

Crystallization behaviour and microstructural evolution of a $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass derived from spodumene mineral

ASTRID NORDMANN, YI-BING CHENG

Department of Materials Engineering, Monash University, Clayton Vic. 3168 Australia

A naturally occurring mineral deposit of α -spodumene has been successfully used to fabricate glasses and glass ceramics in the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) system. TiO_2 is an effective nucleating agent in promoting the crystallization of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$ glass to produce LAS glass-ceramics in which β -quartz_{ss} and β -spodumene_{ss} are the major crystalline phases evolved. The crystallization process and microstructural evolution were monitored using X-ray diffraction and transmission electron microscopy.

1. Introduction

The concept of controlled glass crystallization can be traced back to the original work of Stookey [1, 2] who showed that efficient internal nucleation of a glass enabled the development of a homogeneous, fine-grained microstructure. To achieve this aim it has generally been necessary to incorporate one or more nucleating agents into the parent glass. These additives act as heterogeneous sites at which the nucleation of desired crystalline phases may take place and therefore by adjusting the type and concentration of the nucleating agent used it is possible to exercise some control over the crystallization process.

The important crystalline phases obtained from the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system are β -quartz solid solution (β -quartz_{ss}) and β -spodumene_{ss}, both of composition $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$. Beta-quartz_{ss} is a solid solution based on the hexagonal high-quartz structure and has a thermal expansion coefficient (TEC) $\alpha = 0 \pm 0.15 \times 10^{-6}$ per $^\circ\text{C}$ [3]. Beta-spodumene is a solid solution derived from the tetragonal form of silica known as keatite and has a TEC $\alpha = 1-2 \times 10^{-6}$ per $^\circ\text{C}$ [3]. A stuffed high-quartz solid solution may in general be obtained by heat-treating a glass of the general composition $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-n\text{SiO}_2$ where n ranges from 2–10 or higher. However, the high-quartz solid solution transforms into the keatite solid solution at elevated temperatures only when n is greater than or equal to 3.5 [4]. Materials comprised of β -quartz_{ss} provide superior thermal shock resistance and coupled with their high mechanical strength and optical transparency, offer excellent promise as engineering materials.

One of the earliest studies on the nucleation and crystallization of LAS glasses was conducted by Doherty *et al.* [5]. Transmission electron microscopy (TEM) analyses of glasses containing TiO_2 as a nucleating agent showed that phase separation

occurred on cooling from the melt and subsequent heating caused the formation of a large number of aluminium titanate crystals approximately 5.0 nm in diameter. These crystals acted as sites for heterogeneous nucleation and allowed crystallization of the remaining glass to proceed. Further studies by Barry *et al.* [6] examined a series of TiO_2 -containing LAS glasses in order to seek regularities in the efficiency of additive oxides as a function of the base glass composition. They found that crystal nucleation was particularly efficient in glasses near the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ composition line and ascribed these observations to changes in the fluidity of the glass at the crystal growth front. Maier and Müller [7] studied a lithium aluminosilicate glass ceramic containing TiO_2 and ZrO_2 . They observed the formation of ZrTiO_4 crystallites which acted as precursor nuclei for subsequent crystallization. Similar results were also described by Ramos and Gandais [8].

The present work discusses the crystallization of a lithium aluminosilicate glass containing TiO_2 as a nucleating agent. Conventionally, LAS glasses and glass-ceramics are prepared from Al_2O_3 , SiO_2 and reagent-grade Li_2CO_3 [9–11]. Australia has a relatively large deposit of spodumene minerals which are comprised of Li_2O , Al_2O_3 and SiO_2 in approximately a 1:1:4 molar ratio and a small amount of Na_2O and Fe_2O_3 as impurities. The current study forms a part of an overall project utilizing the naturally occurring mineral to produce glass-ceramics with superior thermal shock resistance. A previous study focused on the characterization of this mineral and its amenability to glass formation and crystallization [12]. That work examined the effect of different concentrations of ZrO_2 and TiO_2 on the crystallization behaviour using differential thermal analysis and X-ray diffraction (XRD). The present study provides a detailed correlation between the microstructural evolution and the crystallization behaviour observed at different

heat-treatment times and temperatures for a glass of fixed composition.

