Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage. [http://researchspace.auckland.ac.nz/feedback](http://researchspace.auckland.ac.nz/feedback)

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the [Library Thesis Consent Form](http://researchspace.auckland.ac.nz/librarythesisconsentform) and [Deposit Licence](http://researchspace.auckland.ac.nz/depositlicence).
FABRICATION, KINETICS AND CRYSTALLOGRAPHY OF LITHIUM DISILICATE GLASS-CERAMICS

SAIFANG HUANG

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemical and Materials Engineering, the University of Auckland

July 2015

© Copyright 2015 by SAIFANG HUANG
This research project mainly focuses on three aspects of investigations on lithium disilicate glass-ceramics, namely, fabrication, kinetics, and crystallography. One of the objectives is to fabricate a high-strength glass-ceramic in complex lithium disilicate glass systems for dental restorative applications by means of compositional design of parent glass and heat treatment optimization. The second objective is to understand the nucleation mechanism and crystallization kinetics of lithium disilicate glasses by in situ and real-time observations of phase transition using X-ray diffraction (XRD) technique with the state-of-the-art synchrotron radiation. In the meantime, it is of interest to systematically study the evolution of crystallographic structure of the involved crystalline phases (mainly lithium metasilicate and/or disilicate), which is refined by Rietveld method from the as-received synchrotron XRD data, and discuss the relationship of phase transition and crystallographic evolution.

Firstly, a lithium disilicate glass-ceramic, based on a well-documented SiO$_2$–Li$_2$O–Al$_2$O$_3$–P$_2$O$_5$–ZrO$_2$ glass system, was developed. This glass ceramic has a three-point flexural strength of 307 MPa and Vickers hardness of 7.9–8.2 GPa. The glass-ceramic demonstrated a zigzag crack path, suggesting the fracture mechanism of crack deflection. The formation of cubic zirconia (c-ZrO$_2$) with a spherical shape was identified (Chapter 4). Built on the experimental findings of Chapter 4, other new glass compositions (glasses B, C, E, and F) were designed, with MgO being a common additive. Glass-ceramics from glass B (Al$_2$O$_3$-free system) showed an optimized flexural strength of 439±93 MPa and Vickers indentation fracture (VIF) toughness of 0.93–1.29 MPa·m$^{1/2}$. Very limited amount of lithium metasilicate (LS) was detected by synchrotron radiation during glass crystallization. The investigation indicates that the crystallization temperature has a more profound effect than holding time on the phase transformation, morphology and crystallite size of these glass-ceramics (Chapter 5).

In addition, a high strength lithium disilicate glass-ceramics with 562±107 MPa were fabricated in a novel glass composition (glass C) with both MgO and Al$_2$O$_3$ additives and crystallised at 505°C/60min + 605°C/60min + 810°C/120min. Such a three-stage annealing profile was optimized step by step. Remarkably in this glass-ceramic, the netting and
interlocking cluster morphology of lithium disilicate (LS<sub>2</sub>) crystals can be controllably achieved, which is highly correlated with the superior mechanical properties of final products (Chapter 6). Its formation mechanism is still unclear and worthy to be investigated in future.

According to the type of crystallization sequences of LS and LS<sub>2</sub>, the developed glass-ceramics can be categorized into the following three types. Type I is the simultaneous nucleation of LS and LS<sub>2</sub> phases, followed by the transformation of LS to LS<sub>2</sub>. Type II is that LS nucleates first and then transforms to LS<sub>2</sub> at a higher temperature. Type III is that LS<sub>2</sub> directly forms in the glasses without the formation of LS. Practically, glasses with types I and II reaction sequences are preferred because LS phase has very attractive machinability that enables the utilization of CAD/CAM technology for the fabrication of dental products with complex shapes.

Secondly, we investigated the role of P_2O_5, the nucleation and crystallization kinetics in a complex lithium disilicate glass (glass Bo) by in situ XRD measurements and Rietveld refinements. As evidenced by high-resolution synchrotron powder diffraction data, the nucleation of LS and LS<sub>2</sub> is triggered by the steep compositional gradients around the disordered Li_3PO_4 (LP) structural units in the glass matrix. The isothermal nucleation and crystallization kinetics were investigated as well. Accordingly, the Avrami exponent n and activation energy E_a of silicate phases were estimated by a modified JMAK equation and Arrhenius assumption (Chapter 7). Owing to its lower activation energy, the LS phase was evidenced to nucleate ahead of LS<sub>2</sub> at the very beginning of glass nucleation. Surprisingly, the phase transformation of glass upon heating and that of glass melt upon cooling were different; that is, no LS<sub>2</sub> was detected during fast cooling of the glass melt. It indicates that the driving force of the cooling process is not enough for activating the nucleation of LS<sub>2</sub> phase. Apart from the phases LP, LS, and β-cristobalite, two hexagonal phases with very close lattice constants to β-quartz were observed and they showed near zero expansion behaviour (Chapter 8). The non-isothermal crystallization kinetics of lithium disilicate glasses (glasses B and Bo) was depicted by the evolution of phase fraction and crystallite size as a function of annealing temperature (Chapter 5 and Chapter 7). It is found that the growth of LS<sub>2</sub> in glasses of type I is probably constrained by LS at the nucleation stage.

Thirdly, from the investigations into the crystallography of the above-discussed three types
of glass-ceramics, a common phenomenon of structural response of Li$_2$Si$_2$O$_5$ along its $c$ axis to other silicon-related phases during glass crystallization was observed unprecedentedly, which was evidenced from the relationship between the crystallographic evolution and phase transition in glasses (AG1, C, and E/F). In addition, the crystallographic evolution of LS$_2$ phase in glass Bo was investigated upon heating and cooling, respectively. It is confirmed in glasses Bo and C that the lattice parameter $c$ of LS$_2$ shows a typical “V”-shape trend in lithium disilicate glasses of type I. In other words, it drops non-linearly when LS is present in the glass-ceramic then rises up linearly after LS disappears. Moreover, upon heating the $c$ axis of LS demonstrates a non-linear shrinking trend; while upon cooling, it has a linear expanding trend against the increasing temperature (i.e. positive correlation). Thus, a close correlation between the structures of LS$_2$ and LS phases during phase transformation is suggested.
ACKNOWLEDGMENTS

Firstly, I would like to express my sincere gratitude to my main supervisor, Associate Professor Peng Cao, who is always supportive, willing to share his expertise and give hand-on supervision on my research project. Also, I am indebted to my co-supervisor, Professor Wei Gao, for his kind guidance, encouragement and support. Besides, special thanks address to Professor Zhaohui Huang, my overseas supervisor at China University of Geosciences (Beijing), for his kind supervision since 2007 and strong support on my study at both universities. I am very grateful to all supervisors for their kind care and guidance on my study, life and future career.

Special thanks to the industry advisor Dr. Bo Zhang who helped me with melting of some glass compositions. Grateful thanks also extend to the Head of Department, Professor Brent Young and Deputy Head Postgraduate, Dr Mark Jones. I also thank technicians Mr Steve Matthews, Dr. Alec Asadov, Ms Laura Liang, and Mr Raymond Hoffmann of Chemical & Materials Department, and Mr. Andres Arcila-Rivera of School of Environmental Science.

I also wish to thank people in the research groups: Dr. Tianping (Balan) Zhu, Dr. Yuxin Wang, Dr. Xin Ouyang, Dr. Gang (Joey) Chen, Dr. Shanghai Wei, Dr. Yangsi Liu, Dr. Ying Ju, Dr. Jie Han, Wei Qu, Ying (Shirley) Li, Chenfei (Tony) Wang, Dr. Changzou (Victor) Yu, Dr. Hailian Bi, Haibo Hou, Dr. Junye Dong, and those who gave all forms of support to my study.

This research was partially undertaken on the Powder Diffraction beamline at the Australian Synchrotron (AS) Centre, Victoria, Australia (under projects: AS123/PD/4411 and AS123/PDFI/5330). I would like to thank the beamline scientists, Dr. Justin Kimpton and Dr. Qinfen Gu, at the Australian Synchrotron Centre for their technical support.

I gratefully acknowledge the China Scholarship Council (CSC) for providing a doctoral scholarship to study at the University of Auckland.

Last but never least, I wish to specially thank my fiancée, Yan Liu, for her sweet love, patience and support during my PhD study in New Zealand. I also wish to thank my parents (Chunxiu Li and Xinglai Huang), uncle (Xinglong Huang), elder brother (Saifei Huang), and all friends for their love and ceaseless encouragement.
# Table of Content

ABSTRACT ................................................................................................................................. i

ACKNOWLEDGMENTS ............................................................................................................... v

Table of Content ....................................................................................................................... vii

List of Figures ............................................................................................................................ xiii

List of Tables ............................................................................................................................. xxi

Chapter 1  Introduction .............................................................................................................. 1
  1.1  Background of the research ............................................................................................... 1
  1.2  Research objectives ........................................................................................................... 2
  1.3  Thesis outline .................................................................................................................... 3
  1.4  References ........................................................................................................................ 3

Chapter 2  Literature Review ...................................................................................................... 5
  2.1  Dental materials for restorative applications .................................................................... 5
    2.1.1  Porcelain-fused-to-metal (PFM) ................................................................................. 5
    2.1.1.1  Advantages & disadvantages ................................................................................ 6
    2.1.2  All-ceramics ............................................................................................................... 7
    2.1.2.1  Advantages & disadvantages ................................................................................ 7
    2.1.3  Glass-ceramics .......................................................................................................... 8
    2.1.3.1  Advantages & disadvantages ................................................................................ 8
  2.1.4  Fabrication methods and properties of dental ceramics ................................................. 9
  2.2  Glass-ceramics .................................................................................................................. 10
    2.2.1  Fabrication of glass-ceramics .................................................................................... 11
  2.2.2  Applications of glass-ceramics ..................................................................................... 12
    2.2.2.1  General applications ............................................................................................. 12
    2.2.2.2  Applications in restorative dentistry ..................................................................... 12
  2.3  Glass nucleation and crystallization .................................................................................. 14
    2.3.1  Nucleation and crystallization mechanisms ............................................................... 14
    2.3.2  Classical nucleation theory (CNT) ............................................................................ 14
  2.3.3  Crystallization kinetics .................................................................................................. 18
    2.3.3.1  Isothermal crystallization (JMAK isothermal kinetic model) ................................ 18
    2.3.3.2  Non-isothermal crystallization ............................................................................ 19
  2.3.4  Measurement of crystal nucleation rate ...................................................................... 20
Chapter 5  Fabrication of a lithium disilicate glass-ceramic from the SiO$_2$–Li$_2$O–MgO–P$_2$O$_5$–ZrO$_2$ glass system ................................................................. 71

5.1 Introduction .................................................................................. 72
5.2 Experimental procedures ............................................................. 72
  5.2.1 Crystallisation process .............................................................. 72
  5.2.2 Characterisation and mechanical testing .................................. 73
5.3 Results ......................................................................................... 74
  5.3.1 In situ high temperature XRD investigations ............................ 75
    5.3.1.1 Laboratory HT-XRD investigation .................................... 75
    5.3.1.2 Synchrotron HT-XRD investigation (Detection of trace phase formation) .... 76
    5.3.1.3 Weight fraction and crystal size evolutions determined by Rietveld refinements ................................................................. 76
  5.3.2 Selection of annealing stages – Set I ........................................ 78
    5.3.2.1 Phase assemblage and mechanical properties of products of Set I .......... 78
    5.3.2.2 Microstructure of products of Set I ..................................... 81
  5.3.3 Optimization of the second stage (nucleation stage) .................. 81
    5.3.3.1 Phase assemblage and microstructure of products of Sets II and III .... 81
      5.3.3.2 Flexural strength of Sets II and III ..................................... 83
5.4 Discussion ................................................................................... 84
5.5 Summary .................................................................................... 86
5.6 References .................................................................................. 86

Chapter 6  Fabrication of high-strength glass-ceramics with a highly networked and interlocked microstructure ......................................................... 89

6.1 Introduction .................................................................................. 89
6.2 Experimental procedures ............................................................. 90
  6.2.1 Glass preparation .................................................................. 90
  6.2.2 Glass-ceramic fabrication ....................................................... 90
  6.2.3 Characterisation methods ....................................................... 91
6.3 Results ....................................................................................... 92
Chapter 7  Crystallization kinetics of a lithium disilicate glass by in situ synchrotron powder diffraction .............................................................. 107
7.1  Introduction .................................................................................. 107
7.2  Experimental procedures ............................................................... 109
7.3  Results and Discussion ................................................................. 111
  7.3.1  Series I: in situ non-isothermal crystallization ......... 111
         7.3.1.1  Volume fraction vs. annealing temperature .......... 113
         7.3.1.2  Crystallite size vs. annealing temperature ...... 114
  7.3.2  Series II: Real time isothermal crystallization .............. 115
  7.3.3  Series III: Real time nucleation kinetics study ............. 117
7.4  Discussion .................................................................................... 119
  7.4.1  Phase formation sequence ....................................................... 119
         7.4.1.1  Series I: non-isothermal crystallization .......... 119
         7.4.1.2  Series II: isothermal crystallization ............ 121
  7.4.2  Role of P2O5 ................................................................. 122
  7.4.3  Isothermal kinetics investigation ......................................... 123
7.5  Summary ....................................................................................... 125
7.6  References ................................................................................... 126

Chapter 8  Crystallographic evolution of a lithium disilicate glass upon heating and cooling ................................................................. 129
8.1  Introduction .................................................................................. 129
8.2  Results ........................................................................................ 131
  8.2.1  Phase transformation upon heating and cooling .............. 131
  8.2.2  Crystallographic evolution ...................................................... 134
         8.2.2.1  Crystallographic evolution upon heating .......... 134
         8.2.2.2  Crystallographic evolution upon cooling ......... 135
8.3  Discussion .................................................................................... 136
  8.3.1  Crystal structure ................................................................. 136
  8.3.2  Lattice parameters evolution of different phases and their correlation ... 137
  8.3.3  The unit cell volume evolution of different phases ........... 138
<table>
<thead>
<tr>
<th>Table of Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3.4 Nucleation/crystallization in the glass melt during cooling</td>
</tr>
<tr>
<td>8.4 Summary</td>
</tr>
<tr>
<td>8.5 References</td>
</tr>
</tbody>
</table>

Chapter 9  Structural response of lithium disilicate in glass crystallization | 145 |
| 9.1 Introduction | 145 |
| 9.2 Experimental Section | 146 |
| 9.3 Results and Discussion | 147 |
| 9.3.1 Phase evolution process in various glasses | 147 |
| 9.3.2 Lattice parameters of lithium disilicate | 149 |
| 9.3.2.1 Glasses AG1, C, E and F | 149 |
| 9.3.2.2 Glass B | 151 |
| 9.3.3 Lattice parameters of lithium metasilicate | 152 |
| 9.3.4 Unit cell volume of silicate phases | 154 |
| 9.4 Discussion | 156 |
| 9.5 Summary | 158 |
| 9.6 References | 158 |

Chapter 10  Summary and Future Work | 161 |
| 10.1 Summary | 161 |
| 10.2 Future work | 163 |
| 10.2.1 Structural evolution monitored by solid-state NMR (Ongoing work) | 163 |
| 10.2.2 Future work | 167 |
| 10.3 References | 168 |

Biography | 169 |
| 1. Journal publications | 169 |
| 2. Manuscripts under review | 169 |
| 3. Patent applications | 170 |
| 4. Conferences | 170 |
List of Figures

Figure 2-1. Long-span six-unit porcelain-fused-to-metal bridge (IPS d.SIGN®) in clinical situation. (A) Preparation of the teeth, (B) the six-unit PFM bridge fabricated on a gypsum model, and (C) cemented bridge.6 ........................................... 6
Figure 2-2. Mechanical properties of dental ceramic materials.38 ........................................... 10
Figure 2-3. Schematic plot for a cycle of processes of glass formation and crystallization for the fabrication of glass-ceramics from monolithic bulk glasses.............................................................................................................................................. 10
Figure 2-4. Reaction routes between the initial glass and the final glass–ceramic (after Stewart).42 ........................................................................................................................................gos 12
Figure 2-5. (a) Products of leucite type glass–ceramics as dental inlay, veneer, and single crown from left; (b) Dental bridge reflected on a mirror to show the interior.46 The 3-unit bridge consists of a framework of lithium disilicate glass-ceramic (IPS Empress®2) veneered with fluoroapatite glass–ceramic (IPS Eris®). ........................................................................................................................................gos 14
Figure 2-6. The relationship between the change in Gibbs free energy (ΔG) and the radius of nucleus (r). After Höland et al.60 ........................................................................................................................................gos 15
Figure 2-7. Model of heterogeneous nucleation. H represents the heterogeneous substrate, S represents the nucleus, and L the parent glass, θ shows the contact angle........................................................................................................................................gos 16
Figure 2-8. Experimental steady-state nucleation rates (a), and induction periods (b) versus temperature and inverse temperature, respectively, for lithium disilicate glass35,61 ........................................................................................................................................gos 17
Figure 2-9. Schematic representation of the classical rates for nucleation and crystallization in glasses. After Karpukhina et al.63 The Ostwald-Miers temperature range is a metastable zone of undercooling. ....................................................... 17
Figure 2-10. A typical curve of the number density of Li2O-2SiO2 crystals in glasses of stoichiometric composition versus time of nucleation obtained by the ‘development’ method.33 ........................................................................................................................................gos 21
Figure 2-11. Function of ΔTp versus temperature of isothermal treatment of a glass according to the Marotta’s method34 ........................................................................................................................................gos 21
Figure 2-12. Crystal structure of stable lithium disilicate viewing from the a axis................. 22
Figure 2-13. Phase diagram of the Li2O–SiO2 system showing solid-solution regions and liquid–liquid phase separation region.90 (c: cristobalite; t: tridymite; L: liquid; ss: solid-solution; q: quartz)........................................................................................................................................gos 24
Figure 2-14. Epitaxial growth of cristobalite (CR), lithium metasilicate (LS), and
lithium disilicate (LS2) on a lithium orthophosphate (LP) crystal.  

Figure 2-15. Schematic diagram of structural changes occurring in the residual glassy phase during crystallization of lithium disilicate glasses involving lithium metasilicate. Left: starting glass; middle: remaining glass phase after nucleation of LS; right: remaining glass phase after transformation of LS to LS2 at a higher temperature. Open circles are demonstrating oxygen atoms.  

Figure 2-16. (a) The evolution of different phosphate units in lithium disilicate glasses at 455 °C, (b) the evolution of $^{31}$P MAS-NMR spectra of a glass after treatment.  

Figure 2-17. The microstructure of (a) a non-annealed bulk lithium disilicate glass and (b) glass-ceramic annealed at 800 °C.  

Figure 2-18. SEM micrograph of lithium disilicate glass-ceramic (a) rod-like, (b) plate-like (this work).  

Figure 3-1. The Powder Diffraction beamline at the Australian Synchrotron Centre. The high temperature furnace (Anton Paar HTK-2000 strip furnace) was setup with a temperature control system.  

Figure 3-2. Schematic idealised plan view and cross-sectional view of (a) Vickers indent radial-median or 'halfpenny' crack system and (b) Vickers indent radial Palmqvist crack system.  

Figure 4-1. Heat treatment temperature profile of the glass with four stages.  

Figure 4-2. DTA analysis of parent glass Bo (ramp rate of 20 °C/min in air).  

Figure 4-3. XRD patterns of samples after heat treatment at first three stages.  

Figure 4-4. XRD patterns of samples (S1-S4) annealed at various final-stage temperatures holding for 20 min.  

Figure 4-5. XRD patterns of samples (M1-M3) heat-treated for different holding time at 770 °C.  

Figure 4-6. Crystalline morphology of lithium disilicate glass-ceramics S1-S4 heat-treated at different temperatures holding for 20 min (etching with 2% HF acid solution for 10s). (a) S1: 770°C, (b) S2: 790°C, (c) S3: 820°C, (d) S4: 850°C. The insets are BSE images.  

Figure 4-7. Morphology of GC samples heat-treated at 770°C, holding for (a) 1 h and (b) 2.5 hrs respectively (etching with 2% HF solution for 10s). The white grains are ZrO$_2$.  

Figure 4-8. (a) Crack propagation in lithium disilicate glass-ceramics (sample S4), (b) the enlarged image of selected area in (a).  

Figure 5-1. Temperature profile of glass annealing for synchrotron measurements.
Figure 5-2. DTA trace of the base glass (ramp rate of 20 K/min in air). ........................................ 75

Figure 5-3. Laboratory HT-XRD of the base glass, where D represents the stable lithium disilicate phase (540–900 °C, orthorhombic, JCPDS no. 70-4856), P = lithium phosphate (750–900 °C, JCPDS no. 83-0339), C = cristobalite (780–870 °C, JCPDS no. 27-0605), and Q = quartz (810–900 °C, JCPDS no. 47-1144). When temperature is >900 °C, the sample was distorted and the data collection failed. The bar in colour indicates the diffraction intensity. .................................................................................. 75

Figure 5-4. (a) In situ high-temperature XRD patterns (in colour contour) of the complex lithium disilicate glass, (b) the line patterns of partial data to show the peaks of LS phase (directed by arrows) and peaks of other unidentified phase (directed by stars). D: lithium disilicate (LS2); M: lithium metasilicate (LS); P: lithium phosphate (LP); C: cristobalite (CR); Q: quartz (QZ). .......................................................................................... 77

Figure 5-5. Weight fraction of phases in the glass-ceramics as a function of temperature. The quantitative results suggest a maximum of ~2 wt% LS precipitated from the glass. .................................................................................. 78

Figure 5-6. The crystallite size of LS2 phase as a function of temperature. The dotted line shows the silicate phase(s) existed in the corresponding temperature range. The crystal growth of LS2 is indicated to be hampered by the existence of LS. .................................................................................. 78

Figure 5-7. RT-XRD patterns of lithium disilicate glass-ceramics crystallised at different stages. ................................................................................................................................. 79

Figure 5-8. SEM images of the lithium disilicate glass-ceramics from Set II: (a) sample 2S, (b) sample 3S, and (c) sample 4S (after polishing and etching); and (d) the fracture surface of sample 3S (without polishing). Scale bar = 5 μm. 80

Figure 5-9. XRD patterns of (a) Set II samples annealed at different temperatures of the second stage for 30 min, and (b) Set III samples annealed at various holding times of the second stage at 675 °C. .......................................................................... 81

Figure 5-10. BSE micrographs of Set II samples treated under different temperatures at the second stage for 30 min (after polishing and etching). (a) sample M1, 620 °C, (b) sample M3, 660 °C, (c) sample M4, 680 °C and (d) sample M6, 720 °C. Scale bar = 5 μm. .................................................................................. 82

Figure 5-11. BSE micrographs of Set III samples treated with different holding times at 675 °C (after polishing and etching). (a) sample T1: 15 min, (b) sample T2: 30 min, (c) sample T5: 120 min. Scale bar = 5 μm. ........................................... 83

Figure 5-12. Bending strength of (a) Set II samples at different holding temperatures (samples M1 to M6) and (b) Set III samples at different holding times
Figure 6-1. In situ synchrotron high temperature XRD patterns of the lithium disilicate glass ................................................................. 84

Figure 6-2. (a) DSC traces of glass C after treatment at different annealing temperatures for 2 h, (b) DSC traces of glass C after treatment at 505 °C for different annealing time. The heating rate was 15 K/min. ...................... 93

Figure 6-3. The shift of the main exothermal peaks of glasses after pre-treatment at various temperature or time from DSC trace of original glass. \( \Delta T_p = T_p - T_p' \) ................................................................. 94

Figure 6-4. XRD patterns of samples at various temperatures or holding times. The first stages are 505 °C for 60 min, and the following two stages are (a) 580-655 °C for 20 min + 830 °C for 30 min, (b) 10-120 min at 605 °C + 830 °C for 30 min, (c) 605°C for 60min and 750-830 °C for 30 min, and (d) 605°C for 60min and 10-120 min at 810 °C............................................. 95

Figure 6-5. Flexural strength of samples at various temperatures or holding times. The first stages are 505 °C for 60 min, and the following two stages are (a) 580-655 °C for 20 min + 830 °C for 30 min, (b) 10-120 min at 605 °C + 830 °C for 30 min, (c) 605°C for 60min and 750-830 °C for 30 min, and (d) 605°C for 60min and 10-120 min at 810 °C............................................. 96

Figure 6-6. (left column) Polished surface and (right column) fracture surface of samples treated with various temperatures at the third stage (30 min). (a) T5- 750°C, (b) T6- 770 °C, (c) T7- 790°C, (d) T8- 810°C ......................... 98

Figure 6-7. (left column) Polished surface and (right column) fracture surface of samples treated with various holding times at the third stage (810 °C). (a) S5 - 10min, (b) S6 - 20min, (c) S7- 60min, (d) S8- 120min...................... 99

Figure 6-8. The typical feature of networked structure widely existing in the high-strength glass-ceramic (sample S8) ................................................................. 100

Figure 6-9. The schematic illustration for the formation of the netted and interlocked clusters of lithium disilicate in the glass-ceramics............................................ 101

Figure 6-10. TEM images of an “H” like microstructure in the glass-ceramic. ..................... 102

Figure 6-11. TEM image of a sample of GCS8 (with flexural strength of ~623 MPa) ....... 103

Figure 6-12. (a) TEM and (b) SAED images of the high-strength lithium disilicate glass-ceramic.................................................................................. 104

Figure 7-1. The temperature profiles of three series of synchrotron XRD experiments. Series I: continuous heating from 500°C to 1010°C; Series II: isothermal annealing at 770°C for 120 min, to study crystallization kinetics; and Series III: isothermal annealing at 560°C, 570°C, and 580°C, respectively,
to study its nucleation kinetics. ................................................................. 110

Figure 7-2. Synchrotron HT-XRD of the lithium disilicate glass when continuously heated from 500 to 1010°C. D: Li₂Si₂O₅ (LS₂); M: Li₂SiO₃ (LS); P: Li₃PO₄ (LP); Z: ZrO₂................................................................. 111

Figure 7-3. Intensities of phases in the Series I sample as a function of temperature. The intensity data are taken from the strongest peak of each phase, i.e. (111) plane of LS₂, LS, and ZrO₂, and (120) of LP......................... 112

Figure 7-4. The XRD patterns showing the initiation of Li₂SiO₃ (marked as “1”) and Li₂Si₂O₅ (marked as “2”) phases observed in the annealing of Series I........... 113

Figure 7-5. Volume fraction of phases as a function of temperature, determined by XRD full pattern quantitative phase analysis......................................................... 114

Figure 7-6. Crystallite sizes of LS, LS₂ and LP phases as a function of temperature....... 115

Figure 7-7. Real time synchrotron HT-XRD of the lithium disilicate glass treated at 770°C with elapsed time of 120 min. D: lithium disilicate, Li₂Si₂O₅; P: lithium phosphate, Li₃PO₄; M: lithium metasilicate, Li₂SiO₃; C: cristobalite; Q: quartz; Z: ZrO₂. A trace amount of ZrO₂ (<0.15 vol.%) precipitated after heating for 24–120 min at this temperature. ................. 115

Figure 7-8. Volume fraction of all phases as function of the elapsed time at 770°C. The total volume fraction of LS, LS₂, QZ and CR against the elapsed time is also plotted. The standard deviations are less than 0.1%. ...................... 116

Figure 7-9. Crystal size of the LS₂ and LS phases with the holding time at 770°C ........ 117

Figure 7-10. Real time synchrotron HT-XRD patterns of the glass at (a) 560, (b) 570, and (c) 580°C. The nucleation and crystallization of LS and LS₂ phases are temperature and time dependent.......................................................... 118

Figure 7-11. Real time synchrotron HT-XRD patterns of the glass at (a) 560, (b) 570, and (c) 580°C. The nucleation and crystallization of LS and LS₂ phases are temperature and time dependent. The standard deviations are less than 0.1%...................................................................................... 119

Figure 8-1. Synchrotron HT-XRD patterns of the lithium disilicate glass sample: (a) heating from 500°C to 1010°C, and (b) cooling from a melt and recording at 1000°C to 520°C. D: Li₂Si₂O₅ (LS₂); M: Li₂SiO₃ (LS); P: Li₃PO₄ (LP); Z: ZrO₂; C: β-cristobalite; Q: β-quartz. Note that the patterns are shown in a continuous 2-dimentional plot where the intensity was displayed by colour contour, while the data were acquired as per the experimental method................................................................. 132

Figure 8-2. The enlarged XRD patterns of different phases in the sample upon cooling (from 950 to 520 °C). M: Li₂SiO₃ (LS); P: Li₃PO₄ (LP); C: β-cristobalite (cubic); Q1/Q2: β-quartz (hexagonal).......................... 133
Figure 8-3. The weight fraction of LS as a function of temperature on cooling. The dotted line used to connect the experimental points is for eye guidance. .......................... 133

Figure 8-4. Lattice parameters of (a) LS₂, (b) LS, (c) LP and (d) ZrO₂ phases as a function of temperature upon heating. The errors for those of LS₂, LS and ZrO₂ phases are very small and not present in Figure 8-4a, 4b and 4d; only the errors for those of LP phase are plotted in Figure 8-4c. ......................... 134

Figure 8-5. Lattice parameters of (a) LS and (b) LP phases as a function of temperature on cooling. ................................................................................................. 136

Figure 8-6. The crystal structures of (a) stable lithium disilicate,²³ (b) lithium metasilicate,²⁶ (c) lithium orthophosphate²⁰ and (d) cubic zirconia.²⁷ .................. 137

Figure 8-7. Selected diffraction patterns of lithium silicate phase during the annealing of the glass: (a) (002) plane and (b) (130), (020) and (111) planes of stable LS₂ transforming at high temperatures. Arrows are added only for eye guidance on the evolution trend of peaks. ....................................................................................... 138

Figure 8-8. Unit cell volumes of (a) LS₂, (b) LS, (c) LP and (d) ZrO₂ as a function of temperature on heating ................................................................................................. 140

Figure 8-9. Unit cell volumes of (a) LS and (b) LP as a function of temperature on cooling. ......................................................................................................................... 140

Figure 9-1. In situ synchrotron XRD patterns of lithium silicate glass-ceramics at high temperatures. (a1 – d1) show the main peaks of crystalline phases formed during the heat treatment process; (a2 – d2) demonstrate the peak evolution of (002) plane of lithium disilicate, and (a3 – d3) depict the peak evolution of its (130), (020) and (111) planes. The letters a, b, c and d represent the glasses AG1, C, E and F, respectively. The letters A, C, D, M, P, Q, T, and U in the (a1–d1) patterns are denoting the crystalline phases of MgAl₂Si₄O₁₂, cristobalite, lithium disilicate, lithium phosphate, quartz, tridymite, and an unidentified phase, respectively. ........................................ 150

Figure 9-2. (a) The lattice parameters and (b) unit cell volume of the LS₂ phase as a function of temperature ........................................................................................................ 151

Figure 9-3. (a) Main peaks of crystalline phases crystallized in the glass as a function of temperature, (b) peak evolution of (002) plane of lithium disilicate phase, (c) peak evolution of its (130), (020), and (111) planes. ....................... 152

Figure 9-4. (a) The lattice parameters of the LS phase in glass AG1 as a function of temperature and (b) the diffraction patterns for (002) plane of LS whose trend is consistent with the evolution trend of the c axis as shown in (a). ...... 152

Figure 9-5. (a) The lattice parameters of LS phase against temperature in glass C, and close-up diffraction patterns for (b) (200), (c) (020) and (d) (002) planes of Li₂SiO₃ (M). ........................................................................................................................................ 153
Figure 9.6. Unit cell volume of (a) LS$_2$ and (b) LS phases in glass AG1 as a function of temperature. ............................................................. 155

Figure 9.7. Unit cell volume of (a) LS$_2$ and (b) LS phases in glass C as a function of temperature. ................................................................. 155

Figure 9.8. Unit cell volume of LS$_2$ phase in (a) glass E and (b) glass F as a function of temperature. ................................................................. 155

Figure 9.9. (a) The (101) peak of LP phase, and (b) the (111) peak of CR phase in glass F. As indicated by arrows, the glass is deformed at temperatures above 960 °C. ................................................................. 156

Figure 10.1. The RT-XRD patterns of glass C treated at various temperatures ....................... 163

Figure 10.2. (a) The $^{31}$P NMR spectra of the glass treated at various temperatures, (b) the fitted $^{31}$P NMR spectra of the glass treated at various temperatures with enlarged bottoms, and (c) the evolution of phosphorus species in the samples (lines along the data points are for eye guidance only). .................. 164

Figure 10.3. The curves of recovered magnetization ($M$) versus relaxation delay ($t$). These curves were used for $T_1$ time determination of $^{29}$Si NMR measurements of samples at various annealing temperatures ................................ 165

Figure 10.4. $^{29}$Si relaxation decay of the samples C0-C6. The differences between the curved and straight portion of the plots are drawn by the dash lines. ............... 167
List of Tables

Table 2-1. Ceramic systems for metal-ceramic/all-ceramic dental restorations.\(^\text{37}\) ............ 9

Table 2-2. Evolution of Glass-ceramic dental restoration products and their detailed scientific information\(^\text{2, 46}\) ........................................................................................................ 13

Table 2-3. Typical values of kinetic exponent for crystallization processes in isothermal conditions\(^\text{59, 65}\) ........................................................................................................ 19

Table 2-4. Patents related to lithium disilicate glass-ceramics for dental applications. ....... 25

Table 2-5. Composition ranges of the patented lithium disilicate glass-ceramics for dental restorations. ........................................................................................................ 26

Table 2-6. The mechanical properties of lithium disilicate glass-ceramics for dental applications covered in the patents listed in Table 2-4............................................. 34

Table 3-1. Nominated compositions of lithium disilicate glasses (in wt%).......................... 48

Table 4-1. Phase assemblage and mechanical properties of lithium disilicate glass-ceramics heat-treated at different final-stage temperatures. ......................... 62

Table 4-2. Phase evolution of lithium disilicate glass as function of temperature.............. 66

Table 5-1. Heat treatment profiles of the lithium disilicate glasses. ................................ 73

Table 5-2. Heat treatment process, crystalline phases, crystallinity, and \(\text{Li}_2\text{Si}_2\text{O}_5\) content in the products, and mean value ± standard deviations for flexural strength (\(\sigma_f\)), Vickers hardness (\(HV\)), VIF fracture toughness (\(K_c\)). .................. 79

Table 6-1. Heat treatment profiles of different glasses. .................................................. 91

Table 6-2. The composition of spots 1–4 in Figure 6-11 detected by EDS. ...................... 103

Table 7-1. Summary of the phase formation sequences in the lithium disilicate glass..... 120

Table 7-2. The induction time (\(t_0\)) and fitted Avrami coefficients (\(n\) and \(k\)) for the nucleation of LS\(_2\) and LS phases at 560, 570 and 580 °C. ............................... 124

Table 8-1. Comparison of phase transformation in the lithium disilicate glass during heating and cooling ................................................................. 131

Table 8-2. Modelling of the unit cell volume for LS, LS\(_2\) and LP phases upon heating or cooling ........................................................................................................ 139

Table 9-1. XRD patterns, evolution of lattice parameters of LS\(_2\), crystalline phases and their temperature ranges for different glasses .............................................. 148

Table 10-1. The fitted results of the relaxation time (\(T_1\)) and ratio of both short and long components in the samples at different annealing stages .......................... 166
Chapter 1 Introduction

1.1 Background of the research

Ceramics have been successfully used in aesthetic dentistry for decades as metal-free restorations with high-quality and natural-appearing features. Glass-ceramics are a class of ceramic materials with appealing physical and mechanical properties achieved by controlled crystallization of base glass. In comparison to glass-ceramics of other types, the lithium disilicate-reinforced glass-ceramics are particularly important owing to their outstanding properties. They have been widely used as dental restorative materials.

