The effects of additives in to heat treatment temperature and time on the crystallinity of lithium silicate glass-ceramic

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Abstract The glass powders were prepared from binary system of 45 wt.% Li₂O and 55 wt.% SiO₂ and melted in platinum crucible (90% Pt- 10% Rh) at 1195 °C for 1:15 hr. The glass molten was rapid cooled in cold water at 3°C and the produced frit was milled in agate mortar and four sample groups were prepared. In the first group the temperature changes of heat treatment 750, 800, 850, 900 and 950°C was studied. Second group the time changes of heat treatment 2, 4, 6, 8 and 10 hr. was examined. Third group the addition effect of P₂O₅ 4, 7, 11, 14 and 18 wt.% as nucleating agent was studied. Fourth group the addition changes of nucleating agent mixing P₂O₅ and TiO₂ (quarter of P₂O₅ percentages as same above) was inspected. XRD, AFM and optical microscope had been done for all four group specimens. Crystalline phase percentages were calculated from XRD histogram by GSAS (General Structure Analysis System) and EXPGUI. The grain size distribution and average diameter of the crystalline phases for all four group specimens were calculated by AFM measurement. The density and mass fraction of crystalline phases were calculated by optical microscope image analyses by image J 1.52i. The results indicated good crystalline phase percentages, phases density, mass fraction and average diameter on nano-scale for 4 wt.% of (3 wt.% P₂O₅- 1 wt.% TiO₂), heat treated at temperature 950°C for 6 hrs.

Keywords: Glass-Ceramic, Powder Technology, Lithium Silicate, GSAS, Image J 1.52i.

1. Introduction

Glass-ceramics are inorganic materials consisting of crystalline phases and amorphous phase (glass phase). It is interesting materials due to its unique mechanical, thermal, chemical and electrical properties. It can be designed for specific application by employing its special properties. It may be produced from a close control of molten glass with seeds (Nucleating agents) like P₂O₅, TiO₂, ZrO₂, MgF₂…..etc., or cooling rate; the crystalline phases is growing in glass matrix [1].

Lithium silicate is first glass-ceramic developed by Stookey (1953, 1959), it produced from binary Li₂O-SiO₂ glass base. The main crystalline phase formed in this glass base could be Li₃Si₂O₇, Li₂SiO₃, Li₂SiO₄, …etc; which depends on particular ratio of Li₂O and SiO₂ and the type of components that introduced the glass base composition and nucleating agents. One of the important properties of lithium silicate is good chemical durability which makes it suitable for biomaterial in human medicine and restorative material in dentistry particularly. The additional properties of lithium silicate such as high flexural strength, fracture toughness, young modulus values are 120.1, 110.7 and 126.7 GPa., along x-, y- and z-axis, electrical resistivity, band gap 5.36 ev. , and low loss factor have increased the demand for this material in electrical applications. Relatively, high thermal expansion coefficient render it proper material for sealing substrates in the electrical industries [2].
The glass powders sintering are one of the glass-ceramic formations in which the glass molten is rapidly cooled in cold water or cold metal rollers. The produced frit may be milled to 5 µm particle size and compacted to bulk material, then put in furnace for firing in which the sintering and crystallization process occur in one firing cycle. It is quite simple forming method and mixing different glass powders to make glass-ceramic composites. The closed pores may still exist in the material prepared by this method which reduces the mechanical strength, dielectric properties such as dielectric breakdown strength. However, we obtain high quality surface finish by this method [3].

2. Materials and Methods

2.1. Base Glass preparation

Base glass is binary system of Li₂O (45%wt) and SiO₂ (55%wt) in which the starting materials were Lithium carbonate Li₂CO₃ (BDH Chemicals Ltd, England, quality 99.5%) and Silicon dioxide SiO₂ (Thomas Baker Chemicals Ltd, India, quality 99%). Starting materials were mixed by using magnetic heating mixer and diluted with water for 1:30 hr. After drying, the mixture was calcined in crucible at 700°C for 1 hr. It was milled in agate mortar for half hour and compressing to cylinder shape with 1.8 diameter × 2.4 heights mm by applying 5 ton pressure and put in platinum crucible (90% Pt-10% Rh). The base glass mixture was melted in furnace at 1195ºC for 1:15 hr., then base glass molten rapidly cooled in cold water at temperature of 3ºC producing a frit.