2. Experimental procedures

2.1. Sample preparation

The glass composition comprised 4 wt% TiO₂ (Dulux®) as a nucleating agent, 1 wt% As₂O₃ (AnalaR®) as a fining agent and 95 wt% spodumene mineral concentrate (obtained from Lithium Australia Ltd). These constituents were hand-mixed for 20 min using an alumina mortar and pestle and then transferred to a platinum crucible. The batch mixture (~80–100 g) was melted in a rapid heating furnace at 1600 °C for 3 h using a heating rate of 20 °C per min. The glass was then removed from the furnace, water-quenched, crushed into small pieces and then remelted twice more under the same conditions to ensure glass homogeneity. Glass-ceramics were prepared by subjecting the glass to single-step heat-treatments at temperatures between 700–1000 °C for a period of 0–8 h using heating and cooling rates of 5 °C per min. A dwell time of zero hour is used here to infer that the sample was immediately cooled as soon as the temperature reached the designated value.

2.2. Sample characterization

XRD experiments were performed using a Rigaku Geigerflex diffractometer operating at 40 kV and 22.5 mA, using Cu K_α radiation and a Ni filter. Samples were crushed to a fine powder and scanned at 2° per min using a step size of 0.05°. Samples for TEM were cut, polished, ion-beam milled to perforation, carbon-coated and then examined either in a Philips EM420 TEM operating at 120 kV or a Philips CM20 TEM operating at 200 kV and equipped with energy dispersive X-ray spectroscopy (EDS) facilities. Due to rapid degradation of the sample by the electron beam in a conventional double-tilt holder, some samples were contained in a liquid nitrogen cooled holder.

3. Results and discussion

3.1. Physical appearance of crystallized glasses

The crystallization sequence expressed itself in visual changes in the appearance of the material. The parent glass was homogeneous and slightly yellow but upon heat treatment displayed changes in its colour and transparency. When heated for 4 h at 700 °C, the sample maintained the same characteristics as the as-cast glass; it was not until heating for 8 h at 700 °C or for 0.5 h at 725 °C that the first visible change became apparent. Under these conditions the glass darkened to a slightly brown colour but retained its transparency. Apparently, the crystallization process can be controlled through judicious alterations to the crystallization temperature for a given time or to the duration of the process at a prescribed temperature. With increasing heat-treatment temperature (750–850 °C), again for a fixed 4 h period, the glass continued darkening in colour and increased slightly in its opacity. At 900 °C it developed a purple haze and by 950 °C

was pale purple and fully opaque. The colour changes from yellow to brown to purple are probably due to changes in the coordination of the Ti⁴⁺ ions with increasing temperature [13]. Additional increments in temperature did not have any further detectable effects on the appearance of the samples.

The observed changes in the optical properties of the samples were accompanied by changes in the grain sizes and phase assemblages within the material. To maintain transparency in a polycrystalline material, the grain size must be smaller than the wavelength of visible light in order to prevent interference effects and subsequent light scattering and the refractive indices of any inclusions must be comparable to that of the surrounding medium. TEM analysis of a sample heated at 950 °C, presented in section 3.3, revealed grain sizes up to 450 nm, a size well beyond the wavelength of light and thereby accounting for the increased opacity. Further contributions to the opacity of the samples result from differences in the birefringence and refractive indices of the phases which they contain. Any minor phases evolved with an increase in the temperature most likely have different refractive indices compared to β-quartz_{ss} and β-spodumene_{ss} and therefore alter the opacity. In addition, thermal stresses will locally change the density of the residual glass and consequently cause directional increases and decreases of refractive index, that is, make the glass birefringent [13].