The application of this type of material, however, is limited to three-unit dental bridge up to premolar due to the relative low mechanical properties. Moreover, the current clinical investigations suggest that glass-ceramics have a lower reliability than the conventional metal-ceramic or zirconia-based 3-unit restorations. Therefore, one of the focuses is strengthening and toughening of lithium disilicate glass-ceramics. High-strength glass-ceramics would enhance the reliability of dental products and also extend its dental applications to bridges involving molar restoration. Ceramic materials have to meet the criteria on mechanical properties and chemical stability set by an ISO standard 6872:2008(E) for dental applications.¹

Involved in turning glass to glass-ceramics is nucleation, which seems simple for a glass with inoculation of $P_2O_5$. Interestingly, the nucleation mechanism of $P_2O_5$-containing glass compositions has attracted wide debate. The contradictory explanations have been reported. An epitaxy growth mechanism was proposed by Headley et al. on a pre-seeded glass which was applied for metal sealing.² However, in a conventional annealing of glasses without pre-seeding of well-crystallized lithium phosphate, it is more likely that the glass nucleation is initiated at phase boundaries between the disordered lithium phosphate phase and glass matrix, as evidenced from a comprehensive NMR study of Bischoff et al.³ This is still an open question for further investigation.

The simple binary $SiO_2$–$Li_2O$ system has been served as an ideal model for the study of nucleation and crystal growth processes in glass. A fundamental understanding of these
processes is vital to the controllable development of glass-ceramics. Several theories have been developed on nucleation and crystallization, such as the classical nucleation theory (CNT), the Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory, and Cahn–Hilliard theory. Dramatic discrepancies between the CNT theory and experiments have been observed with regard to the nucleation rate and surface energy. Although extensive investigations based on the CNT have been done, there still remain fundamental open questions. The JMAK and Cahn–Hilliard theories provide information of the crystallization mechanism and activation energy of glass nucleation with respect to isothermal and non-isothermal crystallization.

The crystallization kinetics of complex glasses (with more than three components) is rarely quantitatively described in the literature. All of the currently used glass-ceramics have complex compositions. The understanding of crystallization kinetics of complex glasses would be of great significance for the fabrication of glass-ceramics with a desired microstructure.

Furthermore, crystallographic evolution of phases was rarely reported during the crystallization of lithium disilicate glasses. It was also seldom studied what the relationship of different phases that crystallized from base glass is, and how the structure responses to each other within these crystalline phases.

Furthermore, the crystallographic evolution of phases was rarely reported during the crystallization of lithium disilicate glasses. Also little is known about the relationship between the different phases that crystallized from base glass and what are the structure responses from each of these crystalline phases.

1.2 Research objectives

In this project three main objectives were proposed and implemented:

(1) Fabrication of lithium disilicate glass-ceramics with high strength of novel glass compositions for restorative dental applications;

(2) Quantitative studies of the nucleation crystallization kinetics of lithium disilicate glasses in complex systems; and

(3) Understanding of the crystallographic evolution and interaction involved during glass crystallization.
1.3 Thesis outline

The thesis is composed of ten chapters. Many chapters are directly based on the published work by the author of this thesis.\textsuperscript{9-16} Chapter 1 is a brief introduction. Chapter 2 presents the literature review on dental materials for restorative dentistry, the formation and applications of glass-ceramics, theories of glass nucleation and crystallization. The fabrication, microstructure, properties and applications of lithium disilicate glass-ceramics are also included. Chapter 3 describes the experimental methods covering the entire thesis. Subsequently, Chapters 4–6 report the fabrication, microstructure and properties of lithium disilicate glass-ceramics from several glasses. Chapter 7 investigates the nucleation and crystallization kinetics of a lithium disilicate glass by \textit{in situ} XRD experiments using synchrotron radiation. The high-temperature crystallographic evolution of crystalline phases, especially lithium disilicate, has been carefully examined in Chapter 8 and Chapter 9, where the first-ever observed phenomenon of structural response of lithium disilicate is presented. Chapter 10 summarizes the main findings of this research and addresses how they relate to each other; it also describes the ongoing work, and proposes the possible future work.

1.4 References


Chapter 2  Literature Review

Materials science and restorative dentistry are changing the lives of people who are missing their teeth and those who just want a big smile rather than covering with hands due to their anaesthetic teeth. Generally, two practical objectives of restorative treatment are recreations of aesthetics and function. The application environment and preferred properties of materials for use in dental implantation and restorative dentistry are completely different. Materials for restorative dental applications must fulfil the requirement of compatibility with the oral environment, but must not be bioactive. The restorative dental materials must resemble natural teeth so that shade, translucency, toughness, wear and chemical resistance properties are important.\(^1\) In contrast, the most critical property for implantation dental material is its bioactivity, so that a strong bonding with bone can be achieved.

2.1 Dental materials for restorative applications

Restorative materials are used to replace and reconstruct the tooth to its original shape and function, and have to meet durability in the oral environment, simulate the natural tooth structure and exhibit high strength and wear resistance.\(^2\) The main types of materials used as dental restorations are porcelain, all-ceramics, metal-ceramics (porcelain-fused-to-metal, \(PFM\)), glass-ceramics and so forth.\(^3\) Depending on their particular characteristics and properties, these materials can be fabricated for the applications of inlay, onlay, crown, veneer, bridge, and denture, which are classified as indirect restorations.\(^4\)

Ideally, apart from durability and biocompatibility, restorative dental materials should also exhibit excellent aesthetic characteristics (such as translucency, natural tooth colour and outstanding light transmission), and optimal mechanical properties (including similar hardness/wear behaviour to real teeth, excellent flexural strength and fracture toughness which should meet the requirements of the indication ranges).\(^5,6\) Besides, restorative materials also should be easily removed when retreatment is required.\(^7\)

2.1.1 Porcelain-fused-to-metal (PFM)

Porcelain-fused-to-metal (PFM, metal-ceramic), a ceramic coating or veneer sintered onto
the metal substructure via multiple furnace-firing processes, was developed in the 1960s.
PFM restorations are still the most widely used type of indirect restorative system with great
success, accounting for 50% of the market throughout the world. The metal alloys used in
these applications include Au, Pd-Ag, Ni-Cr and Co-Cr alloys. The ceramic veneers are
called dental “porcelain” due to the main crystalline phases of feldspar (K₂O·Al₂O₃·6SiO₂)
and leucite (K₂O·Al₂O₃·4SiO₂). These phases are formed in a fast, disordered, almost
uncontrolled crystallization process rather than by controlled nucleation and crystallization as
is the case in glass–ceramics.

2.1.1.1 Advantages & disadvantages

Metal-ceramic restorations have high strength and fracture resistance due to the metal
framework. Less tooth structure needs to be removed to provide a proper structure for the
crown. They have the advantage of good marginal fit and can be individualized by painting
with different coloured and translucent glass ceramic veneers. Many studies have also
showed good in vivo and in vitro long-term survival results of long-span and multiple unit
bridges. It therefore can be fabricated as long span denture with 5 units or more. An example
of long-span six-unit PFM bridge is shown in Figure 2-1.

There are still many disadvantages for this type of restorations. Firstly, different CTEs of
materials may result in the chipping or delamination of veneering material. Secondly, the
time-consuming casting and veneering processes of the metal framework are likely to
generate inhomogeneity which should be avoided in dental products. The aesthetics of PFM is not as good as metal-free restorations (glass-ceramics or all-ceramics) so that it is not preferred for anterior restorations. Besides, corrosion reactions of the metal frameworks can cause metallic taste, oral burning, and allergic reactions in patients.13

2.1.2 All-ceramics

Classification of complications and overall survival rates of all-ceramic restorations were reviewed by Conrad et al.14 who concluded that the major clinical complication resulting in failure is the fracture and/or the coping of the veneering porcelain. Hickel et al15 also summarized that the typical survival rates for all-ceramic restorations are 88%–100% after 2–5 years and 84%–97% after 5–14 years, and the complications resulting in failure are fractures of the ceramic material, endodontic treatment, debonding, tooth fracture, and caries.

Zirconia is one of the most promising restorative materials with very high toughness and strength due to the tetragonal to monoclinic ($t \rightarrow m$) phase transformation (martensitic transformation),16 which can be induced by external stresses and results in a 4% volume increase and the related compressive stresses.17 Transformation toughening, microcrack toughening, contact shielding and crack deflection are the main toughening mechanisms acting in zirconia-based ceramics.18

2.1.2.1 Advantages & disadvantages

In addition to its biocompatibility, zirconia restorations with good marginal fit can be manufactured by CAD/CAM technique.19,20 Besides, they can be aesthetic when coated with the veneering glass-ceramics and their aesthetics can be customized by veneering different colour and translucent pastes.8

However, chipping/delamination of veneered zirconia all-ceramic restorations may occur due to the residual stresses. These stresses are generated from the thermal misfit between veneering material and core ZrO2, development of flaws and structure defects, and their relatively weak bonding strength.21,22 All-ceramic restorations fabricated by CAD/CAM technique may fail from chipping of veneer layers or crack initiation at the interface.23 Although there are short-time studies on the durability of long-span restorations,24,25 long-term data are insufficient to validate the clinical potential of zirconia. The rigidity of
zirconia (high elastic modulus of \(\sim 240\) GPa) causes stress to be transferred to the much less rigid dentin (with elastic modulus of 18–22 GPa\(^{26}\)), resulting in root fractures.\(^7,17\) Furthermore, if root fracture occurs, the zirconia prosthesis is very difficult to remove from the root canal.\(^{27}\)

### 2.1.3 Glass-ceramics

Glass-ceramics are composites containing a residual glassy phase and one or more crystalline phases, and in most cases, with crystallinity of about 30\%–70\%.\(^{28}\) Their mechanical properties are significantly improved via partial crystallization of base glasses. Glass-ceramics of several types have been used as restorative dental materials, such as mica, leucite and lithium disilicate types.

#### 2.1.3.1 Advantages & disadvantages

The making of glass-ceramic begins with a parent glass, and therefore all the well-established glass-forming techniques, including melting, casting, pressing and rolling, can be employed to manufacture components with a variety of complex shapes.\(^{29}\) Based on the glass forming technology, glass-ceramic dental restorations have an important feature that they are suitable for large-scale dental laboratories or mass production. The cost of each product can thus be significantly reduced. Besides, glass-ceramics can be obtained from a wide variety of compositions leading to a wide range of mechanical, optical and thermal properties.\(^{30}\) Such properties are adjustable by compositional adjustment and crystallization control.\(^{29}\) Fully-dense (zero or very low porosity) glass-ceramics with preferable mechanical properties can be easily produced by heat-treating bubble-free glasses;\(^{31}\) in comparison, the preparation of pore-free ceramics from powder is still challenging.\(^{32}\)

Moreover, the optical properties are another advantage of glass ceramics; they are translucent.\(^{33}\) The colour and translucence of glass-ceramic restorations are tuneable by adding colorants in the glass compositions and/or varying crystallinity. These features and self-glazing effect\(^{34}\) enable glass-ceramics being aesthetic and having very similar external appearance to natural teeth.\(^{35}\)

Thus far, the flexural strength and fracture toughness of existing glass-ceramics are not high enough for posterior three-unit restorations (molar). A great deal of work has been reported for strengthening or toughening of glass-ceramics.\(^{36,92}\)
2.1.4 Fabrication methods and properties of dental ceramics

During the past decades, much attention has been paid to fabrication methods, net-shape processing, properties and clinical performance of all-ceramic systems\(^36\). Various fabrication techniques can be used for making metal-ceramic and all-ceramic restorations, such as sintering, heat-pressing, dry pressing and sintering, slip-casting & glass infiltration, soft machining & glass infiltration/sintering, soft machining & sintering & heat-pressing, hard machining.\(^37\)

<table>
<thead>
<tr>
<th>Processing Method</th>
<th>Crystalline phase</th>
<th>Crystallinity (%)</th>
<th>Strength (MPa)</th>
<th>Brand</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered on metal substructure</td>
<td>Leucite</td>
<td>15–25</td>
<td>61 ± 5</td>
<td>Ceramco®3</td>
<td>Dentsply</td>
</tr>
<tr>
<td>Heat-pressed</td>
<td>Leucite</td>
<td>≈ 35</td>
<td>106 ± 17</td>
<td>IPS Empress®</td>
<td>Ivoclar</td>
</tr>
<tr>
<td></td>
<td>Lithium disilicate</td>
<td>65</td>
<td>306 ± 29</td>
<td>IPS Empress®2</td>
<td>Ivoclar</td>
</tr>
<tr>
<td>Dry-pressed and sintered</td>
<td>Alumina</td>
<td>Highly crystalline</td>
<td>607 ± 73</td>
<td>Procera®</td>
<td>Nobel Biocare</td>
</tr>
<tr>
<td>Slip-cast/soft machined and glass-infiltrated</td>
<td>Alumina</td>
<td>67–68</td>
<td>594 ± 52</td>
<td>In-Ceram® Alumina</td>
<td>Vident</td>
</tr>
<tr>
<td></td>
<td>Spinel</td>
<td>65–68</td>
<td>378 ± 65</td>
<td>In-Ceram® Spinell</td>
<td>Vident</td>
</tr>
<tr>
<td></td>
<td>12 Ce-TZP alumina</td>
<td>67</td>
<td>630 ± 58</td>
<td>In-Ceram® Zirconia</td>
<td>Vident</td>
</tr>
<tr>
<td>Soft-machined &amp; sintered</td>
<td>3Y-TZP</td>
<td>Highly crystalline</td>
<td>1087 ± 173</td>
<td>Cercon®</td>
<td>Dentsply</td>
</tr>
<tr>
<td></td>
<td>Alumina</td>
<td>Highly crystalline</td>
<td>700</td>
<td>In-Ceram® AL</td>
<td>Vident</td>
</tr>
<tr>
<td>Hard-machined &amp; crystallized</td>
<td>Leucite</td>
<td>≈ 35</td>
<td>106 ± 17</td>
<td>IPS Empress® CAD</td>
<td>Ivoclar</td>
</tr>
<tr>
<td></td>
<td>Lithium disilicate</td>
<td>65</td>
<td>262 ± 88</td>
<td>IPS e.max CAD</td>
<td>Ivoclar</td>
</tr>
</tbody>
</table>

Table 2-1. Ceramic systems for metal-ceramic/all-ceramic dental restorations.\(^37\)

Table 2-1 shows the processing method, main crystalline phase, crystallinity and strength of restorations produced by different manufacturers. The mechanical properties of dental ceramic materials vary in a wide range, as demonstrated in Figure 2-2. Zirconia-type ceramics possess the highest flexural strength and fracture toughness due to the favourable transformation toughening effect, so they can be used as posterior bridges with over three units in dentistry. In comparison, lithium disilicate glass-ceramics can be used as three-unit anterior bridges up to second premolar, while leucite glass-ceramics can be used up to posterior crowns only.\(^6\)
Glass-ceramics are a type of polycrystalline solid material with a small proportion of residual glassy phase prepared by the controlled crystallization of glasses. They are first formed as glasses, and then subjected to a regulated heat treatment process which allows the nucleation and growth of crystal phases from the parent glasses (Figure 2-3). The earliest literature reporting the formation of crystals from glasses can be dated back to 1739, when a French chemist Réaumur managed to convert glass with sand and gypsum into
opaque porcelain-like object, although the nucleation occurred essentially from glass surface. After his work, Stookey at Corning Glass Works accidentally developed the true glass-ceramics with fine grains in 1957 from photosensitive glasses which contain small amounts of metals. Afterwards, the research and development on glass-ceramics have attracted great interest, and both practical and theoretical investigations have been significantly progressed. Glass-ceramics have been widely used in both domestic and high technological applications for decades. The mechanisms of glass nucleation and kinetics of crystal growth were systematically investigated, leading to the theories of glass nucleation (more details in Section 2.3.2).

2.2.1 Fabrication of glass-ceramics

The heat treatment process is an essential step to convert the bulk glass into crystalline ceramics that possess much better mechanical properties than the original glass. Practically, there are two or more stages for nucleation and crystallization of glasses under a controllable manner (Figure 2-3). The proper nucleation density (the number of nuclei per unit volume), by controlling the nucleation temperature and time, and the subsequent crystal growth process are crucial to the development of fine-grained microstructure in the final glass-ceramic. The heating rate is generally not a key factor, as long as it would not cause cracking due to high stresses. Normally it can be set to 2–5 K/min or up to 10 K/min for thin glass articles.

The crystallization process of glass can be classified into four routes, as shown in Figure 2-4. Route 1 is direct precipitation of the major phase via homogeneous nucleation; route 2 is nucleation via homogeneous process and subsequent precipitation of the major phase on the nucleus surface via heterogeneous process; route 3 is precipitation of the major phase via homogeneous nucleation after phase separation; and route 4 is nucleation of “nucleant phase” via homogeneous process after phase separation, then precipitation of the major phase on the nucleus surface via heterogeneous process.
2.2.2 Applications of glass-ceramics

2.2.2.1 General applications

Glass-ceramics have wide applications in various areas of engineering and technology, including mechanical, thermal, electrical, electronic, aerospace, nuclear, optical, medical and dental fields. Some examples are bearings, heat exchangers, insulators, capacitors, nozzle cones of missiles, glass-ceramic to metal seals, magnetic memory disc substrates, and dental restorations. The biocompatible and bioactive glass-ceramics for medical use have attracted extensive attention for decades.

2.2.2.2 Applications in restorative dentistry

Glass-ceramics had been envisioned for dental use as early as 1968. After that, there are several types of glass-ceramics for restorative dentistry, including mica-based glass-ceramics (DICOR®), leucite-based glass-ceramics (IPS Empress®), and lithium disilicate-based glass-ceramics (such as IPS Empress® 2). They are used as restorative dental materials due to their excellent biocompatibility, desired mechanical and thermal properties, translucency, and chemical durability. Numerous investigations have been done on various glass-ceramic systems during past decades. Table 2-2 lists the evolution timeline of glass-ceramic dental restoration products. The detailed scientific information are also indicated.

The mica-based glass-ceramics are suitable for the applications of veneers, inlays, onlays, as well as dental crowns in restorative dentistry, but not recommended for fixed partial dentures, abutments, or dental bridges. The leucite-based glass-ceramics can be applied as...
laminate veneers, inlays and onlays, and anterior and posterior crowns, but insufficient for posterior fixed dental bridges. The lithium disilicate-based glass-ceramics are an important type of dental restorative material, which will be overviewed in detail in section 2.4. The examples of dental products are shown in Figure 2-5.

<table>
<thead>
<tr>
<th>Year</th>
<th>Product</th>
<th>Main crystal phase</th>
<th>Processing</th>
<th>Mechanism</th>
<th>Indications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1979</td>
<td>DICOR® MGC</td>
<td>tetrasilicic mica (KMg₂Si₂O₉F₂)</td>
<td>moulding, CAD/CAM</td>
<td>internal mechanisms, phase separation</td>
<td>first clinical tests, crowns, inlays</td>
</tr>
<tr>
<td>1991</td>
<td>IPS Empress®</td>
<td>leucite (KAl₂Si₆O₁₈)</td>
<td>moulding, pressing</td>
<td>surface mechanisms</td>
<td>inlays, crowns, veneers</td>
</tr>
<tr>
<td>1997</td>
<td>IPS Empress® Cosmo Post</td>
<td>lithium zirconium silicate (Li₂ZrSi₆O₁₈)</td>
<td>pressing on posts (ZrO₂), moulding</td>
<td>internal mechanisms</td>
<td>fixation of ZrO₂ posts</td>
</tr>
<tr>
<td>1997</td>
<td>IPS ProCAD®</td>
<td>leucite</td>
<td>CAD/CAM</td>
<td>surface mechanisms</td>
<td>inlays, crowns, veneers</td>
</tr>
<tr>
<td>1999</td>
<td>IPS d.SIGN®</td>
<td>leucite, fluoroapatite</td>
<td>sintering on metal frameworks</td>
<td>surface and heterogeneous internal nucleation</td>
<td>crowns and long-span bridges</td>
</tr>
<tr>
<td>2000</td>
<td>IPS Empress® 2</td>
<td>lithium disilicate</td>
<td>pressing</td>
<td>heterogeneous internal nucleation</td>
<td>crowns, three-unit anterior bridges</td>
</tr>
<tr>
<td></td>
<td>IPS Eris® (Eris for E2)</td>
<td>fluoroapatite</td>
<td>sintering on IPS Empress® 2</td>
<td>internal nucleation</td>
<td>veneers</td>
</tr>
<tr>
<td>2004</td>
<td>IPS Empress® Esthetic</td>
<td>leucite</td>
<td>moulding, pressing</td>
<td>inlays, crowns and small dental bridges</td>
<td></td>
</tr>
<tr>
<td>2005</td>
<td>IPS e.max® Press</td>
<td>lithium disilicate</td>
<td>moulding, pressing</td>
<td>inlays, crowns and small dental bridges</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IPS e.max® Zir Press</td>
<td>fluoroapatite</td>
<td>viscous flow on ZrO₂ frameworks</td>
<td>internal nucleation</td>
<td>crowns, posterior bridges</td>
</tr>
<tr>
<td></td>
<td>IPS e.max® CAD</td>
<td>lithium metasilicate/disilicate</td>
<td>CAD/CAM</td>
<td>heterogeneous internal nucleation</td>
<td>inlays, veneers, crowns, bridges</td>
</tr>
<tr>
<td></td>
<td>IPS e.max® Ceram</td>
<td>fluoroapatite</td>
<td>sintering on IPS e.max® CAD</td>
<td>internal nucleation</td>
<td></td>
</tr>
<tr>
<td>2009</td>
<td>IPS e.max® Press HT</td>
<td>moulding</td>
<td>moulding</td>
<td>inlays, onlays</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IPS e.max® CAD HT</td>
<td></td>
<td>CAD/CAM</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: DICOR® MGC is made by Corning Inc./Dentsply Int. ; IPS series are made by Ivoclar Vivadent AG, Schaan, Liechtenstein. Leucite: KAl₂Si₆O₁₈, lithium disilicate: Li₂Si₂O₅, Fluoroapatite: Ca₅(PO₄)₃F.
Figure 2-5.  (a) Products of leucite type glass–ceramics as dental inlay, veneer, and single crown from left; (b) Dental bridge reflected on a mirror to show the interior. The 3-unit bridge consists of a framework of lithium disilicate glass-ceramic (IPS Empress®2) veneered with fluoroapatite glass–ceramic (IPS Eris®).

2.3 Glass nucleation and crystallization

2.3.1 Nucleation and crystallization mechanisms

There are two types of nucleation mechanism: homogeneous and heterogeneous. Homogeneous nucleation deals with a stochastic process that nuclei precipitate in a homogeneous supercooled liquid without the assistance of external catalysts such as the container wall. By contrast, heterogeneous nucleation refers to a process that nuclei form on preferred nucleation sites including pre-existing interfaces, previously nucleated phases, surface defects and container wall. For glass-ceramic materials, there is another common classification of nucleation mechanism according to the location where nucleation takes places, i.e., volume (or bulk) nucleation and surface nucleation.

The kinetics and thermodynamics of nucleation have been well documented, including CNT and JMAK theory.

2.3.2 Classical nucleation theory (CNT)

The classical theory of nucleation phenomenon was first formulated by Volmer and Weber in 1926. The fundamental equations of CNT have been reviewed regularly by, for example James, Kelton, Weinberg, Fokin, and Zanotto.

The nucleation rate, defined as the number of nuclei formed per unit volume in unit time, is given by:

\[
I = I_0 \exp \left( -\frac{W^* + \Delta G_D}{k_B T} \right)
\]
where, $I_o$ is the pre-exponential term and given in Eqn. (2)\(^{53}\) and varies between $10^{41}$ and $10^{42} \text{ m}^{-3} \text{s}^{-1}$ for different condensed systems.\(^{59}\)

$$I_o = 2n_v V^{1/3} \left( \frac{k_B T}{h} \right) \left( \frac{\sigma}{k_B T} \right)^{1/2}$$  \hspace{1cm} (2)

$k_B$ and $h$ are the Boltzmann and Planck constants, respectively; $n_v$ is the number of formula units per unit volume of melt; $\sigma$ is interfacial energy for formation of a new surface of the nucleus; $W^*$ and $\Delta G_D$ are respectively the activation energy barriers for nucleation of a critical sized nucleus and for transfer of atoms through the solid-liquid interface to this nucleus. The critical size, $r^*$, of a spherical nucleus is given by:

$$r^* = \frac{2\sigma}{\Delta G_V}$$ \hspace{1cm} (3)

Figure 2-6. The relationship between the change in Gibbs free energy ($\Delta G$) and the radius of nucleus ($r$). After Höland et al.\(^{60}\)

The activation energy for the formation of a stable nucleus is:

$$W_{homo}^* = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G_V^2}$$ \hspace{1cm} (4)

where, $\Delta G_V = G_l - G_c$ is the difference between the free energies of liquid and crystal per unit volume of the crystal.

It is noted that the above equations are valid for homogeneous nucleation only except for
Eqn (3) that also holds for heterogeneous nucleation. The nucleation process defined by the above equation is steady state nucleation, i.e. time-independent. Unlike in metals, glasses possess very high viscosity and therefore establishing a steady state might take a long time. The time-lag $\tau$, defined as the time for establishing steady-state nucleation in a glass system, is given by

$$\tau = \frac{16h}{\pi} \frac{\sigma}{\Delta G^2 a^4} \exp \left( \frac{\Delta G_D}{k_B T} \right)$$

(5)

where $a$ is the mean size of structural/formula units. For simplicity, the number of super-critical nuclei per unit volume of the system, $N_v$, at time $t$ can be given by:

$$N_v(t) = I_{st} \left( t - \frac{\pi^2}{6} \tau \right)$$

(6)

Then, the time lag $\tau$ can be easily estimated by using the induction period $t_{ind}$.

$$\tau = \frac{6}{\pi^2} t_{ind}$$

(7)

In the case of heterogeneous nucleation (Figure 2-7), steady-state nucleation rate is given by

$$I_{st}^{het} \approx N^S \frac{k_B T}{h} \exp \left( -\frac{W_{het}^* + \Delta G_D}{k_B T} \right)$$

(8)

$$W_{het}^* = W_{home}^* \emptyset$$

(9)

$$\emptyset = f(\theta) = \frac{1}{4} (1 - \cos \theta)^2 (2 + \cos \theta)$$

(10)

where $N^S$ is the number of ‘structural units’ in contact with the catalysing surface per unit volume; $\theta$ is the contact angle.

---

**Figure 2-7.** Model of heterogeneous nucleation. $H$ represents the heterogeneous substrate, $S$ represents the nucleus, and $L$ the parent glass, $\theta$ shows the contact angle.

Two experimental results are shown as examples in Figure 2-8, illustrating the steady-state nucleation rate and induction period of lithium disilicate glass as functions of temperature, $T$. 
or inverse temperature, $1/T$.

Figure 2-8. Experimental steady-state nucleation rates (a), and induction periods (b) versus temperature and inverse temperature, respectively, for lithium disilicate glass.$^{35,61}$

Figure 2-9 illustrates the temperature-dependent nucleation and crystallization rates in glasses. Below the melting temperature ($T_m$), where the melt remains effectively free of nuclei. As the temperature decreases further, $\Delta G_V$ increases, thus decreasing the value of the critical radius, $r^*$. Consequently, the critical radius will be only a few tens of nanometers, and the formation probability of a nucleus will become significant so that nuclei will form in detectable quantities. While, it needs a degree of undercooling to allow the formation of nuclei, so there exists a metastable zone of undercooling in the melt (Figure 2-9).$^{62}$

Figure 2-9. Schematic representation of the classical rates for nucleation and crystallization in glasses. After Karpukhina et al.$^{63}$ The Ostwald-Miers temperature range is a metastable zone of undercooling.
2.3.3 Crystallization kinetics

The understanding of crystallization kinetics of glasses is of essential significance to both glass formation and glass-ceramic fabrication. The effects of annealing temperature and time on the phase transformation and as-received microstructure of glass-ceramics are generally considered, and thus the crystallization kinetics of both the isothermal and non-isothermal processes of glasses have attracted wide interest.\textsuperscript{64}

2.3.3.1 Isothermal crystallization (JMAK isothermal kinetic model)

The theory of crystallization kinetics under isothermal conditions was developed by Johnson and Mehl, Avrami, and Kolmogorov in the late 1930s\textsuperscript{53}. It is well known as JMAK kinetic model which is the basis of kinetic theories of glass formation. Assuming that the transformation is predominantly by nucleation and growth of the crystals, dispersed throughout the volume of the material, the volume fraction $x(t)$ crystallized after time $t$ can be expressed as

$$x(t) = 1 - \exp\left[-g \int_0^t I(t') \left[\int_{t'}^t U(t'') dt''\right]^3 dt'\right]$$  (11)

where, $g$ is the shape factor, equal to $4\pi/3$ for spherical crystals, and $I$ and $U$ are the rates of nucleation and growth, respectively.

A general simple expression is

$$x(t) = 1 - \exp(-Kt^n)$$  (12)

or

$$\ln(-\ln(1 - x)) = \ln K + n \ln t$$  (13)

where Avrami exponent, $n$, varies depending on both nucleation and growth mechanisms (see Table 2-3);\textsuperscript{59} the kinetic constant, $K$, incorporates the rates of nucleation and growth. Specifically,

$$n = 4, \quad K = \frac{g}{4} IU^3$$ (homogeneous nucleation)

$$n = 3, \quad K = gN_o U^3$$ (heterogeneous nucleation)

The values of $K$ and $n$ can be determined by fitting the experimental data of $x(t)$ to Eq. (12). JMAK equations have yielded useful information on nucleation kinetics.

However, it should be emphasized that the application of JMAK equations is based on
several assumptions: (1) isothermal crystallization conditions; (2) random or uniform nucleation; (3) growth rate of new phase is controlled by temperature and is independent of time, which means a steady state. These three assumptions should be carefully considered before the JMAK equation is used. In addition, the JMAK analysis must be supported by complementary studies (such as microscopy), otherwise misinterpretation may occur.

<table>
<thead>
<tr>
<th>Table 2-3. Typical values of kinetic exponent for crystallization processes in isothermal conditions(^{59,65})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transformation</td>
</tr>
<tr>
<td>(I) Polymorphic changes, discontinuous precipitation, eutectoid reactions, interface controlled growth etc.</td>
</tr>
<tr>
<td>Increasing nucleation rate</td>
</tr>
<tr>
<td>Constant nucleation rate</td>
</tr>
<tr>
<td>Decreasing nucleation rate</td>
</tr>
<tr>
<td>Zero nucleation rate (site saturation)</td>
</tr>
<tr>
<td>Grain edge nucleation after saturation</td>
</tr>
<tr>
<td>Grain boundary nucleation after saturation</td>
</tr>
<tr>
<td>(II) Diffusion controlled growth</td>
</tr>
<tr>
<td>All shapes growing from small dimensions</td>
</tr>
<tr>
<td>Increasing nucleation rate</td>
</tr>
<tr>
<td>Constant nucleation rate</td>
</tr>
<tr>
<td>Decreasing nucleation rate</td>
</tr>
<tr>
<td>Zero nucleation rate</td>
</tr>
<tr>
<td>Growth of particles of appreciable initial volume</td>
</tr>
<tr>
<td>Needles and plates of finite long dimensions</td>
</tr>
<tr>
<td>Thickening of long cylinders (needles)</td>
</tr>
<tr>
<td>Thickening of very large plates</td>
</tr>
</tbody>
</table>

### 2.3.3.2 Non-isothermal crystallization

The thermoanalytical techniques, such as differential scanning calorimetry (DSC) or differential thermal analysis (DTA), have been used to study the non-isothermal crystallization kinetics.\(^{67-69}\) Hammetter et al.\(^{70}\) studied the crystallization kinetics of a complex lithium silicate glass-ceramic. The activation energy for crystallization was determined using a variable heating rate method based on the following non-isothermal kinetic models which was extended from JMAK model\(^{71}\):

\[
\nu \exp \left( -\frac{E}{RT_p} \right) = \frac{E}{RT_p^2} \alpha
\]

or
\[
\ln \left( \frac{T_p^2}{\alpha} \right) = \ln \left( \frac{E}{R} \right) - \ln v + \frac{E}{RT_p} \tag{15}
\]

where \( T_p \) is the temperature of the peak maximum, \( \alpha \) is the experimental heating rate, \( E \) is the activation energy, \( v \) is a frequency factor (as it has the unit \( s^{-1} \)), and \( R \) is the gas constant.

It is accepted that the JMAK model has limited applicability for the non-isothermal transformations. One of the reasons is that both nucleation and growth rates are no longer constant under non-isothermal conditions. Málek described several testing methods for checking the applicability of the JMAK model in non-isothermal measurements.\(^{65}\) It is valid only if the crystals of a new phase grow from nuclei of a constant number and the nucleation is completed prior to crystal growth.\(^{72}\) Another method for testing the applicability was proposed by Henderson.\(^{68, 69}\) A general expression\(^{65, 73}\) for the fraction extent of crystallization, \( \alpha_p \), at the DSC/DTA peak is proposed as

\[
\alpha_p = 1 - \exp \left( \frac{1-x_p \pi(x_p)}{n} - 1 \right) \tag{16}
\]

where the temperature integral \( x_p \) is the algebraic ratio of \( \frac{E}{RT_p} \), and \( \pi(x_p) \) is an approximation of \( x_p \) and has a rational expression of \( \frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \).\(^{73}\)

### 2.3.4 Measurement of crystal nucleation rate

#### 2.3.4.1 Measurement methods

In order to measure the nucleation rate, \( I = \frac{dN}{dt} \), by counting the number of the nuclei, these nuclei must be developed to a visible size. There are two most common methods for estimating the nucleation rate by counting the number density of crystals.

If the nucleation and growth rate curves are weakly overlapped as shown in Figure 2-9, i.e., nucleation \( (I) \) and growth \( (U) \) rates meet the conditions of \( I(T_G) \ll I(T_N) \) and \( U(T_G) \gg U(T_N) \), a double-stage annealing (known as Tammann or “development” method) is used.\(^{53}\) That is to say, crystals first nucleate at a low temperature \( T_N \) and then grow up to a detectable size at a higher temperature \( T_G \). Figure 2-10 shows a typical curve, obtained by this method, of the number density of lithium disilicate crystals in a stoichiometric \( \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \) glass versus nucleation time. On the other hand, when the \( I(T) \) and \( U(T) \) curves are considerably overlapped, the number density of crystals can be directly measured by using single-stage annealing (direct method) after heat treatment at \( T_N \).
2.3.4.2 Marotta method

The temperature-dependent nucleation rate of glass can be examined according to Marotta method. Generally, a glass sample without pre-treatment is subjected to thermal analysis at a given ramp rate, where a peak temperature \( T_p \) can be obtained due to the exothermic effect of nucleation. Then, the peak temperatures \( T'_p \) of glass samples that pre-treated at different isothermal conditions (for the same period) are recorded at the same ramp rate. The peak shift, \( \Delta T_p = T_p - T'_p \), can be observed for each measurement.

A larger peak shift reflects a higher nucleation rate at the corresponding temperature of the isothermal condition. A curve incorporating \( \Delta T_p \) and \( T \) is shown in Figure 2-11 as an example.
2.4 Lithium disilicate glass-ceramics

Lithium disilicate glass-ceramics was first investigated by Stookey at Corning Glass Works in the 1950s. They can be fabricated from various glasses in SiO$_2$–Li$_2$O related systems. The volume crystallization throughout the glass can be achieved with P$_2$O$_5$, a most widely used component, act as nucleating agent. Therefore, the glass-ceramics generally consist of a large volume fraction of fine Li$_2$Si$_2$O$_5$ (lithium disilicate, LS$_2$) crystals and a minor amount of Li$_3$PO$_4$ (lithium phosphate, LP) crystals that are uniformly dispersed in the glassy matrix. The common values of flexural strength and fracture toughness are about 215~350 MPa and 3~3.4 MPa·m$^{0.5}$. The linear CTE is about 10.6 ppm/K.

