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EFFECT OF ALUMINA CONCENTRATION ON THERMAL AND STRUCTURAL PROPERTIES OF MAS GLASS AND GLASS-CERAMICS

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Abstract

Magnesium aluminum silicate (MAS) glass samples with different concentrations of alumina (7.58 to 14.71 mol%) were prepared by melt and quench-technique. Total Mg content in the form of MgF_2+MgO was kept constant at 25 mol%. MAS glass was converted into glass-ceramics by controlled heat treatment at around 950°C. Crystalline phases present in different samples were identified by powder X-ray diffraction technique. Dilatometry technique was used to measure the thermal expansion coefficient and glass transition temperature. Scanning electron microscopy (SEM) was employed to study the microstructure of the glass-ceramic sample. It is seen from X-ray diffraction studies that at low Al_2O_3 concentrations (up to 10.5 mol%) both $MgSiO_3$ and fluorophlogopite phases are present and at higher Al_2O_3 concentrations of 12.3 and 14.7 mol%, fluorophlogopite and magnesium silicate (Mg_2SiO_4), respectively are found as major crystalline phases. The average thermal expansion co-efficient (α_{avg}) of the glass samples decreases systematically from 9.8 to $5.5\cdot10^{-6}$ °C^{-1} and the glass transition temperature (T_g) increases from 610.1 to 675°C with increase in alumina content. However, in glass-ceramic samples the α_{avg} varies in somewhat complex manner from 6.8 to $7.9\cdot10^{-6}$ °C^{-1} with variation of Al_2O_3 content. This was thought to be due to the presence of different crystalline phases, their relative concentration and microstructure.

Keywords: glass-ceramics, glass transition temperature, magnesium aluminum silicate, thermal expansion coefficient

Introduction

Magnesium aluminum silicate (MAS) glass-ceramic belongs to technologically important materials due to their wide applications in the fields of high voltage and high vacuum [1, 2]. This material exhibits better thermal stability, superior electrical insulation and higher mechanical strength as compared to the parent glass. The special feature of MAS glass-ceramics is its machinability. This property arises due to the presence of micro-crystalline fluorophlogopite phase having plate-like structure. The

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different properties of these glass and glass-ceramics such as microhardness, average thermal expansion coefficient (α_{avg}), glass transition temperature (T_g), machinability etc., among others, depend on the composition of the base glass and presence of different crystalline phases [3–5]. The effect of sources and concentrations of MgF_2, which acts as the nucleating agent for the formation of micro-crystalline phases, has been studied by Radonjic and Nicholik [6]. In recent years, some studies related to the kinetics of crystallization process in glass and glass-ceramics using thermoanalytical technique, have also been reported [7, 8]. In another study, Shennawai *et al.* [9] have studied the effect of nucleating agent on the nature of the crystalline phases developed in $Li_2O–MgO–SiO_2–Al_2O_3$ glass matrix and inferred that the thermal, mechanical and other properties of these glass-ceramics are significantly affected by the nature and extent of the crystalline phases.

Madhumita *et al.* [10] have also reported the effect of MgF_2 concentration on the thermal, mechanical and other physico-chemical properties of this glass-ceramic. Their study revealed that increase in MgF_2 concentration, increases the formation of fluorophlogopite phase, which leads to its improved machinability. Recently, some studies have been carried out by Hill *et al.* [11, 12] to see the effect of lithia on the crystallization process and the mechanical properties of this material. Present communication deals with the investigations related to the preparation of MAS glass and glass-ceramic samples and the effect of Al_2O_3 concentration on thermal and structural properties. It was observed that the relative concentration of different crystalline phases and the nature of residual glass, depending upon the alumina concentrations have marked effect on the thermal and structural properties.