3.2. XRD analysis

3.2.1. Effect of heat-treatment temperature on crystallization

Table 1 shows the effect of heat-treatment temperature on the phase evolution when a constant crystallization

TABLE I Effect of heat-treatment temperature on crystallization. In each case, a crystallization dwell time of 4 h was used (XRD intensity: m = medium, s = strong)

Temperature (°C)	XRD result	TEM observation
as-cast glass	glass	amorphous
700	glass	amorphous
725	β-quartz _{ss} (m)	dispersion of crystals (<i>d</i> ~ 120 nm) in a glassy matrix, small ppts <i>l</i> ~ 30 nm
750	β-quartz _{ss} (s)	equiaxed grains (<i>d</i> ~ 220 nm), ppts <i>l</i> ~ 45 nm
800	β-quartz _{ss} (s)	*
850	β-quartz _{ss} (s)	equiaxed grains (<i>d</i> ~ 240 nm), ppts <i>l</i> ~ 60 nm, <i>w</i> ~ 10 nm
900	β-quartz _{ss} (s) β-spodumene _{ss} (s)	*
950	β-spodumene _{ss} (s)	equiaxed grains (<i>d</i> ~ 450 nm) ppts <i>l</i> ~ 200 nm, <i>w</i> ~ 15 nm.
1000	β-spodumene _{ss} (s)	*

d = average grain diameter; ppts = precipitates; *l* = average precipitate length; *w* = average precipitate width; *TEM analysis was not performed.

TABLE II Effect of heat-treatment time on crystallization (XRD intensity: m = medium, s = strong)

Crystallization temperature (°C)	Crystallization time (h)	XRD result	TEM observation
725	0	glass	amorphous
	1	glass	amorphous, ppts $l \sim 15$ nm
	2	β -quartz _{ss} (m)	amorphous with crystallites $d \sim 110$ nm, ppts length $l \sim 20$ nm
	4	β -quartz _{ss} (m)	amorphous with crystallites $d \sim 120$ nm, ppts $l \sim 30$ nm
750	0	glass	amorphous
	1	β -quartz _{ss} (s)	equiaxed grains, $d \sim 140$ nm, ppts $l \sim 35$ nm
	2	β -quartz _{ss} (s)	equiaxed grains, $d \sim 140$ nm, ppts $l \sim 35$ nm
	4	β -quartz _{ss} (s)	equiaxed grains, $d \sim 150$ nm, ppts $l \sim 45$ nm
850	0	β -quartz _{ss} (s)	equiaxed grains, $d \sim 240$ nm, ppts $l \sim 60$ nm
	0.25	β -quartz _{ss} (s)	equiaxed grains, $d \sim 240$ nm, ppts $l \sim 60$ nm
	4	β -quartz _{ss} (s)	equiaxed grains, $d \sim 240$ nm, ppts $l \sim 60$ nm

d = average grain diameter; ppts = precipitates; l = average precipitate length (increases in width occur in similar proportions as indicated in Table I)

time of 4 h is employed. It is seen that heat-treatment at 700 °C for 4 h retained the amorphous nature of the parent glass, whereas heat-treatment at temperatures between 725–850 °C for the same time produced samples comprised of a single phase, β -quartz_{ss} according to the XRD analyses. Heat-treatment at 900 °C gave a sample containing predominantly β -spodumene_{ss} with β -quartz_{ss} providing only a minor contribution to the X-ray diffraction spectrum, whereas 950 and 1000 °C for 4 h led to samples comprised entirely of β -spodumene_{ss}. These results suggest that the stability of different phases is strongly temperature dependent; above 850 °C, the β -quartz_{ss} with a low thermal expansion coefficient transformed into the β -spodumene_{ss} which has a relatively higher TEC, and accordingly the material becomes opaque. From this point of view, materials comprised of β -quartz_{ss} are limited to application temperatures less than 850 °C if optical transparency is required.

3.2.2. Effect of heat-treatment time on crystallization

Table II illustrates the influence of the heat-treatment time on the crystallization behaviour. At a low temperature (725 °C) XRD results suggested the retention of a fully amorphous sample when crystallization dwell times of 0 and 1 h were used. Increasing the time to 2 h led to a sample comprised of both glass and small crystallites of β -quartz_{ss} while a further increment to 4 h resulted in a slight growth of these

β -quartz_{ss} crystals. At an intermediate temperature (750 °C), a heat-treatment time of 0 h still retained the glass, however, crystallization times of 1, 2 and 4 h generated samples which, based on XRD results, were fully crystallized β -quartz_{ss}. Subsequent TEM observations indicated differences in the average grain size of these materials. In contrast, the heat-treatment time at a high temperature (850 °C) did not significantly affect the nature of crystallization. Crystallization dwell times of 0, 0.25 and 4 h at 850 °C all produced samples comprised of β -quartz_{ss} without displaying any discernible differences in the microstructure. From these results, 750 °C seems to be an appropriate temperature for the formation of β -quartz_{ss}-containing glass-ceramics. These observations on the spodumene mineral-derived materials are consistent with other studies which used reagent-grade chemicals to fabricate LAS glasses and glass-ceramics in which TiO₂ was used as a nucleating agent [14, 15], and therefore provides encouraging evidence of directly utilizing the natural mineral for this application.