The Li$_2$SiO$_3$ (lithium metasilicate, LS) phase may (but does not necessarily have to) form in the glasses, depending on the glass composition. The LS possesses relatively lower strength and hardness than lithium disilicate phase. This feature offers a favourable advantage that the partially crystallized materials have superior machinability via the CAD/CAM method and then can be fully crystallized.

In terms of crystal structure, the stable lithium disilicate (Li$_2$Si$_2$O$_5$) is an orthorhombic layer silicate with space group ccc2 (at room temperature: $a = 5.807$ Å, $b = 14.582$ Å, $c = 4.773$ Å), and its crystal structure is presented in Figure 2-12. Interestingly, a metastable lithium disilicate with orthorhombic space group $Pbcn$ ($a = 5.683$, $b = 4.784$, $c = 14.648$, Å) was reported by Smith et al. 

![Crystal structure of stable lithium disilicate viewing from the a axis](image)

Figure 2-12. Crystal structure of stable lithium disilicate viewing from the a axis
2.4.1 Fabrication techniques

There are generally two methods for the fabrication of lithium disilicate glass–ceramics. One is to apply thermal treatment on a bulk glass after melting and shaping.\textsuperscript{2, 31, 34, 77-79} With this method, the base glass will be converted into a fine grained ceramic by an appropriate heat treatment.\textsuperscript{31} Generally, a special nucleating agent is employed for the bulk nucleation (heterogeneous) and crystallization of glass. A typical two-stage treatment profile is shown in Figure 2-3. More holding stages may be adopted to adjust the microstructure development. Chemically homogeneous and bubble-free glass is critical to ensure the crystallised microstructure and the properties attained in the final glass-ceramics.

The other method is via sintering of compacted powders which can be either glass only (glass frits\textsuperscript{80, 81} or sol-gel\textsuperscript{82}) or a mixture of glass and ceramic. This method can take on various shaping techniques such as cold pressing, slip casting, tape casting, or powder coating, followed by sintering to achieve full densification.\textsuperscript{83} It also allows the addition of reinforcing phases into the glass powder for enhancing/toughening the glass-ceramics,\textsuperscript{84} or to include some pigments to impart the end product with tooth-like optical properties.\textsuperscript{85} Besides, the powdered glass results in uniform surface nucleation during heat treatment, so no special nucleating agent is required.\textsuperscript{44} Since surface nucleation and crystallization take place during sintering, strong tendency of generating internal nucleation is not required for the base glasses of the sintered glass-ceramics.\textsuperscript{86} Accordingly, it is possible to produce glass-ceramics from a much wider range of composition by this method without the selection of a proper nucleating agent.

However, the issue of densification arises, and correspondingly the potential effect of porosity on both mechanical properties and translucency\textsuperscript{87} has to be considered. This method essentially follows the principles of conventional powder metallurgical technology.\textsuperscript{88, 89}

2.4.1.1 Phase diagram of binary SiO\textsubscript{2}–Li\textsubscript{2}O system

The binary SiO\textsubscript{2}–Li\textsubscript{2}O system (Figure 2-13) was regarded as a model system for the study of glass nucleation and crystallization mechanisms. Especially the stoichiometric 2SiO\textsubscript{2}–Li\textsubscript{2}O system received extensive investigation as it forms lithium disilicate (Li\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}). For improving the properties of this material, additional components have been added to the
nonstoichiometric glass system. Thus, varieties of multi-component lithium disilicate glass systems have been developed. Their excellent flexural strength and toughness have expanded the range of indications of glass–ceramics to dental bridges involving anterior region.\textsuperscript{46}

![Phase diagram of the Li\textsubscript{2}O–SiO\textsubscript{2} system showing solid-solution regions and liquid–liquid phase separation region.\textsuperscript{90} (c: cristobalite; t: tridymite; L: liquid; ss: solid-solution; q: quartz)](image)

\textbf{2.4.1.2 General chemical compositions}

The base glasses for the production of glass-ceramics must meet two requirements: they must not devitrify during the glass-forming process, while they are able to crystallise on reheating. For these purpose, a glass normally consists of conventional glass-forming oxides (such as SiO\textsubscript{2}) and special modifying oxides having small cations (such as Li\textsuperscript{+}, Mg\textsuperscript{2+} and Zn\textsuperscript{2+}) with high field strength for the promotion of phase separation.
Chapter 2 | Literature Review

Table 2-4. Patents related to lithium disilicate glass-ceramics for dental applications.

<table>
<thead>
<tr>
<th>Group</th>
<th>Patent Name</th>
<th>Patent No.</th>
<th>Year</th>
<th>Inventor</th>
<th>Company</th>
<th>Info</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Lithium disilicate-containing glass-ceramics some of which are self-glazing</td>
<td>US5219799</td>
<td>Jun 1993</td>
<td>Beall, G. H. Echeverria, L.M. Morrissey, J. Pierson, J.</td>
<td>Corning Inc. @NY, USA</td>
<td>Certain compositions within covered ranges are self-glazing.</td>
</tr>
<tr>
<td>C</td>
<td>Lithium disilicate glass ceramics dental product /Sinterable lithium disilicate glass ceramic</td>
<td>US6342458/US5614893 US6606884</td>
<td>Jan 2002/Jan 2003 Feb 2003 Aug 2003</td>
<td>Schweiger, M. Frank, M. Rheinberger, V. Höland, W.</td>
<td>above</td>
<td>High-strength sinterable lithium disilicate glass ceramics are described which can be further processed in particular by pressing in the viscous state to shaped dental products.</td>
</tr>
<tr>
<td>H</td>
<td>High-strength dental restorations</td>
<td>EP1797015 WO06042046</td>
<td>Jun 2007 Apr 2006</td>
<td>Brodkin, D. Panzera, C. et al.</td>
<td>Pentron Laboratory Technologies, LLC @CT, USA</td>
<td>The glass-ceramics have good pressability.</td>
</tr>
<tr>
<td>I</td>
<td>Castable glass-ceramic composition useful as dental restorative</td>
<td>US4515634</td>
<td>May 1985</td>
<td>Wu, J. M. Cannon, W. R. Panzera, C.</td>
<td>Johnson &amp; Johnson Dental Products Company @NJ, USA</td>
<td>With 8%~10% of GeO₂ in the final composition. The material has improved castability.</td>
</tr>
<tr>
<td>J</td>
<td>Lithium silicate glass ceramic for fabrication of dental appliances</td>
<td>US20090258778</td>
<td>Oct 2009</td>
<td>Castillo, R.</td>
<td>James R. Glidewell Dental Ceramics, Inc. @CA, USA</td>
<td>Lithium disilicate glass ceramics can be easily mechanically machined in an intermediate stage of the crystallization and represent high-strength, highly translucent and chemically stable glass ceramics after complete crystallization.</td>
</tr>
<tr>
<td>K</td>
<td>Lithium disilicate glass ceramics, method for the production thereof and use thereof</td>
<td>US20120309607</td>
<td>Jun 2011</td>
<td>Durschang, B. Probst, J. Thiel, N. Bibus, J. Vollmann, M. Schusser, U.</td>
<td>Fraunhofer Ges Forschung, etc. @Munich, Germany</td>
<td>Lithium disilicate glass ceramics can be easily mechanically machined in an intermediate stage of the crystallization and represent high-strength, highly translucent and chemically stable glass ceramics after complete crystallization.</td>
</tr>
</tbody>
</table>
Table 2-5. Composition ranges of the patented lithium disilicate glass-ceramics for dental restorations.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>SiO₂</th>
<th>Li₂O</th>
<th>ZnO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>ZrO₂</th>
<th>Al₂O₃</th>
<th>B₂O₃</th>
<th>Me₈O</th>
<th>colorants</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>65-80</td>
<td>8-19</td>
<td>0-7</td>
<td>0-7</td>
<td>0-5</td>
<td>1.5-7</td>
<td>0-3</td>
<td>0-11</td>
<td></td>
<td></td>
<td>Ca 0-10 Sr 0-6 Ba 0-6</td>
<td>/0-0.1%Pd</td>
</tr>
<tr>
<td>B-C</td>
<td>57-80</td>
<td>11-19</td>
<td>0-8</td>
<td>0-13.5</td>
<td>0-11</td>
<td>0-10</td>
<td>0-5</td>
<td></td>
<td></td>
<td></td>
<td>Mg 0-5, MgZn 0.1-9</td>
<td>0-8, La 0.1-6</td>
</tr>
<tr>
<td>D</td>
<td>64-73</td>
<td>13-17</td>
<td>0.5-6</td>
<td>2-5</td>
<td>0-2</td>
<td>2-5</td>
<td>0-2</td>
<td>0.5-5</td>
<td></td>
<td></td>
<td>MgCaSrBa 0-7</td>
<td>0.5-7.5</td>
</tr>
<tr>
<td>E</td>
<td>64-75</td>
<td>13-17</td>
<td>free</td>
<td>2-5</td>
<td>0-2</td>
<td>2-5</td>
<td>0.1-4</td>
<td>0.5-5</td>
<td></td>
<td></td>
<td>MgCaSrBa 0-3</td>
<td>0.5-7.5</td>
</tr>
<tr>
<td>F-H</td>
<td>62-85</td>
<td>8-19</td>
<td>0-5</td>
<td>0-5</td>
<td>0.5-12</td>
<td>0-3</td>
<td>1.5-10</td>
<td>0-4.9</td>
<td>Ca 0-7, Mg 0-2, Ba 0-7</td>
<td>YCeEuTbTa</td>
<td>wt%</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>37-74.3</td>
<td>24-33</td>
<td>0-2</td>
<td>0-2.4</td>
<td>0-4</td>
<td>0.5-4</td>
<td>Ca 1-10</td>
<td>Mg 0-2</td>
<td>Ti 0-4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>53-59</td>
<td>14-16</td>
<td>-</td>
<td>3.5-4.1</td>
<td>2.7-4</td>
<td>2.5-6</td>
<td>2.5-3.4</td>
<td>Ti 0.5-1.8, Ge 0-8.4, Sm 0-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>55-70</td>
<td>10-15</td>
<td>0.1-5</td>
<td>10-20</td>
<td>0.1-5</td>
<td>BPBaNaZnCaYTiNiTaLa 0-10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note 1 – All elements in the table denote the oxides of them; letters A-K in ref column denote the groups in Table 2-4.

A wide range of compositions have been investigated in the literature and patents. Table 2-4 summarizes the patent search with regard to lithium disilicate glass-ceramics for dental restorative applications. Table 2-5 presents the patented chemical compositions of lithium disilicate glass-ceramics. Some components are incorporated in to the base glass to obtain the desired properties of final glass-ceramic products. For instance, Al₂O₃ and K₂O can improve the chemical durability of lithium disilicate glass-ceramics with nonstoichiometric compositions to a significant extent by forming a glass matrix similar to that of feldspar, K₂O·Al₂O₃·6SiO₂. Some other oxides such as TiO₂, CeO₂ and Fe₂O₃ (see patents US6514893/ US6606884) are used as colorants.

2.4.1.3 Effect of nucleating agents

Bulk nucleation in some glass-ceramic systems such as the Na₂O-BaO-SiO₂ system is able to accomplish without the aid of special additives. More commonly, the following additives are used as nucleating agents in glass, to promote phase separation: TiO₂, ZrO₂, P₂O₅, Ta₂O₅, WO₃, Fe₂O₃, and F (fluorides).

2.4.1.3.1 TiO₂

In 1956, Stookey invented highly crystallized glass-ceramics by incorporating 2 to 20 wt% TiO₂ into the SiO₂-Al₂O₃-Li₂O and SiO₂-Al₂O₃-MgO systems for the development of
glass-ceramics with minimal thermal expansion and high strength, respectively.\textsuperscript{41, 93} Since then, TiO\textsubscript{2} is widely used as an efficient nucleating agent for the fabrication of glass-ceramics. TiO\textsubscript{2} is soluble in a variety range of molten glasses. It can also act as fluxing agent.\textsuperscript{86} Its high ionic field strength tends to encourage the liquid–liquid phase separation phenomenon.\textsuperscript{94} The phase separation may be initiated during the cooling of melt, which plays an important role in the controlled glass crystallization. As titania does not form crystal phases at the early stage of crystallization but it is normally detected after the precipitation of other phases,\textsuperscript{39} the heterogeneous nucleation of main crystalline phases from parent glasses is led by the formation of TiO\textsubscript{2}-rich droplets rather than the related crystals.

Specifically, TiO\textsubscript{2} does not have nucleating effect unless there are certain divalent metal oxides (RO) in the glasses, such as MgO. Under this circumstance, the titania-rich droplets crystallize in the form of titanates (RO\textcdot TiO\textsubscript{2}) with hexagonal ilmenite-type structure, rather than the crystalline TiO\textsubscript{2} phases at the late stages.\textsuperscript{95} The reason from the structural aspect is that, Ti\textsuperscript{4+} ion, with ionic radius of 0.68 Å, would occupy the tetrahedral (four-fold coordinated) network-forming sites during melting. It tends to revert to its low-temperature state of six-fold coordination and thus be trapped in the silicate network. With a divalent metal oxide, titania is then likely to form a separate phase under reheating.

\textbf{2.4.1.3.2 ZrO\textsubscript{2}}

Zirconia is another example of intermediate oxide that exhibit similar behaviour with titania. The use of zirconia in glasses as nucleating agent was first described by Sawai in 1961.\textsuperscript{96} The solubility of ZrO\textsubscript{2} is limited to about 4 wt%, much less than that of titania. Thus, it cannot act as fluxing agent but will increase the liquidus temperature of the glass. Tashiro \textit{et al.} used zirconia to produce a transparent low-expansion glass-ceramic “Neoceram”.\textsuperscript{43, 97} They found that the solubility of ZrO\textsubscript{2} is significantly increased when P\textsubscript{2}O\textsubscript{5} is present in silicate melts. As P\textsubscript{2}O\textsubscript{5} also has nucleating effect, it is hard to tell which constituent contributes to the improved nucleation of glasses with both oxides present. Schweiger \textit{et al.}\textsuperscript{98} prepared the SiO\textsubscript{2}–Li\textsubscript{2}O–ZrO\textsubscript{2}–P\textsubscript{2}O\textsubscript{5} glass-ceramics with 15 wt% and 20 wt% ZrO\textsubscript{2} as a dentin buildup material, by hot-press sintering with glass powder. Apel \textit{et al.} illustrated that zirconia influences the crystallization by hampering crystal growth of both LS and LS\textsubscript{2} in the
same system.\textsuperscript{91}

ZrO\(_2\) has another advantage that it does not give any tinge to the products even when used in large amounts.\textsuperscript{86} Further, the inclusion of zirconia may enhance the toughness of glass-ceramic if it crystallizes in tetragonal zirconia polycrystal (TZP) phase, a partially stabilized ZrO\(_2\) with 3 mol\% Y\(_2\)O\(_3\). However, the transformation toughening effect\textsuperscript{18} may not be achieved, if zirconia crystallizes as a stable cubic polymorph or it may not precipitate from the glass matrix at all.

2.4.1.3.3 \(\text{P}_2\text{O}_5\)

The phosphorus pentoxide (\(\text{P}_2\text{O}_5\)) as nucleating agent was discovered in 1963 by McMillan and Partridge.\textsuperscript{99} The phosphorus ion (P\(^{5+}\)) of this oxide has a charge difference with that of the principal network-forming ion (Si\(^{4+}\)), which gives a double-bonded oxygen ion within the silicate network favouring the separation of phosphorus groups from the network.\textsuperscript{39} Moderate amount (~1 mol\%) of \(\text{P}_2\text{O}_5\) can induce amorphous phase separation and increase the crystal nucleation rate, simultaneously.\textsuperscript{31, 94, 100} The lithium disilicate glass with less \(\text{P}_2\text{O}_5\) shows surface crystallization.\textsuperscript{77} Besides, it was observed that \(\text{P}_2\text{O}_5\) in small addition reduced the crystal growth rates of glasses in Li\(_2\)O-SiO\(_2\) related systems, thereby suppressing glass crystallization, at the glass-working temperature range.\textsuperscript{39}

The nucleating mechanism of \(\text{P}_2\text{O}_5\) has been widely debated over decades. Headley \textit{et al.} (1984)\textsuperscript{101} studied the crystallization mechanism of a special lithium disilicate glass (for the metal-sealing applications) where Li\(_3\)PO\(_4\) crystals was precipitated at sealing temperature of glass to metal (1000 °C, for 20 min). Within the sealing step, the Li\(_3\)PO\(_4\) crystals grow via Ostwald ripening, and then act as nucleating sites for cristobalite (SiO\(_2\)), Li\(_2\)SiO\(_3\) and Li\(_2\)Si\(_2\)O\(_5\) during the subsequent heat treatment process, as shown in Figure 2-14.\textsuperscript{101} These results lead to a heterogeneous nucleation process of crystals by epitaxial growth on exposed facets of Li\(_3\)PO\(_4\) crystallites. Some other investigations\textsuperscript{18, 33} support this epitaxial growth mechanism in which the Li\(_3\)PO\(_4\) crystals act as heterogeneous nucleation sites in the conventional heat treated glasses.\textsuperscript{31, 100} It is noted, however that no convincing data were provided.
Figure 2-14. Epitaxial growth of cristobalite (CR), lithium metasilicate (LS), and lithium disilicate (LS2) on a lithium orthophosphate (LP) crystal.  

In a typical heat treatment of lithium disilicate glasses for dental applications, however, the epitaxy mechanism is questionable because the above “seeding” process of Li$_3$PO$_4$ crystals is generally not applied in the case of dental applications. Instead, Li$_3$PO$_4$ crystals precipitated after the formation of LS and/or LS$_2$. It therefore indicates that the silicate phases may not be directly nucleated by Li$_3$PO$_4$ crystals; more possibly, the nucleation of lithium disilicate is triggered by the steep compositional gradients resulting from microstructural heterogeneities. The phosphorus species in the initial glass would lead to a phase separation into silica rich droplets and lithia rich matrix phases on heat treatment, which was evidenced by solid state nuclear magnetic resonance (NMR) results of Bischoff et al.

2.4.1.4 Role of other oxides

Alkali metal oxides, such as Li$_2$O, Na$_2$O and K$_2$O, can lower the melting temperature of glasses, while high proportions of them may lead to poor chemical stability of glasses or glass-ceramics. The “mixed alkali effect”, by mixing two or more alkali metal oxides, will improve the chemical stability, compared to the situation of using either oxide alone with the same total concentration.

The alumina, zinc oxide, and alkaline earth oxides (e.g. MgO and CaO) are beneficial to the chemical stability of glasses; and in some composition, boric oxide (B$_2$O$_3$) in small additions tends to be concentrated in residual glassy phase thus enhances its chemical stability. ZnO variation mainly influenced the translucency of the glass-ceramics. Vanadium pentoxide (V$_2$O$_5$) can also act as nucleating agent like P$_2$O$_5$ to lithia-silica related glasses attributing to
the similar structural role, but are less effective. Fluorides such as NaF, Na₃AlF₆ and Na₂SiF₆, are not suitable for nucleating agents as only very small amounts can be dissolved in silicate glasses.³⁹

During the compositional design of glass-ceramics, the possibility of devitrification in a controllable manner is important to ensure that glassy structure is retained after cooling down to room temperature, i.e. devitrification should be avoided. Alumina will suppress the devitrification during cooling of the glass, even in a few percent, and so does zinc oxide. However, B₂O₃ may lower the refractoriness of glassy phase when its content excesses a certain limitation (2 or 3 wt%).³⁹

2.4.2  Phase formation mechanisms

In lithium disilicate glass-ceramics, lithium disilicate and metasilicate are dominant phases during the glass crystallization. They are generally formed via the reactions given in Eqns. 20–21.³¹ The formation mechanism for them has been widely investigated by various methods, including XRD, TEM,⁹⁰, ¹⁰⁶ NMR,¹⁰⁷, ¹⁰⁸ IR, and Raman spectroscopy or their combination.¹⁰⁹

Based on powder diffraction studies, the mechanisms for the formation of lithium metasilicate (LS) and disilicate (LS₂) can be given by Eqns. (17–19). Instead, ²⁹Si NMR spectrum is able to provide information on the local environments of silicon. Bischoff et al. investigated the phase evolution in lithium disilicate glass-ceramics of a SiO₂–Li₂O–P₂O₅–Al₂O₃–K₂O–(ZrO₂) system by a comprehensive solid state NMR study,¹⁰⁴ in which the LS and LS₂ phases nucleated in simultaneously. The structural evolution from glass to glass-ceramic (Figure 2-15) can be interpreted by quantitative analyses of overall NMR results. The formation of LS phase from glass is quantitatively revealed to be via Eqn. 21.¹⁰⁴ The transformation of LS phase to LS₂ at a higher temperature is via Eqn. 22.

\[
\text{Li}_2\text{O (glass) + SiO}_2\ (\text{glass}) = \text{Li}_2\text{SiO}_3\ (\text{cryst}) \quad \text{Eqn. 17}
\]
\[
\text{Li}_2\text{SiO}_3\ (\text{cryst}) + \text{SiO}_2\ (\text{glass}) = \text{Li}_2\text{Si}_2\text{O}_5\ (\text{cryst}) \quad \text{Eqn. 18}
\]
\[
\text{Li}_2\text{O (glass) + 2 SiO}_2\ (\text{glass}) = \text{Li}_2\text{Si}_2\text{O}_5\ (\text{cryst}) \quad \text{Eqn. 19}
\]
\[
3 \text{Li}_2\text{O (glass) + P}_2\text{O}_5\ (\text{glass}) = 2 \text{Li}_3\text{PO}_4\ (\text{cryst}) \quad \text{Eqn. 20}
\]
Figure 2-15. Schematic diagram of structural changes occurring in the residual glassy phase during crystallization of lithium disilicate glasses involving lithium metasilicate. *Left:* starting glass; *middle:* remaining glass phase after nucleation of LS; *right:* remaining glass phase after transformation of LS to LS$_2$ at a higher temperature. Open circles are demonstrating oxygen atoms.$^{104}$

Figure 2-16. (a) The evolution of different phosphate units in lithium disilicate glasses at 455 °C, $^{106}$ (b) the evolution of $^{31}$P MAS-NMR spectra of a glass after treatment$^{104}$.

The crystallization of Li$_3$PO$_4$ is given by Eqn. 20. Holland *et al.* investigated the early stages of crystallization of simple lithium disilicate glasses containing P$_2$O$_5$, and the evolution of local structure was detected by applying days of annealing at 455 °C (Figure 2-16a).$^{106}$ There are dominant ortho- and minor pyro- phosphate species (with chemical shift of 9.7±0.3 ppm and 0.0±0.2 ppm, respectively) in the base glass, and significant reduction of orthophosphate species to form others (pyro- and meta- species) is concurrent with the
crystallization of silicate phases (Eqn. 23).
\[ 2 Q^{(3)} \text{(glass)} = Q^{(2)} \text{(cryst)} + Q^{(4)} \text{(glass)} \]  
\[ Q^{(2)} \text{(cryst)} + Q^{(4)} \text{(glass)} = Q^{(3)} \text{(cryst)} \]  
\[ \text{ortho-P (glass)} = \text{pryo-P + meta-P (cryst)} \]

Eqn. 21
Eqn. 22
Eqn. 23

The role of P$_2$O$_5$ on glass nucleation is generally concerned for the understanding of the nucleation mechanism. Headley et al. suggested an epitaxial growth mechanism of silicate phases on LP crystals which were pre-seeded in base glass.$^{101}$ In a conventional process, however, the crystallization of Li$_3$PO$_4$ has been widely observed to take place after nucleation of LS and LS$_2$. Such a controversy deserves further investigations into the role of P$_2$O$_5$ and by which route (in Figure 2-4) the glasses nucleate. Bischoff et al. found that the P-containing phases are strongly disordered at low temperatures and retained until the transformation of LS to LS$_2$ is observed at 850 °C.$^{104}$

2.4.3 Microstructure

As the development of glass-ceramics is based on lithium disilicate glasses, their microstructure is also related to the initial structure of parent glasses. The phenomenon of phase separation could result in a heterogeneous mixture of two immiscible amorphous phases in the parent glasses (Figure 2-17).$^{110}$ It may also be effective in increasing the driving force for the precipitation of crystalline phases from glass matrix. Some typical morphologies of lithium disilicate glass-ceramics are shown in Figure 2-18.

Figure 2-17. The microstructure of (a) a non-annealed bulk lithium disilicate glass and (b) glass-ceramic annealed at 800 °C.$^{110}$
It is well recognized that microstructure is the key to the mechanical and optical properties of glass-ceramics. The development of a desired microstructure is highly correlated to the glass composition and also controlled by annealing processes. Therefore, the fabrication of high performance glass-ceramics essentially requires an appropriate glass compositional design and microstructure tailoring.

The precipitated phases, crystallinity, and crystal morphologies, specific ratio, grain sizes and distribution, as well as the chemical composition of residual glassy phase, are important factors contributing to the mechanical properties. The crystallinity also largely determines the translucency of glass-ceramics.

2.4.4 Properties

The term “restorative material” is describing a material that is utilized to replace the incisal and/or dentinal portion of the tooth and to reconstruct the tooth to its original shape and function, rather than dental implants and root fillers which are inserted into human body. For dental restorative applications, the candidate materials need to fulfill the standards (ISO 6872) such as high chemical durability, adjustable optical properties, and excellent mechanical properties. In terms of the optical properties, dental materials must exhibit the translucency, colour, opalescence, and fluorescence of natural teeth. In order to achieve long service life, mechanical properties such as flexural strength and fracture toughness even have to surpass those of natural teeth to withstand any masticatory stress induced on the restoration, and are particularly important for dental bridges. The properties such as shade,
wear, hardness of dental restorations should be similar to natural tooth. Lastly, the restorative
dental materials must not be bio-active. \(^{52}\)

### 2.4.4.1 Mechanical properties

Apart from its appearance like natural teeth, lithium disilicate glass-ceramics as a dental
restorative material are required to have high mechanical properties to withstand the normal
masticatory forces and stresses that exist within an oral environment. Glass-ceramics have
proven to be reliable in the application of single-unit dental crowns. Nevertheless, the strength
and/or toughness may not be adequate for the fabrication of multi-unit restorations. According
to the ISO standard 6872:2008(E), the minimum mechanical requirements of dental
ceramics for posterior 3-unit dental bridge involving molar (i.e. ceramics in Class 5)
restorations are 500 MPa for flexural strength and 3.5 MPa\(\cdot m^{0.5}\) for fracture toughness.

It is well known that the glass-ceramics of lithium disilicate type have significantly better
mechanical properties than other dental glass-ceramics such as the ones of leucite type. The
flexural strength of commercial dental products of them, IPS Empress®2 and IPS Empress®,
are 400±40 and 112±10 MPa, and the toughness are 3.3±0.3 and 1.3±0.1 MPa m\(^{1/2}\),
respectively. \(^{112}\) This is attributed to the presence of the layer silicate phase of lithium
disilicate.

### Table 2-6. The mechanical properties of lithium disilicate glass-ceramics for dental applications covered in
the patents listed in Table 2-4.

<table>
<thead>
<tr>
<th>Patent group</th>
<th>Flexural strength, MPa</th>
<th>Toughness, MPa m(^{1/2})</th>
<th>Referred patent No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>336–450 (3-point)</td>
<td>3.0</td>
<td>US6420288</td>
</tr>
<tr>
<td>C</td>
<td>200–400 (3-point)</td>
<td>3.0–4.5</td>
<td>US6342458</td>
</tr>
<tr>
<td>D</td>
<td>250–472 (biaxial)</td>
<td>1.6–2.4 (Indentation method)</td>
<td>US8042358</td>
</tr>
<tr>
<td>E</td>
<td>479–786 / 608–828 (biaxial)</td>
<td>--</td>
<td>US7871948</td>
</tr>
<tr>
<td>F</td>
<td>360–480 (3-point)</td>
<td>--</td>
<td>US6455451</td>
</tr>
<tr>
<td>G</td>
<td>400–440 (3-point)</td>
<td>--</td>
<td>US6517623</td>
</tr>
<tr>
<td>H</td>
<td>400–440 (3-point)</td>
<td>--</td>
<td>EP 1797015 A2</td>
</tr>
<tr>
<td>J</td>
<td>305–340 (3-point)</td>
<td>--</td>
<td>US20090258778</td>
</tr>
<tr>
<td>K</td>
<td>356–418 (3-point)</td>
<td>--</td>
<td>US20120309607 A1</td>
</tr>
</tbody>
</table>

Nevertheless, further improvement of the mechanical properties of lithium disilicate
glass-ceramics is still in demand, in order to enhance the reliability of material and the service
life of dental products. High strength lithium disilicate glass-ceramics have attracted great interest, as shown in the literature\textsuperscript{34,91} and patent database (see Table 2-4). Correspondingly, the mechanical properties reported in those patents are listed in Table 2-6. The surprisingly high values of over 700 MPa determined by biaxial strength testing was reported in a ZnO-free glass by Apel \textit{et al.} (see patent group E in Table 2-4). Unfortunately, there is no three-point bending data of these glass ceramics reported by these authors,\textsuperscript{91} and the values from these two testing methods are not comparable.

\subsection*{2.4.4.2 Chemical stability}

Lithium disilicate glass-ceramics are best known as a biomaterial in human medicine,\textsuperscript{46} particularly as a restorative material in dentistry.\textsuperscript{2} Apart from its widely accepted advantage of biocompatibility,\textsuperscript{113} the chemical durability is no doubt an important feature. The incorporation of Al\textsubscript{2}O\textsubscript{3} and K\textsubscript{2}O components has been reported to improve the chemical stability considerably.\textsuperscript{78,114,115} According to the ISO standard 6872:2008(E),\textsuperscript{111} the maximum chemical solubility of dental ceramics, depending on the application, is 100 or 2000 μg⋅cm\textsuperscript{-2} as aesthetic ceramic or substructure ceramic, respectively. The lithium disilicate glass ceramics meet these requirements set in the ISO standard.

\subsection*{2.4.4.3 Optical properties (translucency & colour)}

Aesthetic restorations are required in clinical situations, while matching the optical properties of artificial teeth to the natural teeth is a significant challenge in dentistry. Natural translucency is needed to achieve an appearance similar to that of human teeth.\textsuperscript{8} Lithium disilicate glass-ceramics have displayed excellent aesthetic features, such as translucency, self-grazing and colour adjusting by adding colorants.

Clinically, the optical behaviour of a ceramic restoration is highly determined by the colour of underlying tooth structure, thickness of ceramic, and colour of cement. Their effects on the resulting optical colour of a lithium disilicate-reinforced glass-ceramic crown were investigated by Chaiyabutr \textit{et al.}\textsuperscript{116} Sometimes, a fluoroapatite glass-ceramic veneer is applied on the IPS e.max\textsuperscript{®} core restoration to imitate the optical characteristics of natural teeth.\textsuperscript{117}

\subsection*{2.4.5 Dental Applications}

The lithium disilicate glass-ceramics have been introduced for use in dentistry as
restorative materials by Ivoclar Vivadent AG (Schaan, Liechtenstein). They are commercially available as an ingot that can be press-fit (IPS e.max Press) and as a block that can be milled with CAD/CAM technology (IPS e.max CAD).\textsuperscript{118} The development of lithium disilicate glass-ceramics has been focused on clinical applications including dental inlays, onlays, crowns, bridges and anterior fixed partial dentures (FPDs) (IPS e.max Press and IPS Empress 2).\textsuperscript{14} Among all-ceramics, only zirconia-based systems are approved for 3-unit restorations involving a molar so far.\textsuperscript{119}

The chairside crowns (from IPS e.max CAD) performed well without clinical failures after two years of clinical service.\textsuperscript{118} When lithium disilicate glass-ceramic is utilized for 3-unit FPDs replacing up to the first premolar, an acceptable clinical success rate was achieved.\textsuperscript{120} Makarouna \textit{et al.} found that the survival rate was 63\% after 6-year clinical service, whereas 95\% in the control group of conventional metal-ceramic.\textsuperscript{121} A long-term evaluation was reported in 2013 which demonstrates a survival rate of 71.4\% after 10-year service.\textsuperscript{122} According to a systematic review, the clinical outcomes of lithium disilicate single crowns show excellent short-term survival rates, and those of PFD prostheses are fair. For instance, the 5-year cumulative survival rate is 97.8\% and 78.1\%, respectively; while, the medium term (5-10 years) performance is not promising for the use of FPDs.\textsuperscript{123}

Although the trials of posterior FPDs have been made, the clinical performance is not as competitive as zirconia type FPDs. According to Esquivel-Upshaw \textit{et al.}, their results showed that three-unit posterior FPDs from IPS Empress\textsuperscript{®}2 have a 93\% (28/30) survival rate within the 2-year evaluation period, where the failure was associated with fracture due to short connector height or the greatest occlusal force.\textsuperscript{124} Taskonak \textit{et al.} investigated the clinical performance of the same type of material as crowns and FPDs of both anterior and posterior for the identical length of period. The single unit crowns demonstrated a satisfactory clinical performance during the 2-year period, however, a failure rate of 50\% of FPDs occurred.\textsuperscript{125} Kern \textit{et al.} suggested that 3-unit FDPs made from monolithic lithium disilicate glass-ceramic may be a safe alternative to metal-ceramic FDPs if the manufacturer’s recommendations are followed.\textsuperscript{126} The success rate, defined as remaining unchanged and free of complications, of FDPs (6 anterior and 30 posterior teeth) was 91.1\% after five years and 69.8\% percent after 10 years, that were similar to those of conventional metal-ceramic FDPs.
2.5 Motivation of the current research

As is discussed above, the clinical performance of lithium disilicate glass-ceramic restorations is urged to be improved. This greatly relies on the enhancement of mechanical properties of the material. Aside from that, glass forming technology has superior advance for mass-production and quality control. We therefore propose to fabricate a lithium disilicate glass-ceramic that is strong and preferably, tough enough for posterior 3-unit dental bridge by heat treatment of bulk glass.

On the other hand, as mentioned earlier (section 2.3.3.1) that the CNT theory is based on several assumptions. Although it gives reasonable qualitative interpretations on the temperature and time dependences of nucleation rates, this theory encounters with serious problems quantitatively. Moreover, glasses in practical applications are more complex than those of simple systems discussed by CNT. By accessing the state-of-the-art synchrotron facilities in the Australian Synchrotron Centre (projects AS123/PD/4411 (Round 2012/1) and AS123/PD(PDFI)/5330 (Round 2012/3)), we proposed an in situ observation of nucleation and crystallization of several complex lithium disilicate glasses using high-temperature X-ray diffraction. The synchrotron radiation can provide high intensity patterns on a considerably short time scale for quantitative phase and structural analyses. Ultimately, the transformation kinetics can be better understood and therefore it is possible to achieve the desired microstructure and properties of glass-ceramics..

In summary, with the overall aim of achieving both the fabrication of strengthened lithium disilicate glass-ceramics and the investigation of crystallization kinetics and mechanisms of lithium disilicate glasses, several specific objectives of this project are listed as follows:

(1) To fabricate novel lithium disilicate glass-ceramics with appropriate mechanical properties for the possible application of three-unit prostheses involving molar.

(2) To investigate the crystallization, microstructure and mechanical properties of lithium disilicate glass-ceramics in different glass systems.

(3) To revisit the role of P₂O₅ on the crystallization of lithium disilicate glasses using synchrotron X-ray diffraction (XRD).

(4) To quantitatively analyse the kinetics of a complex LS₂ glass during nucleation and
crystallization.

(5) To study the crystallographic evolution behaviour of crystalline phases in the same glass upon heating and cooling.

(6) To investigate the structural response of LS$_2$ phase to other phases in various LS$_2$ glasses.

2.6 References


40 M. Réaumur. The art of making a new type of porcelain by very simple and easy methods of transforming glass into porcelain, Part I. Memoires de l'Academie Royale des Sciences, 370-388 (1739).
52 W. Höland & G. H. Beall. in Glass-Ceramic Technology Ch. 4, 252-353 (John Wiley & Sons, Inc., 2012).
2714 (2006).
60 W. Höland & G. H. Beall. in Glass-Ceramic Technology Ch. 1, 1-74 (John Wiley & Sons, Inc., 2012).