2.2. Specimen preparation

The produced frit was milled in agate mortar for 1 hour to get a fine glass powder. A 5 g specimen in the shape of a disc (10 mm diameter by 2.5 mm thickness) was prepared by using biaxial pressing. Four groups were studied in this work; in the first group (G1) the change of heat treatment temperatures as 750 0ºC, 800 0ºC, 850 0ºC, 900 0ºC and 950 0ºC was studied. In the second group (G2) the change of heat treatment times as 2, 4, 6, 8 and 10 hrs was inspected. In the third group (G3) the change of addition percentage of P₂O₅ (Fluka AG, Buchs SG, quality 99%) 4, 7, 11, 14 and 18% as nucleating agent was examined. In the fourth group (G4) the change of addition percentage of mixing P₂O₅ and TiO₂ (BDH Chemicals Ltd, England, quality 98%) as nucleating agents was studied. The corundum (α-Al₂O₃) (BDH Chemicals Ltd, England, quality 99%) as reference material for XRD specimens, table (1) shows all four groups and their changes that studied in this work.

2.3. Testing Methods and Measurements

XRD was done by X-ray diffractometer (XRD-6000 Shimadzu, German) with measurement conditions as shown in table (2). In this work, general structure analysis system (GSAS & EXPGUI) which is comprehensive system for the refinement of structural models for both single crystals and powder diffraction data was employed [6]. The grain size measurements for all four groups in this work were used atomic force microscope analysis (AFM) (type SPM-AA3000, Angstrom, USA). Optical microscope and image J 1.52i software were used to measure the crystalline phases density and mass fraction for four group specimens. The optical microscope was polarizing microscope model MT9430 transmitted illuminator, MEIJI Techno Co. LTD, Japan with digit camera of type canon DSI26431, Canon Inc., Japan connecting to computer.
Table 1. Four groups and their changes.

|                  | G11 | G12 | G13 | G14 | G15 |
|------------------|-----|-----|-----|-----|-----|
| **First Group G1** |     |     |     |     |     |
| Temperatures °C  | 750 | 800 | 850 | 900 | 950 |
| Time hr          | 4   | 4   | 4   | 4   | 4   |
| Nucleating Agent % | 0   | 0   | 0   | 0   | 0   |
| **Second Group G2** |     |     |     |     |     |
| Temperatures °C  | 800 | 800 | 800 | 800 | 800 |
| Time hr          | 2   | 4   | 6   | 8   | 10  |
| Nucleating Agent % | 0   | 0   | 0   | 0   | 0   |
| **Third Group G3** |     |     |     |     |     |
| Temperatures °C  | 800 | 800 | 800 | 800 | 800 |
| Time hr          | 4   | 4   | 4   | 4   | 4   |
| Nucleating Agent % | 4   | 7   | 11  | 14  | 18  |
| **Forth Group G4** |     |     |     |     |     |
| Temperatures °C  | 800 | 800 | 800 | 800 | 800 |
| Time hr          | 4   | 4   | 4   | 4   | 4   |
| Nucleating Agent % | 3   | 1   | 5.25 | 1.75 | 8.25 |

Table 2. XRD Measurement Conditions.

|                     |                  |                  |                  |                  |                  |
|---------------------|------------------|------------------|------------------|------------------|------------------|
|                     | **X-ray Tube**   |                  |                  |                  |                  |
| Target              | Cu               |                  |                  |                  |                  |
| Voltage KV          | 40               |                  |                  |                  |                  |
| Current mA          | 30               |                  |                  |                  |                  |
| Wavelength ˚A       | 1.5418           |                  |                  |                  |                  |
| **Scanning**        |                  |                  |                  |                  |                  |
| Scan Range 2θ (deg) | 10-80            |                  |                  |                  |                  |
| Scan Mode           | Continuous Scan  |                  |                  |                  |                  |
| Scan Speed (deg/min)| 8                |                  |                  |                  |                  |
| Sampling Pitch (deg)| 0.02             |                  |                  |                  |                  |

3. Results and discussion

Figure (1) is showing XRD histogram of base glass, G12, G32 and G42, there is 7.5 wt.% crystalline phase in base glass XRD histogram due to the ratio of Li₂O to SiO₂ is non-stoichiometric. A phenomenon occurred in this state called "Phase Separation" render the base glass certain opacity and phase separation is playing a part in the nucleation of lithium silicate glass-ceramics [4]. Primary phase 5.3 wt.% Li₄SiO₄ and secondary phase 2.2 wt.% SiO₂ in base glass, they are considered as nuclei for growing the crystalline phases in heat treatment later.

It is obvious from figure (1); the base glass shows lower intensity values which mean low reflections from low content of crystalline phases, while G32 and G42 showed higher intensity values from high reflections of high content of crystalline phases [5].
Figure 1. XRD histogram of base glass, G12, G32 and G42.

Corundum ($\alpha$-Al$_2$O$_3$) was used as reference material for crystalline phase percentage calculations from EXPGUI and which add 1g for each specimen and done by [7]:

$$P_f = \frac{C_A}{C_m} \times P_m$$  \hspace{1cm} (1)

Where $P_f$ is crystalline phase fraction, $C_A$ is Addition fraction of Corundum in specimen, $C_m$ is Mass fraction of Corundum that calculated from EXPGUI and $P_m$ is Mass fraction of crystalline phase that calculated from EXPGUI.

$$G_f = 1 - \sum_{i=0}^{i} P_f$$  \hspace{1cm} (2)

Where $G_f$ is Glass fraction.