Experimental

Different batches of glass samples, weighing approximately 100 g each, were prepared as per the compositions given in Table 1. The concentration of Al_2O_3 was varied from 7.58 to 14.71 mol% and Mg content in the form of MgF_2+MgO was kept nearly constant at 25 mol%. Initial charge was prepared using either carbonates or oxides of the constituents and calcined at maximum temperature of 950°C for 24 h with predetermined heating schedule. MgF_2 was added as nucleating agent. Melting of calcined charge was carried out in a covered Pt-Rh crucible at about 1500°C in a raising and lowering hearth furnace (Model OKAY, 70R10, M/s Bysakh, Kolkata) and held for 1–2 h for complete homogenization. The molten charge was poured in a preheated graphite/brass moulds and so formed glass was transferred to a specially designed annealing furnace operating at temperature about 600°C. Sample was annealed for 3–4 h and cooled to room temperature in a programmed manner. The base glass was converted to glass-ceramics by nucleating at the temperature around 650°C for 4–6 h and followed by controlled crystallization in the temperature range of 900–970°C using a programmable resistance-heating furnace. Detailed procedure has been reported earlier by Madhumita *et al.* [13].

Table 1 Nominal compositions of MAS samples in mol%

Batch No.	SiO_2	MgO	Al_2O_3	B_2O_3	K_2O	MgF_2
Sample#1	52.8	21.49	7.58	6.82	6.88	4.4
Sample#2	51.9	21.27	8.89	6.76	6.83	4.31
Sample#3	51.0	20.91	10.42	6.64	6.71	4.29
Sample#4	50.09	20.52	12.34	6.46	6.6	4.15
Sample#5	48.6	19.93	14.71	6.22	6.42	4.08

The nature of glassy state and different crystalline phases were identified by powder X-ray diffraction (XRD) technique using CuK_α as radiation source. The thermal expansion coefficient (TEC) and glass transition temperature were measured using Thermo Mechanical Analyser (TMA) (Model TMA 92, Setaram, France) over the temperature range of 30–750°C using silica as probe in an inert (Ar) atmosphere. The average value of TEC over the temperature range of 30–300°C was calculated. SEM studies were carried out using Jeol make JSM-T330A machine to see the microstructure of the glass-ceramics sample after etching the fractured surface with 5% HF solution for 5 s.

Results and discussion

Figure 1 shows the XRD pattern of a representative base glass sample before crystallization. A broad peak observed at $2\theta\approx25°$, indicates the glassy nature of the sample. Figure 2 shows the XRD patterns of glass-ceramic samples. It is clear that these samples contain significant amount of crystalline phases dispersed in the glassy matrix. A broad background peak at $2\theta\approx25°$, indicates the presence of residual glassy phase in all samples. For sample with 7.58 mol% of Al_2O_3, both $MgSiO_3$ and fluorophlogopite crystalline phases are formed. With increase in Al_2O_3, there is an increase in the relative intensity of the fluorophlogopite phase, reaching nearly single phase at 12.34 mol% of Al_2O_3. However, with further increase of Al_2O_3 content (>12.34 mol%), the Mg_2SiO_4 (forstetite phase) becomes the major crystalline phase.