91 E. Apel, C. van't Hoen, V. Rheinberger & W. Höland. Influence of ZrO$_2$ on the


108 R. Dupree, D. Holland & M. G. Mortuza. A MAS-NMR investigation of lithium


Chapter 3 Experimental Methods

This chapter presents the compositional design and procedures employed in this project. Techniques such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC), X-ray diffraction at either room temperature (RT-XRD) or high temperature (HT-XRD) were employed to study the thermal behaviour and crystalline phase evolution of materials as functions of temperature and time. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) as well as energy-dispersive X-ray spectrometer (EDS) were used for the microstructural observation of materials. Nuclear magnetic resonance (NMR) was combined with XRD to determine the structural change of glass and crystal phases.

3.1 Base glasses

3.1.1 Compositional design and glass melting

Before we designed our own glass recipes, we conducted systematic patent search on the currently reported glass compositions (as summarized in Table 2-4 and Table 2-5). Then, we screened several glass compositions to achieve an ideal glass-ceramic structure where lithium disilicate (Li$_2$Si$_2$O$_5$) serves as the main phase whereas rhenanite (CaNaPO$_4$), enstatite (MgSiO$_3$), or cordierite (Mg$_2$Al$_4$Si$_5$O$_{18}$) consists in the residual glass matrix. Table 3-1 lists the composition of several glasses that were studied in the entire thesis. The glass AG1 is a documented glass in the literature which was reported to be of high flexural strength, and glass Bo is of similar composition in the same system. In glass Bo, the effect of P$_2$O$_5$ on the crystallization of lithium disilicate glass-ceramics was investigated. Several experimental glasses were designed for the development of high-strength lithium disilicate glass-ceramics, including the glasses B, C, E and F (Table 3-1).

3.1.2 Glass melting

As per the prescribed recipes listed in Table 3-1, these glasses are melted in crucibles by Gaffer Coloured Glass Ltd (Auckland, New Zealand). The starting materials (and the corresponding component) for the melting of these glasses were: index sand (SiO$_2$), lithium carbonate (Li$_2$O), ammonium phosphate (P$_2$O$_5$), alumina (Al$_2$O$_3$), calcite (CaO), magnesium
carbonate (MgO), dolomite (CaO and MgO), zircon (ZrSiO₄), potash or potassium nitrate (K₂O), soda ash or sodium nitrate (Na₂O), manganese dioxide (MnO), antimony trioxide (Sb₂O₃). The starting materials with prescribed weight ratio were dry-mixed before putting into alumina crucibles. To achieve the homogeneous base glasses, the powder mixtures were melted at temperatures above 1300 °C for several hours, depending on the compositions. Glass rods were drawn from glass melt at 1050°C with diameters of 5–10 mm.

Table 3-1. Nominated compositions of lithium disilicate glasses (in wt%)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Bo</th>
<th>AG1</th>
<th>B</th>
<th>C</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol ratio of SiO₂/Li₂O</td>
<td>2.51</td>
<td>2.41</td>
<td>2.40</td>
<td>2.55</td>
<td>2.50</td>
<td>2.50</td>
</tr>
<tr>
<td>SiO₂</td>
<td>75.1</td>
<td>74.27</td>
<td>70.61</td>
<td>68.52</td>
<td>75.80</td>
<td>75.80</td>
</tr>
<tr>
<td>Li₂O</td>
<td>15.0</td>
<td>15.42</td>
<td>14.69</td>
<td>13.41</td>
<td>15.13</td>
<td>15.13</td>
</tr>
<tr>
<td>MgO</td>
<td>0</td>
<td>1.97</td>
<td>1.80</td>
<td>4.07</td>
<td>4.07</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.6</td>
<td>3.55</td>
<td>4.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>4.9</td>
<td>3.38</td>
<td>4.48</td>
<td>4.17</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.52</td>
<td>0.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>2.74</td>
<td>2.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>1.7</td>
<td>3.26</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.7</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The glass-ceramic fabrications from glasses Bo, B and C will be discussed in Chapter 4, Chapter 5 and Chapter 6, respectively. In Chapter 7 and Chapter 8, the crystallization kinetics and crystallographic evolution in glass Bo will be discussed. In Chapter 9, the structural response phenomenon will be discussed with the glasses AG1, C, E, and F.

3.2 Heat treatment

The bulk glasses underwent heat treatment in air in a muffle furnace. The profile of annealing was designed to be multiple stages (2 to 4) according to their thermal characteristics. The effects of both temperature and holding time on the phase transformation, microstructure, and properties were investigated.
3.3 Characterization

3.3.1 Thermal analysis

Thermal analyses (differential thermal analysis (DTA) and differential scanning calorimetry (DSC)) were carried out to determine the glass transition temperature, nucleation and crystallization temperature. DTA was performed using a 2960 SDT thermoanalyzer. Heating rate for all DTA runs was 20 °C/min. DSC measurements were conducted on a DSC 404 F3 Pegasus® (NETZSCH, Germany) at a heating rate of 15 K/min in argon gas, unless specified otherwise. Thermal analysis data were used to devise the heat treatment procedure. Marotta’s method²⁻³ was used for determining the nucleation temperature and holding time.

3.3.2 Phase identification

The phase evolution analysis of lithium disilicate glass-ceramics were carried out with laboratory X-ray diffraction (XRD), at either room temperature (RT) or high temperature (HT), and in situ synchrotron HT-XRD techniques.

3.3.2.1 Laboratory (conventional) X-ray diffraction (XRD)

Phase identification of glass-ceramics were identified by X-ray powder diffraction (XRD; D2-Phaser, Bruker, Germany) with Cu Kα radiation (λ = 1.5418 Å) operating at 30 kV and 10 mA. Data were recorded over the 2θ range of 10°–90° with a step increment of 0.02°.

The crystal phase evolution during heat treatment of parent glasses was examined by in situ HT-XRD on another laboratory diffractometer (D8 Advance, Bruker, Germany) with a high temperature chamber (Anton Paar HTK 1200), operating at 40 kV and 30 mA. Monolithic glass samples in dimensions of about Φ12mm×0.8mm were mechanically grinded. The data were recorded from room temperature up to 1000 °C with an increment of 20 or 30 °C and 2θ range of 10–40 °, with a step size of 0.02° and a measuring time of 1 s.

3.3.2.2 Synchrotron X-ray diffraction (SXRD)

In situ SXRD of all parent glasses was performed on the Powder Diffraction (PD) beamline at the Australian Synchrotron Centre. The glasses were mechanically cut and grinded to dimensions of about 5 mm × 5 mm × 0.4 mm (monolithic). An Anton Paar HTK-2000 strip furnace (with a platinum (Pt) resistance strip heater) and a Mythen II
microstrip detector were attached to the state-of-the-art synchrotron beamline. The high-resolution data collection was on the Bragg-Brentano diffraction configuration, using X-ray beam energy of 11 keV (\(\lambda = 1.1273\ \text{Å}\)). The glass specimens were heated up at a rate of 400 K·min\(^{-1}\). For non-isothermal annealing, the diffraction patterns were recorded at the holding stages to detect the phases within the range of 500–1010 °C, and at each stage the X-ray beam was switched on for 4 min. For isothermal annealing, the data were recorded at the subscribed temperatures and X-ray was on every 15 s.

Due to the special configuration of detector modules (with gaps of 0.2° in every 5°), dataset pairs (p1 and p2) were collected at two detector settings shifted by 0.5° to ensure full coverage. In our case, p1 covered a 2θ angle of 6.2 to 86° while p2 covered 6.7 to 86.5°, respectively. After data collection, the dataset pairs were merged to remove the gaps by using the tool PDViPeR.

![Figure 3-1. The Powder Diffraction beamline at the Australian Synchrotron Centre. The high temperature furnace (Anton Paar HTK-2000 strip furnace) was setup with a temperature control system.](image-url)
3.3.2.3 Rietveld Refinements

A software MAUD, written by Lutterotti on the basis of the full-pattern analysis using Rietveld method, was employed for quantitative phase analysis. For such refinements, a Delf line broadening model was used, adopting an iterative least-square procedure by minimizing the residual parameters $R_{wp}$, $R_B$ and $R_{exp}$. The crystallite size and the microstrain (root mean square, r.m.s. strain, $\langle \varepsilon^2 \rangle^{1/2}$) were evaluated using an isotropic size-strain model.

The entire suite of data sets was refined sequentially, and crystallinity, volume fraction and crystallite size of each phase were obtained as a function of temperature and holding time. The information retrieved was then used to investigate the phase formation, nucleation and crystallization kinetics.

3.3.3 Nuclear magnetic resonance (NMR)

All solid-state NMR experiments were carried out on dry powder samples using a Bruker AVANCE 300 standard bore magnet system (7.05 T) operating at 59.62 MHz for $^{29}$Si resonance and 121.50 MHz for $^{31}$P resonance. The parameters for $^{29}$Si spectroscopy were: a 90° pulse width of 4.2 μs, and a different recycle delay ($d_1$) depending on the spin-lattice (or longitudinal) relaxation time $T_1$ with a spectral-width of 50.125 kHz. NMR Experiments were carried out at ambient temperature using samples enclosed in the zirconium oxide (ZrO$_2$) 7 mm rotors. The $^{29}$Si chemical shift scale was referenced to tetramethylsilane (TMS). The parameters for $^{31}$P spectroscopy were: a 90° pulse width of 4.6 μs, a different recycle delay was applied depending on the $T_1$ with a spectral-width of 50.125 kHz was used. The spinning speed for $^{29}$Si and $^{31}$P experiments was 5 and 7 kHz, respectively. The $^{31}$P chemical shift scale was referenced to 85% H$_3$PO$_4$.

The saturation recovery method was adopted for the measurement of relaxation times of the $^{29}$Si species, where a train of 50 90° pulses was applied followed by an observe pulse. Recycle delay was 1 s, while the delay in saturation pulse train was 5 ms.

3.3.4 Microstructure

3.3.4.1 Scanning electron microscopy (SEM)

The heat treated glass-ceramic samples were mechanically ground and finally polished with 1μm diamond suspension, followed by etching with 2% hydrofluoric (HF) acid solution.
for 15 s. The fracture surfaces were directly etched for 25 s without grinding. A conductive Pt layer was coated onto the surface of the samples using the machine Quorum (Q150RS). Microstructural observation of the glass-ceramic samples was performed by using an environmental scanning electron microscope (ESEM; FEI Quanta 200F) equipped with a SiLi energy dispersive X-ray spectroscope (EDX, EDAX Pegasus EDS detector).

3.3.4.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) investigations were carried out on an electron microscope (FEI Tecnai F20-G2, FEGTEM, Tokyo, Japan) equipped with a cold-stage (for cooling down the specimen to –173 °C), and with Oxford INCA (Oxfordshire, UK) energy-dispersive X-ray spectrometer (EDX) for microprobe elemental analysis. For the preparation of thin foils for the TEM observation, standard methods of grinding were applied to achieve a thickness of about 15 μm, and then ion beam thinning (IBT) was conducted on an IBT machine (Gatan Model 691 PIPS), operating at a voltage of 4.5 keV and with an angle of 10° (beam currents of left gun 25 μA and right gun 28 μA) for 170 min until a central hole was obtained. After that, a further milling was performed at 4.5 keV + 6° for 2 min, and lastly 3.4 keV + 4° for 16 min (beam currents of left gun 18 μA and right gun 17 μA).

3.3.5 Mechanical properties measurements

3.3.5.1 Vickers Hardness

Microhardness testing was conducted on the polished cross sections of the glass-ceramic samples, using an Ernst Leitz Wetslar GmbH microscope with a load of 9.8 N and dwell time of 10 s. Approximately 10 hardness readings were recorded for each sample. The Vickers hardness of samples were calculated with the equation \( H_V = \frac{2F \sin 68°}{d^2} \), where \( F \) is the load and \( d \) is the mean length of the impression diagonals.

3.3.5.2 Fracture toughness

3.3.5.2.1 Indentation fracture toughness

Figure 3-2 shows the schematic views of Vickers indent radial-median and radial-Palmqvist crack systems. The formulas for calculation are reviewed in the literature.\(^5\) It is noted that,
although the indentation methods have been discredited in recent years, the Vickers Indentation fracture (VIF) toughness was still employed using the Anstis crack-length method. This is because a large body of fracture toughness data is available in the literature and also because the method is simple and straightforward. The fracture toughness is calculated using the following formula:

$$K_{ic} = 0.016(E/H)^{0.5}(P/c^{1.5})$$

where, $E$ is Young’s modulus, $H$ is hardness, $P$ is load, and $c$ is the length of crack from the impression centre. The Young’s modulus ($E$) of lithium disilicate glass-ceramics was taken to be 99 GPa.

![Figure 3-2. Schematic idealised plan view and cross-sectional view of (a) Vickers indent radial-median or 'halfpenny' crack system and (b) Vickers indent radial Palmqvist crack system.](image)

### 3.3.5.2.2 Fracture toughness by SENB method

The fracture toughness of optimized glass-ceramics was also measured by single-edge notched beam (SENB) three-point bending test according to a more accepted ISO standard. Rectangular samples were cut with a diamond saw and ground to the dimensions of 2×4×40 mm$^3$, and then notched with a depth of about 2 mm.

According to ASTM C1421–09 standard, the fracture toughness under SENB three-point...
flexure \((K_{1c})\) can be calculated by using Eqn. (2),

\[
K_{1c} = g \left[ \frac{P_{max} S_o 10^{-6}}{BW^3} \right] \left[ \frac{3 \left[ \frac{a}{W} \right]^2}{2 \left[ 1 - \frac{a}{W} \right]^2} \right]
\]

where,

\[
g = g \left( \frac{a}{W} \right) = \frac{1.99 - \left[ \frac{a}{W} \right]}{1 + 2 \left[ \frac{a}{W} \right]} \left[ 2.15 - 3.93 \left[ \frac{a}{W} \right] + 2.7 \left[ \frac{a}{W} \right]^2 \right]
\]

where:

- \(K_{1c}\): fracture toughness \((MPa\sqrt{m})\),
- \(P_{max}\): maximum force \((N)\),
- \(S_o\): outer span \((m)\),
- \(B\): side to side dimension of the specimen perpendicular to the crack depth \((m)\),
- \(W\): top to bottom dimension of the specimen parallel to the crack depth \((m)\),
- \(a\): crack depth \((m)\), and
- \(g = g \left( \frac{a}{W} \right)\): function of the ratio \(a/W\) for three-point flexure.

### 3.3.5.3 Three-point flexural strength

Flexural strength was measured at room temperature using a three-point bending test on an INSTRON 3367 machine. Average values were taken from 4–8 sample bars. The span of the samples was 32 mm and a crosshead speed of 0.5 mm\(\cdot\)min\(^{-1}\) was used. The flexural strength was determined using cylindrical specimens by the equation of \(\sigma=8P/l\pi d^3\), where \(P\), \(l\), and \(d\) are the maximum load, span and diameter, respectively.

### 3.4 References


Chapter 4 Phase formation, microstructure and properties of a lithium disilicate glass-ceramic in the SiO$_2$–Li$_2$O–Al$_2$O$_3$–P$_2$O$_5$–ZrO$_2$ system

This chapter aims to investigate the crystalline phase formation, microstructure and mechanical properties of a lithium disilicate glass-ceramic (Glass Bo) from the SiO$_2$–Li$_2$O–Al$_2$O$_3$–P$_2$O$_5$–ZrO$_2$ glass system. A four-stage heat treatment process was used for crystallization of the glass. The effects of holding time and temperature at the final stage on the crystalline morphology of the glass-ceramic were studied. The DTA results revealed two crystallization peaks at 672 °C and 839 °C. At temperatures lower than 770 °C with holding time of 20 min, the LS phase forms in the glass-ceramic as revealed by XRD. When the glass was heated to a higher temperature or held for a longer time, the LS$_2$ phase dominates and some other minor phases such as cristobalite and LP emerge. Backscattering SEM and EDX revealed a large number of nanosized ZrO$_2$ particles when the crystallisation temperature was above 790 °C. Vickers hardness of the lithium disilicate glass-ceramic was about 8.1–8.4 GPa and flexural strength in the range of 282–307 MPa. Crack deflection was observed along the LS$_2$ cluster boundaries. The crystallisation sequence was proposed to explain the observed microstructure and phases.

The main results have been published in:


4.1 Introduction

Lithium disilicate glass-ceramics have a much higher flexural strength and fracture toughness than glass-ceramics of other types, such as leucite-type (KAlSi$_2$O$_6$), mica-type (KMg$_2$Si$_4$O$_{10}$F$_2$), fluorapatite (Ca$_5$(PO$_4$)$_3$F), and leucite-apatite. Thus they are of particular importance for dental restorative applications and have been acquiring wide applications. 

---

1 This chapter is presented in a journal publication manner. Note that this format is accepted as per the Guide to Theses and Dissertations of the University of Auckland. The same format is also used for the subsequent chapters 5–9, with some modifications.
recent years, the nucleation mechanism and crystalline phase formation in the binary SiO$_2$-Li$_2$O system has been extensively investigated and a large body of information is available in the literature. Apart from that, glass-ceramics from multi-component SiO$_2$–Li$_2$O based systems have also attracted substantial research interest and a number of such have been widely used clinically.

The nucleation and crystal phase formation is complicated in multi-component lithium disilicate glass systems, and largely affected by the additives to glasses. In the development of multi-component lithium disilicate glass, phosphorus pentoxide is a common additive as a nucleation promoter since 1963. McMillan and Partridge found that P$_2$O$_5$ catalyses the crystallisation of a wide range of glass compositions derived from the Li$_2$O-Al$_2$O$_3$-SiO$_2$, Li$_2$O-MgO-SiO$_2$ and MgO-Al$_2$O$_3$-SiO$_2$ systems. Since then there have been a large number of follow-up investigations on how P$_2$O$_5$ affects nucleation and crystallisation in glass. Although the exact role that P$_2$O$_5$ plays and its interaction with other oxides is not well understood, it is generally agreed that P$_2$O$_5$, in the form of either phosphorus pentoxide or lithium orthophosphate (Li$_3$PO$_4$), promotes phase separation in Li$_2$O-SiO$_2$ glasses. By exploring the effectiveness of P$_2$O$_5$, Höland et al. developed a multi-component non-stoichiometric SiO$_2$–Li$_2$O–Al$_2$O$_3$–K$_2$O–ZrO$_2$–P$_2$O$_5$ system, which was reported to possess a (biaxial) flexural strength of 726 MPa after crystallisation.

Inspired by their work, we used a similar glass as a model material in the SiO$_2$–Li$_2$O–Al$_2$O$_3$–P$_2$O$_5$–ZrO$_2$ system. In this non-stoichiometric composition glass, small amounts of P$_2$O$_5$ and trace amounts of ZrO$_2$ were added as nucleating agents. A four-stage heat treatment was designed to crystallize this glass. The main purpose is to study how the crystalline phases emerge and the microstructural evolution during the crystallization process.

### 4.2 Experimental procedures

The glass Bo was melted in a Pt crucible at 1500 °C for 3 h. The molten glass was poured into a graphite mould that was preheated to 500 °C, to obtain cylindrical glass rods 10 mm in diameter and 60 mm long. A multi-stage heat treatment profile, as shown in Figure 4-1, was designed upon DTA trace. The effects of the last-stage temperature (770–850 °C for 20 min,
samples S1–S4) and holding time (770 °C for 20 min–2.5 h, samples M1–M3) on the phase formation, microstructure and mechanical properties were investigated.

Figure 4-1. Heat treatment temperature profile of the glass with four stages.

The 3-point flexural strength, Vickers Hardness, and Vickers indentation fracture (VIF) toughness of glass-ceramics were measured as per the methods described in Section 3.3.5. The crystalline phases of glass-ceramics at different heat treatment stages were identified on a D2-Phaser X-ray diffractometer. Microstructural observation of the as-received glass-ceramic samples was performed on the polished and etched cross sections by ESEM and EDX.

4.3 Results

4.3.1 DTA analysis

The DTA trace for glass Bo is shown in Figure 4-2, in which three featured temperatures were identified. The first endothermic peak at ~473 °C can be regarded as the glass transition temperature⁷ or annealing point of the glass.¹⁷,¹⁸ There are two exothermic peaks at 672 °C and 839 °C, which are associated to the formation of crystalline phases.

4.3.2 XRD analysis

Figure 4-3 presents the XRD patterns of the glass samples subjected to sequential heat treatment. It is clear that no crystallographic peaks can be defined in the glass sample that was heated at 520 °C for 20 min. A sequential heat treatment at 620 °C for 20 min causes the
formation of both Li$_2$SiO$_3$ (LS thereafter) and Li$_2$Si$_2$O$_5$ (LS$_2$ thereafter), while LS$_2$ starts to dominate after the sample was further treated at 740 °C/20 min.

![DTA analysis of parent glass Bo (ramp rate of 20 °C/min in air).](image1)

**Figure 4-2.** DTA analysis of parent glass Bo (ramp rate of 20 °C/min in air).

In addition, the final heat treatment stage was investigated by XRD analysis. Figure 4-4 shows the XRD patterns for the glass samples that were heat treated at different final stage temperatures. At a relatively low temperature 770 °C, two major phases – LS and LS$_2$ – coexist. In remarkable contrast, when the final stage temperature increases to 790 °C, the LS peaks disappear while ZrO$_2$ peaks emerge. The intensity of the ZrO$_2$ peaks gradually increases.

![XRD patterns of samples after heat treatment at first three stages.](image2)

**Figure 4-3.** XRD patterns of samples after heat treatment at first three stages.
with increasing temperature from 790 °C to 850 °C. Also some extra peaks, weak but noticeable, emerge and can be indexed to cristobalite.

Figure 4-4. XRD patterns of samples (S1-S4) annealed at various final-stage temperatures holding for 20 min.

Figure 4-5. XRD patterns of samples (M1-M3) heat-treated for different holding time at 770 °C.
The effect of holding time at the final stage is shown in Figure 4-5, in which the peaks of LS disappear if the samples were held for 1 h or longer at 770 °C. ZrO$_2$ was detected at this temperature when holding for 2.5 h. Table 4-1 summarises the major crystalline phases observed in the glass samples when subjected to different heat treatment cycles.

Table 4-1. Phase assemblage and mechanical properties of lithium disilicate glass-ceramics heat-treated at different final-stage temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. final stage (°C)</th>
<th>Phase assemblage$^a$</th>
<th>Flexural strength (MPa)</th>
<th>Hardness (GPa)</th>
<th>$K_{IC}$ (MPa m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>770</td>
<td>LS, LS$_2$</td>
<td>246 ± 11</td>
<td>7.9 ± 0.1</td>
<td>1.17</td>
</tr>
<tr>
<td>S2</td>
<td>790</td>
<td>LS$_2$, minor phases</td>
<td>282 ± 32</td>
<td>8.1 ± 0.2</td>
<td>1.14</td>
</tr>
<tr>
<td>S3</td>
<td>820</td>
<td>LS$_2$, minor phases</td>
<td>283 ± 34</td>
<td>8.4 ± 0.1</td>
<td>1.23</td>
</tr>
<tr>
<td>S4</td>
<td>850</td>
<td>LS$_2$, minor phases</td>
<td>307 ± 16</td>
<td>8.2 ± 0.2</td>
<td>1.12</td>
</tr>
</tbody>
</table>

$^a$ LS: Li$_2$SiO$_3$, LS$_2$: Li$_2$Si$_2$O$_5$, minor phases: Li$_3$PO$_4$, β-cristobalite (SiO$_2$) and ZrO$_2$

4.3.3 Microstructure

Figure 4-6 shows the microstructure observed in the glass-ceramic samples when subjected to four different temperatures: 770°C, 790°C, 820°C and 850°C. After heat treatment at 770 °C for 20 min, the main phases are LS and LS$_2$. For further clarification of Figure 4-6a, the dendrite-shaped etched pits represent the crystalline LS dendrites (as it can be easily etched by HF acid solution),$^6$ and the LS$_2$ matrix was left there. This observation is in agreement with the report by Höland et al.$^7$ and Apel et al.$^{19}$ In addition, there are also pits left by LP crystals. The etching of all solvable crystals makes “pores” in SEM images presented throughout the thesis. In the glass samples that were treated at a temperature higher than 790 °C, those dendritic LS virtually disappear and nanosized LS$_2$ clusters have become predominant (Figure 4-6b-d). It is also interesting to note that back scattered electron (BSE) micrographs show a number of white spherical particles delineated at the boundaries of the LS$_2$ clusters. Energy dispersive spectrometry (EDS) results suggest that these spherical particles probably are ZrO$_2$ which is a minor additive in the glass composition.
Similar to the heat treatment temperature, the holding time also plays an important role in the microstructural evolution. Figure 4-7 represents SEM micrographs of the samples treated at 770 °C but held for different time. In contrast to Figure 4-6a, LS₂ is the only crystal phase that is present in the samples when held for 1 h or longer at 770 °C. The microstructures of glass-ceramics show little difference when held for 1–2.5 h at 770°C.

Figure 4-6. Crystalline morphology of lithium disilicate glass-ceramics S1-S4 heat-treated at different temperatures holding for 20 min (etching with 2% HF acid solution for 10s). (a) S1: 770°C, (b) S2: 790°C, (c) S3: 820°C, (d) S4: 850°C. The insets are BSE images.

Figure 4-7. Morphology of GC samples heat-treated at 770°C, holding for (a) 1 h and (b) 2.5 hrs respectively (etching with 2% HF solution for 10s). The white grains are ZrO₂.
4.3.4 Mechanical properties and fracture

After heat treatment, the glass-ceramic samples were mechanically tested to determine the flexural strength and hardness. The results are also summarized in Table 4-1. In general, a higher heat treatment temperature enhances the flexural strength and microhardness. For instance, samples S2-S4 have a flexural strength of about 282~307 MPa, in comparison to 246 MPa for sample S1. The Vickers hardness of samples S2-S4 were about 8.1~8.4 GPa, slightly higher than that of sample S1 (7.9 GPa).

We also estimated the fracture toughness and studied the crack propagation behaviour using Vickers indentation. The value of $K_{ic}$ was calculated to be 1.12 MPa\(\sqrt{m}\), as per the formula $0.016(E/H)^{0.5}(P/c^{1.5})$ proposed by Anstis et al.\textsuperscript{20} Figure 4-8 shows the crack propagation in sample S4. Some LS\textsubscript{2} clusters are pulled apart (Figure 4-8a), while at the tip of the main crack, the crack deflection occurs along the LS\textsubscript{2} cluster boundaries in a zigzag fashion (Figure 4-8b).

![Figure 4-8](https://example.com/image.png)

Figure 4-8. (a) Crack propagation in lithium disilicate glass-ceramics (sample S4), (b) the enlarged image of selected area in (a).
4.4 Discussion

It is known that a fine-grained microstructure is attainable by controlled crystallization (devitrification) processes. The technique used to obtain such a fine microstructure is to generate crystal nuclei at a temperature giving a high nucleation rate but a low crystal growth rate. The addition of nucleating agents such as P$_2$O$_5$ has become a common practice of glass-ceramic technology. Apparently the selection of the heat treatment temperature is critical for controlling crystallization and attendant microstructure. A differential thermal analysis (DTA) or differential scanning calorimetry (DSC) trace is usually used to devise the heat treatment temperatures. The DTA scan in this work shows two strong exothermic peaks, which indicate the crystallization of lithium metasilicate (Li$_2$SiO$_3$) and lithium disilicate (Li$_2$Si$_2$O$_5$). Höland et al.\textsuperscript{7} reported a similar DSC result and nucleation temperature range (500 – 540 °C). It is reasonably assumed that nucleation temperature in our work is also in the similar range, which is much higher than that in binary Li$_2$O-SiO$_2$ glasses (~450 °C\textsuperscript{2, 3, 21}). This can be contributed to the nucleating agent P$_2$O$_5$, which reduces the nucleation undercooling.

Headley et al.\textsuperscript{22} studied the growth mechanism of lithium disilicate glass-ceramics doped with P$_2$O$_5$ by transmission electron microscopy (TEM). They introduced the Li$_3$PO$_4$ nuclei by preheating the glass at 1000 °C, and found that cristobalite (SiO$_2$), Li$_2$SiO$_3$ and Li$_2$Si$_2$O$_5$ crystallize via epitaxial growth on several specific crystallographic facets of Li$_3$PO$_4$ crystallites in the subsequent heat treatment stages. On the contrary, most of other investigations employed a conventional heat treatment regime without a pre-nucleation stage of Li$_3$PO$_4$. In these non-prenucleation cases, Li$_3$PO$_4$ crystals were formed after the crystallization of LS and LS$_2$, which indicates that the silicate phases may not be directly nucleated on Li$_3$PO$_4$. More likely, the nucleation of lithium disilicate was triggered by the steep compositional gradients resulting from microstructural heterogeneities.\textsuperscript{23} Amorphous phosphate species in the initial glass would still lead to a phase separation into silica-rich droplet and lithia-rich matrix phases upon heat treatment.\textsuperscript{24} This proposed mechanism was also supported by a recent solid-state nuclear magnetic resonance (NMR) study on a
non-stoichiometric multi-component system by Bischoff et al.\textsuperscript{16}

In our current study, the Li\textsubscript{3}PO\textsubscript{4} particles were not detected at low temperatures (<770 °C) by laboratory XRD, probably because the crystallites were too small or the phosphate species remained amorphous at these temperatures. At higher temperatures, P\textsubscript{2}O\textsubscript{5} reacts with Li\textsubscript{2}O to form the crystalline Li\textsubscript{3}PO\textsubscript{4} particles which act as nucleation sites for LS.\textsuperscript{8} Thus, the phosphate component transforms from disordered species to well-ordered crystalline states at a temperature of about 790 °C. This was clarified by Bischoff et al. with the evidence of line broadening of \textsuperscript{31}P MAS-NMR spectra of multi-component lithium disilicate systems at low temperatures.\textsuperscript{16} The Li\textsubscript{3}PO\textsubscript{4} phase was detected concomitant with cristobalite at 790~850 °C. The concomitant existence of Li\textsubscript{3}PO\textsubscript{4} and cristobalite could be a result of nucleation and growth of cristobalite on lithium phosphate nuclei.\textsuperscript{22} It also suggests that the Li\textsubscript{3}PO\textsubscript{4} particles are less likely to directly nucleate LS\textsubscript{2}. We therefore propose the following phase formation sequence, as listed in Table 4-2.

\textbf{Table 4-2. Phase evolution of lithium disilicate glass as function of temperature}

<table>
<thead>
<tr>
<th>Step</th>
<th>Temp. Range</th>
<th>Reaction and phase formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>520 – 620 °C</td>
<td>Nucleation and probable slow growth of LS and LS\textsubscript{2}</td>
</tr>
<tr>
<td>2</td>
<td>620 – 770 °C</td>
<td>Rapid growth of LS to maximum, little growth of LS\textsubscript{2}</td>
</tr>
<tr>
<td>3</td>
<td>790 – 850 °C</td>
<td>Decomposition and transition of LS; crystallization of Li\textsubscript{3}PO\textsubscript{4} and cristobalite, growth of LS\textsubscript{2}; formation of ZrO\textsubscript{2}</td>
</tr>
</tbody>
</table>

The following reactions can be proposed for the formation of the above phases.

\begin{align*}
\text{Li}_2\text{O} \text{ (glass)} + \text{SiO}_2 \text{ (glass)} &= \text{Li}_2\text{SiO}_3 \text{ (crystal)} \\
\text{Li}_2\text{O} \text{ (glass)} + 2 \text{SiO}_2 \text{ (glass)} &= \text{Li}_2\text{Si}_2\text{O}_5 \text{ (crystal)} \\
\text{Li}_2\text{SiO}_3 \text{ (crystal)} + \text{SiO}_2 \text{ (glass)} &= \text{Li}_2\text{Si}_2\text{O}_5 \text{ (crystal)} \\
3\text{Li}_2\text{O} \text{ (glass)} + \text{SiO}_2 \text{ (glass)} + \text{P}_2\text{O}_5 \text{ (glass)} &= 2\text{Li}_3\text{PO}_4 \text{ (crystal)} + \text{SiO}_2 \text{ (cristobalite)}
\end{align*}
A large number of nanosized ZrO$_2$ are observed in the samples when they were heated to a temperature $\geq 790$ °C (Figure 4-6b–d). This result is consistent with the XRD results as shown in Figure 4-4. It is therefore speculated that ZrO$_2$ particles act as nucleants for LS$_2$. The use of ZrO$_2$ as a nucleating agent was reported by Sawai.$^{25}$ Similar to TiO$_2$, zirconia is soluble in molten glasses but during cooling or subsequent reheating nanosized or submicroscopic particles are precipitated and these precipitates serve as nucleating agents. It is not clear whether and how the two oxides P$_2$O$_5$ and ZrO$_2$ play a synergistic role in nucleation and crystallization. As to the aluminium component, it does not participate in the crystallization processes, but is located in a four-coordinate network-forming species in the amorphous matrix.$^{16}$ It is also unclear how the aluminium influences the nucleation and crystallization of glasses and/or the properties of glass-ceramics.

Mechanical properties of the lithium disilicate glass-ceramics can be improved by a proper heat treatment. A finer grained lithium disilicate is favourable for enhanced strength. In order to obtain a fine grain structure, large numbers of nuclei that are uniformly distributed are required. In the subsequent crystallization, each of these nuclei should develop a grain, while grain growth, in particular abnormal grain growth should be limited. Only in this way, a fine grain structure and high mechanical strength can be achieved.

### 4.5 Summary

In this chapter, we investigated the crystalline phase formation, microstructure and mechanical properties of a lithium disilicate glass-ceramic. The following conclusion can be drawn:

1. At low temperature the main phase is LS with a minor LS$_2$ phase, while at a relatively high temperature LS$_2$ is dominant. The LS phase disappears when the heat treatment temperature reaches 790 °C or when holding for more than 1 h at 770 °C.

2. The co-existence of LP and cristobalite at a temperature $> 790$ °C suggests that the nucleation and growth of cristobalite strongly depend on well-crystallized LP particles.

3. Nanosized ZrO$_2$ particles were identified in the samples when they were heat treated at a high temperature of $> 790$ °C and LS$_2$ was the major crystalline phase. It is therefore
speculated that ZrO$_2$ acts as a nucleating agent for LS$_2$ phase.

(4) Fracture cracks were observed to deflect along the LS$_2$ cluster boundaries. The crack deflection is the main toughening mechanism in this glass ceramic.

4.6 References


Chapter 5  Fabrication of a lithium disilicate glass-ceramic from the SiO2–Li2O–MgO–P2O5–ZrO2 glass system

In this chapter, a lithium disilicate glass ceramic was developed in the SiO2–Li2O–MgO–P2O5–ZrO2 glass system as a candidate material for dental restorative applications. Three sets of samples were employed to investigate the effects of heating profile, crystallisation annealing temperature and holding time on the phase evolution, microstructure and mechanical properties. The glass-ceramics derived from this composition have an optimized flexural strength of 439±93 MPa. Additional higher temperature annealing stages were of little help for the improvement of bending strength, but did enhance the Vickers indentation fracture toughness (VIF) from 0.93 to 1.29 MPa·m\(^{1/2}\). It is found that both the crystallization temperature and holding time affect the phase transformation, morphology and crystallite size of these glass-ceramics, but the crystallisation temperature has a more profound effect than the holding time. Although no peaks of LS were detected with laboratory X-ray source, the formation of a trace amount of LS was successfully evidenced by synchrotron-based X-ray diffraction (XRD). Accordingly, the crystallization mechanism involved in this glass is suggested to be the co-nucleation of lithium metasilicate and disilicate, rather than the nucleation of lithium disilicate only. Some intermediate phases in trace amounts were also detected. It clearly demonstrates that the advanced synchrotron-based X-ray enables the detection capability of powder diffraction technique.