Figure (2) shows the changes of heat treatment temperatures, time and nucleating agent percentages with crystalline phase percentages. The increasing of heat treatment temperature and time lead to increasing in crystalline phase percentages as seen in figure (2) a and b. Figure (2) c shows the crystalline phases increasing with adding percentage of nucleating agent which has been done for a certain limit. This behavior is attributed to increasing interfacial energy ($\gamma$) or energy barrier value which is restricting the crystalline phase growing and depending on viscosity of the glass-ceramic composition [8]. The crystalline phase percentages in forth group (G4) higher than third group (G3) because of producing viscosity depending on the type and amount of nucleating agents added to the base glass.
Figure 2. Heat treatment temperature, time and nucleating agent percentage. (a) First group (G1), (b) Second group (G2), (c) Third (G3) and fourth (G4) group.

Figure (3) shows the growing crystalline phases in base glass have primary phase and secondary phases. The primary phase may be low or high percentage but still dominant phase and secondary phase percentages less than primary phase. The primary phase which limits the glass-ceramic properties which are depending on chemical composition and crystalline structure of the primary phase and secondary phases are making differences in the glass-ceramic properties [8].

Figure 3. Primary phase and secondary phase percentages. (a) First group (G1), (b) Second group (G2), (c) Third group (G3), (d) Fourth group (G4).
The primary phase in this work is lithium silicate Li$_2$SiO$_3$ has an orthorhombic structure with lattice constants (a, b, c) = (9.396, 5.396, 4.661 Å) [space group Cmc2$_1$ (No.36)]. It has four molecular units (24 atoms) per cell, consisting of one type of Li atoms with site of 8b, one type of Si atoms with site of 4a, and two types of O atoms with site of 8b and 4a, respectively. Li$_2$SiO$_3$ have number of properties such as low electric conductivity, high mechanical resistance, high thermal stability, mechanically stable structure and good young modulus values [9]. Figure (3) indicates existence of crystalline phases in a and b and vanishing in c and d while absence in a and b like Li$_4$SiO$_4$ and SiO$_2$, appear new crystalline phases in c and d while absence in a and b like Li$_3$PO$_4$, Li$_{22}$Si$_5$O$_{22}$, TiO$_2$...etc. This means the secondary phases is metastable phases which their existence or vanishing is depending on the chemical composition, mixing and addition percentage of base glass and nucleating agents, temperature and time of the heat treatment. Whereas primary phase Li$_2$SiO$_3$ exists in a, b, c and d of figure (3) which meaning stable phase.

The grain size measurement range on all specimens is 25 × 25μm and choice has been done for one specimen from each group as shown in Figure (4).

![Figure 4](image-link)  
**Figure 4.** Grain size distribution for selecting specimen. (a) G12, (b) G23, (c) G32 and (d) G42.

The grain size results of crystalline phases in lithium silicate glass-ceramic for all four group specimens are nano-scale, average diameter from 64 nm to 108 nm. As seen in figure (4), c is high grain size distribution (0<ps<40 nm) because of P$_2$O$_5$ helps in growing of the crystalline phases and has high energy of reaction with others oxides to creating new compounds of crystalline phases. The rest of figure (4), a, b are (0<ps< 14 nm), (0.03<ps< 14.03 nm) and d show low grain size distribution (0<ps< 13.7 nm) in above figure, TiO$_2$ was reduced from P$_2$O$_5$ activity to larger crystalline phases in diameter but increased the density of crystalline phase with 13.7 nm diameter as comparison with c.

Figure (5) shows the temperature, time of heat treatment and addition percentage of nucleating agent changes with average diameter was studied. It may be seen an increasing to a certain limit and begun to decrease except for G3 (P$_2$O$_5$) curve in c, the average diameter increases with addition percentage of nucleating agents.
A wide range at high temperature, the glass is semi-liquid solid material and crystalline phases are lookalike islands in the middle of glass. The large crystalline phase (low energy) is encountering glass barrier (high energy) leading to broken parts of crystalline phase (island) and small pieces of crystalline phase are begin to grow up [10]. As mention before, $P_2O_5$ has high energy to reaction and get attracting the ions in glass and building order arrangement by increasing the diffusion rate of ions in glass.