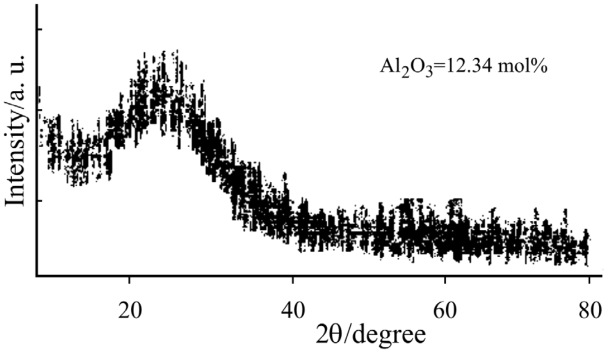

Fig. 1 XRD pattern of a representative glass sample

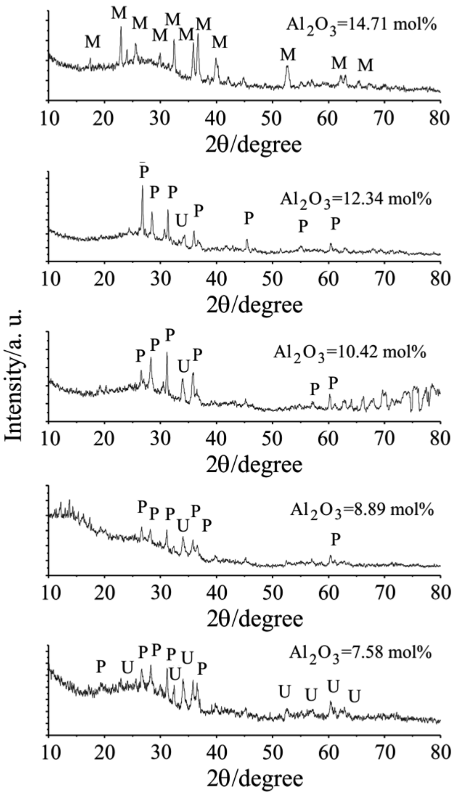

Fig. 2 XRD patterns of different batches of glass-ceramic samples; M – Mg_2SiO_4, P – fluorophlogopite, U – $MgSiO_3$

Figure 3 shows a typical displacement *vs*. temperature plot of TMA for a glass and glass-ceramic samples. This shows that the change in displacement is higher for the base glass sample as compared to the glass-ceramics over the same temperature range. The change in slope indicates the glass transition temperature, which is different for the glass and glass-ceramics samples and basically depends upon the composition of residual glassy phase.

Figure 4 shows the variation of α_{avg} and T_g as a function of Al_2O_3 content for glass samples. From this figure it is clear that with the increase in Al_2O_3 content from 7.6 to 14.7 mol%, the α_{avg} shows a systematic decrease from 9.8 to $5.5\cdot10^{-6}$/°C, and a systematic increase from 640 to 676°C for T_g. As alumina goes to tetrahedral co-ordination with oxygen and acts as glass network-former [14], an increase in Al_2O_3 content thus increases the rigidity of the glass structure. This is consistent with the reduction in the values of thermal expansion coefficient and increase in the values of glass transition temperature.

Figure 5 shows the variation of α_{avg} and T_g as a function of Al_2O_3 content for glass-ceramics samples. Unlike the glass samples, variation of α_{avg} and T_g is not

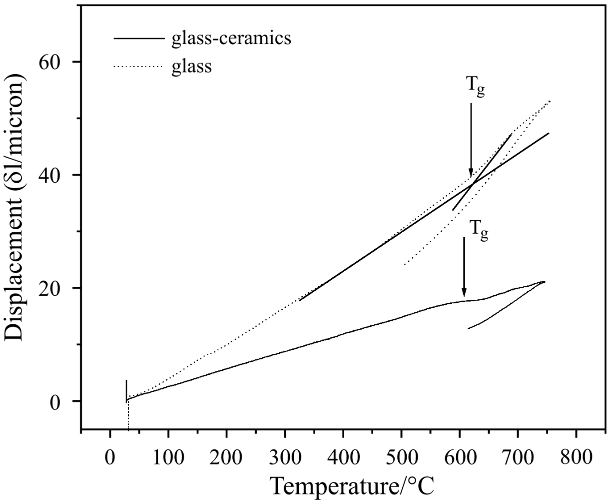

Fig. 3 Typical displacement *vs.* temperature plot of TMA for glass and glass-ceramic samples

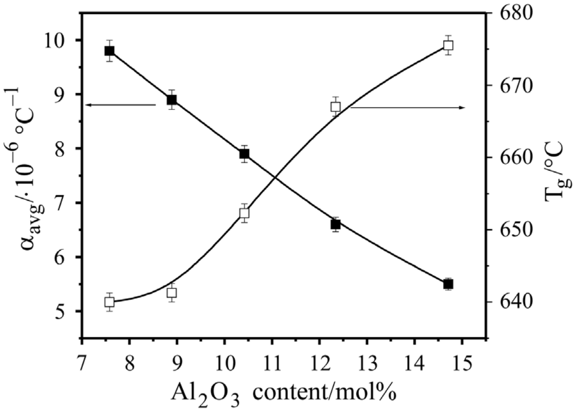

Fig. 4 Variation of ■ – α_{avg} and □ – T_g as a function of alumina contents for glass samples

monotonic for the glass-ceramics. It may be mentioned that the decrease in the values of α_{avg} is significantly larger for the glass-samples as compared to glass-ceramics over the same concentration range of Al_2O_3. The glass transition temperature shows marginal increase up to 10.42 mol% of Al_2O_3 sample and then there is a sharp increase in the values of glass transition temperature for higher concentrations of alumina. The change in glass transition values for glass-ceramics samples may be because of the nature of the residual glass phase in the sample.