The main results in this chapter have been published in:


5.1 Introduction

Lithium disilicate glasses have been extensively studied\textsuperscript{1-5} and have been clinically applied in dental restoration. Desired physical and mechanical properties can be attainable through a controlled annealing procedure. The annealing process controls the phase formation and transformation, microstructure, crystallinity and hence properties of the glass-ceramics. The reported values of flexural strength and fracture toughness for lithium disilicate glass-ceramics are generally 215–350 MPa using three-point or four-point bend test and 3–3.4 MPa-m\textsuperscript{0.5} using single-edge notched beam (SENB) method.\textsuperscript{6} Glass-ceramics having high strength and high fracture toughness are in increasing demand in dental restorative applications. von Clausbruch et al. from Ivoclar Vivadent AG\textsuperscript{5} reported a ZnO-containing lithium disilicate with a flexural strength of 440 MPa in the SiO\textsubscript{2}–Li\textsubscript{2}O–K\textsubscript{2}O–ZnO–P\textsubscript{2}O\textsubscript{5} system using three-point bending test. Ivoclar has also reported a high flexural strength of 726 MPa in a ZnO-free SiO\textsubscript{2}–Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3}–K\textsubscript{2}O–ZrO\textsubscript{2}–P\textsubscript{2}O\textsubscript{5} system,\textsuperscript{3,7} using a biaxial bending method as per ISO standard 6872. To the best of our knowledge, the three-point flexural strength of such a glass-ceramic is not available in the literature. In our work described in Chapter 4, we tested a similar composition glass by three-point bending and only attained 307 MPa.\textsuperscript{8}

The key factors affecting the properties of glass-ceramics include the chemical composition, nucleants added, annealing profile, crystallinity, crystalline phases present, and crystal morphology of the glass-ceramics. In the work covered in this chapter, we developed a high-strength lithium disilicate glass-ceramic that has a non-stoichiometric composition in a SiO\textsubscript{2}–Li\textsubscript{2}O–MgO–P\textsubscript{2}O\textsubscript{5}–ZrO\textsubscript{2} glass system. Three sets of annealing were designed to study the influences of heating profile, crystallisation temperature and holding time on the phase evolution, microstructure and mechanical properties of the lithium disilicate glass-ceramics.

5.2 Experimental procedures

5.2.1 Crystallisation process

Three sets of experiments were designed according to the differential thermal analysis
(DTA) curve of glass B (Figure 5.2, in Section 5.3). In the first set, we investigated how annealing stages affect the crystallization process (see Set I in Table 5.1). The first stage (530 °C, 90 min) is designed for nucleation, while the other stages are for crystallisation. Set II aims to study the effect of crystallization temperature at the 2nd stage (samples M1–M6 in Table 5.1). Similarly, Set III aims to study the effect of holding time at the 2nd stage (samples T1–T5 in Table 5.1). It is noted that the temperatures for Set II and III were selected in the range within the major exothermal peak of the DTA curve. The last stage in Set II and Set III was at 800 °C, which is 20 °C higher than the third stage of Set I.

Table 5.1. Heat treatment profiles of the lithium disilicate glasses.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Annealing profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st stage</td>
</tr>
<tr>
<td>Set I</td>
<td></td>
</tr>
<tr>
<td>2S</td>
<td>530 °C/90 min</td>
</tr>
<tr>
<td>3S</td>
<td>530 °C/90 min</td>
</tr>
<tr>
<td>4S</td>
<td>530 °C/90 min</td>
</tr>
<tr>
<td>Set II</td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>530 °C/90 min</td>
</tr>
<tr>
<td>M4</td>
<td></td>
</tr>
<tr>
<td>M5</td>
<td></td>
</tr>
<tr>
<td>M6</td>
<td></td>
</tr>
<tr>
<td>Set III</td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td></td>
</tr>
<tr>
<td>T2</td>
<td></td>
</tr>
<tr>
<td>T3</td>
<td>530 °C/90 min</td>
</tr>
<tr>
<td>T4</td>
<td></td>
</tr>
<tr>
<td>T5</td>
<td></td>
</tr>
</tbody>
</table>

5.2.2 Characterisation and mechanical testing

Crystalline phases of the glass-ceramics treated at different annealing stages were identified by laboratory RT-XRD on a D2-Phaser diffractometer. Laboratory HT-XRD measurements were performed on a D8 Advance diffractometer with a high temperature chamber. Continuous XRD patterns were recorded at temperatures in the range of 480–930 °C with step interval of 30 °C (a total of 16 measurements). The average heating rate in the monitored range was about 1 K·min⁻¹. Synchrotron HT-XRD measurements were also performed. There
were 22 holding stages within the temperature range of 500–920 °C, with an interval of 20 °C (Figure 5-1), for recording the diffraction patterns. At each stage, X-ray was switched on for 4 min to detect the phases at corresponding temperatures.

![Figure 5-1](image.png)

**Figure 5-1.** Temperature profile of glass annealing for synchrotron measurements.

Microstructural observation of the glass-ceramic samples was performed on the polished cross sections and un-polished fractured surface by ESEM and EDX. Flexural strength was measured by three-point bending tests. Average values were calculated from 5–7 samples. Vickers microhardness and Vickers indentation fracture (VIF) toughness were evaluated as per the description in Section 3.3.5.

### 5.3 Results

Figure 5-2 presents a differential thermal analysis (DTA) trace for the glass. A major exothermic peak is recorded at 674 °C and a glass transition temperature at 451 °C. There are additional two weak peaks at ~725 °C and 775 °C, which might be attributed to the crystallisation of some minor crystalline phases. The annealing profiles are designed as per these DTA peaks, as shown in Table 5-1.
5.3.1 In situ high temperature XRD investigations

5.3.1.1 Laboratory HT-XRD investigation

Figure 5-3 displays the HT-XRD patterns of the glass in the range of 480–900 °C in a two-dimensional view. No diffraction peaks was noticeable if the temperature is below 540 °C. It is found that the stable LS$_2$ phase formed directly in the glass. No peaks of LS phase were
detected throughout the entire laboratory HT-XRD measurements. The formation of LS$_2$ phase is considered via the reaction:

$$\text{Li}_2\text{O} \text{ (glass)} + 2 \text{SiO}_2 \text{ (glass)} = \text{Li}_2\text{Si}_2\text{O}_5 \text{ (cryst)}$$

The intensity of LS$_2$ increases with temperature till 840 °C, after which it decreases with temperature (Figure 5-3). The volume fraction of the crystallized LS$_2$ phase quickly increases to a maximum amount in the as-prepared glass-ceramic at 630 °C. It is also observed that a higher temperature (>840 °C) gives rise to more glassy phase at the expense of LS$_2$ crystals in the glass-ceramic. As seen in Figure 5-3, LP phase starts to emerge at 750 °C; its fraction also increases with temperature. In addition, β-cristobalite (JCPDS 27-0605, cubic) and β-quartz (JCPDS 11-0252, hexagonal) crystals formed at 780–870 °C and 810–900 °C, respectively. XRD data acquisition failed at a temperature >930 °C because the sample is significantly distorted.

5.3.1.2 Synchrotron HT-XRD investigation (Detection of trace phase formation)

With the scheduled annealing profile in Figure 5-1, the in situ high-temperature XRD patterns of the complex lithium disilicate glass were acquired and depicted in a two-dimensional pattern in Figure 5-4a where the intensities are illustrated in colour. No diffraction peaks were observed at temperatures below 580 °C. There are five crystalline phases identified from the synchrotron diffraction patterns: LS, LS$_2$, LP, β-cristobalite (CR), and β-quartz (QZ).

The diffraction peaks initiated at 580 °C can be assigned to LS and LS$_2$ phases. The intensity of LS phase (~500 counts) is considerably lower than that of LS$_2$ phase (~160,000 counts), as shown in Figure 5-4b. Such a high intensity ratio of LS$_2$ to LS (over 300 times) may explain why the precipitation of LS in this glass was hardly detected by the laboratory X-ray source. Due to the distortion of the sample, data acquisition of synchrotron powder diffraction of this glass failed at a temperature ≥920 °C where melting was accelerated.

5.3.1.3 Weight fraction and crystal size evolutions determined by Rietveld refinements

The weight fractions of involved phases, as shown in Figure 5-5, were determined by applying Rietveld refinement using synchrotron powder diffraction data. Both LS and LS$_2$
phases were detected at 580 °C, with a limited quantity of 0.09 wt% and 0.08 wt% respectively as determined by quantitative phase analysis. The LS$_2$ phase dominated the glass-ceramic during crystallization, which reached a fraction of above 50 wt% at 660 °C. The crystallization of LS$_2$ reached a maximum of ~63 wt% at ~760 °C. In this glass, LS with a maximum amount of ~2 wt% formed and completely disappeared at 700 °C although its diffraction intensity is extremely low.

![Image](image.png)

Figure 5-4. (a) In situ high-temperature XRD patterns (in colour contour) of the complex lithium disilicate glass, (b) the line patterns of partial data to show the peaks of LS phase (directed by arrows) and peaks of other unidentified phase (directed by stars). D: lithium disilicate (LS$_2$); M: lithium metasilicate (LS); P: lithium phosphate (LP); C: cristobalite (CR); Q: quartz (QZ).

The silica phases including β-cristobalite and β-quartz crystallized when the temperature reached 780 and 820 °C, respectively. As indicated in Figure 5-5, LP, CR and QZ showed a linear increasing trend after their precipitation. The complete crystallization of LP gave a maximum fraction of ~4 wt%, whereas the maximum fraction of CR and QZ was about 2 wt% and less than 1 wt%, respectively.

The evolution of crystallite size of LS$_2$ with temperature is shown in Figure 5-6. The size of LS$_2$ crystals was refined to be about 200 nm at 600 °C. Very interestingly, the crystallite size of LS$_2$ remained in the same level at 600–700 °C where the LS phase co-existed with LS$_2$. Similar trend was also observed in glass Bo (see Figure 7-6 in Chapter 7). Right after the disappearance of LS at 700 °C, the LS$_2$ phase showed a gradual crystal growth.
Figure 5.5. Weight fraction of phases in the glass-ceramics as a function of temperature. The quantitative results suggest a maximum of ~2 wt% LS precipitated from the glass.

Figure 5.6. The crystallite size of LS$_2$ phase as a function of temperature. The dotted line shows the silicate phase(s) existed in the corresponding temperature range. The crystal growth of LS$_2$ is indicated to be hampered by the existence of LS.

5.3.2 Selection of annealing stages – Set I

5.3.2.1 Phase assemblage and mechanical properties of products of Set I

After being subjected to multi-stage heat treatments, the glass-ceramic samples are white, which is favourable to the subsequent colour tuning for dental restorations. The evolution of the crystalline phases and the properties of lithium disilicate glass-ceramics were studied in the first set of experiments listed in Table 5-1. The nucleation stage was kept constant at
Chapter 5 | Fabrication of a lithium disilicate glass-ceramic from the SiO\textsubscript{2}–Li\textsubscript{2}O–MgO–P\textsubscript{2}O\textsubscript{5}–ZrO\textsubscript{2} glass system

530 °C for 90 min. At this stage, the samples are still transparent, which means the LS\textsubscript{2} and LP nucleus are invisible to naked eye. Crystallisation is achieved by the subsequent heat treatments, up to four stages. The phase assemblage and mechanical properties of the heat treated samples are listed in Table 5-2.

Table 5-2. Heat treatment process, crystalline phases, crystallinity, and Li\textsubscript{2}Si\textsubscript{2}O\textsubscript{5} content in the products, and mean value ± standard deviations for flexural strength (\(\sigma_f\)), Vickers hardness (HV), VIF fracture toughness (\(K_c\)).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystalline phase</th>
<th>Crystallinity (%)</th>
<th>Li\textsubscript{2}Si\textsubscript{2}O\textsubscript{5} (wt%)</th>
<th>(\sigma_f) (MPa)</th>
<th>HV (GPa)</th>
<th>(K_c) (MPa\textsuperscript{m\textfrac{1}{2}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-stage, 2S</td>
<td>Li\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}+Li\textsubscript{3}PO\textsubscript{4}</td>
<td>60.7 ± 5.1</td>
<td>57.6 ± 2.5</td>
<td>439 ± 93</td>
<td>7.83 ± 0.20</td>
<td>0.93 ± 0.01</td>
</tr>
<tr>
<td>3-stage, 3S</td>
<td>Li\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}+Li\textsubscript{3}PO\textsubscript{4}</td>
<td>64.9 ± 6.2</td>
<td>61.5 ± 4.2</td>
<td>418 ± 53</td>
<td>7.24 ± 0.23</td>
<td>1.15 ± 0.02</td>
</tr>
<tr>
<td>4-stage, 4S</td>
<td>Li\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}+Li\textsubscript{3}PO\textsubscript{4}</td>
<td>61.7 ± 7.6</td>
<td>58.0 ± 5.3</td>
<td>371 ± 49</td>
<td>6.39 ± 0.25</td>
<td>1.29 ± 0.07</td>
</tr>
</tbody>
</table>

As shown in Figure 5-7 and also summarised in Table 5-2, the crystalline phases are LS\textsubscript{2} and LP for all these three cases, i.e., 674 °C/30 min (sample 2S), 780 °C/30 min (sample 3S), and 850 °C/30 min (sample 4S). XRD patterns suggest that the content of LP phase increases with increasing temperature (Figure 5-7). No silica phases appeared in the conventionally annealed glass-ceramics, which is obviously different from the results of in situ HT-XRD investigation (Figure 5-3). The crystallinity and fraction of LS\textsubscript{2} phase in the glass-ceramics are summarised in Table 5-2, showing that the product after 3-stage treatment possesses the highest crystallinity and LS\textsubscript{2} content.

Figure 5-7. RT-XRD patterns of lithium disilicate glass-ceramics crystallised at different stages.
Table 5-2 also presents the bending strength ($\sigma_f$), Vickers hardness ($HV$), fracture toughness ($K_c$) determined with Vickers indentation technique (VIF) of the lithium disilicate glass-ceramics. Both flexural strength and hardness decrease with the number of heat treatment stages. On the contrary, an additional higher temperature treatment is beneficial for the fracture toughness (Table 5-2), which increased from 0.93 MPa-m$^{1/2}$ for 2-stage annealing to 1.29 MPa-m$^{1/2}$ for 4-stage annealing.

![Figure 5-8. SEM images of the lithium disilicate glass-ceramics from Set II: (a) sample 2S, (b) sample 3S, and (c) sample 4S (after polishing and etching); and (d) the fracture surface of sample 3S (without polishing). Scale bar = 5 µm](image)

It is noted that, in spite of low fracture toughness, the flexural strengths in the range of 370 to 440 MPa are comparable with, or slightly better than the commercial IPS Empress 2 glass ceramic.$^1$ $^{10}$ $^{11}$ The low VIF toughness value is also similar to those reported in Ref. $^{12}$ (1.5~1.7 MPa·m$^{1/2}$). It is proposed that for an identical glass-ceramic the fracture toughness values measured by SENB method are much higher (2.5~3.3 MPa·m$^{1/2}$)$^{12}$. 
5.3.2.2 Microstructure of products of Set I

Figure 5-8 a–c show the microstructure in the polished glass-ceramics crystallised with different stages. It can be seen that the LS₂ crystal size increases with annealing stage, from ~0.5 μm in sample 2S to ~2 μm in sample 4S. In the 2-stage sample (2S), the LS₂ crystallites are of equiaxed morphology; and nano-sized pits were observed. These nano-sized pits are thought to be the etched-out LP crystals. By increasing the annealing temperature, the aspect ratio of LS₂ crystallites increases to 3–4 (Figure 5-8c), suggesting that a higher temperature promotes a preferential crystal growth and results in an elongated morphology of the LS₂ crystallites. In addition, LP crystallites also grow into a rod-like morphology with submicron size at 780 and 850 °C. Figure 5-8d illustrates the fracture surface showing that LS₂ grains have a rod-like morphology.

5.3.3 Optimization of the second stage (nucleation stage)

5.3.3.1 Phase assemblage and microstructure of products of Sets II and III

The crystalline phase assemblage of Set II samples (M1 – M6) is shown in Figure 5-9a. Apart from the main phases of LS₂ and LP, a phase with diffraction peak located at 2θ = 31.90° was identified in the samples M2 – M5. However, this peak could not properly match any JCPDS cards and is referred to as an unknown phase. Set III samples (T1 – T5) had similar XRD patterns to the samples M2 – M5 and displayed in Figure 5-9b.

![Figure 5-9](image-url)
min, and (b) Set III samples annealed at various holding times of the second stage at 675 °C.

The morphology of selected samples of Set II (M1, M3, M4, M6) are illustrated in Figure 5-10. It can be seen that their microstructures are similar except for the crystallite size. Samples M1 and M6 have a larger crystallite size than samples M3 and M4. In addition, nano-sized crystallites with different contrast (brighter than that of LS₂ crystallites) were present in the backscattered electron images (Figure 5-10b–c), which might be the unknown phase, as identified by XRD (Figure 5-9). It is noted that this unknown phase only existed in the samples with crystallisation temperatures of 640–700 °C. The unknown phase might be a variant of zirconia or zircon-related phase and its nucleation may only take place in a specific temperature range. The effect of holding time on the microstructure of the glass ceramics is shown in the backscattered electron micrographs (Figure 5-11). Similar microstructures to those in samples M3 and M4 of Set II are observed, except that the Set III samples had slightly larger crystallite sizes.

![Figure 5-10](image)

**Figure 5-10.** BSE micrographs of Set II samples treated under different temperatures at the second stage for 30 min (after polishing and etching). (a) sample M1, 620 °C, (b) sample M3, 660 °C, (c) sample M4, 680 °C and (d) sample M6, 720 °C. Scale bar = 5 μm.
As discussed above, it demonstrates that the crystallization temperature is more critical than the holding time on the morphology and crystallite size of lithium disilicate glass-ceramics in our glass system. This is because crystallisation of glass is a diffusion-controlled process.

Figure 5-11. BSE micrographs of Set III samples treated with different holding times at 675 °C (after polishing and etching). (a) sample T1: 15 min, (b) sample T2: 30 min, (c) sample T5: 120 min. Scale bar = 5 μm.

5.3.3.2 Flexural strength of Sets II and III

After heat treatment, the glass-ceramic samples were tested using the 3-point bending
method to determine the flexural strength. The mean values and standard deviations of the bending strength are summarized in Figure 5-12. In comparison with the first set, the second and third sets of samples were of lower mean flexural strength in the range of 280~345 MPa. However, it should be noted that these two sets of glass-ceramics were produced from a different batch of glass melt. Although the difference in the flexural strength among these samples is not significant, as a rule of thumb, a higher crystallization temperature increases the flexural strength. A higher temperature enhances the development of the LS$_2$ crystallites, which in turn increases the flexural strength.

![Figure 5-12](image)

**Figure 5-12.** Bending strength of (a) Set II samples at different holding temperatures (samples M1 to M6) and (b) Set III samples at different holding times (samples T1 to T5).

### 5.4 Discussion

The additive P$_2$O$_5$, most likely in the form of Li$_3$PO$_4$, acts as heterogeneous nucleation sites during the crystallisation of lithium disilicate glasses.$^4$ These Li$_3$PO$_4$ nuclei not only nucleate precursor LS,$^2$ but also directly initiate LS$_2$ crystals especially if the glass does not involve the formation of LS. On the contrary, in the current glass the LP phase was observed at 700 °C and above, which was after the crystallization of LS and LS$_2$. This suggests that LP nuclei with short range order (which cannot be notably detected by XRD) form in the glass at an early stage, which then trigger the compositional gradients of parent glass and lead to the nucleation of silicate phases.$^{13, 14}$

It is noteworthy that the LS phase in this glass was not detected by the conventional X-ray source, either *in situ* or *ex situ*. With the laboratory data, the crystallization of glass B should
be regarded via a “LS-free” nucleation mechanism as the LS phase was blindly neglected due to the weakness of the laboratory X-ray source. On the contrary, with the aid of the advanced synchrotron radiation, we managed to track the trace phase formation of LS, from a trace amount as low as 0.08 wt% to the maximum fraction of ~2 wt% (Figure 5-5), which nucleated simultaneously with LS$_2$ at 580 °C. Correspondingly, the mechanism is revised to be the simultaneous nucleation of both LS and LS$_2$ phases. The formation of limited fraction of LS phase has also been reported by Soares Jr et al. during the investigation of crystallization of binary Li$_2$O-SiO$_2$ glasses.$^{15}$ The LS phase coexisted with LS$_2$ up to 120 hours at the glass transition temperature, suggesting the same reaction sequence in the glasses involving the formation of trace LS phase.

Besides, it is interesting that there were no peaks of zirconia (ZrO$_2$) identified in the diffraction peaks in the entire temperature range. This is different from glass Bo (a similar glass in SiO$_2$-Li$_2$O-Al$_2$O$_3$-P$_2$O$_5$-ZrO$_2$ system) we previously investigated (see Chapter 4) where cubic ZrO$_2$ was detected in the products even though glass Bo contains a lower amount of ZrO$_2$.\textsuperscript{8}

The crystallite size of LS$_2$ at the temperature range where LS crystallizes remains at the same level of around 200 nm, and then it gradually increases (Figure 5-6). A similar trend was reported in other lithium disilicate glasses.$^{13}$ This may imply that the existence of LS in the glass not only affects the crystallographic structure of LS$_2$ but also hampers its crystal growth capability.

The mechanical properties (flexural strength decreases and toughness increases) showed opposite trends against temperature (Table 5-2), the reasons for which are not well understood. The total crystallinity or the quantity of the LS$_2$ phase is seemingly not the reason. We therefore postulate that the decreased flexural strength and hardness with additional annealing stages might be attributed to the increased fraction of the LP phase present in the glass (see Figure 5-8 in the subsequent section). The increased VIF fracture toughness could be ascribed to the elongated LS$_2$ crystallites (Figure 5-8c in Section 5.3.2.2).
5.5 Summary

In this work, we studied the phase evolution of a complex lithium disilicate glass in the SiO\textsubscript{2}-Li\textsubscript{2}O-CaO-P\textsubscript{2}O\textsubscript{5}-ZrO\textsubscript{2} system by high-temperature XRD, and investigated the effects of heating profile, annealing temperature and holding time for crystal growth on phase composition, microstructure and mechanical properties of the derived glass-ceramics. The following conclusions can be made:

1. In Set I, the lithium disilicate glass-ceramics possess 57-62 wt% lithium disilicate crystals measured by semi-quantitative analysis. By increasing the multi-stage annealing temperature, the Vickers hardness of the glass-ceramics decreases from $7.83 \pm 0.20$ GPa to $6.39 \pm 0.25$ GPa, while the fracture toughness of the products increases from 0.93 to $1.29 \text{ MPa}\cdot\text{m}^{1/2}$. These glass ceramics showed excellent flexural strength of $439 \pm 93$ MPa when heat treated at 675 °C in the second stage.

2. The crystallization temperature plays a more critical role than the holding time in affecting the phase transformation, morphology and crystal size of the glass-ceramics (Sets II and III).

3. No lithium metasilicate was detected during the crystallisation process of lithium disilicate glass. The phase evolution process of the glass during conventional annealing process was different from that under the annealing of the \textit{in-situ} high temperature XRD investigation.

This high-strength glass composition is promising for dental restorative applications, especially for posterior three-unit bridge dental restoration.

5.6 References


Chapter 6  Fabrication of high-strength glass-ceramics with a highly networked and interlocked microstructure

This chapter aims to develop a high-strength lithium disilicate glass-ceramic from a novel glass composition for dental restorative applications. A complex lithium disilicate glass composition (Glass C) was designed in the SiO$_2$–Li$_2$O–MgO–Al$_2$O$_3$–P$_2$O$_5$–ZrO$_2$ glass system. Four sets of samples were employed to investigate the effects of heating profile, crystallisation annealing temperature and holding time on the phase evolution, microstructure and mechanical properties. A three-stage heat treatment schedule was investigated step by step in order to maximize the mechanical properties of the products. The highest average bending strength, 562 ± 107 MPa was obtained using a three-stage heat treatment of 505°C/60min + 605°C/60min + 810°C/120min. The high bending strength of the product was elucidated by the unique networking and interlocking feature. The LS$_2$ (Li$_2$Si$_2$O$_5$) crystals are combined with each other and such a novel microstructure gives rise to a higher strength. The as-developed glass-ceramic could be a good candidate for dental restorative applications, especially for posterior three-unit bridges.

The main results in this chapter will be reported in:


6.1  Introduction

Lithium disilicate glass-ceramics as a promising dental restorative material have been well known for its high mechanical properties and excellent translucency.$^1$ The commercial dental products (such as IPS Empress®2) have a typical flexural strength of 400±40 MPa and toughness of 3.3±0.3 MPa m$^{1/2}$. Nevertheless, the current products are not yet commercially used for multi-unit restorations involving a molar.$^3$ This is because the attained strength and fracture toughness in the IPS Empress®2 do not meet the requirements for multi-unit applications.
In the past years, efforts have been made to enhance the reliability and service life of lithium disilicate glass-ceramic dental products by improving their mechanical properties.\textsuperscript{4, 5} For this purpose, zirconia, best known for its transformation toughening effect,\textsuperscript{6, 7} is added to reinforce lithium disilicate glass-ceramics.\textsuperscript{5, 8} Such a toughening effect, however, may be questionable if the effective tetragonal zirconia polycrystals (TZP) do not precipitate in the glass-ceramics.\textsuperscript{4, 8, 9} Alternatively, a high crystalline interlocking microstructure is preferably expected for enhancement of the mechanical properties,\textsuperscript{2, 4, 10-12} which is basically dependent on glass composition and the thermal annealing process. In 2007, Apel et al. reported a lithium disilicate glass-ceramic with a high biaxial flexural strength (>700 MPa) in the SiO\textsubscript{2}–Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3}–K\textsubscript{2}O–P\textsubscript{2}O\textsubscript{5}–ZrO\textsubscript{2} glass system.\textsuperscript{5} In addition, three-point flexural strength measurements on similar glasses in the same system do not indicate such high strength, but with mean values of 307–394 MPa instead.\textsuperscript{9, 11} Very interestingly, Zhang \textit{et al.} reported that an additional annealing stage could release the internal stress of the glass-ceramics and therefore largely improve the flexural strength to ~581 MPa.\textsuperscript{11}

In this chapter, we developed a high-strength lithium disilicate glass-ceramic in the complex SiO\textsubscript{2}–Li\textsubscript{2}O–MgO–Al\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5}–ZrO\textsubscript{2}–K\textsubscript{2}O–CaO system. The optimization of heat treatment of glass for the high strength glass-ceramics was carefully implemented. The evolution of microstructure was observed and revealed a novel effective interlocking structure which contributes to the enhanced properties.

6.2 Experimental procedures

6.2.1 Glass preparation

The non-stoichiometric multi-component lithium disilicate glass (i.e., glass C) was designed in the SiO\textsubscript{2}–Li\textsubscript{2}O–MgO–Al\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5}–ZrO\textsubscript{2}–K\textsubscript{2}O–CaO system, whose chemical composition as given in Table 3-1. The glass was melted at 1350 °C for 18 h in an alumina crucible. After melting, the molten glass was drawn into rod samples of 4–7 mm in diameter.

6.2.2 Glass-ceramic fabrication

We adopted a three-stage annealing profile for glass crystallization, and optimized the properties of the as-received glass-ceramics from the designed glass composition. The first
stage was optimized by the so-called “Marotta method”. Furthermore, it is known from previous work that the selection of intermediate crystallization (or “mid-stage”) temperature would have considerable influence on the phase composition and microstructure of the glass-ceramics. Thus, in this study we designed four sets of experiments as follows (Table 6-1). The first stage (505 °C, holding time 60 min) was kept the same to initiate glass nucleation to a similar extent for all experiments. Sets I and II aim to study the effects of temperature (580–655 °C, samples T1–T4) and holding time (10–120 min, samples S1–S4) at the mid-stage of the crystallization process of the glass. Sets III and IV were adopted to study the influence of temperature (750–830 °C, samples T5–T8 & S3) and holding time (10–120 min, samples S5–S8) at the third stage on the microstructure and flexural strength of glass-ceramics. The favoured temperature or holding time was adopted for the optimization of the next set of experiment, which was done one after another from set I to set IV.

Table 6-1. Heat treatment profiles of different glasses.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1st stage</th>
<th>2nd stage</th>
<th>3rd stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>505°C/60 min</td>
<td>580°C/20min</td>
<td>830°C/30min</td>
</tr>
<tr>
<td>T2</td>
<td></td>
<td>605°C/20min</td>
<td></td>
</tr>
<tr>
<td>T3</td>
<td></td>
<td>630°C/20min</td>
<td></td>
</tr>
<tr>
<td>T4</td>
<td></td>
<td>655°C/20min</td>
<td></td>
</tr>
<tr>
<td>Set II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>505°C/60 min</td>
<td>605°C/10min</td>
<td>830°C/30min</td>
</tr>
<tr>
<td>S2</td>
<td></td>
<td>605°C/30min</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td></td>
<td>605°C/60min</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td></td>
<td>605°C/120min</td>
<td></td>
</tr>
<tr>
<td>Set III</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T5</td>
<td>505°C/60 min</td>
<td>605°C/60min</td>
<td>750°C/30min</td>
</tr>
<tr>
<td>T6</td>
<td></td>
<td></td>
<td>770°C/30min</td>
</tr>
<tr>
<td>T7</td>
<td></td>
<td></td>
<td>790°C/30min</td>
</tr>
<tr>
<td>T8</td>
<td></td>
<td></td>
<td>810°C/30min</td>
</tr>
<tr>
<td>Set IV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>505°C/60 min</td>
<td></td>
<td>810°C/10min</td>
</tr>
<tr>
<td>S6</td>
<td></td>
<td></td>
<td>810°C/20min</td>
</tr>
<tr>
<td>S7</td>
<td></td>
<td></td>
<td>810°C/60min</td>
</tr>
<tr>
<td>S8</td>
<td></td>
<td></td>
<td>810°C/120min</td>
</tr>
</tbody>
</table>

6.2.3 Characterisation methods

Firstly, the DSC trace of the original glass without any pre-treatment was recorded at a
heating rate of 15 K/min in argon gas. To evaluate the effectiveness of nucleation temperature and time, the glass specimens were subjected to further DSC measurements by pre-annealing it at various temperatures (465–545 °C, for 2 h) or holding times (15 min to 4 h, at the optimized temperature 505 °C) according to the Marotta method by applying the same heating rate. The shifts of exothermal peaks of the DSC traces with respect to the original glass (without any pre-treatment) were then carefully determined.

Crystalline phases of glass-ceramics treated at different annealing stages were identified by XRD on a laboratory D2-Phaser diffractometer at room temperature.

In situ synchrotron X-ray diffraction (SXRD) was performed to the parent glass at elevated temperatures. The diffraction patterns were recorded at 23 holding stages to detect the phases within the range of 500–940 °C, with an interval of 20 °C. At each stage the X-ray beam was switched on for 4 min. Microstructural observation of glass-ceramic samples was performed by ESEM and EDX. TEM and SAED were carried out on a FEI Tecnai F20-G2 electron microscope as described in Section 3.3.4.2.

6.3 Results

6.3.1 HT-XRD investigation

The in situ high-temperature diffraction patterns were recorded in the range of 480–900 °C, which are plotted in Figure 6-1 (top: 3D contour; bottom: 2D contour). No diffraction peaks was noticeable if the temperature was below 580 °C. The lithium metasilicate (Li$_2$SiO$_3$, LS) phase nucleated at 580 °C and then transformed to lithium disilicate phase (orthorhombic Li$_2$Si$_2$O$_5$, LS$_2$) at 700 °C via the reaction Eqn (1).

\[
\text{Li}_2\text{SiO}_3 \text{(cryst)} + 2 \text{SiO}_2 \text{(glass)} = \text{Li}_2\text{Si}_2\text{O}_5 \text{(cryst)} \tag{1}
\]

At the higher temperatures, the crystal growth of lithium disilicate during the measurement (>700 °C) accompanied with the crystallization of other minor phases, including lithium phosphate (Li$_3$PO$_4$, LP, ≥780 °C), β-quartz (SiO$_2$, QZ, 840–900 °C) and a possible phase of MgAl$_2$Si$_4$O$_{12}$ (820–900 °C). Temperatures of over 840 °C gave rise to more glass
phase at the expense of LS$_2$ crystals in the glass-ceramic. Accurate XRD data acquisition failed at 920 °C due to the sample melting and distortion.

![In situ synchrotron high temperature XRD patterns of the lithium disilicate glass](image)

6.3.2 Design of pre-nucleation stage via Marotta method

As described in the experimental section, we conducted a step-by-step optimization of mechanical properties for the fabrication of glass-ceramics using a three-stage annealing profile. The first stage of the annealing profile aims to precipitate suitable nuclei for the latter two stage crystallization. We employed thermal analyses via the Marotta method$^4$, $^{13}$ to interpret the effects of temperature and time on nucleation. To be specific, the DSC traces of glasses with or without pre-treatment are plotted in Figure 6-2. In the DSC trace of the original glass, there are two major exothermal peaks at approximately 603.2 °C and 742.2 °C, respectively. The glass transition temperature is ~460 °C. The shifts in the exothermal peaks were demonstrated in Figure 6-3a, which indicate an optimal nucleation temperature of 505 °C where the first exothermal peak almost disappeared. The shift of the second exothermal peak at this temperature also reached the maximum, which has been widely observed in other experiments.$^4$, $^{13}$ On the other hand, the shifts against holding time are shown in Figure 6-3b, which suggests that duration of 1 h at 505 °C could introduce an efficient number of nuclei. The first exothermal peak was noticeable within 2 h.
Figure 6-2. (a) DSC traces of glass C after treatment at different annealing temperatures for 2 h, (b) DSC traces of glass C after treatment at 505 °C for different annealing time. The heating rate was 15 K/min.

Figure 6-3. The shift of the main exothermal peaks of glasses after pre-treatment at various temperature or time from DSC trace of original glass. $\Delta T_p = T_p - T_p'$

6.3.3 Optimization of mechanical properties

On the basis of above results, we used the optimal temperature of 505 °C and holding
time of 1 h to introduce nuclei for the following two annealing stages. Four sets of experiments (Table 6-1) were designed to optimize the annealing profile and improve the flexural strength of glass-ceramics.

![XRD patterns of samples at various temperatures or holding times](image)

Figure 6-4. XRD patterns of samples at various temperatures or holding times. The first stages are 505 °C for 60 min, and the following two stages are (a) 580-655 °C for 20 min + 830 °C for 30 min, (b) 10-120 min at 605 °C + 830 °C for 30 min, (c) 605°C for 60min and 750-830 °C for 30 min, and (d) 605°C for 60min and 10-120 min at 810 °C.

The phase assemblages in the as-crystallized glass-ceramics were investigated as shown in Figure 6-4. The four sets of samples all composed of lithium disilicate (main phase) and lithium phosphate. The variation of temperature at this stage affected the phase composition in
the products (set I: T1–T4). This can be seen from the relative intensity of quartz phase and from the appearance of some additional peaks (noted by “S” and “T”) in the powder diffraction patterns in Figure 6-4a. The sample T2 in this set showed higher flexural strength (369±77 MPa) than others (Figure 6-5a). Accordingly, the temperature of mid-stage was preferably selected to be 605 °C and the influence of holding time at this temperature was then investigated (set II: S1–S4).

![Graph showing flexural strength and holding time](image)

Figure 6-5. Flexural strength of samples at various temperatures or holding times. The first stages are 505 °C for 60 min, and the following two stages are (a) 580-655 °C for 20 min + 830 °C for 30 min, (b) 10-120 min at 605 °C + 830 °C for 30 min, (c) 605°C for 60min and 750-830 °C for 30 min, and (d) 605°C for 60min and 10-120 min at 810 °C.

