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Preparation of Lithium Disilicate Glass-Ceramics as Dental Bridge Material

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Abstract

Sintering and crystallization behaviors of three lithium-silicate-based glass compositions were determined by heating the pressed specimens above their DTA crystallization peak temperatures.

The crystallization procedure and microstructure of the heat-treated specimens were investigated by means of differential thermal analysis, X-ray diffraction and scanning electron microscopy.

According to the results, while P_2O_5 encouraged the crystallization of both Li_2SiO_3 and $Li_2Si_2O_5$ phases, ZrO_2 did not show such capability. Furthermore, while Li_2SiO_3 was crystallized directly as the result of a bulk crystallization mechanism, $Li_2Si_2O_5$ tended to crystallize epitaxially on the surface of the previously precipitated Li_2SiO_3 particles.

Keywords: Lithium disilicate, glass ceramic, dental

I. Introduction

Since the 1990s, efforts have been made to develop biomaterials for restorative dentistry based on the production of metal-free systems [1,2]. Lithium disilicate ($Li_2Si_2O_5$) glass ceramics with major uses in all-ceramic restorative dentistry were produced for the first time in 1995 [2]. This material is suitable for fabricating restorative prostheses of any kind, from dental inlays, onlays, veneers and crowns to multi-unit bridges, mainly owing to its desirable strength and fracture toughness [1–10], which are essential properties in dental materials as they guarantee the long lifetime of the restoration against various mechanical and thermal stresses. These properties can be achieved with certain microstructural modifications like uniform distribution of crystalline phase in the glass matrix and interlocking of needle and plate- like lithium disilicate crystals [5,11,12], which can be obtained only with the bulk crystallization mechanism.

The principal method of producing multi-unit bridges is based on the viscous flow of a glass specimen, consisting of sintering of a compacted powder frit, or melt casting, and then hot pressing of the resulting glassy ingots into a lost-wax mould [1].

Like other glass-ceramics, lithium disilicate glass-ceramics need suitable nucleating agents for bulk crystallization. Precious metals, e.g. Ag, Cu, and Pt, and oxides like ZrO_2 and P_2O_5, with no undesirable coloring effects, seem suitable in this respect [11–13]. In the present work the above-mentioned oxides were adopted as nucleants and their effects on the sintering and crystallization behaviors of the compacted bodies were compared. These behaviors have not yet been studied sufficiently for this glass system.

II. Experimental Procedure

The chemical compositions of the prepared glasses are shown in Table 1. Reagent grade SiO_2 (acid-washed, purity ≥ 99 %), Al_2O_3 (MR70), Li_2CO_3 (Merck, 1.05671), KNO_3 (Merck, 1.05061), P_2O_5 (Merck, 1.00540), H_3BO_3 (Merck, 1.05061) and ZrO_2 (Merck, 1.00757) powders were used as raw materials. The glass compositions were melted in high-alumina crucibles in an electric furnace, at 1350 °C for 1 h. The obtained glass melts were cooled rapidly by quenching into distilled water.

Table 1: Chemical compositions of the three glasses.

Constituent (wt%)	G_B	G_{BZ}	G_P
SiO_2	74.2	74.2	74.2
Al_2O_3	3.54	3.54	3.54
Li_2O	15.40	15.40	15.40
K_2O	3.25	3.25	3.25
P_2O_5	-	-	3.37
B_2O_3	3.37	3.37	-
ZrO_2	-	3.37	-

Then the resulting frits were fast-milled to particle sizes smaller than 75 μm. Subsequently, cylindrical specimens measuring 4.5 mm in height and 15 mm in diameter were pressed at a pressure of 45 MPa.

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The compacted powders were sintered in the range 800–900 °C for 2 h. The optimum sintered specimens (ingots) were then re-fired at 950 °C for 15 min instead of the usual heat-pressing operation, which is the required procedure for shaping the final restorative.