3.3. Microstructures

Representative TEM micrographs of several samples are now presented. Fig. 1a depicts a low magnification micrograph of the parent glass which indicates a homogeneous and essentially featureless morphology, although at a higher magnification (Fig. 1b) a fine-scale morphology which may be indicative of phase separation via spinodal decomposition is revealed.

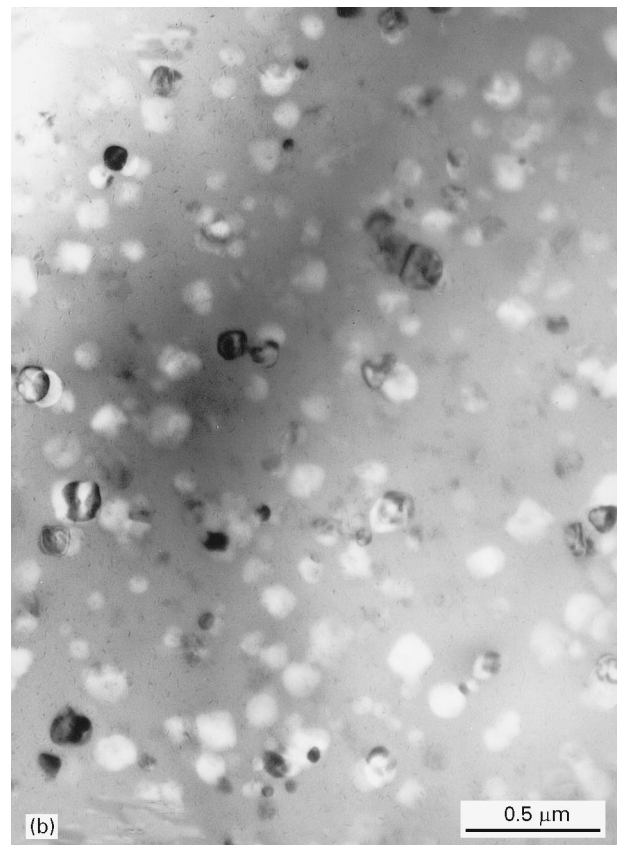
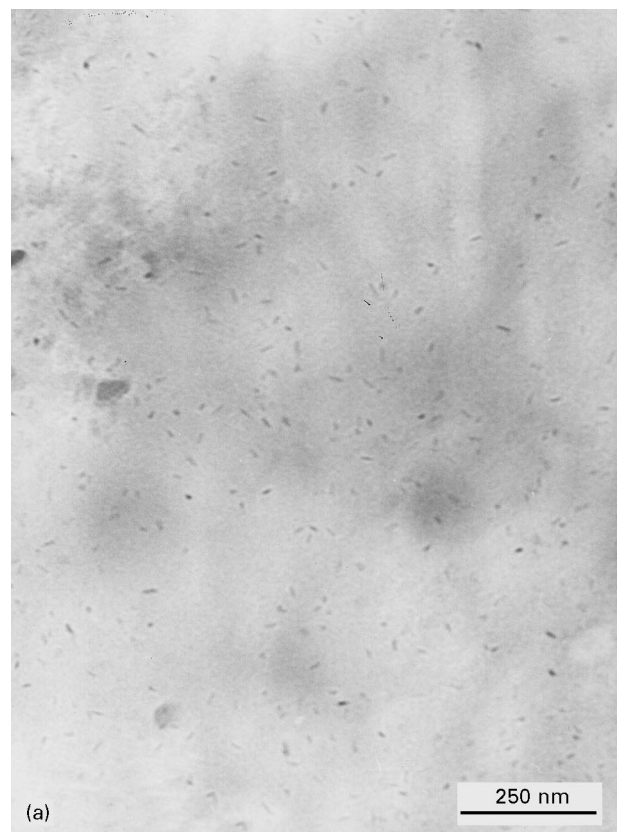
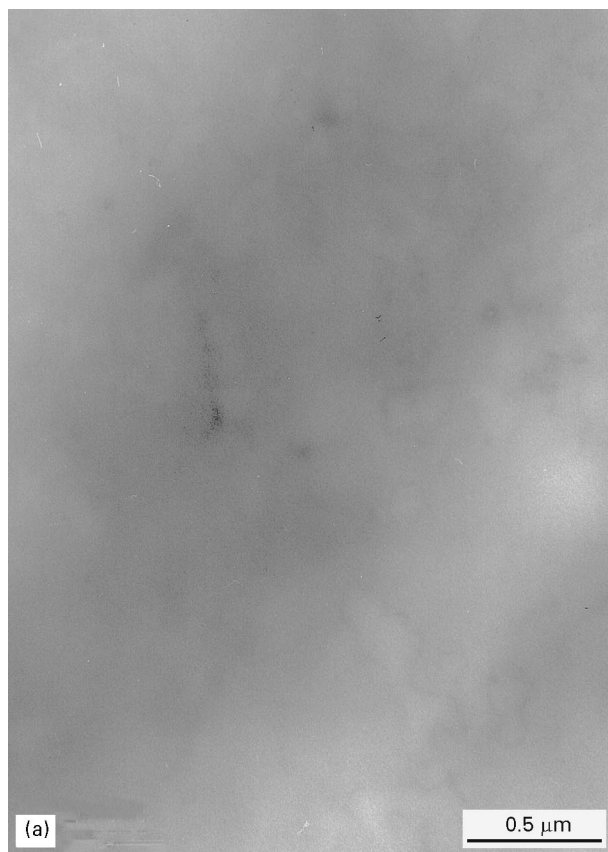