It is noted that the holding time of the second stage had considerable effect on the crystallization of this glass (Figure 6-4b). To be specific, a medium length of holding period (20–60 min) for glass nucleation at the mid-stage resulted in the precipitation of hexagonal phases (quartz and/or MgAl2Si4O12) in final products (samples T1–T4 and S2-S3), whereas
none of these phases crystallized in the samples (S1 and S4) when much shorter (10 min) or longer (120 min) holding time were employed at this stage. Interestingly, the samples with the hexagonal phases demonstrated higher flexural strength (369–407 MPa) than other samples without these phases (242–272 MPa), as shown in Figure 6-5b. This probably indicates that the existence of hexagonal phases could be beneficial to the enhancement of mechanical properties of glass-ceramics. The optimal duration time at the mid-stage was then optimized to be 60 min.

To explore the effect of temperature and time at the third stage, the sets III and IV were designed. Although all samples (T5–T8 and S5–S8) possessed the same phase assemblage (Figure 6-4 c–d), higher temperature and longer time are contributing to the enhancement of mechanical properties of lithium disilicate glass-ceramics. When temperature is in the range of 790–830 °C, the flexural strength of glass-ceramics was over 400 MPa. The optimal temperature at the third stage could be 810 °C as the corresponding glass-ceramics illustrated the highest strength of 417±66 MPa (Figure 6-5c). The effect of holding time was investigated at this temperature, and clearly showed a gradual increase in the flexural strength with an increasing period of annealing (Figure 6-5d). When applying a short holding time of 10 min at the optimized temperature, the as-prepared glass-ceramics only showed a mean strength of 276 ± 85 MPa. The glass-ceramics demonstrated significant improvement of flexural strength (exceed 500 MPa) with a holding time of 1 h and longer. The mean strength of the lithium disilicate glass-ceramics was 562±107 MPa when extend the holding time to 2 h at 810 °C during the final stage.

### 6.3.4 Microstructure of high-strength lithium disilicate glass-ceramics

To trace the influence of heat treatment temperature and time on the microstructure of glass-ceramics, samples were carefully polished and etched with 2 vol% HF acid solution to expose the grains of lithium disilicate and other phases. Nevertheless, the crystals of lithium phosphate phase cannot withstand the HF acid solution and were easily dissolved off, leaving with voids in the cross section or fracture surface of samples.
Figure 6-6. (left column) Polished surface and (right column) fracture surface of samples treated with various temperatures at the third stage (30 min). (a) T5 - 750°C, (b) T6 - 770°C, (c) T7 - 790°C, (d) T8 - 810°C

The microstructure evolution of glass-ceramics with temperature and time are shown in Figure 6-6 and Figure 6-7, respectively. Homogeneous equiaxed grains formed in nanoscale were observed in the sample T5 which annealed at 750 °C (Figure 6-6a). It was observed that the higher heat treatment temperature at the third stage led to apparent crystal growth in the glass-ceramics. Although the crystal length reached a maximum (~2 μm), the main phase lithium disilicate crystallized in a unique microstructure of networking and interlocking (Figure 6-6d). A large amount of lithium disilicate grains networked and interlocked to form the novel morphology. In addition, many elongated voids can be observed in such
morphology of lithium disilicate. These voids could be left from the dissolving of either crystalline phase(s) or glass. By annealing at 810 °C, the formation of such morphology requires a minimum holding time of 20 min (Figure 6-7). Longer holding time led to an increase in the fraction of this type of grains. Some round grains or “X”-shape morphology can also be observed in the glass-ceramics (e.g. Figure 6-6d and Figure 6-7c), which are probably the minor phase quartz or MgAl$_2$Si$_4$O$_{12}$ formed in the material.

Figure 6-7. (left column) Polished surface and (right column) fracture surface of samples treated with various holding times at the third stage (810 °C). (a) S5 - 10min, (b) S6 - 20min, (c) S7- 60min, (d) S8- 120min.
Figure 6-8. The typical feature of networked structure widely existing in the high-strength glass-ceramic (sample S8).

6.4 Discussion

6.4.1 Formation process of the unique microstructure

In comparison with the glass-ceramics that developed from glasses Bo and B, the glass-ceramic from glass C has much higher flexural strength. To be specific, the optimized
strength of glass-ceramic from glass Bo is only 307 MPa and mean strength of glass-ceramic from glass B is 439 MPa. From glass C, the lithium disilicate glass-ceramic has a mean value of 562 MPa, with a maximum strength of 712 MPa. In addition, it is noted that the glass-ceramic may be further improved if an additional annealing stage was applied to relieve the stress in the material. The benefit of such procedure was reported to be obvious on enhancing the flexural strength of glass-ceramic by Zhang et al.\textsuperscript{11}

The high strength glass-ceramic has a highly networked, interlocked, and clustered microstructure. Such a microstructure is clearly developed from nano-size particles to interlocked submicron rods then to the networked and interlocked grain clusters (Figure 6-6). The above results, particularly those of sample set IV (Figure 6-7), lead to a strong indication that the significant enhancement of flexural strength of lithium disilicate glass-ceramics is highly correlated to the novel microstructure of lithium disilicate phase. The submicron elongated rods coalesced to form the layered clusters and interlocked throughout the materials, which constructed a firm structural unit that is harder to break down comparing with the unnetted rods. A schematic illustration is plotted as the experimental results (Figure 6-9).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6-9.png}
\caption{The schematic illustration for the formation of the netted and interlocked clusters of lithium disilicate in the glass-ceramics.}
\end{figure}
To evaluate the fracture toughness of this glass-ceramic, a glass disc was subjected to heat treatment by applying the optimized temperature profile. Then, rectangular bars were wire cut by diamond saw to the dimensions of about 2×4×40 mm$^3$ (Section 3.3.5.2.2). After grinding, polishing and notching (depth of about 2 mm), five standard specimens were tested using three-point flexure via the SENB method as per the ASTM standard C-1421-09, with a span of about 20 mm. The average toughness was calculated to be $3.45 \pm 0.08$ MPa m$^{0.5}$.

### 6.4.2 Understanding of the intrinsic formation mechanism

To interpret the formation mechanism of lithium disilicate grains with the as-observed novel morphology, a rod sample of S8 (with flexural strength of 623 MPa) was subjected to further TEM investigation. The thinned area of the glass-ceramic cannot withstand an accelerating voltage of 100 keV if a cold stage is not used. The thinnest edge collapsed dramatically if the focused electron beam was on, indicating that the local heat was quite high that the specimen was rapidly perforated. In this case, high resolution observation is impossible. To solve this problem, the TEM specimen was placed in a cold stage filled with liquid nitrogen which cooled the specimen down to about -173 °C. However, the specimen also encountered severe shifting problem during the observation under a magnification of above 50000×. So far, no high resolution TEM images were acquired.

![TEM image of an “H” like microstructure in the glass-ceramic.](image)
Chapter 6 | Fabrication of high-strength glass-ceramics with a highly networked and interlocked microstructure

103

Figure 6-11. TEM image of a sample of GCS8 (with flexural strength of ~623 MPa)

Table 6-2. The composition of spots 1–4 in Figure 6-11 detected by EDS.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>Spot 1</th>
<th>Spot 2</th>
<th>Spot 3</th>
<th>Spot 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>63.85</td>
<td>64.54</td>
<td>68.06</td>
<td>64.08</td>
</tr>
<tr>
<td>Si</td>
<td>30.57</td>
<td>32.56</td>
<td>28.85</td>
<td>32.80</td>
</tr>
<tr>
<td>Al</td>
<td>3.21</td>
<td>1.65</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>2.35</td>
<td>0.41</td>
<td>3.01</td>
<td>0.99</td>
</tr>
<tr>
<td>Ca</td>
<td>0.37</td>
<td></td>
<td>0.29</td>
<td>0.36</td>
</tr>
<tr>
<td>Mg</td>
<td>0.29</td>
<td></td>
<td></td>
<td>0.33</td>
</tr>
<tr>
<td>Na</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An “H” like microstructure of LS₂ crystals was observed during TEM measurement (Figure 6-10). Such a structure represents the interlocking feature of even two paralleling elongated crystals by the bonding crystal in the middle. Among them, there is a glassy matrix phase as evidenced by SAED observation. This TEM observation is consistent with the SEM observation on the netting and interlocking microstructure of layered crystal clusters.

Figure 6-11 shows the high-angle annular dark-field (HAADF) STEM images of the high-strength lithium disilicate glass-ceramic. Apart from the elongated crystals in 100–300 nm, some round/ellipse grains can be observed in the microstructure. By EDS analysis of
these grains, Si and O are the main elements of their compositions. Interestingly, minor amount of Al was detected in spots 1, 2 and 4, and much lower amounts of Mg and Ca were detected in spot 2 and spot 4 (Table 6-2). Lithium is out of the detection limit of EDS technique, so these grains have the possibility of being lithium-containing. Thus, the grain indicated by spot 1 could be (lithium-) aluminosilicates, the one at spot 2 may be magnesium/calcium aluminosilicate, the grain at spot 3 may be silica, and that of spot 4 may be lithium disilicate doping with Al. The detected phosphorus in the composition may indicate the inclusion of lithium phosphate nuclei in the grains. This is evidenced by the observed nano-sized crystals in Figure 6-12a, which dispersed throughout the glass-ceramics.

![Fig 6-12](image)

Figure 6-12. (a) TEM and (b) SAED images of the high-strength lithium disilicate glass-ceramic.

The selected area electron diffraction (SAED) images of four grains are shown in Figure 6-12b. As the cold-stage is single-tilt, it is really hard to adjust to high-axis direction when performing the SAED of the grains. The diffraction patterns in the SAED images of Figure 6-12b indicate multi-crystalline nature of the detected grains at spots 1 and 2. The round grains at spots 3 and 4 have regular electron diffraction patterns, indicating an orthorhombic and monoclinic structure, respectively.

As indicated from HT-XRD data, both β-quartz and MgAl$_2$Si$_4$O$_{12}$ (which have orthorhombic symmetry) can be crystallized from the glass. The EDS results further suggest that both Mg, Al and Ca in a limited amount enter into crystalline structures, and possibly
form phases like (Mg, Ca)Al$_2$Si$_4$O$_{12}$. A crystal with Si, O and Al (but without Mg) was identified by EDS as well, demonstrating possibility of the formation of petalite LiAlSi$_3$O$_8$ (JCPDS 75-1716), which has a monoclinic structure as observed in the electron diffraction data of spot 4 in Figure 6.12b.

It is pity that the high-resolution lattice observation of the crystal clusters was not successful. Thus, no direct evidence can be used to deduct the formation process of the unique microstructure. Even though, the current TEM data do enable us to see the microstructure of glass-ceramic without acid etching treatment of specimen. In the glass-ceramics, there are lath-like LS$_2$, round-shape QZ crystals, and nano-sized LP nuclei. The EDS analysis of crystals confirmed the presence of Mg, Al, Ca, and K in some of the crystals.

6.5 Summary

High-strength lithium disilicate glass-ceramics were developed in the SiO$_2$–Li$_2$O–MgO–Al$_2$O$_3$–P$_2$O$_5$–ZrO$_2$–K$_2$O–CaO system by annealing profile optimization in a step-by-step manner. From the in situ synchrotron high-temperature XRD study, the phase transition process of the complex parent glass was revealed, and illustrated that the lithium metasilicate form solely then transform to lithium disilicate phase at around 700 °C with other minor phases (MgAl$_2$Si$_4$O$_{12}$ and β-quartz) forming at temperatures of above 820 °C. The pre-nucleation temperature and time were investigated by a thermal analysis (DSC) method, and the optimization of intermediate stage and final stage of heat treatment were investigated by mechanical testing and microstructure observation. It shows that the bending strength of lithium disilicate glass-ceramics was significantly enhanced from 276 ± 85 to 562 ± 107 MPa by applying an optimized three-stage annealing profile of 505°C/60min + 605°C/60min + 810°C/120min. We successfully developed a novel microstructure composed of networked and interlocked clusters in the high-strength glass-ceramics, which can effectively enhance the mechanical properties. TEM study suggests that the components MgO and Al$_2$O$_3$ in the parent glass precipitate to form the crystalline phases like (Mg,Ca)Al$_2$Si$_4$O$_{12}$ and LiAlSi$_3$O$_8$. The high-strength glass-ceramic is promising for dental restorative applications, especially for posterior three-unit bridge dental restoration.
6.6 References


Chapter 7  Crystallization kinetics of a lithium disilicate glass by in situ synchrotron powder diffraction

The high-temperature phase transformation of a multi-component lithium disilicate glass (glass Bo) was investigated by in situ and real time synchrotron X-ray diffraction in the SiO$_2$–Li$_2$O–P$_2$O$_5$–Al$_2$O$_3$–ZrO$_2$ glass system. Quantitative phase analysis via Rietveld method was performed on the high-resolution data aiming to reveal the crystallization sequence, crystallization kinetics and the role of P$_2$O$_5$ on nucleation. It is found that the nucleation of lithium metasilicate (LS) and lithium disilicate (LS$_2$) in this complex glass is triggered by the steep compositional gradients associated with the disordered lithium phosphate (LP) precursors in the glass matrix. The LS$_2$ crystals grow at the expense of the LS, cristobalite and quartz phases in the glass during the isothermal crystallization process at 770°C. The nucleation kinetics is temperature dependent, and the induction period of nucleation is longer at a lower temperature.

The main results in this chapter have been published in:


7.1 Introduction

Glass-ceramics with desired properties can be produced by designing glass recipe and controlling crystallization of the parent glasses.$^1$ There have been extensive fundamental studies on the mechanisms, kinetics and thermodynamics of nucleation and crystallization of base glasses.$^{2-10}$ The Li$_2$O–SiO$_2$ glass systems are one of the most extensively investigated glasses since its discovery in the 1950s.$^{11, 12}$ In the regime of Li$_2$O–SiO$_2$ systems, stoichiometric binary Li$_2$O–2SiO$_2$ glass serves as an ideal model material for studying nucleation mechanism and primary phase formation$^{2, 5, 13, 14}$ while multi-component glasses have been developed for various engineering applications.$^9, 15$ The addition of some indispensable, either minor or major, constituents significantly alters the nucleation and
crystallization kinetics and/or phase formation scenarios, which in most cases are more complex than those in the binary Li$_2$O–SiO$_2$ systems.

P$_2$O$_5$ is one of the most widely used nucleating agents for glass. McMillan and Partridge$^{16,17}$ first discovered the nucleating potency of P$_2$O$_5$ in a number of ternary glass compositions such as Li$_2$O–Al$_2$O$_3$–SiO$_2$, Li$_2$O–MgO–SiO$_2$, and MgO–Al$_2$O$_3$–SiO$_2$. Due to a charge difference between the two network-forming ions, P$^{5+}$ and Si$^{4+}$, one phosphorus-oxygen bond per [PO$_4$] tetrahedron must be a double-bond. The presence of this double-bonded oxygen ions leads to a favourable phase separation of phosphate grouping from the silicate network. Follow-up work on adding Li$_3$PO$_4$ to binary Li$_2$O–SiO$_2$ revealed that substitution of 1 mol% P$_2$O$_5$ for the equivalent amount of SiO$_2$ results in significant phase separation.$^{18}$ McMillan et al. also observed that the addition of 1 mol% P$_2$O$_5$ resulted in a much finer grained microstructure.$^{19,20}$

The work prior to the late 1980s have been summarized in the literature.$^{11,21}$ Significant efforts have been devoted to understanding the mechanisms by which P$_2$O$_5$ addition controls crystallization in glass. One plausible model is epitaxial growth of the crystallizing phase on the nucleating agent or on a phase that incorporates it. Conceptually this model is supported by the close lattice match, i.e. small lattice disregistry, between Li$_3$PO$_4$ and Li$_2$Si$_2$O$_5$ crystals. The first piece of experimental evidence in favour of this model was given by Headley and Loehmann in 1984.$^{22}$ They observed epitaxial growth of cristobalite (CR), LS, and LS$_2$ on the LP crystals. In their work,$^{22}$ well-crystallized LP precipitation had been obtained by an initial high temperature treatment at 1000°C for 20 min, prior to their crystallization study. It is therefore questionable whether LP actually nucleates the silicate phases. Using X-ray diffraction (XRD), Iqbal et al. detected crystallization of Li$_3$PO$_4$ phase in a Li$_2$O–SiO$_2$ system containing 5 mol% P$_2$O$_5$ when the glass was heated at 476°C.$^{23}$ However, their transmission electron microscopy (TEM) work did not provide direct evidence of the presence of LP. Furthermore, they found that in a glass system containing less than 3 mol% P$_2$O$_5$, such LP crystals could not be detected by XRD and TEM if the glass is nucleated in an optimal temperature range (450–550°C).$^{23}$ Due to the technical difficulties of laboratory XRD and microscopy in detecting crystalline phases as they are either in small quantity or small size, the fundamental understanding of the crystallization process is incomplete, and the real role of
Li$_3$PO$_4$ as a nucleating agent is still unclear.

In addition to the conventional laboratory XRD, microscopy, differential thermal analysis (DTA) and physical property measurements, nuclear magnetic resonance (NMR), has been performed to give a quantitative description of silicate framework species, its interaction with Li ions and the structural changes of the minor constituents such as P and Si.$^{23-27}$ Most recently, Bischoff et al.$^{28}$ revisited the crystallization process in a lithium disilicate glass using $^{29}$Si single and double resonance solid state NMR spectroscopy. Their NMR results negate the epitaxial growth model previously proposed by Headley and Loehmann,$^{22}$ and instead suggest that the nucleation of LS and LS$_2$ both initiate at the phase boundary between the disordered LP and glass matrix. However, both Headley et al.$^{22}$ and Bischoff et al.$^{28}$ were unable to reveal what relationship exists between LS and LS$_2$ during nucleation and crystal growth.

In the past decades, thermodynamic and kinetic aspects of nucleation and crystal growth have been extensively investigated, particularly in simple glass systems.$^8$ In most cases the crystallization kinetics follows the well-known Avrami equation, or more accurately KM-JMA equation,$^{29-31}$ named after Russian mathematician Kolmogorov and metallurgist Mirkin, and American metallurgists Johnson, Mehl and Avrami. Due to the experimental difficulties in obtaining high-quality nucleation data by the conventional methods such as DTA or laboratory XRD,$^5$ the understanding of the crystallization kinetics in complex lithium disilicate glasses is still limited.

In this chapter, we employed X-ray powder diffraction in using synchrotron radiation to reveal the structural changes of the parent glasses in situ and real-time, by monitoring spontaneous change in the XRD spectra of during glass crystallization. With the high-resolution XRD data, we revisited the nucleation and crystallization processes by quantitatively analysing the changes of fraction and crystallite size of each phase during both non-isothermal and isothermal crystallization processes, from the very beginning of nucleation to the completion of crystallization. Specifically, the nucleation and crystallisation kinetics are investigated in this study.

### 7.2 Experimental procedures

In this chapter, a multi-component lithium disilicate glass containing both P$_2$O$_5$ and ZrO$_2$
(glass Bo) was employed, which has already been documented in the literature.\textsuperscript{15, 32, 33} Three series of \textit{in situ} synchrotron HT-XRD experiments were conducted to study the nucleation and crystallization kinetics of the lithium disilicate glass (Figure 7-1).

![Figure 7-1](image)

Figure 7-1. The temperature profiles of three series of synchrotron XRD experiments. Series I: continuous heating from 500°C to 1010°C; Series II: isothermal annealing at 770°C for 120 min, to study crystallization kinetics; and Series III: isothermal annealing at 560°C, 570°C, and 580°C, respectively, to study its nucleation kinetics.

(I) Non-isothermal crystallization by continuously heating to 1010°C

A glass sample was quickly heated from room temperature (~25°C) to 500°C in 1 min and then continuously heated to 1010°C with a ramp rate of 400 K/min in a stepwise manner. The fast ramp rate was employed to minimize the additional nucleation or crystal growth during the heating process. The XRD patterns were continuously recorded from 500 to 1010°C at an interval of 10 to 30°C. At each temperature, the sample was held for 4 min for XRD recording.

(II) Isothermal crystallization at 770°C

To study the crystallization kinetics, the lithium disilicate glass was heated to a crystallization temperature of 770°C with a ramp rate of 400 K/min, and then held at this temperature for up to 120 min. A total of 200 patterns were recorded during the 120 min holding period.

(III) Isothermal nucleation kinetics study at 560–580°C

The glass samples were heated from room temperature to a temperature of 560–580°C.
When the temperature reached the prescribed setting, the XRD data were collected. All data were automatically recorded for a fixed collecting time of 30 s (at 560 and 570°C) or 45 s (at 580°C) per dataset. This ensures achieving high quality spectra and real time measurements.

After data acquisition, phase analysis was conducted to figure out the involved phase evolution, and then full-pattern analysis via Rietveld method was performed using the software MAUD to retrieve the quantitative phase content, crystallite size, crystallographic parameters and other information.

7.3 Results and Discussion

7.3.1 Series I: in situ non-isothermal crystallization

Figure 7-2 shows the synchrotron HT-XRD data of the lithium disilicate glass recorded from 500 to 1010°C (Series I). The intensity change of each phase with temperature and/or holding time qualitatively reflects the trend of its volume fraction in the glass samples. In this regard, the strongest peak intensity of each phase, i.e. (111) for LS₂, LS, ZrO₂ and (120) for LP, is shown in Figure 7-3 as a function of temperature.

Figure 7-2. Synchrotron HT-XRD of the lithium disilicate glass when continuously heated from 500 to 1010°C.

D: Li₂Si₂O₅ (LS₂); M: Li₂SiO₃ (LS); P: Li₃PO₄ (LP); Z: ZrO₂.
As presented in Figure 7-2 and Figure 7-3, the intensity of LS phase increases sharply from 580°C to 640°C and then gradually to 750°C, after which the intensity decreases quickly and vanishes at 780°C. In contrast, the LS\textsubscript{2} intensity drastically increases at 730–780°C, and then levels off until 850°C, followed by a quick decrease and complete vanishing at 950°C. The ZrO\textsubscript{2} intensity demonstrates a similar trend to the LS\textsubscript{2}. It seems that when the LP intensity rapidly increases at 850°C, the LS\textsubscript{2} intensity starts to drop.

![Graph showing phase intensities](image)

**Figure 7-3.** Intensities of phases in the Series I sample as a function of temperature. The intensity data are taken from the strongest peak of each phase, i.e. (111) plane of LS\textsubscript{2}, LS, and ZrO\textsubscript{2}, and (120) of LP.

A close-up XRD pattern (Figure 7-4) reveals that the LS peaks emerged at 560°C while the LS\textsubscript{2} peaks emerged at 580°C, suggesting that LS nucleates slightly prior to LS\textsubscript{2}. This is a new finding in terms of phase transition sequence as most laboratory XRD investigations are unable to identify this sequence in such a narrow temperature range.
Chapter 7 | Crystallization kinetics of a lithium disilicate glass by in situ synchrotron powder diffraction

7.3.1.1 Volume fraction vs. annealing temperature

The p1-pattern of each XRD dataset was used for full pattern analysis by Rietveld refinement. Figure 7-5 presents the temperature-dependent volume fraction of each phase evolved during the continuous heating process (Series I). This agrees with the qualitative analysis results in Figure 7-3. As shown in Figure 7-5, in the temperature range of 560 to 750°C, the volume fraction of LS phase is greater than that of LS$_2$ phase. At a temperature between 750 and 780°C, the volume fraction of LS phase rapidly decreases to 0.6 vol.% whereas LS$_2$ phase increases dramatically from 23.4 vol.% to 66.6 vol.%.

Above 780°C, the glass-ceramic contains crystalline phases of LS$_2$, LP and ZrO$_2$. With increasing temperature, the fraction of LS$_2$ phase decreases whereas that of LP phase is almost constant below 950°C. It must be pointed out that the X-ray diffractogram of LP phase below 780°C is a broad hump, which can be attributed to the disordered (amorphous) LP species. The formation of such disordered species may be due to the clustering of phosphorous and lithia in the glass matrix. Nevertheless, it is observed that such disordered LP species tends to become ordered when the temperature increases and eventually the well-ordered LP crystals form at a temperature >780 °C. $^{31}$P MAS-NMR results by Bischoff et al.$^{28}$ present a similar phenomenon. The volume fraction of ZrO$_2$ phase is significantly small (refer to the inset in Figure 7-5). The highest amount of ZrO$_2$ is 0.73 vol.% at 820°C. Nevertheless it has a similar relationship with temperature as the LS$_2$ phase does in the range of 770–930°C.
Figure 7-5. Volume fraction of phases as a function of temperature, determined by XRD full pattern quantitative phase analysis.

7.3.1.2 Crystallite size vs. annealing temperature

Our previous research shows that the well-crystallized LS and LS$_2$ phases are of short rod shape in this glass-ceramic. In order to evaluate the crystal growth rate during crystallization process, the mean crystallite sizes of LS, LS$_2$ and LP were determined using an isotropic size-strain model during the Rietveld refinement process, and the results are shown in Figure 7-6. It is noted that the holding time at each temperature was 4 min during XRD data acquisition. It can be seen that the LS$_2$ crystallite size increases from 83 to 817 nm when the temperature rises from 580 to 930°C (note that the LS$_2$ phase disappeared at 950°C). Concomitantly the LS crystals grow from 44 to 161 nm as the temperature increased from 580 to 780°C. In the temperature range of 800 to 950°C, the LP crystallite size increases from ~25 nm to ~430 nm. The crystallite sizes of each phase can be fitted to an exponential model as shown in Figure 7-6.
7.3.2 Series II: *Real time isothermal crystallization*

In order to study the crystallization kinetics of this glass, we chose a temperature of 770°C at which a major LS\(_2\) phase and a certain amount of LS phase exist. Figure 7-7 displays the synchrotron HT-XRD patterns recorded at this temperature with elapsed time of 120 min. Six phases emerged in the entire process: Li\(_2\)Si\(_2\)O\(_5\) (LS\(_2\)), Li\(_2\)SiO\(_3\) (LS), Li\(_3\)PO\(_4\) (LP), ZrO\(_2\), cristobalite (CR) and quartz (QZ).

Figure 7-7. Real time synchrotron HT-XRD of the lithium disilicate glass treated at 770°C with elapsed time of 120 min. D: lithium disilicate, Li\(_2\)Si\(_2\)O\(_5\); P: lithium phosphate, Li\(_3\)PO\(_4\); M: lithium metasilicate, Li\(_2\)SiO\(_3\); C: cristobalite; Q: quartz; Z: ZrO\(_2\). A trace amount of ZrO\(_2\) (<0.15 vol.%) precipitated after heating for 24–120 min at this temperature.
The data shown in Figure 7-7 were further processed for quantitative phase analysis. The volume fractions of both amorphous and crystalline phases at 770°C against the time are plotted in Figure 7-8. Within the first 15 seconds (when first dataset was recorded), 27.5 vol.% LS and 3.5 vol.% LS$_2$ emerged and the remaining (~70 vol.%) was still glass phase. After the instantaneous advent of LS$_2$ and LS, the glassy portion decreased quickly from ~70 vol.% to less than 50 vol.% within the subsequent 24 min. The amount of ~20 vol.% glassy phase has been transformed to crystalline LS$_2$, cristobalite and quartz, while the amount of LS phase remains unchanged. After 24 min of holding, the volume fractions of LS, cristobalite and quartz decreased while the fraction of LS$_2$ increased, suggesting that the formation of LS$_2$ was formed at the expense of LS, quartz and cristobalite. This postulation is supported by the fact that the total amount of these four phases did not vary with the holding time (~51 vol.% in total).

![Figure 7-8. Volume fraction of all phases as function of the elapsed time at 770°C. The total volume fraction of LS, LS$_2$, QZ and CR against the elapsed time is also plotted. The standard deviations are less than 0.1%.](image)

Apart from the volume fraction change, the crystallite size of the LS and LS$_2$ phases also changed during the crystallization process. As shown in Figure 7-9, the LS$_2$ crystallite size follows a power curve while the LS crystallite size follows an exponential curve. The difference in crystal growth velocity may be ascribed to the different mechanisms of crystal growth for LS and LS$_2$. The exponential form of the LS crystallite size curve implies that LS crystal growth proceeds by attaching larger ordered clusters to the advancing front of LS. These larger ordered clusters could be formed by phase separation in the glass. On the other
hand, the LS$_2$ growth may be accomplished by single-atom jumping. This different growth mechanisms have been observed in crystallisation of Ni-P glass.$^{34}$ The crystallite sizes of LS phase after 80 min holding are excluded in Figure 7-9 due to significant errors in the course of Rietveld refinement.

![Graph showing crystallite size vs time for LS and LS$_2$ phases](image)

Figure 7-9. Crystal size of the LS$_2$ and LS phases with the holding time at 770°C

### 7.3.3 Series III: Real time nucleation kinetics study

Figure 7-10 shows the real time synchrotron XRD patterns at 560, 570 and 580°C. At such a nucleation temperature, only the diffraction peaks of crystalline LS and LS$_2$ phases were observed. The induction time, within which no nucleation is noticeable, gradually reduces with increasing temperature. For example, at 560°C noticeable LS peaks emerge after 10 min while at 580°C the LS peaks become visible after 3 min.
Figure 7-10. *Real time* synchrotron HT-XRD patterns of the glass at (a) 560, (b) 570, and (c) 580°C. The nucleation and crystallization of LS and LS$_2$ phases are temperature and time dependent.

The volume fraction of the LS$_2$ and LS phases as a function of nucleation temperature are plotted in Figure 7-11. At a lower temperature, the induction time of nucleation is longer. The induction time for nucleation of disilicate and metasilicate glasses were also studied by Deubener *et al.*, but using an indirect method of analysis. They indicated that the induction time analysis may be able to distinguish the nucleation process being homogeneous or heterogeneous or tell whether there is a metastable precursor. All the curves have a typical sigmoidal shape wherein an initial slow rise is followed by a rapid rise and slows down again towards the completion of crystallization. The LS phase takes longer time to reach the maximum volume fraction (i.e. saturation state of nuclei) than LS$_2$ phase at each nucleation temperature. Besides, the time expected for the saturation of LS nuclei is also much longer at lower temperatures. The kinetics calculation is presented in the subsequent section.
Chapter 7 | Crystallization kinetics of a lithium disilicate glass by in situ synchrotron powder diffraction

7.4 Discussion

7.4.1 Phase formation sequence

7.4.1.1 Series I: non-isothermal crystallization

The phase evolution in this glass over temperature can be divided into several stages (Figure 7-5): (i) induction period, (ii) nucleation of LS and LS$_2$, (iii) saturated nucleation stage, (iv) LS-to-LS$_2$ transformation, (v) crystal growth of LS$_2$ and LP, (vi) dissolution of LS$_2$, and (vii) dissolution of LP. In this work we observed the precipitation of ZrO$_2$ during Stages (v) and (vi), even though a trace amount of ZrO$_2$ (0.73 vol.%) was added. LS$_2$ exists and grows in the temperature range of 580 to 930°C, whereas LS and crystalline LP emerge and grow from 560 to 780°C, and from 780 to 1010°C respectively. When the temperature is higher than 1010°C, the glass is completely melted. The phase formation sequences in the lithium disilicate glass are summarized in Table 7-1.

Based on the observations made in this study and the NMR work of Bischoff et al$^{28}$ whose glass has a similar composition to ours, we propose the following phase formation sequence. At 580–620°C (Stage ii, Figure 7-5), the crystalline LS is nucleated from Q$^{(2)}$(glass) and Q$^{(3)}$(glass) via the following Eqns. 1 and 2, whereas the formation of LS$_2$ is probably via Eqn. 3. During 620–730°C (Stage iii), the content and crystallite size of silicate phases have
little change.

Table 7-1. Summary of the phase formation sequences in the lithium disilicate glass.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temp range / °C</th>
<th>Reaction sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>500–580</td>
<td>induction period for nucleation</td>
</tr>
<tr>
<td>(ii)</td>
<td>580–620</td>
<td>nucleation of LS and LS$_2$</td>
</tr>
<tr>
<td>(iii)</td>
<td>620–730</td>
<td>nuclei of both LS and LS$_2$ saturated; formation of LP embryos with short-range order (poorly-crystallized)</td>
</tr>
<tr>
<td>(iv)</td>
<td>740–780</td>
<td>LS-to-LS$_2$ transformation</td>
</tr>
<tr>
<td>(v)</td>
<td>780–860</td>
<td>crystal growth of LS$_2$; formation of LP crystals (well-crystallized); the precipitation of ZrO$_2$</td>
</tr>
<tr>
<td>(vi)</td>
<td>860–950</td>
<td>dissolution of LS$_2$ and ZrO$_2$</td>
</tr>
<tr>
<td>(vii)</td>
<td>950–1010</td>
<td>dissolution of LP</td>
</tr>
</tbody>
</table>

The observation that LS formed earlier than LS$_2$ (Figure 7-4) is in agreement with the nucleation kinetics calculation of LS and LS$_2$ phases as LS has a lower activation energy.\textsuperscript{9} Besides, the evolution of LS$_2$ in this glass is closely related to LS at 580–780°C. More detailed crystallographic study of the glass-ceramic will be reported elsewhere.

At 740–780°C (Stage iv, Figure 7-5), the rapid increase of LS$_2$ and decrease of LS and glass phase suggest that, at this stage LS phase likely transforms into LS$_2$ phase via Eqn. 4. It is not clear whether or not LP plays a role in promoting the LS-to-LS$_2$ transition as the well-crystallized LP emerges only at a temperature $>$800°C. Subsequently, when the temperature was higher than 800°C (Stages v–vii), the amount of glass phase starts to increase while the amounts of LS$_2$ and ZrO$_2$ decrease. Also in this temperature range, the LP phase forms via Eqn. 5 and some of LS$_2$ and ZrO$_2$ crystals are melted back to the glass.

LS$_2$ exists and grows in the range of 580 to 930°C, whereas LS and crystalline LP emerge and grow from 560 to 780°C, and from 780 to 1010°C respectively. When the temperature is higher than 1010°C, the glass-ceramic is completely melted.

\[
\text{Li}_2\text{O (glass) + Q}^{(2)}\text{ (glass) = Li}_2\text{SiO}_3\text{ (cryst)} \quad \text{Eqn. 1}
\]
Crystallization kinetic of a lithium disilicate glass by *in situ* synchrotron powder diffraction

\[ \text{Li}_2\text{O} \text{ (glass)} + Q^{(3)} \text{ (glass)} = \text{Li}_2\text{SiO}_3 \text{ (cryst)} + Q^{(4)} \text{ (glass)} \]  
Eqn. 2

\[ \text{Li}_2\text{O} \text{ (glass)} + 2Q^{(3)} \text{ (glass)} = \text{Li}_2\text{Si}_2\text{O}_5 \text{ (cryst)} \]  
Eqn. 3

\[ \text{Li}_2\text{SiO}_3 \text{ (cryst)} + Q^{(4)} \text{ (glass)} = \text{Li}_2\text{Si}_2\text{O}_5 \text{ (cryst)} \]  
Eqn. 4

\[ 3 \text{Li}_2\text{O} \text{ (glass)} + P_2\text{O}_5 \text{ (glass)} = 2 \text{Li}_3\text{PO}_4 \text{ (cryst)} \]  
Eqn. 5

It is noted that the temperature range for the existence of LS phase is dependent on the glass compositions. In our glass with a SiO$_2$/Li$_2$O molar ratio of 2.5, the LS phase exists between 580 and 770°C, and disappears at ~780°C. In the lithium disilicate glass system with SiO$_2$/Li$_2$O molar ratio of ~2.8 as reported by Headley *et al.*,\(^{22}\) LS phase remained with a large amount at a higher temperature of 820°C. Another glass system we recently investigated (SiO$_2$/Li$_2$O molar ratio of ~2.4)\(^{36}\) shows that the formation of LS is very limited or even cannot be detected during the entire phase evolution process. Therefore it is worth to point out that the formation of LS in a lithium disilicate glass is largely dependent upon the overall glass composition, and cannot be merely judged from the molar ratio of SiO$_2$/Li$_2$O.