The crystallization mechanism, crystallinity and microstructure of the sintered specimens were investigated respectively by means of differential thermal analysis (STA, Polymer Laboratories 1640), X-ray diffraction (Jeol-JDX 8030) and scanning electron microscopy (Philips XL30) techniques. Differential thermal analysis was performed with a heating rate of 10 °K/min in air atmosphere and the XRD patterns were recorded for two theta values from 5° to 80° with a step size of 0.02°. The accuracy of the XRD analyzer in determination of the d-spacing of the crystalline phases was ±0.02. The microstructures were evaluated via polishing and then etching of the specimens in 5 % HF for 30 s.

III. Results and Discussion

(1) Sintering and crystallization behaviours of glasses

Fig. 1 shows the DTA traces of the glasses. Accordingly, while the DTA curves of G_B and G_{BZ} show a single exothermic peak, there are two peaks in the G_P thermograph. Endothermic peaks at 944, 934 and 950 °C, respectively, in the thermographs of glasses G_B, G_{BZ} and G_P can be attributed to their liquidus temperatures. Furthermore, the dilatometric softening points (T_s) of glasses G_B and G_P are about 465 °C and that of G_{BZ} is about 490 °C. This means that ZrO_2 has increased the viscosity and so the crystallization temperature of G_{BZ}. In addition, comparison of the glasses shows that G_P exhibits a higher peak intensity than the other glasses, which means it has been crystallized more extensively during the DTA run.

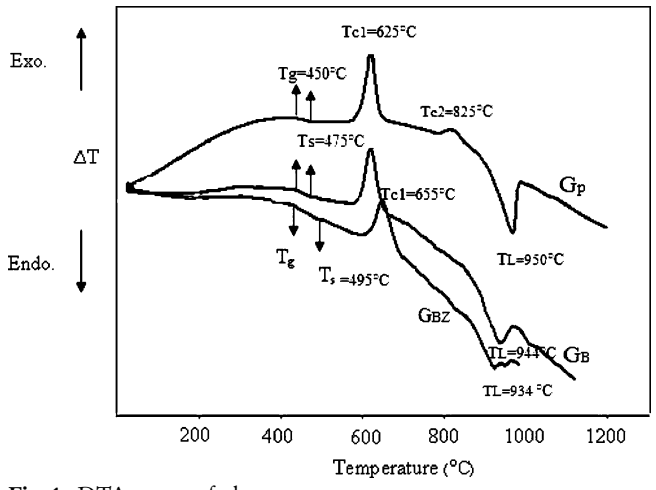

Fig. 1: DTA traces of glasses.

Fig. 2 shows the X-ray diffraction patterns of the G_P glasses, after heat treatment at their first and the second crystallization peak temperatures for 2 h. Accordingly, the first peak in the DTA traces represents the crystallization of lithium metasilicate (Li_2SiO_3) and the second one, which only emerges in the DTA curve of specimen G_P at 825 °C, represents the crystallization of lithium disilicate ($Li_2Si_2O_5$). Crystallization of $Li_2Si_2O_5$ in G_B and G_{BZ} during the heat treatment at 825 °C and the lack of a distinctive second exothermic peak in their DTA thermographs mean that surface crystallization is the dominant mechanism for the crystallization of $Li_2Si_2O_5$ in them.

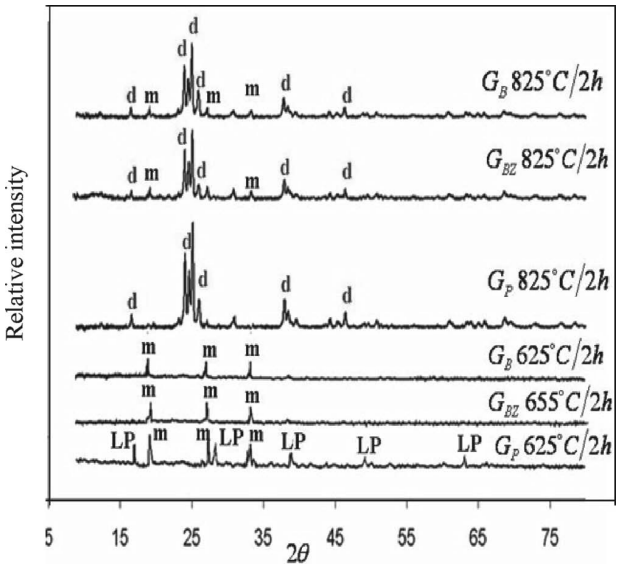

Fig. 2: XRD patterns of the glasses heat-treated for 2 h at their first and second exothermic peak temperatures of G_P, d: lithium disilicate, m: lithium meta-silicate, LP: Li_3PO_4.