Figure 1 Bright field TEM micrographs of as-cast glass at (a) low magnification and (b) high magnification.

Figure 2 Bright field TEM micrographs of LAS glass heat-treated at 725 °C for (a) 1 h and (b) 4 h.

However, it is unclear whether this is genuine evidence for phase separation or whether it is merely an artefact arising from the carbon coating on the specimen, since both phenomena may have a similar interconnected

network on a structural scale of 5–10 nm. Although nucleation via glass-in-glass phase separation in the LAS glass-ceramics was reported previously [6, 16–18], the results of the present study favour the

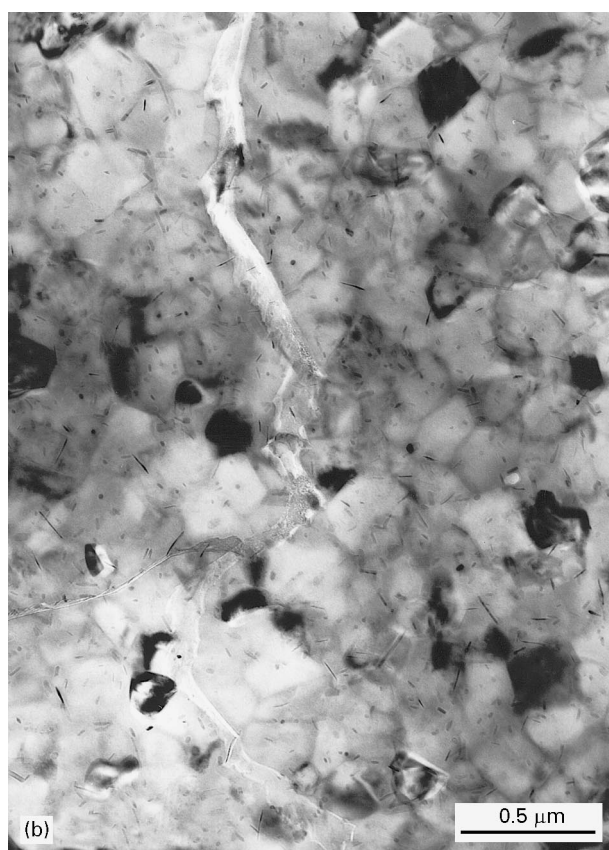
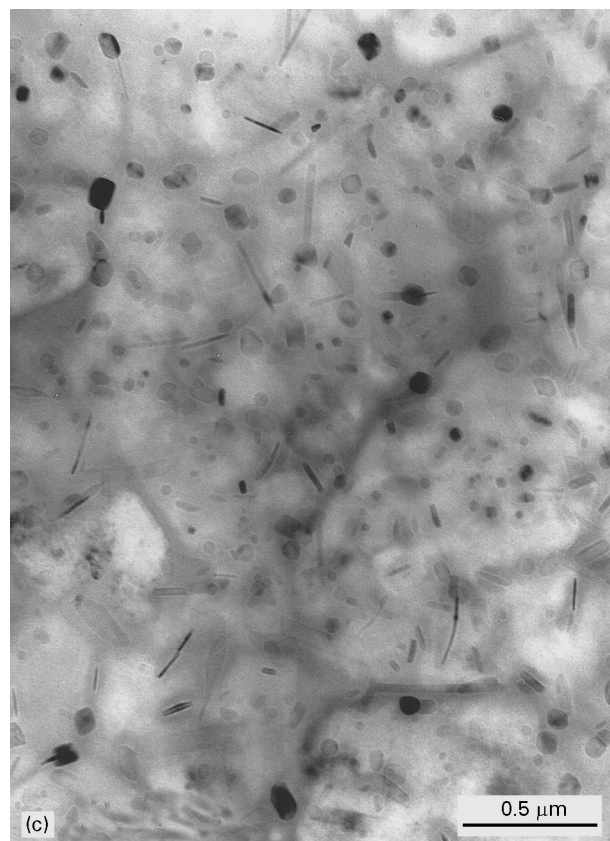
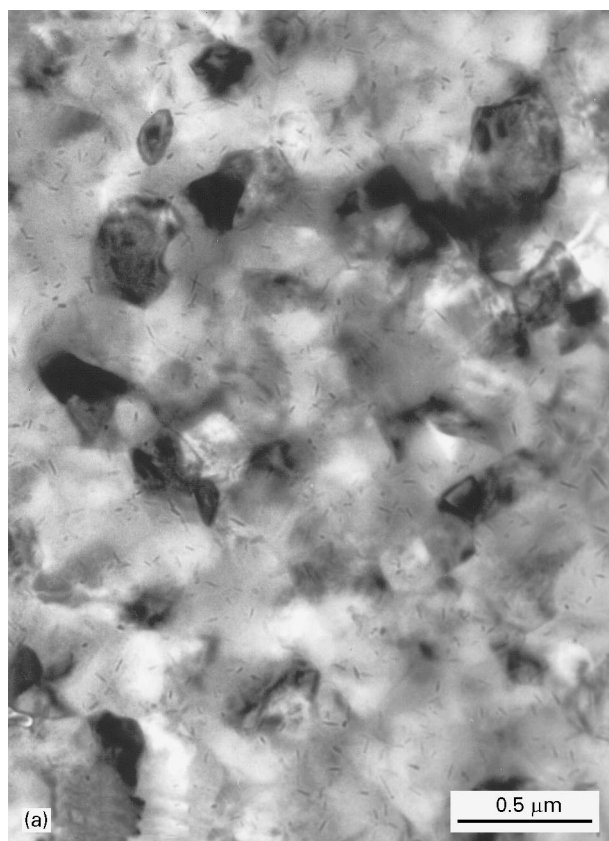


Figure 3 Bright field TEM micrographs of LAS glass heat-treated for 4 h at (a) 750 °C, (b) 850 °C and (c) 950 °C.

notion of heterogeneous nucleation, as will be discussed here.

Fig. 2 (a and b) illustrates glass samples heat-treated at 725 °C. When heated for 1 h at 725 °C (Fig. 2a) an