**7.4.1.2 Series II: isothermal crystallization**

The Rietveld refinement results reveal the correlation between volume fraction of each phase and holding time at 770°C (Figure 7-8). It is found that when the glass was directly heated to 770°C devoid of a nucleation stage, two silica phases – cristobalite (CR) and quartz (QZ) – formed in the sample within a few minutes. The formation of these phases is proposed to be achieved via the reaction Eqns. 3, 6, 7 and 8.

\[ \text{SiO}_2 \text{ (glass)} = \text{quartz} \text{ (cryst), after heating for } \sim 2 \text{ min} \]  
Eqn. 6

\[ \text{SiO}_2 \text{ (glass)} = \text{cristobalite} \text{ (cryst), after heating for } \sim 6 \text{ min} \]  
Eqn. 7

\[ \text{Li}_2\text{SiO}_3 \text{ (cryst)} + \text{SiO}_2 \text{ (QZ/CR) = Li}_2\text{Si}_2\text{O}_5 \text{ (cryst) (with <50 vol.% glass)} \]  
Eqn. 8

It is noted from Figure 7-8 that almost instantaneously, the fraction of LS, LS$_2$ and LP reaches 27.5 vol.%, 3.5 vol.% and 0.4 vol.%, respectively. Due to the significant change in atomic mobility with structural relaxation at 770°C, these initial amounts of crystallized phases are determined by the phase equilibrium in this glass system (lever rule). The variation
of volume fractions of $\text{LS}_2$ (Figure 7-8) suggests that the formation of $\text{LS}_2$ is at the expense of $\text{LS}$, $\text{CR}$ and $\text{QZ}$ via Eqn. 8. This postulation is supported by the fact that the total amount of these four phases does not vary with the holding time (amounting to $\sim$51 vol.% in total). The gradually reduced growth rate of $\text{LS}_2$ (Figure 7-9) could be ascribed to the reduced amounts of the reactants $\text{LS}$, $\text{CR}$ and $\text{QZ}$ available in the glass. Besides, the changing composition of the glass is also likely to affect both the thermodynamic and kinetic parameters during crystallization.\(^{10}\)

It is also noted that the types of silica phase precipitates in this glass depends on the heat treatment procedures. For example, with the isothermal profile of Series II, two types of silica phases ($\text{QZ}$ and $\text{CR}$) formed. In the same glass, however, only cristobalite precipitated in a conventional annealing process (i.e. separate nucleation and crystallization), as reported in our previous study;\(^{33}\) and no silica phase formed during the 23-step non-isothermal process of Series I. This strongly suggests that the silica phases (quartz and cristobalite) preferably crystallize when a relatively large amount of glassy phase is left in the lithium disilicate glass-ceramics at high temperatures. It is based on the fact that there are sufficient ingredients in the base glass for the formation of various phases in Series II.

In comparison however, for a non-isothermal annealing process, the formation of silica phases is limited. This is probably because a considerable amount of $\text{SiO}_2 + \text{Li}_2\text{O}$ ingredients are consumed during the nucleation and crystallization of silicate phases ($\text{LS}$ and $\text{LS}_2$) at the initial stages. The results also indicate that the properties of glass-ceramics can be tailored via a finely controlled phase transformation process.

### 7.4.2 Role of $\text{P}_2\text{O}_5$

The broad hump-like diffraction peak of LP phase, located at 20 angle of 16°–17°, was observed in the high-resolution real-time synchrotron XRD patterns. It is suggested that $\text{P}_2\text{O}_5$ species is being transformed to short-range order LP embryos (8–20 nm). LP embryos are poorly-crystallized with disordered structure at 580–770°C. This is consistent with the NMR findings of Bischoff et al. who suggested that phosphate acts as a lithium ion scavenger via formation of orthophosphate ($\text{P}^{(0)}$) and/or pyrophosphate ($\text{P}^{(1)}$) species.\(^{28}\) It is probably more accurate to state that the LP phase is amorphous or disordered glassy phase at the nucleation
period via Eqn. 5.

The volume fraction of glass phases is drawn in Figure 7-5. It has two downward trends in the ranges of 560–620°C and 750–780°C due to the nucleation and rapid LS-to-LS₂ transformation (via Eqn. 4), respectively. Below 780°C, the disordered structure of LP glassy phase gradually shifted toward ordered structure of crystalline LP phase (~5.5 vol.%), and contributed to the phase separation of silica rich droplets and lithia rich matrix phases from the base glass.³⁷ The boundaries of amorphous LP species were therefore regarded as the nucleation sites for lithium silicate phases. The formation of crystalline LP may contribute to the rapid transformation of LS₂ from LS via Eqn. 4.

From the evolution of phosphorus species as discussed above, it is suggested that the addition of P₂O₅ in the glass results in microstructural heterogeneities and steep compositional gradients in the glass at the early stage of nucleation. These results support the speculation of Höland et al.¹ on the nucleation mechanism, and in good agreement with the suggestion of Bischoff et al.²⁸ It is believed that the nucleation of LS and LS₂ phases in a conventional annealing process, in which no LP crystals are pre-seeded, is initiated by the disordered phosphorus species.

The cubic zirconia phase crystallized in the glass has little positive contribution to the crystallization of Li₂Si₂O₅, but will hamper the crystal growth as suggested in the literature.¹⁵, ³⁸ This type of zirconia also has no obvious contribution to the mechanical properties of lithium disilicate glass-ceramics.³³

### 7.4.3 Isothermal kinetics investigation

A simplified expression for the KM-JMA is given by Eqn. 9

\[ x(t) = 1 - \exp(-Kt^n) \quad \text{Eqn. (9)} \]

where \( x(t) \) is the volume fraction of a crystalline phase transformed, and \( k \) is a rate constant which incorporates the nucleation rate and the rate of radial growth of the newly nucleated nuclei. The value of Avrami exponent \( n \), which varies between 0.5 and 4, provides information on the crystallization mechanism.³⁹

In many cases, the sigmoidal shape curves involve an induction period \( (t_0) \) beyond which nucleation is negligible. As such, a modified formula is usually used and given by Eqn. 10:
\[ x(t) = 1 - \exp(-k(t - t_0)^n) \quad \text{Eqn. (10)} \]

By fitting experimental data, the Avrami exponent, \( n \), and rate constant, \( k \), for each crystalline phase, were calculated and summarized in Table 7-2. The value of \( n \) for LS\(_2\) phase (1.74–1.84) is higher than that for LS phase (1.24–1.49), while the rate constant \( k \) of LS\(_2\) is smaller than that of LS phase. The rate constant, \( k \), of both LS\(_2\) and LS phases increased with increasing temperature.

These data are used to calculate the activation energy with an Arrhenius assumption. The activation energies \( E_a \) of LS\(_2\) and LS are 275 and 213 kJ/mol, respectively and are relatively smaller than those reported by Hammetter et al. from DTA investigations, i.e. 360 kJ/mol for nucleation of LS\(_2\) and 270 kJ/mol for LS.\(^9\)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>( t_0 ) (min)</th>
<th>( n )</th>
<th>( \ln k )</th>
<th>( t_0 ) (min)</th>
<th>( n )</th>
<th>( \ln k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>560</td>
<td>12.5</td>
<td>1.82</td>
<td>-9.20</td>
<td>8.3</td>
<td>1.49</td>
<td>-7.07</td>
</tr>
<tr>
<td>570</td>
<td>5.6</td>
<td>1.74</td>
<td>-8.70</td>
<td>4.2</td>
<td>1.37</td>
<td>-6.77</td>
</tr>
<tr>
<td>580</td>
<td>3.6</td>
<td>1.84</td>
<td>-8.27</td>
<td>1.8</td>
<td>1.24</td>
<td>-6.35</td>
</tr>
</tbody>
</table>

In a similar way, the crystallization kinetics analysis is carried out. The Avrami exponent \( n \) of LS\(_2\) crystallisation is about 0.85. It may suggest that the LS\(_2\) crystals grow with limited dimensions.\(^{39}\) This suggestion is assisted by the microstructure of this glass-ceramic reported previously,\(^{33}\) i.e. LS\(_2\) clusters crystallized with lengths of 0.5–1 μm, and also by the refined crystallite size of LS\(_2\) in Figure 7-9. The LP phase is continuously precipitating as time elapses at 770°C. The kinetic study shows that its Avrami exponent \( n \) is 0.79.

It has to be noted that the above kinetics analysis is based on an indirect measurement of volume fractions of crystallites. A direct count of crystal number and measurement of their sizes is necessary if the technique permits.
7.5 Summary

The crystallization kinetics of a multi-component lithium disilicate glass was investigated by in situ and real time synchrotron high-temperature X-ray diffraction (HT-XRD) in the SiO$_2$–Li$_2$O–P$_2$O$_5$–Al$_2$O$_3$–ZrO$_2$ system. With the high resolution synchrotron XRD data, the effects of temperature and holding time on the phase transformation, crystallite size, and crystallinity was studied by quantitative phase analysis using the Rietveld full-pattern fitting method.

The in-situ synchrotron HT-XRD experiments have proved that, without pre-crystallization of lithium phosphate (Li$_3$PO$_4$), the nucleation mechanism of lithium metasilicate (Li$_2$SiO$_3$) and disilicate (Li$_2$Si$_2$O$_5$) in the complex lithium disilicate glass were triggered by the steep compositional gradients arising from the disordered lithium phosphate structural units in the glass matrix. This finding is in good agreement with the solid-state NMR results reported by Bischoff et al. (2011), and is different from the epitaxial growth mechanism in the glasses with the aid of well-crystallized Li$_3$PO$_4$ nucleating agent suggested by Headley et al. (1984).

Moreover, Li$_2$SiO$_3$ was evidenced to nucleate ahead of Li$_2$Si$_2$O$_5$, rather than simultaneously, at the very beginning of the nucleation of this glass. But it cannot answer whether the nucleation of Li$_2$Si$_2$O$_5$ relied on the pre-formation of Li$_2$SiO$_3$. The crystallinity of this glass reached ~72.6 vol.% at 780°C. The crystallite size of each phase increased obviously at the corresponding temperature range of crystal growth stage.

Li$_2$Si$_2$O$_5$ continued to grow at the expense of Li$_2$SiO$_3$, cristobalite and quartz when the glass was quickly heated to 770°C and held for 2 hours. The volume fractions of the related crystalline phases were fitted according to the KM-JMA model; and crystallization of cubic zirconia was modelled with a linear function, and its growth rate is about 0.19% per minute at 770°C.

The nucleation of the complex lithium disilicate glass was heterogeneous non-steady state and its kinetics was temperature dependent. At a lower temperature, the induction period of nucleation was longer. The volume fractions at different nucleation temperatures were modelled according to a modified KM-JMA equation $x(t) = 1 - \exp\left(-k(t - t_0)^n\right)$ to
incorporate the initial induction period. The Avrami exponent \( n \) of LS\(_2\) phase (1.74–1.84) was higher than that of LS phase (1.24–1.49), indicating different nucleation mechanisms. The activation energy \( E_a \) of LS\(_2\) and LS are calculated to be 275 and 213 kJ/mol, respectively.

### 7.6 References

Chapter 7 | Crystallization kinetics of a lithium disilicate glass by in situ synchrotron powder diffraction

26 M. Mortuza, M. Ahsan, R. Dupree & D. Holland. Disproportionation of Q$_m^m$ (0 $\leq$ m $\leq$ 4) species in partially devitrified Li$_2$Si$_2$O$_5$ glasses with small amounts of P$_2$O$_5$. *J. Mater. Sci.* **42**, 7950-7955 (2007).
Chapter 8  Crystallographic evolution of a lithium disilicate glass upon heating and cooling

In Chapter 7, the nucleation and crystallization kinetics of a complex lithium disilicate glass was investigated by in situ synchrotron X-ray powder diffraction. In this chapter, the crystallographic evolution trends of crystalline phases in the same glass (glass Bo) during the relevant annealing processes were further discussed. The experimental procedures employed are the same with those in Section 7.2. The lattice parameters and unit cell volume of crystalline phases as a function of temperature were determined upon heating. It is found that the lattice parameter \( c \) of LS\(_2\) shows a “V”-shape trend during heating. The crystallographic evolution of LS\(_2\) phase has a close correlation with LS phase, indicating the mutual interaction between LS and LS\(_2\) phases along \( c \) axis during the nucleation/crystallization process. The phase evolution processes were different upon heating and cooling, and the unit cell volume of both LS and LP phases demonstrated different change rates. In this glass system, no LS\(_2\) was detected during cooling and the main phases formed during cooling process were LP, LS, \( \beta \)-cristobalite and \( \beta \)-quartz. The crystallographic evolution mechanism is discussed.

The main results in this chapter have been published in:


8.1 Introduction

Lithium disilicate (Li\(_2\)O·2SiO\(_2\)) glasses have been well documented in both theoretical investigations and practical applications. It is well known that the simple binary Li\(_2\)O·SiO\(_2\) glass system has been served as a good model for fundamental understandings of the mechanism and kinetics of nucleation and crystal growth in glasses.\(^1\)\(^-\)\(^5\) In the past decades, extensive work has been devoted to interpreting nucleation and crystallization in multi-component glasses.\(^6\)\(^-\)\(^8\) In the multi-component glasses, nucleating agents, such as P\(_2\)O\(_5\),
TiO$_2$, and ZrO$_2$, are commonly added in order to facilitate nucleation of lithium silicate phases. Among these agents, P$_2$O$_5$ is by far the most common nucleant to promote heterogeneous bulk nucleation and hinder surface nucleation. However, with decades of extensive investigations and practice, we have not seen a general consensus with regards to the role of P$_2$O$_5$ on the crystallization of glasses. Thus far two mechanisms have been proposed. In a multi-component glass with well pre-crystallized Li$_3$PO$_4$ (LP) seeds, the silicate phases show an epitaxial growth mechanism, as reported by Headley et al. While, in lithium disilicate glasses without pre-seeding LP crystals, heterogeneous nucleation is initiated by steep compositional gradients. In the case of crystallisation of lithium disilicate glass-ceramics, the observed compositional gradient somehow resembles the constitutional undercooling in metal solidification. With regard to thermal undercooling, it is relatively small during metal solidification whereas viscosity plays a large role during glass formation.

Using high-resolution synchrotron X-ray powder diffraction, we detected the formation of disordered/amorphous LP species which triggered the nucleation of silicates phases. The interfaces between amorphous LP species and the glass matrix serve as nucleating sites in the glasses, which is suggested by solid-state NMR and synchrotron XRD studies. It is also necessary to point out that lithium disilicate glass-ceramics with fine-grained microstructure have attracted great attention for dental restorative applications due to their charming merits, such as excellent aesthetics, high strength, mild hardness, and good chemical stability. The lithium disilicate glass-ceramics with high-strength tend to show better performance for the dental restorations during clinical applications.

The simultaneous nucleation of Li$_2$SiO$_3$ (LS) and Li$_2$Si$_2$O$_5$ (LS$_2$) phases is an important phase transformation sequence for lithium disilicate glass-ceramics, which may result in a highly crystalline interlocking microstructure. In some glass compositions, the crystals of LS$_2$ nucleate simultaneously (observed via ex situ methods) with LS at low temperatures, in both the binary Li$_2$O·2SiO$_2$ system and the P$_2$O$_5$ doped systems. More recently, we found that LS formed slightly earlier than LS$_2$ from a time-resolved basis using synchrotron radiation X-ray, which can be explained by the lower activation energy for LS to initiate nucleation than that for LS$_2$. Apart from the parallel sequence, there are other two types of
reaction sequence: one is that LS crystals nucleate first and then LS$_2$ crystals nucleate heterogeneously on LS,\textsuperscript{16} and the other is that merely LS$_2$ crystals nucleate and LS crystals do not crystallize at all.\textsuperscript{19}

Although there are extensive studies on lithium disilicate glasses, the relationship between crystallographic evolutions of crystalline phases is poorly understood. Furthermore, our understanding of the relationship between lithium disilicate glasses during nucleation and crystallization processes is limited. In the present study, we investigated the crystallographic evolution of crystalline phases in the glass we previously studied\textsuperscript{8} upon heating and cooling. The relationship of high-temperature structural evolution of LS$_2$ and LS upon heating will be discussed, and some phenomena during the cooling process will be demonstrated as well.

8.2 Results

8.2.1 Phase transformation upon heating and cooling

The synchrotron HT-XRD patterns displayed in Figure 8-1a illustrate the phase transformation of the lithium disilicate glass during the heating process from 500 to 1010 °C. It is confirmed by the straight lines for peaks of LP in Figure 8-1a that the possibility of sample distortion was eliminated after re-melting before data collection. The phase evolution process and crystallization kinetics have been discussed elsewhere,\textsuperscript{8} and the phase evolution sequence is briefly summarized in Table 8-1.

<table>
<thead>
<tr>
<th>Heating of the glass</th>
<th>Cooling of the melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp range / °C</td>
<td>event</td>
</tr>
<tr>
<td>500–580</td>
<td>induction period</td>
</tr>
<tr>
<td>580–620</td>
<td>nucleation of LS and LS$_2$</td>
</tr>
<tr>
<td>620–730</td>
<td>saturated nucleation stage</td>
</tr>
<tr>
<td>740–780</td>
<td>LS-to-LS$_2$ transformation</td>
</tr>
<tr>
<td>800–860</td>
<td>crystal growth of LS$_2$ and LP</td>
</tr>
<tr>
<td>860–950</td>
<td>melting of LS$_2$ and ZrO$_2$</td>
</tr>
<tr>
<td>&gt;950</td>
<td>melting of LP</td>
</tr>
</tbody>
</table>
The cooling of glass melt was started from 1200 °C, then cooled down to 520 °C and eventually to room temperature. Considering the total dwell time for data acquisition, the overall cooling rate from 1200 to 520 °C was 8.5 K·min⁻¹. No crystalline phase was detected from 1200 °C to 1000 °C. During the cooling process, the precipitated crystalline phases are shown in Figure 8-1b. It is found that the LP crystals formed first at 950 °C, followed by LS and β-cristobalite crystals at 850 °C and a type of β-quartz crystals (Q1) at 840 °C. However, no LS₂ phase was detected during the entire cooling process. As LS₂ needs higher activation energy for nucleation than LS, LS₂ is more difficult to nucleate than LS. Therefore the LS phase emerged during cooling, while the nucleation of LS₂ was inhibited, either directly from the melt or by transforming LS in the glass. It is inferred that the driving force during the cooling event is sufficient for the nucleation of LS and silica phases, but not for the nucleation of LS₂. It may be also postulated that the rheological conditions of glass are not favourable for LS₂ to nucleate.

It is interesting to note that when cooling down to 770 °C, a new set of peaks emerged. These peaks can be assigned to β-quartz phase (Q2), as shown in Figure 8-2, which is an enlarged XRD pattern of Figure 8-1b within the selected 20 ranges. The phase evolution events during heating and cooling are compared in Table 8-1. The Q2 phase started to form at
770°C where the crystallization of other phases was saturated. It is thus hypothesized that these two β-quartz (Q1 and Q2) originate from different glass components in the matrix. The underlying reason for such a structural difference is not clear yet.

Figure 8-2. The enlarged XRD patterns of different phases in the sample upon cooling (from 950 to 520 °C). M: Li_2SiO_3 (LS); P: Li_3PO_4 (LP); C: β-cristobalite (cubic); Q1/Q2: β-quartz (hexagonal).

The crystallization kinetics of LS during cooling was studied by quantitative phase analysis. The weight fraction of LS as a function of temperature is given in Figure 8-3, which shows that LS crystallizes rapidly with 13.5 wt% at 850 °C, then levels off at 770 °C with ~20.8 wt%. It is much less than the maximum weight fraction of LS (~34.5 wt%) crystallized upon heating at 640–730 °C. Meanwhile, ~5.7 wt% β-cristobalite, ~1.8 wt% β-quartz and ~3.0 wt% LP crystallized during cooling.

Figure 8-3. The weight fraction of LS as a function of temperature on cooling. The dotted line used to connect the experimental points is for eye guidance.
8.2.2 Crystallographic evolution

8.2.2.1 Crystallographic evolution upon heating

During the heating process (Figure 8-1a), the LS phase forms in the range of 580–780 °C, and LS\(_2\) phase presents at 580–930 °C. The lattice parameters of each phase as a function of temperature are shown in Figure 8-4 in the corresponding temperature range. As to the LS\(_2\) phase, it shows an interesting phenomenon: the lattice parameter \(c\) decreases with increasing temperature from 580 to 780 °C, and then steadily increases with temperature up to 900 °C (Figure 8-4a). Both lattice parameters \(a\) and \(b\) of the LS\(_2\) phase increase with temperature. As with the LS phase, the lattice parameters \(a\) and \(b\) increase linearly with annealing temperature, while \(c\) decreases non-linearly (Figure 8-4b). The trends of all lattice parameters of LS were fitted by functions as shown in the figure. It is noted that the standard derivation of lattice parameters of LS\(_2\) and LS phases are much less than \(3 \times 10^{-4}\) Å and \(5 \times 10^{-4}\) Å, and too small to be plotted in Figure 8-4a-b.

![Lattice parameters of (a) LS\(_2\), (b) LS, (c) LP and (d) ZrO\(_2\) phases as a function of temperature upon heating. The errors for those of LS\(_2\), LS and ZrO\(_2\) phases are very small and not present in Figure 8-4a, 4b and 4d; only the errors for those of LP phase are plotted in Figure 8-4c.](image-url)
Other phases such as LP and ZrO$_2$ are also presented in Figure 8-4c-d. At low temperatures (580–780 °C), diffractograms related to LP phase are obscure and hump-like, rather than well-defined peaks. It is difficult to compute accurate parameters by performing the refinement process. Therefore, the values of LP phase at this temperature range are excluded. Nevertheless at 800–950 °C, the lattice parameters increase with temperature and can be fitted to linear functions as shown in Figure 8-4c. With these functions, the calculated lattice parameters at room temperature are: $a = 6.074$ Å, $b = 10.486$ Å, $c = 4.928$ Å, which are very close to the reported values.

The lattice parameter $a$ of cubic zirconia increases monotonically with temperature, as shown in Figure 8-4d. The values can be perfectly fitted to a linear function $y = 1.605 \times 10^{-4} x + 5.3162$. With this function the lattice constant for cubic zirconia at room temperature is calculated to be 5.320 Å. The structural role of ZrO$_2$ as a nucleating agent will not be addressed in the present study of the lithium disilicate glass. Nevertheless, some studies have reported its structural role on glass systems such as MgO–Al$_2$O$_3$–SiO$_2$.

### 8.2.2.2 Crystallographic evolution upon cooling

The crystallographic evolutions of LP and LS during cooling are shown in Figure 8-5, demonstrating a different behaviour in comparison with that in the heating profile (Figure 8-4b-c). Both LS and LP show a linear change of lattice parameters upon cooling. Linear fitting to the data in Figure 8-5 reveals that the shrinkage rates of $a$, $b$, and $c$ for LS are $2.02 \times 10^{-4}$ Å·K$^{-1}$, $1.46 \times 10^{-4}$ Å·K$^{-1}$, and $0.83 \times 10^{-4}$ Å·K$^{-1}$, respectively. The shrinkage rates of $a$, $b$, and $c$ for LP are $1.67 \times 10^{-4}$ Å·K$^{-1}$, $1.97 \times 10^{-4}$ Å·K$^{-1}$, and $1.56 \times 10^{-4}$ Å·K$^{-1}$, respectively. Upon heating, however, the expansion rates of lattice parameters $a$, $b$, and $c$ for LP are $1.95 \times 10^{-4}$ Å·K$^{-1}$, $1.62 \times 10^{-4}$ Å·K$^{-1}$, and $1.23 \times 10^{-4}$ Å·K$^{-1}$, respectively (Figure 8-4c). The crystal structure of LS shows anisotropic expansion during the heating process (Figure 8-4b).

In contrast, all the three precipitated silica phases ($\beta$-quartz denoted by Q1 and Q2, and $\beta$-cristobalite by C) show zero shifts of peak positions upon cooling (Figure 8-2). This indicates that these silica phases have near zero expansion/shrinkage, or at least very small change in the lattice parameters. By cooling from 850 °C to 520 °C, lattice parameter $a$ of $\beta$-cristobalite is kept at 7.140 Å, which is very close to the room temperature value of 7.147 Å.
Similarly, the two forms of β-quartz (Q1 and Q2) showed very little peak shifts (Figure 8-2). Both forms have the same phase structure but slightly different lattice parameter values: Q1 has \(a = 5.037 \, \text{Å}\) and \(c = 5.455 \, \text{Å}\), and Q2 has \(a = \sim5.045 \, \text{Å}\) and \(c = \sim5.470 \, \text{Å}\). The lattice parameters of the Q1 closely match, whereas the Q2 phase show larger lattice values than, β-quartz in the ICSD database (\(a = 4.998 \, \text{Å}\) and \(c = 5.406 \, \text{Å}\), see ICSD-64980).

**Figure 8-5.** Lattice parameters of (a) LS and (b) LP phases as a function of temperature on cooling

### 8.3 Discussion

#### 8.3.1 Crystal structure

Lithium disilicate (LS₂, Li₂Si₂O₅) is a layer silicate with two different structures: one is stable structure and the other is metastable.²² Both structures are orthorhombic. The stable LS₂ belongs to space group ccc2 with lattice parameters of \(a = 5.807 \, \text{Å}\), \(b = 14.582 \, \text{Å}\), and \(c = 4.773 \, \text{Å}\) at room temperature.²³ Its crystal structure piles with corrugated sheets of \((\text{Si}_2\text{O}_5)^2-\) on the (010) plane as illustrated in Figure 8-6a,²⁴ which contributes to excellent mechanical properties of the LS₂ glass-ceramics. Besides, a metastable LS₂ with space group Pbcn (\(a = 5.683 \, \text{Å}\), \(b = 4.784 \, \text{Å}\), \(c = 14.648 \, \text{Å}\)) was reported by Smith *et al.*,²⁵ which would not transform to a stable form of LS₂ below 400 °C. Iqbal *et al* also observed it in the early stage crystallization of a LS₂ glass.²²
Lithium metasilicate (LS, Li$_2$SiO$_3$) is also orthorhombic (space group $Cmc\overline{2}1$), with a chain silicate structure as depicted in Figure 8-6b. Its lattice parameters are $a = 9.396$ Å, $b = 5.396$ Å, $c = 4.661$ Å at room temperature. The crystal structure of orthorhombic lithium phosphate (LP, Li$_3$PO$_4$) is shown in Figure 8-6c, with space group of $Pmn\overline{b}$ (at room temperature ($a = 6.111$ Å, $b = 10.461$ Å, $c = 4.921$ Å). The crystal structure of cubic zirconia with space group of $Fm-3m$ is shown in Figure 8-6d. It has been reported that the lattice parameter $a$ of cubic yttria doped ZrO$_2$ is 5.135–5.174 Å at room temperature. The predicted value for the lattice parameter $a$ of zirconia (5.320 Å at room temperature) is somewhat larger than those reported values for yttria doped ZrO$_2$, which may suggest that the nucleated cubic ZrO$_2$ was stabilized by some ions with bigger ionic radii in this glass system than yttrium ion.

8.3.2 Lattice parameters evolution of different phases and their correlation

As shown in Figure 8-4, the change of lattice parameter $c$ of LS$_2$ followed two trends. With increasing temperature, it decreases first in a non-linear manner up to 780 °C, and then steadily increases at higher temperatures ("V" shape). This result is also reflected by the diffraction peak of (002) plane of LS$_2$, as shown in Figure 8-7a. In this figure, it is clear that the (002) peak shift to a higher angle (i.e. lower lattice spacing) direction first and then to a lower angle direction, which is different from others such as (130) and (020) in Figure 8-7b.
The different evolution behaviours of LS phase upon heating or cooling, as discussed previously, along with the interesting crystallographic evolution behaviour of LS₂ upon heating, strongly indicate that the crystal structure of LS and LS₂ should have a certain correlation during their nucleation period. One of the possible interpretations for this is that simultaneous nucleation of silicate phases affects the crystal structure of each other, especially in the c axis direction. It is evident that the lattice parameter c of both phases unexpectedly decreases with temperature in the nucleation temperature range; while the c value of LS₂ starts to increase with temperature at >780°C when LS phase starts to disappear. This is strong evidence showing the mutual interaction between LS and LS₂ phases along c axis during the nucleation/crystallization process upon heating.

At 930 °C, the values of lattice parameters deviate from their trends. This could be attributed to the collapse of its crystal structure before melting. In comparison, no such interrupted trend is observed during the structure evolution of LP phase around this temperature.

### 8.3.3 The unit cell volume evolution of different phases

Although there is a “V”-shape trend for lattice parameter c, the unit cell volume of LS₂ in the entire temperature range does not have a similar trend. It rather increases steadily, simply
because the increased values of $a$ and $b$. Upon heating, there are two linear models (Eqns. 1-2, in Table 8-2) for the trend of the unit cell volume of LS$_2$ and one model (Eqn. 3, in Table 8-2) for LS, which are derived from Figure 8-8. It is therefore suggested that such a behaviour for LS$_2$ is due to the spontaneous nucleation of silicate phases. For LS$_2$, the change in unit cell volume is approximately $1.26 \times 10^{-2} \, \text{Å}^3 \cdot \text{K}^{-1}$ and $1.79 \times 10^{-2} \, \text{Å}^3 \cdot \text{K}^{-1}$ for the periods of 580–780 °C and 780–930 °C, respectively; and $1.79 \times 10^{-2} \, \text{Å}^3 \cdot \text{K}^{-1}$ for LS.

Table 8-2. Modelling of the unit cell volume for LS, LS$_2$ and LP phases upon heating or cooling

<table>
<thead>
<tr>
<th>Phase and condition</th>
<th>Temp range</th>
<th>Model</th>
<th>Eqn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS$_2$ on heating (model I)</td>
<td>580–780 °C</td>
<td>$y = 0.0126 , x + 408.779$, $R^2 = 0.9951$</td>
<td>(1)</td>
</tr>
<tr>
<td>LS$_2$ on heating (model II)</td>
<td>780–930 °C</td>
<td>$y = 0.0179 , x + 404.697$, $R^2 = 0.9973$</td>
<td>(2)</td>
</tr>
<tr>
<td>LS on heating</td>
<td>580–780 °C</td>
<td>$y = 0.0151 , x + 235.686$, $R^2 = 0.9935$</td>
<td>(3)</td>
</tr>
<tr>
<td>LS on cooling</td>
<td>850–520 °C</td>
<td>$y = 0.0161 , x + 233.781$, $R^2 = 0.9985$</td>
<td>(4)</td>
</tr>
<tr>
<td>LP on heating</td>
<td>800–950 °C</td>
<td>$y = 0.0237 , x + 312.924$, $R^2 = 0.9926$</td>
<td>(5)</td>
</tr>
<tr>
<td>LP on cooling</td>
<td>950–520 °C</td>
<td>$y = 0.0252 , x + 310.461$, $R^2 = 0.9935$</td>
<td>(6)</td>
</tr>
<tr>
<td>LS$_2$ on heating$^*$</td>
<td>885–950 °C</td>
<td>$y = 0.0157 , x + 406.382$, $R^2 = 0.9778$</td>
<td>(7)</td>
</tr>
<tr>
<td>LS on cooling$^*$</td>
<td>875–765 °C</td>
<td>$y = 0.0179 , x + 232.712$, $R^2 = 0.9989$</td>
<td>(8)</td>
</tr>
</tbody>
</table>

$^*$ Eqns. 7 and 8 were reported in ref. 30.

On the other hand, the evolutions of the unit cell volume for LS and LP upon cooling (Figure 8-9), are different from that in the heating process, as summarized as Eqns. (3) vs (4), and Eqns. (5) vs (6) in Table 8-2. As to the lattice parameters of the LS phase, different behaviours against temperature were observed, i.e. nonlinear for heating while linear for cooling. This might be due to the mutual interaction between LS and LS$_2$ phases along $c$ axis during the nucleation and crystallization process upon heating, whereas no LS$_2$ phase was observed to precipitate upon cooling and therefore no such a relationship exists. To the best of our knowledge, this is the first report of the crystallographic interaction between the two silicate phases. However, it must be pointed out that the X-ray diffraction observation on such a mutual interaction of the two phases can only serve as indirect evidence; a direct in situ observation using microscopic techniques is still necessary.
Figure 8-8. Unit cell volumes of (a) LS$_2$, (b) LS, (c) LP and (d) ZrO$_2$ as a function of temperature on heating.

Figure 8-9. Unit cell volumes of (a) LS and (b) LP as a function of temperature on cooling.

Furthermore, it is found that a higher change rate was observed for both phases in the cooling process than that in heating. This observation suggests that the relaxation of crystal structure in the shrinkage process is easier than in expansion. O’Donnell et al.\textsuperscript{30} reported the expansion rate of LS$_2$ and shrinkage rate of LS based on neutron diffraction experiments, as given in Eqns. (7-8) (Table 8-2). However, they did not detect LP during cooling but did
identify it by XRD after neutron diffraction. In their study the shrinkage rate of LS (1.79×10^{-2} Å³·K^{-1}) was also slightly higher than that reported in our study. The modelling for the unit cell volume of LS, LS₂ and LP phases upon heating or cooling are summarized in Table 8-2.

In the case of LS and LP, the unit cell volumes are different at the same temperatures when we compare the heating and cooling processes. This can probably be ascribed to the different formation processes of the crystals. Comparing Figure 8-4 and Figure 8-5 suggests that the evolution behaviours of lattice parameters upon heating and cooling are different. This may also explain why the slope of unit cell volume during cooling is larger than that during heating.

Referring to ICSD card No. 100402, the unit cell volume of LS phase is 236.32 Å³ at 25 °C. This unit cell volume is close to the one (235.92 Å³) estimated according to Eqn. (3). Besides, the unit cell volume of LP phase is 314.59 Å³ at 25 °C as reported in ICSD card no. 79427, which is also close to the value (313.52 Å³) estimated from the linear model Eqn. (5) for the heating process.

### 8.3.4 Nucleation/crystallization in the glass melt during cooling

To investigate the nucleation/crystallization of the glass melt during cooling, the XRD patterns as shown in Figure 8-1b were acquired at several temperatures with a holding time of 6 min for each. Apart from LS, the crystalline silica phases, i.e. cristobalite and quartz, were observed during cooling of the glass melt. This is consistent with O’Donnell et al.’s work.³⁰ The cristobalite phase (at 850 °C) emerges slightly earlier than quartz (at 840 °C), which has also been observed in isothermal annealing of the glass at 770 °C.⁶ During the cooling process, LP crystals started to form at 950 °C. It should be noted that the formation of LP is only observed when the glass melt is slowly cooled down (the overall cooling rate was 8.5 K/min in this study). In the normal glass-making process, this phase does not necessarily form. It is then speculated that, if the LP crystals do form during glass making, they could well serve as nucleiants for the precipitation and growth of LS crystals at low temperatures. The crystallization of LS may follow the epitaxial growth model suggested by Headley et al.⁶

On the other hand, the crystallization kinetics of LS is depicted by the quantitative results
in Figure 8-3. From the weight fraction curve of LS, it is suggested that the crystallization of LS is very fast at the beginning (850 °C), and then slows down at lower temperatures (<770 °C). Besides, the crystallite size of LS is approximately 1 µm at the beginning (850 °C). This is very different from the evolution of crystallite size in the heating process where the nuclei follow a controlled growth manner. The reason for such a large size in this study is unclear.

8.4 Summary

We used a synchrotron X-ray powder diffraction beamline to investigate the crystallographic evolution of crystalline phases in a complex lithium disilicate glass where Li₂SiO₃ (LS) and Li₂Si₂O₅ (LS₂) nucleate simultaneously. The crystallographic change with temperature has been modelled. We found that the lattice parameter c of LS₂ shows a “V”-shape trend, i.e. dropping non-linearly when LS is present in the glass-ceramic then rising up linearly after LS disappears. With the co-existence of LS₂, the LS phase also demonstrates a non-linear decreasing trend in the lattice parameter c, while it has a linear increasing trend when there is no LS₂ upon cooling. A close correlation between LS₂ and LS phases is confirmed. This finding may shed light on a better understanding of nucleation and crystal growth of LS₂ and LS in similar glass systems. The phases of LS and LP showed different change rates in unit cell volume upon heating and cooling. Besides, the phase transformation of the glass (or glass melt) upon heating and cooling were different. No LS₂ was detected during cooling of the glass melt, while two forms of β-quartz with slightly different lattice constants was observed in addition to LP, LS, and β-cristobalite. The silica phases show near zero expansion behaviour.