A clearly observable exothermic peak in G_P and higher intensities of its related XRD patterns indicate that bulk crystallization is probably the mechanism of crystallization for its crystalline phases. Moreover, firing of samples at 825 °C has led to a considerable reduction of Li_2SiO_3 in G_B and G_{BZ} and the complete disappearance of this phase in G_P. Therefore, it can be concluded that besides surface crystallization, $Li_2Si_2O_5$ also precipitates epitaxially on the Li_2SiO_3 crystals and grows at the expense of the latter phase. The role of Li_2SiO_3 as a precursor for crystallization of $Li_2Si_2O_5$ has been mentioned by other researchers [1,7].

Table 2 shows the characteristics of the three compacted glasses, after firing respectively at 800, 850, 875 and 900 °C for 2 h. These results showed that the optimum sintering temperature of G_P was 875 °C and that of the two other glasses was 800 °C. It should be noted that the latter specimens were deformed above 850 °C. It seems that a higher degree of crystallization in G_P is responsible for its higher sintering temperature.

Figs. 3, 4 and 5 show the XRD patterns of the G_B, G_{BZ} and G_P after firing at different temperatures. It can be seen that both $Li_2Si_2O_5$ and Li_2SiO_3 are present in the G_B and G_{BZ} specimens and the amounts of these phases decrease slightly with temperature. On the other hand, apart from the specimens heat-treated at 900 °C, $Li_2Si_2O_5$ was the only crystalline phase detected in the G_P glasses. Increasing the firing temperature to 900 °C caused a slight amount of Li_2SiO_3 to recrystallize in the G_P specimen, apparently at the expense of $Li_2Si_2O_5$. It seems that $Li_2Si_2O_5$ particles dissolve into the residual glass phase at higher temperatures and re-precipitate in the form of Li_2SiO_3 at about 625 °C during cooling of these specimens.

Table 2: Sinterability of the three glasses at different temperatures.

Sintering temperature (°C)		800	850	875	900
Water absorption (%)	G_B	3.11	1.32	1	-
	G_{BZ}	1.74	0.91	-	-
	G_P	5.60	2.90	0.63	0.62
Firing shrinkage (%)	G_B	16.00	14.40	13.98	-
	G_{BZ}	19.00	16.24	-	-
	G_P	8.11	14.02	15.50	15.12
Bulk density (g/cm^3)	G_B	2.89	2.46	2.63	-
	G_{BZ}	3.05	2.83	-	-
	G_P	2.30	2.44	2.81	2.05
Relative density (%)	G_B	91.2	87.3	89.1	-
	G_{BZ}	90.2	89.6	-	-
	G_P	72.9	81.3	91.8	90.1
Porosity (%)	G_B	8.8	12.7	10.9	-
	G_{BZ}	9.8	10.4	-	-
	G_P	27.1	18.7	8.2	9.9

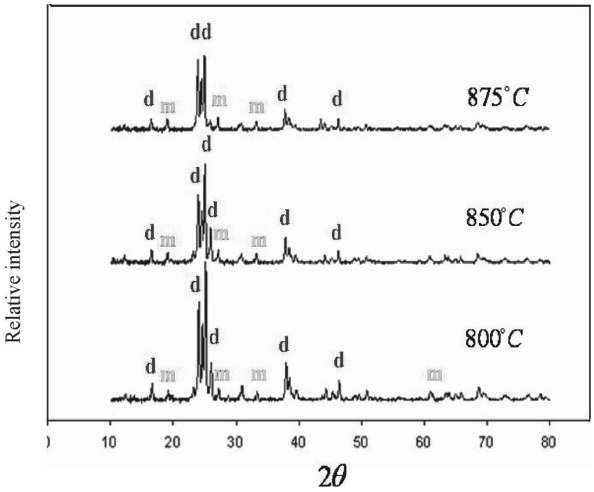

Fig. 3: XRD patterns of G_B specimens after firing at different temperatures, d: lithium disilicate, m: lithium metasilicate.