essentially amorphous structure is observed in which extremely fine whisker-like precipitates, approximately 15 nm long, are distributed. Electron diffraction patterns recorded from this sample show a glassy halo but this may be attributed to the strong diffraction of the glassy matrix masking the diffraction from crystalline nuclei. These precipitates acted as nuclei for subsequent crystal growth and their size also grew with further increase in temperature (Fig. 3a–c). Due to their extremely fine size it was very difficult to positively identify the characteristics of the nuclei formed at the initial stage of the heat-treatment; however, EDS analysis was performed on the sample heat-treated at 950 °C for 4 h, in which extensive growth of these precipitates made the examination possible. As indicated in Fig. 3c the precipitates have two distinct morphologies; long thin rods approximately 200 nm long and 15 nm wide, and small spherical inclusions approximately 40 nm in diameter. Representative EDS spectra recorded from the precipitates and from the surrounding matrix are shown in Fig. 4(a and b) respectively. Fig. 4a indicates a high concentration of titanium and oxygen within the precipitates, regardless of their morphology, whereas spectra recorded from the aluminosilicate matrix (Fig. 4b) suggest the presence of Si, O and Al only. Lithium is not detectable with the present EDS facility. Therefore, the precipitates are believed to be rutile (TiO_2) or other Ti-containing phase [9, 19]. X-ray analysis of the current samples failed to indicate the presence of rutile because it is present in very small concentrations. However, studies in which higher concentrations of

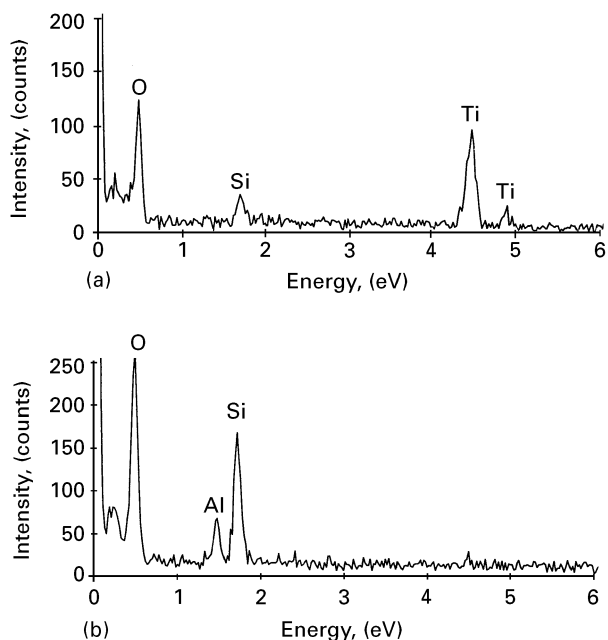


Figure 4 EDS spectra recorded from the sample prepared by heat-treatment for 4 h at 950 °C. Spectra depicted are representative of (a) the round precipitates and (b) the surrounding matrix of the sample shown in Fig. 3c.

TiO₂ were used (e.g., 4.75–10 wt%) showed that rutile contributed to the X-ray spectrum only at high temperatures (e.g., 950–1050 °C) [5, 20]. A similar analysis conducted on Li₂O–Al₂O₃–4SiO₂ glasses showed that the transformation of β-quartz_{ss} to β-spodumene_{ss} is accompanied by the formation of a Ti-rich phase mainly as grain boundary particles but also within the grains themselves [10]. A further study using analytical electron microscopy and high resolution TEM confirmed that TiO₂ remains in the form of anatase particles inside the grains and that although the particles grew with increasing temperature they retained their chemical composition [21]. When heated for 4 h at 725 °C the initial stage of crystallization is readily seen as β-quartz_{ss} emerges as a dispersion of crystallites (~120 nm diameter) in a glassy matrix (Fig. 2b). The dispersion of very fine precipitates of a size similar to those shown in Fig. 2a was observed inside the large crystals. These observations suggest that nucleation is initiated by the fine-scale precipitates and that subsequent crystal growth occurs at these sites.

Fig. 3a presents the microstructure of a glass sample heated for 4 h at 750 °C. Under these conditions the sample was fully crystallized and comprised of uniform, equiaxed grains with an average grain size of approximately 220 nm, while the fine rod-shaped precipitates have grown to approximately 60 nm in length. When the glass was heat-treated for 1 or 2 h at 750 °C (microstructures not shown here), average grain diameters of approximately 140 nm and 160 nm respectively were observed. Fig. 3b shows the microstructure obtained when the glass was heat-treated at 850 °C for 4 h, conditions under which an average grain size of approximately 250 nm was obtained. As a result of the one-step heat-treatment process employed for the crystallization study in this work, the

conditions for nucleation varied in different samples. The fact that the size of nuclei increased with temperature indicates that a two-step heat-treatment process may be more appropriate during which an optimum nucleation stage can be applied to ensure the formation of a large number of fine nuclei. When heated for 4 h at 950 °C, Fig. 3c, the average diameter of the grains increased to approximately 450 nm, while the rod-shaped precipitates grew in similar proportions. X-ray analysis indicated that the crystalline phase detected in this sample was β-spodumene_{ss}, suggesting that the transformation of β-quartz_{ss} to β-spodumene_{ss} occurs somewhere between 850–900 °C.

