Effect of alkali and alkaline earth oxides on crystallization of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses

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Abstract. The effect of alkali and alkaline earth oxides on the crystallization of lithia–alumina–silica glasses has been studied. Crystallization behaviour of glasses has been investigated using DTA and XRD techniques. The principal crystallization phases are identified as β -spodumene solid solution and lithium metasilicate. The crystallization temperature of glasses decreases with increase in the values of the ionic field strength of the alkali and alkaline earth cations. Addition of these oxides at lower concentrations has no significant effect on the crystalline phases.

Keywords. Crystallization temperature; ionic field strength; lithia–alumina–silica glasses; glass ceramics; nucleating agents.

1. Introduction

Glass ceramics have achieved an important place in materials technology because of their unique combination of properties which has resulted in a number of engineering and other applications. Low thermal expansion crystallized glasses are becoming established in several applications where the dimensional stability and the ability to resist thermal shock are important. These materials are produced by controlled crystallization of glasses and have properties superior to those of the parent glasses. Preparation of glass ceramics consists of making a homogeneous glass, shaping it to the desired form and finally heat-treating it to produce a glass ceramic body. These are free from pores. Absence of pores imparts higher mechanical strength (McMillan 1979). Glass ceramic bodies in various shapes and with close dimensional tolerances can be produced by commercial methods. In recent years several studies on nucleation and crystallization behaviour of glasses (Stookey 1961; MacDowell 1966; Patridge 1982) have been carried out. The study of the crystallization of glasses has significant importance both scientifically and technologically.

The glass forming system, lithia–alumina–silica, for producing glass ceramics has been studied by many authors (Patridge and McMillan 1963; Samdani *et al* 1969; Rapp 1973). In this system the crystallization is effected easily and a low thermal expansion phase is also formed. Preparation of a satisfactory glass ceramic depends on crystallizing the desirable phases under controlled conditions to provide a fine microstructure. Although major work has been carried out on various nucleating agents (Zdaniewski 1975; Barry *et al* 1970) and their behaviour on crystallization, no studies on crystallization with alkali and alkaline earth oxides have been carried out. Hence the present work was undertaken.

2. Experimental

The specimens used in this study were prepared by using reagent (LR) quality materials

(table 1), mixed thoroughly and melted in a sillimanite crucible at 1450°C for 2 h in an electric muffle furnace under normal atmospheric conditions. The molten glass was cast in the form of discs on steel plates and was allowed to cool rapidly in air. The specimens were not annealed because thermal history effects are minimized. Heat treatment was carried out at 550°C for 2 h followed by 750°C for 1 h at a rate of 5°C/min and was furnace-cooled.

Differential thermal analysis (DTA) was carried out on powdered glass on a Leeds and Northrup instrument. Calcined alumina was used as the inert material and the rate of heating was 12.5°C/min. The crystallized glass powders were subjected to X-ray diffraction analysis (XRD) for the identification of phases formed during crystallization. A Phillips X-ray diffractometer (PW 1051) was used.

3. Results and discussion

Glasses containing TiO₂ are light yellow in colour whereas those containing ZrO₂ and P₂O₅ are colourless. The progress of crystallization is marked by the changes in the appearance of the material. All the glasses become opaque and white during crystallization. Crystallization of glasses is followed by exothermic peaks as recorded in DTA. Table 2 summarises these results along with the phases identified by XRD and field strength of oxides for different nucleating agents. The peaks in figures 1–4 show DTA and XRD patterns respectively. It can be seen that TiO₂ and

Table 1. Glass ceramic compositions (wt. %).

Constituent	Batch numbers				
	1	2	3	4	5
SiO ₂	66.50	66.50	66.50	66.50	66.50
Al ₂ O ₃	13.70	13.70	13.70	13.70	13.70
Li ₂ O	16.80	16.80	16.80	16.80	16.80
Na ₂ O	2.00	—	—	—	—
CaO	—	2.00	—	—	—
BaO	—	—	2.00	—	—
MgO	—	—	—	2.00	—
K ₂ O	—	—	—	—	2.00

In each batch 3 wt.% each nucleating agents (TiO₂, ZrO₂ and P₂O₅) were added.

Table 2. Crystallization temperature (°C) of the glasses (DTA).

Oxides	Nucleating agents			Field strength (Z/r ²)*	Crystalline phases (XRD)
	TiO ₂	ZrO ₂	P ₂ O ₅		
Na ₂ O	610	705	570	1.04	β-Spodumene and lithium meta silicate
K ₂ O	630	710	580	0.57	—do—
MgO	615	675	570	3.29	—do—
CaO	630	680	630	1.79	—do—
BaO	645	665	555	0.98	—do—

*Based on Pauling's ionic radius.

Figure 1. DTA curves of TiO_2 nucleated glasses.

Figure 2. DTA curves of ZrO_2 nucleated glasses.

Figure 3. DTA curves of P_2O_5 nucleated glasses.

Figure 4. XRD patterns for crystallized glasses.

ZrO₂ nucleated glasses crystallized at higher temperatures as compared to P₂O₅ nucleated glasses. This could be due to the glass-forming nature of P₂O₅ and its ability to induce phase separation at lower temperatures. Phase-separation in the glass may be due to the charge difference between the principal glass network-forming ions, Si⁴⁺ and the foreign network-forming ions, P⁵⁺. Pure glass crystallizes at 605°C. Addition of alkali and alkaline earth oxides has thus changed the crystallization temperature of glasses.

An interesting observation as indicated in table 2 is the effect of the ionic field strength of the alkali and alkaline earth cations on the crystallization temperature. The crystallization temperature of glasses in general decreases with higher values of field strength. This could be due to the fact that the cations of higher field strength can facilitate crystallization in glasses. X-ray patterns, shown in figure 4, for glasses crystallized at 550°C followed by 750°C are almost the same. These analyses reveal that the principal crystalline phases appearing for all the oxides are the β -

spodumene ($\text{Li}_2\text{Al}_2\text{Si}_4\text{O}_{12}$) solid solution and lithium metasilicate (Li_2SiO_3). Addition of these oxides has no significant effect on the crystallized phases.

4. Conclusion

Crystallization temperatures of lithia–alumina–silica glasses decrease with increase in the values of field strength of the alkali and alkaline earth oxides. Addition of these oxides in lower concentrations has no significant effect on the crystalline phases.

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References

- Barry T I, Lay L A and Miller R P 1970 *Discuss. Faraday Soc.* **5** 214
MacDowell J F 1966 *Ind. Eng. Chem.* **58** 45
McMillan P W 1979 *Glass ceramics* (London: Academic Press) pp 158
Patridge G 1982 *Glass Technol.* **23** 133
Patridge G and McMillan P W 1963 *Glass Technol.* **6** 4
Rapp J E 1973 *Ceram. Bull.* **52** 6
Samdani S G, Prasad V M and Abid Ali 1969 *Trans. Indian Ceram. Soc.* **1** 9
Stookey S D 1961 *Chem. Eng. News* **39** 116
Zdaniewski W J 1975 *Am. Ceram. Soc.* **58** 163