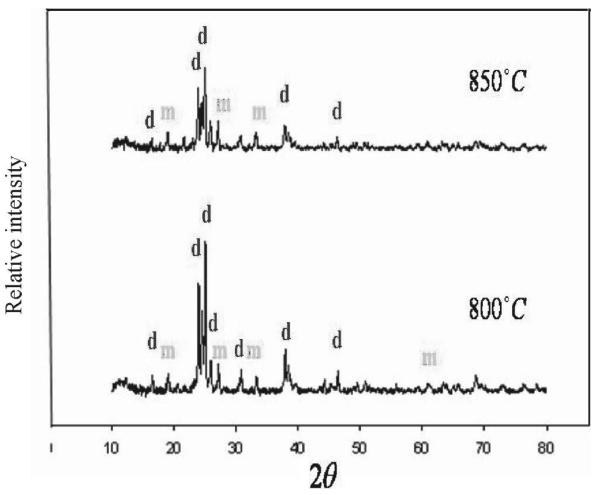

Fig. 4: XRD patterns of G_{BZ} specimens after firing at different temperatures, d: lithium disilicate, m: lithium metasilicate.

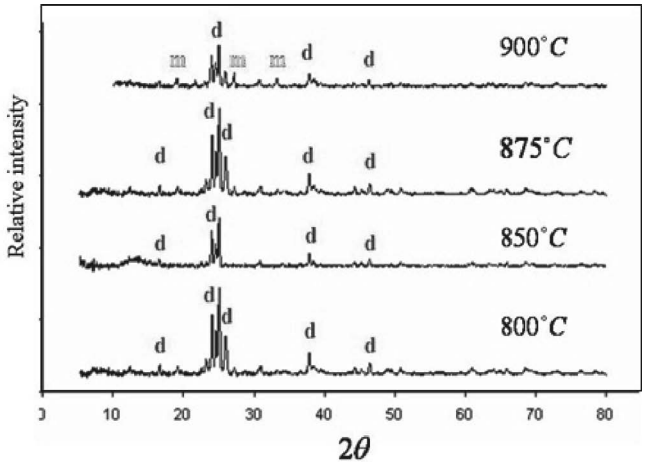

Fig. 5: XRD patterns of G_P specimens after firing at different temperatures, d: lithium disilicate, m: lithium metasilicate.

As the crystalline phases may be altered during hot pressing at higher temperatures, e.g. 950 °C in the usual lost wax method, the prepared glassy ingots were re-fired at the above-mentioned temperature. As it was assumed that application of pressure was ineffective in the crystallization process during re-firing, the pressure parameter was omitted in this experiment. Fig. 6 shows the XRD patterns of the re-fired glassy ingots (15 min). As it can be seen, re-firing has caused the complete conversion of lithium disilicate to lithium meta-silicate in the specimens G_B and G_{BZ}, as a result of the dissolution of the former phase into the residual glass and recrystallization in the form of lithium meta-silicate during the cooling cycle. A higher initial amount of lithium disilicate and a different residual glass composition in the ingot G_P has probably led to the saving of this phase in the re-fired G_P specimen. Lithium-disilicate-containing glass-ceramics are stronger, with regard to mechanical strength, than lithium meta-silicate-based glass-ceramics. Therefore, it seems that G_P is a more suitable composition for restorative prosthesis in respect of the mechanical properties.

(2) Glass-ceramics microstructures

Fig. 7 shows the microstructures of different glasses sintered at their optimum temperatures. The needle-like particles are $Li_2Si_2O_5$ crystals. The comparison of microstructures also shows that G_p, even with its higher firing temperature, has crystalline particles smaller than 2 μm. This observation and the presence of lithium phosphate in the XRD patterns of G_p, heat-treated at 650 °C, confirms again the earlier report [6] indicating that P_2O_5 helps $Li_2Si_2O_5$ crystals to precipitate more easily, through the formation of lithium phosphate, which acts as an effective nucleant for crystallization of Li_2SiO_3 and subsequently $Li_2Si_2O_5$. Apel *et al.* [12] also reported that P_2O_5 affects crystallization by reducing the thermodynamic barrier for nucleation of Li_2SiO_3, rather than the kinetic free energy barrier.