The average thermal expansion coefficient values showed systematic decreases up to 10.42 mol% of Al_2O_3 and a sharp decrease for the sample with 12.34 mol% of Al_2O_3. This decrease is attributed to the progressive increase in the formation of

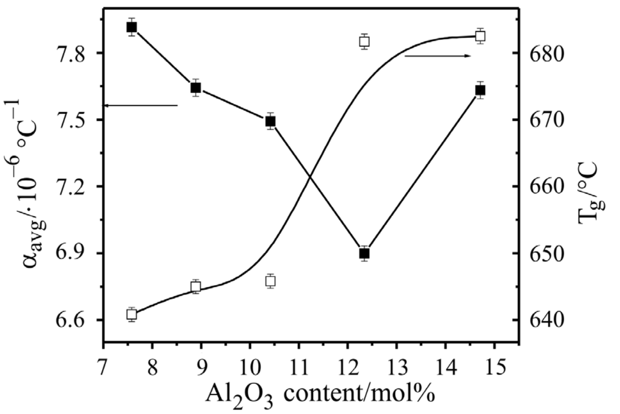

Fig. 5 Variation of ■ – α_{avg} and □ – T_g as a function of alumina contents for glass-ceramic samples

fluorophlogopite phase. Further increase in Al_2O_3 content leads to increase in α_{avg} for the sample containing 14.71 mol% of Al_2O_3. The increase in α_{avg} for alumina content more than 12.34 mol% is thought to be due to formation of magnesium silicate (major phase), which has higher thermal expansion coefficient [15].

Figure 6 shows the SEM pictures of the representative region of glass-ceramics samples. For sample having 7.58 mol% of Al_2O_3, existence of both fluorophlogopite and $MgSiO_3$ phases in the form of large flake like structure and fine grains are seen in Fig. 6a. Figure 6b shows the SEM picture of the sample containing 12.34 mol% of Al_2O_3 which

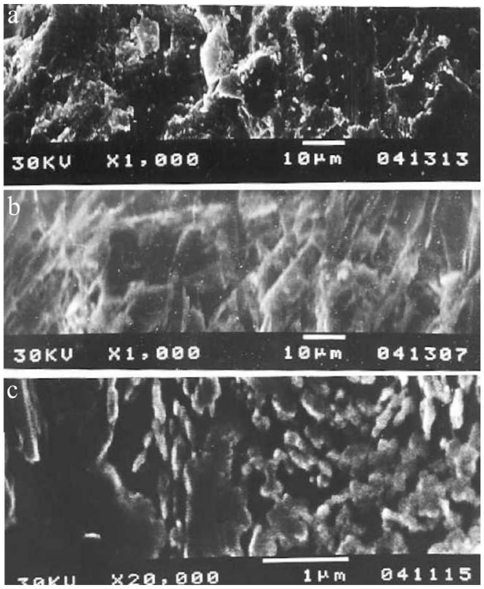

Fig. 6 SEM micrographs of MAS glass-ceramic samples containing different concentration of alumina

is exhibiting plate like structure of single fluorophlogopite phase. Figure 6c shows the SEM picture of the glass-ceramic sample containing 14.71 mol% of Al_2O_3. This pattern is quite different from that of the other two samples and is arising due to the existence of crystalline Mg_2SiO_4 phase, as inferred from its X-ray diffraction studies.

Conclusions

Magnesium aluminum silicate glass and glass-ceramic samples with different amount of alumina were prepared. The increase in Al_2O_3 content which act as glass network-former increases the rigidity of the glass structure, thereby, decreasing the thermal expansion coefficient and increase in glass transition temperature. Unlike this, for glass-ceramics samples, most of the thermo-physical properties are controlled by the relative concentration and chemical composition of different phases present in the system and the morphology of the crystalline phases. From SEM studies of glass-ceramics samples, it is clear that there is wide variation in morphology of the crystalline phases with the change in Al_2O_3 content. Consequently, the physical properties of these glass-ceramics with different types of crystalline phases show somewhat complex behaviour.

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