The specimens were grind with silicon carbide paper 1200 mesh and 1500 mesh and polishing with cloth and alumina paste for half hour. Etching has been done by dilute solution with 3% HF concentration for 2 min; the optical microscope images were analyzed by image J 1.52i. The optical microscope images were magnified force (100X) and image size 1×1mm. The analysis of images had been done by image J1.52i indicating that black dots are representing the crystalline phases in white area which is glass phase. The calculation of crystalline phase's number in 1 mm$^2$ area which represents density of crystalline phases in image J 1.52i, the mass fraction calculation of crystalline phases had been done by limiting all crystalline phases (black dots). The image J 1.52i is calculating the total area (pixel) of the crystalline phases and by dividing on image area (pixel) can got on mass fraction of crystalline phases in 1 mm$^2$ area [11].
The density and mass fraction of crystalline phases were studied with temperature, time of heat treatment and addition percentage of nucleating agent changes, as shown in figure (6) and (7). Figure (6) a and b are shows increasing of crystalline phases density with temperature and time of heat treatment. Figure (6) c increasing of crystalline phase's density reaches to a certain value and begins to decreasing for G3 and G4 curves. This due to increase in the viscosity with nucleating agent addition, but G4 curve shows higher values than a, b and G3 curve in c. The obvious of figure (7), a was little increased of mass fraction with heat treatment temperature up to 900°C, sharp increase was begun due to the reducing viscosity of base glass composition and diffusion rate increased.

**Figure 6.** Crystalline phases density (No. /mm²) with (a) Heat treatment temperature (G1), (b) Heat treatment time (G2) and (c) Addition percentage of nucleating agents (G3) and (G4).

![Figure 6](image)

Figure (7) b and c were increased of mass fraction with heat treatment time and addition percentage of nucleating agents until 8 hrs and 4% in G4 curve and 11% in G3 curve of c are begin to decrease. This related to breaking the crystalline phases to tiny pieces and reaction with softening base glass. Generally, crystalline phases were increased with temperature and time of heat treatment and nucleating agent percentages comparison to base glass. The mass fraction values are so little with comparison to high values of crystalline phases density, this meaning the particle size for all crystalline phases on small scale. Small scale is nano-scale and down and these results provide good agreement and confirmation with AFM results.
4. Conclusion

1- The non-stoichiometric ratio (Li₂O:SiO₂) can be used to making glass-ceramics without adding nucleating agents due to phase separation phenomena that creating crystalline phases which consider nuclei for crystalline phases growing at heat treatment. This state is need for high temperature and more time of heat treatment.

2- Chemical composition of crystalline phases are coming from chemical composition of base glass, so it can governing of the crystalline phase types of the glass-ceramic by type of oxides that forming base glass and their percentage.

3- P₂O₅ is very active nucleating agent for crystalline phases growing of lithium silicate free-alumina glass-ceramic or with little alumina content.

4- A little addition of TiO₂ as nucleating agent with P₂O₅ get higher values for crystalline phase percentages, average diameter and mass fraction when using P₂O₅ alone, i.e. good work for a certain value, but then decreasing is occur.

5- The best results from point view of the work is 4% nucleating agent P₂O₅ and TiO₂, heat treatment temperature is 950 °C and heat treatment time is 6 hr. The glass-ceramic is become good percentage with crystalline phases, high phases density and good mass fraction with interesting in nano-scale.

References

[1] Schmitt, T.J., Tomiyama, M., Folgueras, M.V. and Bahr, F.L., 2012. *Materials Science Forum* **727**:1308-1312. Trans Tech Publications.
[2] Holand, W. and Beall, G.H., 2012. *Glass ceramic technology*. John Wiley & Sons, pp. 75-80.

[3] Ponsot, I., Detsch, R., Boccaccini, A.R. and Bernardo, E., 2015 *Advances in Applied Ceramics*, **114**:S17-S25.

[4] Hijiya, H., Kishi, T. and Yasumori, A., 2009 *Journal of the Ceramic Society of Japan*, **117**:1361:120-126.

[5] Kniess, C.T., de Lima, J.C. and Prates, P.B., 2012. IntechOpen, pp. 295-297.

[6] RBV, L.A.D., 2004. *General structure analysis system (GSAS)*. Los Alamos National Laboratory Report LAUR: 86-748, pp. 51-60.

[7] Gualtieri, A.F., 2003. A guided training exercise of quantitative phase analysis using EXPGUI. *GSAS Tutorials and Examples*.

[8] Prado, M.O., Nascimento, M.L.F. and Zanotto, E.D., 2008 *Journal of Non-Crystalline Solids*, **354** 40-41:4589-4597.

[9] Tang, T. and Luo, D.L., 2010. *J. At. Mol. Sci.*, **1**, pp.185.

[10] Karmakar, B., Rademann, K. and Stepanov, A. eds., 2016. *Glass nanocomposites: synthesis, properties and applications*, William Andrew, pp. 13-19.

[11] Ferreira, T. and Rasb, W., 2012. ImageJ user guide: *IJ* **1.46 r**, pp. 29-34.