The microstructures of the re-fired glassy ingots are shown in Fig. 8. Accordingly, while the re-fired G_P exhibits crystalline particles smaller than 10 μm, which according to XRD results (Fig. 6) are attributed to lithium

disilicate phase, the two other glassy ingots consist of large grown crystals of lithium meta-silicate.

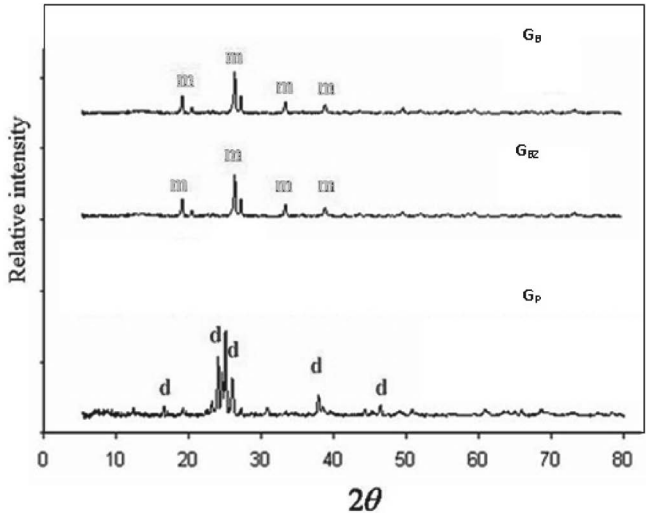

Fig. 6 : XRD patterns of the ingots after re-firing at 950 °C for 15 min.