4. Conclusions

Lithium aluminosilicate glasses and glass-ceramics have been prepared from a naturally occurring spodumene mineral. TEM and XRD results have revealed the various stages of crystallization of the LAS glasses. It was found that the nucleation mechanism and crystalline phase assemblages were similar to those observed in identical materials prepared from reagent grade chemicals. This indicates the great potential of directly using the mineral in LAS glass-ceramic fabrication. It was shown that partial control may be exerted over the crystallization process through judicious alterations to the temperature and duration of the heat-treatment schedule. At low temperatures (725–750 °C) the size and density of crystalline regions within the glass may be varied by adjusting the heat-treatment time accordingly. In contrast, no such control is possible at high temperatures (T ≥ 850 °C) at which fully crystalline samples with a crystal size greater than 250 nm are always obtained regardless of the crystallization time. X-ray diffraction analyses have also shown that the transformation of β-quartz_{ss} to β-spodumene_{ss} occurs at approximately 850–900 °C.

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References

1. S. D. STOOKEY, US Patent 2 920 970, January (1960)
2. *idem Ind. Engng. Chem.*, **51** (1959) 805.
3. H. SCHEIDLER, and E. RODEK, *Amer. Ceram. Soc. Bull.* **68** (1989) 1926.
4. L. CHI-TANG, *Z. Kristallogr.* **132** (1970) 118.
5. P. E. DOHERTY, D. W. LEE and R. S. DAVIS, *J. Amer. Ceram. Soc.* **50** (1967) 77.
6. T. I. BARRY, L. A. LAY and R. P. MILLER, *Discuss. Faraday Soc.* **50** (1970) 214.
7. V. MAIER and G. MÜLLER, *J. Amer. Ceram. Soc.* **70** (1987) C176.

8. A. RAMOS and M. GANDAIS, *J Cryst. Growth* **100** (1990) 471.
9. C. K. CHYUNG, *J. Amer. Ceram. Soc.* **52** (1969) 242.
10. M. H. LEWIS, J. METCALF-JOHANSEN and P. S. BELL, *ibid* **62** (1979) 278.
11. A. ABDE, *Trans. Indian. Ceram. Soc.* **27** (1968) 140.
12. A. NORDMANN and Y. B. CHENG, Proceedings of the 17th International Congress on Glass, Vol. 16 p. 45–50, Chinese Ceramic Society, Beijing (1995).
13. F. V. TOOLEY in “The Handbook of Glass Manufacture” Vol. II. (Ashlee Publishing Co. New York, 1984) p. 961.
14. J. Y. HSU and R. F. SPEYER, *J. Amer. Ceram. Soc.* **72** (1989) 2334.
15. Y. M. SUNG, S. A. DUNN and J. A. KOUTSKY, *J. Eur. Ceram. Soc.* **14** (1994) 455.
16. R. ROY, in Proceedings of the Symposium on Nucleation and Crystallization in Glasses and Melts. Toronto 1962 (*American Ceramics Society* Westerville OH (1962) p. 39.
17. S. M. OHLBERG, H. R. GOLOB and D. W. STRICKLER *ibid* p. 55.
18. J. F. MACDOWELL and G. H. BEALL, *J. Amer. Ceram. Soc.* **52** (1969) 17.
19. G. H. BEALL and D. A. DAVID in “Glass-Ceramic Technology; Science and Technology” Vol 1, (Academic Press. New York 1980) p. 403.
20. A. W. A EL-SHENNANI, A. A. OMAR and E. R. EL-GHANNAM, *Ceram Int* **16** (1990) 47.
21. P. L. GAI and Q. Q. CHEN, *Acta. Cryst.* **A38** (1982) 741.

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