8.5 References

Chapter 8 | Crystallographic evolution of a lithium disilicate glass upon heating and cooling


Chapter 9  Structural response of lithium disilicate in glass crystallization

The classical nucleation theories in glass science have been well-documented, and advanced the fabrication technology and application of glass-ceramics. The mutual interaction within crystalline phases, however, during glass crystallization is rarely reported from a microscopic perspective. In this chapter, the structural response of the $c$ axis of LS$_2$ to other crystalline phases in different types of lithium disilicate glasses was demonstrated using \textit{in situ} synchrotron X-ray powder diffraction. The evolution characteristic of the $c$ axis of LS$_2$ at the nucleation stage behaves differently if the crystallization sequence of silicates varies. The whole evolution trend shows a silica-controlled fashion. These findings may initiate a novel crystallographic approach for analysing the intrinsic mechanisms of reaction, nucleation or crystallization in systems involving crystalline phases.

The main results in this chapter have been published in:


9.1 Introduction

The discovery of glass-ceramics in the 1950s\textsuperscript{1} launched several decades of extensive work into the interrelations of their structure, processing, properties and applications.\textsuperscript{2-5} The classical nucleation and crystal growth theories dedicated to glass\textsuperscript{6-8} have largely contributed to the advancement of glass-ceramics. Li$_2$O-SiO$_2$ glasses serve as an important system for investigating the nucleation theories of glass.\textsuperscript{8-10} The lithium disilicate (Li$_2$O-2SiO$_2$) glasses are of commercially significance, as the derived glass-ceramics have been widely used for dental restorative applications\textsuperscript{3, 4, 11} owing to their desirable performances for clinical use, such as biocompatibility, translucency, mild hardness, good chemical stability, high flexural strength and relatively high toughness.\textsuperscript{12-16}
In lithium disilicate glass systems, lithium disilicate (LS$_2$: Li$_2$Si$_2$O$_5$) and metasilicate (LS: Li$_2$SiO$_3$) are the main crystalline phases crystallizing from base glasses, and their crystallization sequence mainly take on three distinct types. The first type of phase transformation sequence (type I) is simultaneous nucleation of LS and LS$_2$ phases at low temperatures.\textsuperscript{12-14, 17-19} In the second type sequence (type II), LS nucleates solely and then transforms to LS$_2$ at a higher temperature.\textsuperscript{19-21} The temperatures for nucleation of LS and phase transformation of LS to LS$_2$ vary in different compositions. In the third type (type III), only the LS$_2$ phase nucleates from the beginning while LS is not present at all.\textsuperscript{22, 23} Owing to the attractive machinability of LS, the former two types of glass are usually preferred for the manufacturing of dental glass-ceramic products with desirable geometries using standard CAD/CAM systems.\textsuperscript{24, 25} Glasses of type III are however not very common in the literature, which is probably because that it is technologically not emphasized due to the absence of the intermediate phase.

\textit{In situ} experimentation, using either neutrons or synchrotron X-rays, is crucial to monitoring the structural changes in a material system that take place under certain circumstances, such as precipitation in solutions or solid-solutions,\textsuperscript{26} crystallization of amorphous materials,\textsuperscript{27} decomposition of compounds,\textsuperscript{28} synthesis or sintering of polycrystalline materials,\textsuperscript{29} and electrochemical activity in lithium-ion batteries.\textsuperscript{30} In a simple system, structural evolution of a crystal could be a linear trend against temperature if there is no phase transition: a perovskite-type material La$_{0.63}$(Ti$_{0.92}$, Nb$_{0.08}$)O$_3$ is such an example.\textsuperscript{31} What if in the case of a reacting system involving multiple phases? Will these phases still keep the original trend, or, do they affect each other? Here we demonstrate the structural response of LS$_2$ to silica phases in complex lithium disilicate glasses with different nucleation sequences as described above, by monitoring the crystallographic evolution of silicate phases.

\section*{9.2 Experimental Section}

Several complex lithium disilicate glasses with main compositions as shown in Table 3-1 and minor additives (selected from Na$_2$O, K$_2$O, CaO, MnO, Sb$_2$O$_3$) were melted in a Pt crucible at 1500 \degree C for 3 hours. To investigate the crystallographic evolution behaviour of the lithium disilicate glasses, \textit{in situ} HT-XRD experiments of these glasses were conducted on the
Powder Diffraction beamline at the Australian Synchrotron centre. The glasses were cut and ground to thin monolithic samples with dimensions of approximately 5 mm × 5 mm × 0.4 mm for the in situ synchrotron experiments. There were holding stages within the temperature range of 500–1,000 °C with a fixed interval of 20 °C for recording the powder diffraction data throughout the annealing process of each glass. At each stage, X-ray was on for 4 min to detect the phases at the corresponding temperature. The evolution of lattice parameters (a, b and c) of silicate phases at different temperatures were carefully examined by performing Rietveld refinements.

9.3 Results and Discussion

9.3.1 Phase evolution process in various glasses

I made several lithium disilicate glasses which were dedicated to different phase evolution sequences of lithium silicates at elevated temperatures (Type I: glass AG1; Type II: glass C; Type III: glasses E and F). Each glass experienced a continuous annealing process while powder diffraction patterns at subscribed temperatures were recorded in situ using hard X-ray from synchrotron radiation. The crystallographic information of crystalline phases were resolved by structure refinement using Rietveld method. The corresponding in situ powder diffraction patterns, lattice parameters of lithium disilicate, and the phase assemblages of glasses at the temperature stages are listed in Table 9-1.

The phase transformation process in glass AG1 is summarized as follows. LS and LS$_2$ nucleated at 580°C at the same time, and subsequently LS transformed to LS$_2$ at 820°C and this completed at 860°C. This glass shows type I nucleation sequence. The cristobalite (CR) and lithium phosphate (LP) crystallized at 840°C and 880°C, respectively. The slight deformation of the sample was detected at the temperatures higher than 980°C owing to the dissolution of crystals. CR, LP and LS$_2$ phases remained in the glass-ceramics at 1000°C.

Glass C shows type II nucleation sequence. The LS phase nucleated exclusively at 560°C. Very weak peaks of the LS$_2$ phase were detected at 700°C indicating its formation at this temperature. The content of LS$_2$ crystals dramatically increased to over 60 wt% at 760 °C according the quantitative phase analysis, whereas the LS phase disappeared. It indicates that the transformation of LS$_2$, from either LS or glass matrix, completed at 760°C.
Table 9-1. XRD patterns, evolution of lattice parameters of LS$_2$, crystalline phases and their temperature ranges for different glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>In situ high-temperature XRD patterns</th>
<th>Evolution of lattice parameters of LS$_2$</th>
<th>Temp range [°C]</th>
<th>Phase Assemblage</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG1</td>
<td><img src="image1.png" alt="XRD pattern" /></td>
<td><img src="image2.png" alt="Lattice parameters" /></td>
<td>580–860</td>
<td>M: LS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>580–1000</td>
<td>D: LS$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>840–1000</td>
<td>C: CR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>880–1000</td>
<td>P: LP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;960</td>
<td>Slightly deformed</td>
</tr>
<tr>
<td>C</td>
<td><img src="image3.png" alt="XRD pattern" /></td>
<td><img src="image4.png" alt="Lattice parameters" /></td>
<td>560–740</td>
<td>M: LS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>700–900</td>
<td>D: LS$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>720–900</td>
<td>P: LP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>840–900</td>
<td>Q: QZ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>820–900</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;860</td>
<td>Slightly deformed</td>
</tr>
<tr>
<td>E</td>
<td><img src="image5.png" alt="XRD pattern" /></td>
<td><img src="image6.png" alt="Lattice parameters" /></td>
<td>560–980</td>
<td>D: LS$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>760–980</td>
<td>C: CR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>800–980</td>
<td>P: LP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>860–980</td>
<td>T: TM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>940–960</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;960</td>
<td>Slightly deformed</td>
</tr>
<tr>
<td>F</td>
<td><img src="image7.png" alt="XRD pattern" /></td>
<td><img src="image8.png" alt="Lattice parameters" /></td>
<td>600–1000</td>
<td>D: LS$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>780–1000</td>
<td>C: CR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>800–1000</td>
<td>P: LP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>860–980</td>
<td>Q: QZ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>960–1000</td>
<td>T: TM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;960</td>
<td>Slightly deformed</td>
</tr>
</tbody>
</table>

[a] LS: lithium metasilicate; LS$_2$: lithium disilicate; LP: lithium phosphate; CR: cristobalite (JCPDS 27-0605, cubic); TM: tridymite (JCPDS 50-1432, orthorhombic); QZ: quartz (JCPDS 11-0252, hexagonal); S: MgAl$_2$Si$_2$O$_8$; U: unidentified phase (with peaks at d = 3.330, 2.483, and 1.405 Å)
In Glass C, the LP phase crystallized at 720°C and reached a maximum of ~6 wt% at 820°C, and quartz (QZ) formed at 840°C as a trace phase with a maximum amount of ~0.4 wt%. Another trace phase MgAl$_2$Si$_4$O$_{12}$ with a similar content (~0.5 wt%) appeared in this glass at 820°C and melted completely at 900°C. The sample slightly deformed at above 860°C.

The glasses E and F are demonstrating the type III nucleation sequence, i.e. only the LS$_2$ phase nucleates while LS phase does not throughout the annealing process. In fact, these two glasses share similar composition but glass E has 0.43 mol% ZrO$_2$ as shown in Table 3-1. In glass F, the LS$_2$ and LP phases nucleated at 560 and 800°C, respectively; silica phase including CR and tridymite (TM) formed in this glass at 760 and 860°C, respectively. These crystalline phases melted dramatically in this glass at 980°C and completed at 1,000°C.

In glass F, the LS$_2$ and LP phases nucleated at 600 and 800°C, respectively; three types of silica phases including CR, QZ and TM formed in this glass at 780, 840 and 960°C, respectively. The quartz phase melted at 980°C while other crystalline phases still remained in the sample at 1,000°C. This glass showed slight deformation at 960 °C during the annealing process.

### 9.3.2 Lattice parameters of lithium disilicate

#### 9.3.2.1 Glasses AG1, C, E and F

Figure 9-1 illustrates the relationship of phase evolution and peak shift in the as-discussed glasses. To be specific, Figure 9-1(a1-d1) display the XRD patterns of lithium disilicate glasses AG1, C, E and F, respectively. The intensity (in counts) of the powder diffraction patterns is indicated by colours. The expanded patterns of lithium disilicate phase at the selected 2θ ranges are given in Figure 9-1(a2-d2) and Figure 9-1(a3-d3) which are demonstrating the evolution trend of (002) plane and other main peaks of (130), (020) and (111) planes, respectively.

Interestingly, the trends of lattice parameter $c$ of lithium disilicate are different in the three glass systems (types I, II and III), as shown in Table 9-1. With careful examination of the diffraction patterns of lithium disilicate phase forming in the glass samples, we found that the (002) plane changes in different fashions, as shown in Figure 9-1(a2–d2). This observation
confirms that the \(c\) axis of the \(\text{LS}_2\) phase changes in the trends as presented in Table 9-1. The red arrows, for the ease of reading, are drawn in Figure 9-1 for each glass to show the corresponding events at each inflection point of the (002) peak evolution, i.e. lattice parameter \(c\), of lithium disilicate (Table 9-1). There is no similar phenomenon for \(a\) and \(b\) axes. These reflection points of the trends can be associated with the disappearance of LS and the formation of silica phases.

Figure 9-1. *In situ* synchrotron XRD patterns of lithium silicate glass-ceramics at high temperatures. (a1 – d1) show the main peaks of crystalline phases formed during the heat treatment process; (a2 – d2) demonstrate the
peak evolution of (002) plane of lithium disilicate, and (a3 – d3) depict the peak evolution of its (130), (020) and (111) planes. The letters a, b, c and d represent the glasses AG1, C, E and F, respectively. The letters A, C, D, M, P, Q, T, and U in the (a1–d1) patterns are denoting the crystalline phases of MgAl2Si4O12, cristobalite, lithium disilicate, lithium phosphate, quartz, tridymite, and an unidentified phase, respectively.

9.3.2.2 Glass B

The evolution of lattice parameters of LS2 as a function of temperature in glass B is presented in Figure 9-2a. A complex trend was observed in the lattice parameter c of LS2. Specifically, it started with a dramatic decrease at 600–700 °C, followed by a slight increase until the LS phase disappeared. The inflection point at 660 °C was found to hold a precipitation event of an unidentified intermediate phase. After the completion of LS-to-LS2 transformation at 700 °C, the parameter c showed a reverse trend in that it decreased again until 780 °C where a silica phase of β-cristobalite precipitated. From 800 °C where another silica phase (β-quartz) crystallized, it began to increase instead. The events at transition points of the evolution trend are highlighted by the selected peaks in Figure 9-3.

![Figure 9-2. (a) The lattice parameters and (b) unit cell volume of the LS2 phase as a function of temperature](image)

The crystallographic a and b axes do not have similar trends as in the c axis, which was observed in all glasses, rather they increased with temperature. As the small amounts of additives (other than SiO2, Li2O, P2O5) was not detected to crystallize from the glass matrix, the influence of them on the change of the c-axis of LS2 is unclear at the time being. The as-measured unit cell volume (V) of the LS2 phase shows a near linear increasing trend as a function of temperature (Figure 9-2b).
Figure 9-3. (a) Main peaks of crystalline phases crystallized in the glass as a function of temperature, (b) peak evolution of (002) plane of lithium disilicate phase, (c) peak evolution of its (130), (020), and (111) planes.

9.3.3 Lattice parameters of lithium metasilicate

In glass A, the lattice parameters of the LS phase against temperature (600–860°C) are present in Figure 9-4a; the diffraction pattern of (002) plane is shown in Figure 9-4b confirming the trend of the lattice parameter c. The critical point at 760°C may suggest the transformation of LS to LS2 is initiating at this temperature. In glass C, the evolution of lattice parameters of the LS phase are shown in Figure 9-5a, and close-up diffraction patterns are illustrated in Figure 9-5(b-c) for (200), (020) and (002) planes, respectively. The c axis of the LS phase in glass C has a similar evolution trend with that in glass Bo, i.e. decreasing non-linearly against temperature. In glasses E and F, however, there is no LS phase forming from the glass matrix during the whole annealing process.

Figure 9-4. (a) The lattice parameters of the LS phase in glass A as a function of temperature and (b) the diffraction patterns for (002) plane of LS whose trend is consistent with the evolution trend of the c axis as shown in (a).
In type I glass (AG1) where LS$_2$ and LS phases nucleate simultaneously, the parameter $c$ of LS$_2$ phase presents a typical “V”-shaped fashion which consists of a non-linear decreasing curve in the LS–LS$_2$ co-existing range (600–860 °C) and a straight increasing line in the LS$_2$-only range (860–1,000 °C). Such a phenomenon was also observed in another lithium disilicate glass that has the same nucleation sequence. On the other hand, both parameters $a$ and $b$ have an increasing trend, although there is a jump at 860 °C (shown in Table 9-1). The lattice parameters of the LS phase against temperature (600–860°C) are present in Figure 9-4a; the diffraction pattern of (002) plane is shown in Figure 9-4b confirming the trend of the lattice parameter $c$. The critical point at 760°C may suggest that the transformation of LS to LS$_2$ is initiated at this temperature. Nevertheless, the suggested influence of the precipitation of silica phase (cristobalite), i.e. reversing the evolution trend of $c$ axis of LS$_2$, at 840°C may be associated with the similar effect of LS on it.

Figure 9-5. (a) The lattice parameters of LS phase against temperature in glass C, and close-up diffraction patterns for (b) (200), (c) (020) and (d) (002) planes of Li$_2$SiO$_3$ (M).
In type II glass (C) where LS nucleates initially and then transforms to LS2, the declining trend of lattice parameter $c$ of LS2 terminates and shows a slight increase at 840–860 °C where quartz was detected. On the other hand, the parameter $c$ of LS in glass E decreases non-linearly against temperature upon heating, whereas parameters $a$ and $b$ increase (Figure 9-5a). Correspondingly, the diffraction patterns of (200), (020) and (002) planes are shown in Figure 9-5(b–d). Such a trend for the LS phase was also observed in type I glasses (AG1 and Bo). It may suggest that the LS phase has intrinsic behaviour of compression in $c$ axis upon heating, as no interaction with other crystalline phases (e.g. LS2) is present in the glass.

In type III glasses (E and F), the trends of parameter $c$ of LS2 phase are “N”-shaped with two inflection points, namely an increase-drop-increase trend. At each inflection point, the change of trends could be ascribed to the formation of silica phases in the glasses (Table 9-1 and Figure 9-1). For the first section of crystallographic evolution (below 760 °C), the lattice parameter $c$ of LS2 shows an increasing trend against annealing temperature. It could be the intrinsic nature of LS2 phase because no other phases nucleate/crystallize. Then, it changes to a decreasing mode since the appearance of cristobalite at 760 °C (glass E) or 780 °C (glass F), until the crystallization of tridymite phase (glass E) or quartz phase (glass F) at 860 °C occurs. Thus, the lattice parameter $c$ of LS2 phase shows a reversed trend when a silica phase forms.

9.3.4 Unit cell volume of silicate phases

The unit cell volumes of lithium disilicate phase in glasses AG1, C, E and F against temperature are shown in Figure 9-6 to Figure 9-8, respectively.

In type I glass AG1, the unit cell volume of the LS phase may be expressed by a linear equation during the crystallization; while that of LS2 phase can be fitted into two equations separated at 860°C where LS disappeared (Figure 9-6). It is consistent with the modelling for the type I glass Bo. Thus we can draw an indication that such a common feature can readily exist in the glass system with simultaneous nucleation of LS and LS2.

In glass C, the unit cell volume of both LS and LS2 phases can be well fitted using a straight line. The fitting results are displayed in Figure 9-7. The influence of both LS and QZ phases on the fitting for LS2 is slight, ascribing to the reasons that (1) LS phase diminished when LS2 formed, and (2) quartz formed at the end of crystallization period of LS2.
Figure 9-6. Unit cell volume of (a) LS$_2$ and (b) LS phases in glass AG1 as a function of temperature.

Figure 9-7. Unit cell volume of (a) LS$_2$ and (b) LS phases in glass C as a function of temperature.

Figure 9-8. Unit cell volume of LS$_2$ phase in (a) glass E and (b) glass F as a function of temperature.

In glasses E and F, the unit cell volume of LS$_2$ cannot be well fitted by one linear equation. This is owing to the complex trends (i.e. increase-drop-increase), affected by the precipitation of silica phases (CR, QZ and TM), of c axis of the LS$_2$ phase. We therefore
applied two linear equations for fitting in each glass as given in Figure 9-8.

Figure 9-9 shows the XRD patterns of the splitting (111) peak of CR and the affected (101) peak evolution of LP (glass F). It is known that the CR phase have near zero expansion rate, which is also evidenced in our previous study in a lithium disilicate glass. With this observation, we can judge the melting phenomenon of samples at high temperature and check the reliability of crystallographic evolution trends of crystalline phases in all glasses.

Owing to the reversed trend of lattice parameter $c$, the unit cell volume for lithium disilicate does not show an overall linear relationship in glasses AG1, E and F. However, it does show a linear trend for each period, separated by the precipitation events of silica phases, if there are sufficient data points. For glass C, one linear equation can be well applied to the data points in the temperature range of 700–860 °C. The influence of the QZ phase on the unit cell volume of LS$_2$ in glass E (Figure 9-7) and that of the TM phase in glass E (Figure 9-8) are obscure ascribing to their weak effects on crystal lattices of LS$_2$ (Figure 9-4). The difference in the fitted coefficients of the linear equations can be ascribed to the evolution-dependent lattice parameters of lithium disilicate in each glass.

![Figure 9-9. (a) The (101) peak of LP phase, and (b) the (111) peak of CR phase in glass F. As indicated by arrows, the glass is deformed at temperatures above 960 °C.](image)

### 9.4 Discussion

In type I glasses (AG1 and Bo), a significant reverse of trend can be observed for the lattice parameter $c$ of LS$_2$ when the LS phase disappeared. It evidently shows the strong restraint on the crystallographic structure of LS$_2$ during the crystallization process of silicate
On the other hand, in other types of glasses, there is a silica precipitation event taking place at each inflection point. More specifically, in glass C (type II), the decreasing trend of \( c \) terminates at 820-840 °C where QZ forms; in glass F (type III), the “N”-shaped trend of \( c \) has inflection points at 760 and 860 °C which correspond to the precipitation temperatures of CR and QZ, respectively. Such a phenomenon indicates the close relationship between the crystallographic change along \( c \) axis of lithium disilicate and the precipitation of silica phases from the glass matrix. Thus it is evident that the refined lattice parameters of lithium disilicate phase (Table 9-1) are somehow correlated with the silicon-related phases including LS, cristobalite (CR), quartz (QZ), and tridymite (TM). On the other hand, cell parameters \( a \) and \( b \) of LS\(_2\) in all glasses have in common the normal increasing trend without significant change.

From the crystallographic aspect, it has been found that the initial evolution trend of the \( c \) axis of LS\(_2\) was opposite in the glasses of type I and III sequences, i.e., decreasing and increasing respectively.\(^{33,34}\) Thus, crystallographic interaction within silicates is indicated. The observed mode of crystallographic evolution of LS\(_2\) in this glass is consistent with that in the glasses of type I sequence, rather than those of type III sequence. A slight change in the evolution trend of lattice parameter \( a \) was observed at 700 °C (Figure 9-2a), which probably indicates the effect of the disappearance of LS phase on this crystallographic axis.

From the observations in the crystallographic study, we believe that a common phenomenon of structural response takes place during the crystallization of lithium disilicate glasses. To be specific, the crystallographic change of LS\(_2\) in \( c \) axis was largely affected from a normal increasing trend (if no LS precipitated, i.e., the case in type III sequence) to the opposite with the existence of LS phase (i.e., the cases in types I and II sequences). In addition, the silicon-related phase formation will also affect the evolution trend. The reversed trend has been observed in all glasses herein investigated upon the precipitation of the crystalline phases that share the [O–Si–O] source from glass matrix, such as silicates (LS, LS\(_2\)), silica (CR, QZ, etc.) and other Si-related phases. Unsurprisingly, the unidentified intermediate phases also have an effect on such a trend (Figure 9-2a), indicating that it may be silicon-containing in composition.
9.5 Summary

In summary, as indicated from the synchrotron XRD study of several glasses as discussed above, the results confirm a strong link within the crystallographic $c$ axis of lithium disilicate and the precipitation of silica phases. Besides, the crystallization sequence of silicate phases has an impact on the crystallographic structure of lithium disilicate; as a consequence, the evolution trend of its $c$ axis at early stages differs in the glasses AG1, C, E and F. The first ever observation of such a structural response of lithium disilicate in crystallographic lattice level suggests the mutual interaction of crystalline phases that crystallized from base glasses. These findings may shed new light on the nucleation mechanism of the related glasses from a crystallographic perspective.

The mechanism for the silica-controlled crystallographic evolution of lithium disilicate is unclear so far, and would be a scientific question remained for more future investigations using in situ experiments and/or first-principle simulations. We anticipate our work will initiate more experimental or modelling studies in either the glass systems or other chemical reaction systems involving crystalline phases. For instance, it may be insightful to study the crystallographic change of phases to understand the intrinsic mechanisms of the reaction, nucleation, precipitation and/or transformation in polycrystalline materials, glasses, sol-gels, solid solutions, solvent solutions and so forth.

9.6 References

Chapter 9 | Structural response of lithium disilicate in glass crystallization


24 W. Höland, V. Rheinberger, E. Apel & C. van't Hoen. Principles and Phenomena of


Chapter 10  Summary and Future Work

10.1 Summary

In this research project, a high-strength lithium disilicate glass-ceramic was developed in a SiO$_2$–Li$_2$O–MgO–Al$_2$O$_3$–P$_2$O$_5$–ZrO$_2$ system with a novel glass composition (glass C). The glass-ceramic demonstrates a flexural strength of 562±107 MPa. The material could possibly be used for restorative dental applications as three-unit posterior bridges. The optimization of annealing profile (505 °C/60 min + 605 °C/60 min + 810 °C/120 min) was conducted in a step-by-step manner, where Marotta’s method was adopted for setting the pre-nucleation temperature and time (i.e. the first stage). The microstructure of the high-strength glass-ceramics featured highly networked and interlocked clusters of lithium disilicate. This novel microstructure effectively contributed to the improvement of flexural strength of lithium disilicate glass-ceramics. In addition, other crystalline phases (β-quartz, MgAl$_2$Si$_4$O$_{12}$, and Li$_3$PO$_4$) in minor amounts embedded within the clusters and residual glass matrix could strengthen the glass-ceramics further. The development process of such a novel microstructure is proposed, and its formation mechanism could possibly be correlated to the addition of minor additives, especially the combination of Al$_2$O$_3$, MgO and/or CaO.

In terms of lithium disilicate glasses, there are mainly three types of phase transformation sequence during glass crystallization. Type I is simultaneous nucleation of LS and LS$_2$ phases at low temperatures. Type II involved LS nucleating initially and then transforming to LS$_2$ at a higher temperature. For type III, only the LS$_2$ phase nucleates while LS is not present at all. Due to the attractive machinability of LS, types I and II are preferred for the manufacturing of dental restorations using standard CAD/CAM systems. Even though large amounts of work have been reported in the literature, the fundamental reasons that regulate the crystallization behaviour of lithium disilicate glasses are as yet unclear, and thus deserve more future research. This study has shown that the crystallization behaviour is probably controlled by a complex mechanism that involves several factors including (1) the molar ratio of SiO$_2$/Li$_2$O, (2) the type and amount of additives (Al$_2$O$_3$, MgO, K$_2$O etc.) in
glasses, and (3) crystallisation parameters such as temperature and time.

This study also involved in situ XRD measurements with the aid of the state-of-the-art synchrotron radiation to analyse both non-isothermal and isothermal crystallization kinetics of lithium disilicate glasses. It is interesting that during the cooling process of a lithium disilicate glass melt, lithium metasilicate forms with a large crystal size at its first appearance, while no lithium disilicate phase crystallized. This is a new and interesting phenomenon. Moreover, synchrotron XRD have provided evidence that the nucleation of Li$_2$SiO$_3$ and Li$_2$Si$_2$O$_5$ is triggered by the steep compositional gradients, and also enabled the detection of a trace amount of Li$_2$SiO$_3$. With quantitative phase analysis, the weight/volume fraction of phases and crystallite size as a function of annealing temperature (or time) can be analysed, depicting the crystallization kinetics of glasses.

Furthermore, the identified crystallographic relationship in the glass-ceramic is an important contribution of this research. A strong link was found between the crystallographic $c$ axis of lithium disilicate and the precipitation of silica phases; this relationship affirms the structural response of Li$_2$Si$_2$O$_5$ to other phases that crystallized from base glasses. Although the intrinsic mechanism is so far unclear, these findings may shed new light on the investigation of nucleation mechanism of the related glasses from a crystallographic aspect. This work provides useful information about the intrinsic mechanisms for the reaction, nucleation, precipitation and/or transformation in polycrystalline materials, glasses, sol-gels, solid solutions, solvent solutions and so forth.

In summary, the key factors that affect the mechanical properties of glass-ceramics could be the type of crystal phases, crystal size and aspect ratio, crystallinity, and microstructure. These factors are closely related to the composition of the base glass and more critically, the applied heat treatment profile. Therefore, design strategies of a glass-ceramic with desired properties should be able to be drawn from the knowledge of (1) the roles of each component in glass composition, (2) the impact of additives and their contents, (3) nucleation mechanism, (4) crystallization kinetics, (5) effects of temperature and time (of each annealing stage) on microstructural development, and (6) the relationship between properties and microstructure.
of the final glass-ceramics. In terms of compositional design in this research, non-stoichiometric ratio of SiO$_2$:Li$_2$O and a certain amount of potassium oxide, alumina and/or magnesia are preferred. Specifically in this research, a three-stage annealing profile is recommended for the heat treatment of lithium disilicate glasses involving the crystallization of lithium metasilicate.

10.2 Future work

10.2.1 Structural evolution monitored by solid-state NMR (Ongoing work)

In order to interpret the structural change of the high-strength lithium disilicate glass-ceramic from glass C, we are performing solid-state NMR measurements ($^{31}$P and $^{29}$Si) to a series of samples that annealed at various stages, to characterize the local atomic environment of silicon and phosphor at respective annealing stage. The XRD patterns are plotted in Figure 10-1.

![Figure 10-1. The RT-XRD patterns of glass C treated at various temperatures](image-url)
Figure 10-2. (a) The $^{31}$P NMR spectra of the glass treated at various temperatures, (b) the fitted $^{31}$P NMR spectra of the glass treated at various temperatures with enlarged bottoms, and (c) the evolution of phosphorus species in the samples (lines along the data points are for eye guidance only).
The $^{31}$P NMR spectra of samples are plotted in Figure 10-2a. Much narrower peaks of the NMR spectra observed in the samples annealed at 675 °C and above, indicating the crystallization tendency of phosphorous species in the glass. After deconvolution of the $^{31}$P NMR spectra (Figure 10-2b), the evolution of phosphorous species is shown in Figure 10-2c. The peak at 1 ppm can be assigned to $Q^1$ species, i.e. pyrophosphate [P$_2$O$_7$] (note as “pyro”). It is observed that the “pyro” species significantly decreased when the LP embryo (medium-range ordered) formed at 675 °C, and disappeared at 700 °C when poorly crystallized LP crystals formed. The $Q^0$ species with chemical shift of ~12 ppm should be the orthophosphate [PO$_4$] component of crystalline LP phase (note as “orth-1”). This is in line with the increasing percentage of this species (from 6.9% to 95.4%) against the annealing temperature. Another $Q^0$ species with chemical shift of 10.4–10.9 ppm can be also assigned to orthophosphate [PO$_4$] component (note as “orth-2”), but it disappeared at above 750 °C. This may suggest that the “orth-2” species is connecting to other cations (such as Na and K) in glass matrix.

![Figure 10-3. The curves of recovered magnetization (M) versus relaxation delay (t). These curves were used for $T_1$ time determination of $^{29}$Si NMR measurements of samples at various annealing temperatures.](image)

The paramagnetic impurity 0.1 mol% MnO is assumed to be uniformly distributed throughout the glass batch and provides centres for paramagnetic relaxation via spin diffusion. The curves of recovered magnetization (M) versus relaxation delay (t) is presented in Figure
10-3, which were used for spin-lattice relaxation time ($T_1$) time determination of $^{29}\text{Si}$ NMR measurements of the samples annealed at different stages. The glass-in-glass phase separation in the parent glass was identified by measurements of $T_1$.

The data processing was as per the method as documented by Mortuza et al.\(^1\) The data points were fitted as per the following Eqn. (1), and the fitting results are listed in Table 10-1.

$$y = m \times (1 - \exp(-x/a)) + n \times (1 - \exp(-x/b))$$

(1)

where the coefficients $m$ and $n$ represent the ratio of short and long components in the glass ($m+n=1$), and $a$ and $b$ denote the relaxation time ($T_1$) for short and long components, respectively.

The diagrams in Figure 10-4 are drawn accordingly for each sample, which clearly show two relaxation components, i.e., short components (amorphous part) and long components (crystalline part). This implies the presence of glass-in-glass structure present in the parent glass. The relaxation times increase with temperature due to the presence of crystalline phase. The ratio of long component in the samples C1-C3 increased due to nucleation of LS and crystallization of LS\(_2\) (Table 10-1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing temperature</th>
<th>$T_1_{\text{short}}$ (a), sec</th>
<th>$T_1_{\text{long}}$ (b), sec</th>
<th>ratio short ($m$)</th>
<th>ratio long ($n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>(not treated)</td>
<td>12.0</td>
<td>232.0</td>
<td>0.33</td>
<td>0.67</td>
</tr>
<tr>
<td>C1</td>
<td>525</td>
<td>4.8</td>
<td>146.2</td>
<td>0.16</td>
<td>0.84</td>
</tr>
<tr>
<td>C2</td>
<td>675</td>
<td>17.0</td>
<td>581.0</td>
<td>0.08</td>
<td>0.92</td>
</tr>
<tr>
<td>C3</td>
<td>700</td>
<td>24.0</td>
<td>643.0</td>
<td>0.11</td>
<td>0.89</td>
</tr>
<tr>
<td>C4</td>
<td>750</td>
<td>17.0</td>
<td>380.0</td>
<td>0.32</td>
<td>0.68</td>
</tr>
<tr>
<td>C5</td>
<td>800</td>
<td>43.0</td>
<td>1460.0</td>
<td>0.24</td>
<td>0.76</td>
</tr>
<tr>
<td>C6</td>
<td>850</td>
<td>45.0</td>
<td>1600.0</td>
<td>0.17</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Table 10-1. The fitted results of the relaxation time ($T_1$) and ratio of both short and long components in the samples at different annealing stages.
### 10.2.2 Future work

Whilst this thesis has addressed a number of aspects such as, fabrication of high strength lithium disilicate glass-ceramics, crystallization kinetics, and crystallographic response within crystalline phases, there are still many issues that need to be further explored. These include but are not limited to the proposed work as given below.

A recent paper shows that the release of internal stress in the glass-ceramics by an extra stage at 550 °C will greatly enhance the flexural toughness from 392 to 581±25 MPa. This would encourage the revisiting of our high-strength glass-ceramics, especially glass C, by adding such an annealing stage. Better performance of dental products could be expected if it comes out with even higher flexural strength.
It is of great interest to study the formation mechanism of the novel microstructure of the high-strength glass-ceramics. The techniques including high-resolution TEM and X-ray absorption near-edge structure (XANES) may provide direct evidences for the interpretation of its formation mechanism. Moreover, the mechanical contribution from the netted and interlocked clusters in the glass-ceramics may be evaluated by modelling.

Moreover, the effects of Al$_2$O$_3$ and MgO in glass composition on the crystallization and properties of high-strength glass-ceramics from glass C deserve further investigations.

From the preliminary NMR results, it is also hoped to extend our research into a deeper understanding on how the glass structure changes into a glass-ceramic and what the key factors controlling the crystallization sequence are.

10.3 References


Biography

1. Journal publications

The selected publications are based on the doctoral research related to “lithium disilicate glass-ceramic” at the University of Auckland.\textsuperscript{1-6}


2. Manuscripts under review


[3] \textbf{Saifang Huang}, Ying Li, Zhaohui Huang, Shanghai Wei, Wei Gao and Peng Cao*. Fabrication of a high-strength lithium disilicate glass-ceramic with a netting and interlocking microstructure. for submission.
3. Patent applications

1) **Saifang Huang**, Peng Cao, Zhaohui Huang, Wei Gao. High-strength lithium disilicate glass ceramic and method for production thereof. Chinese Invention Patent, Application number: 201410393275.6. Publication number: CN104108883A

4. Conferences

1) **Contributed presentation**: **Saifang Huang**, Peng Cao, Zhaohui Huang, Wei Gao, Trace phase formation in a lithium disilicate glass-ceramic probed by synchrotron XRD technique. *The 11th Asia-Pacific Conference on Materials Processing (APCMP 2014)*, The University of Auckland, New Zealand, July 6-11, 2014

2) **Contributed presentation**: **Saifang Huang**, Peng Cao, Zhaohui Huang, Wei Gao, A Multi-Component High-Strength Lithium Disilicate Glass-Ceramic. (Symposium 23: Advances in Biomineralized Ceramics, Bioceramics, and Bioinspired Designs). *The 10th Pacific Rim Conference on Ceramic and Glass Technology* including GOMD 2013 – Glass & Optical Materials Division Annual Meeting (*PacRim 10*), California, USA, June 2-7, 2013