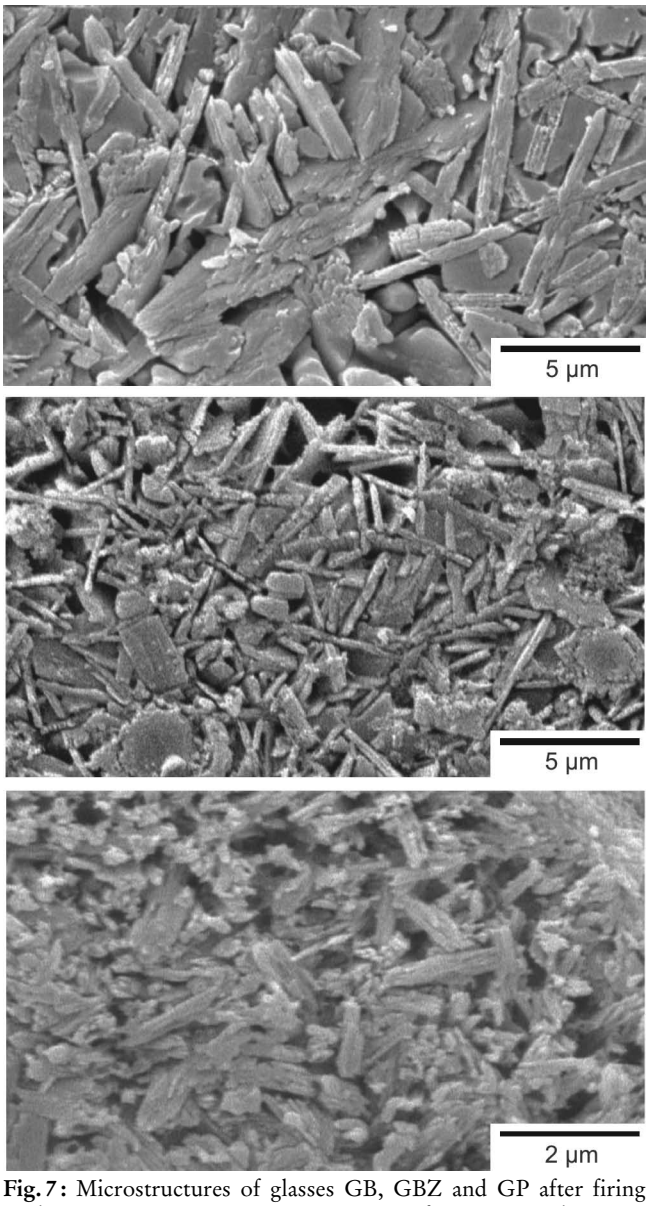

Fig. 7 : Microstructures of glasses GB, GBZ and GP after firing at their optimum sintering temperatures of 800, 800 and 875 °C, respectively.

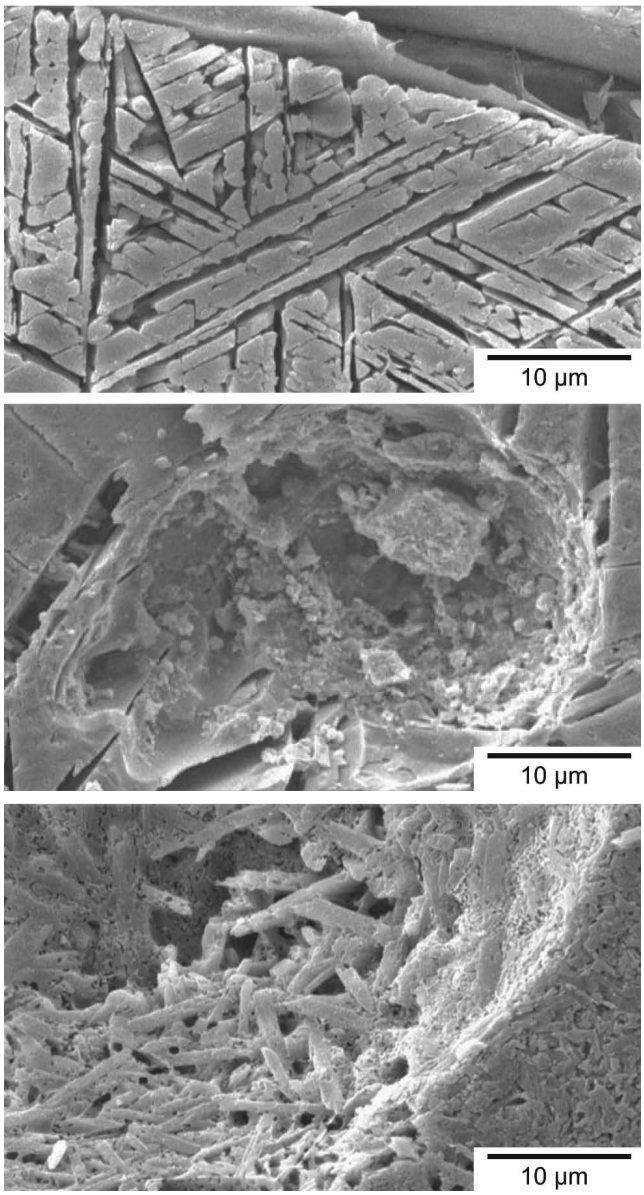

Fig. 8 : Microstructures of the re-fired ingots a) GB, b) GBZ and c) GP.

IV. Conclusions

It was shown that while ZrO_2 did not affect the crystallization behavior of the base glass, the intensity of both lithium meta-silicate and disilicate were increased with addition of P_2O_5.

Lithium phosphate was detected in the P_2O_5-containing glass after its heat treatment at the first DTA peak temperature. Lithium phosphate acted as a nucleating agent for crystallization of Li_2SiO_3 and consequently $Li_2Si_2O_5$. Crystallization of lithium phosphate is responsible for the finer texture, higher amounts of crystalline phases and hence higher sintering temperature of the P_2O_5-containing glass.

According to the re-firing results of glassy ingots, while lithium disilicate converts to meta-silicate in the G_B and G_{BZ} specimens, it remains unchanged in the P_2O_5-containing glass composition. This means that P_2O_5 is an essential constituent of glasses in the manufacture of lithium-disilicate-based glass ceramics.

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