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Study on thermophysical properties and phase evolution in Nd doped Li_2O-Al_2O_3-SiO_2 glass nucleated by multiple nucleating agents

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ABSTRACT

Lithium aluminium silicate (LAS) glasses of compositions (wt%) (1) LASa: $59SiO_2$-$19Al_2O_3$-$3.5Li_2O$-$5B_2O_3$-1.5ZnO-1MgO-$2TiO_2$-$2ZrO_2$-$7P_2O_5$ and (2) LASb: $58SiO_2$-$19Al_2O_3$-$3.5Li_2O$-$5B_2O_3$-1.5ZnO-1MgO-$2TiO_2$-$2ZrO_2$-$7P_2O_5$-$1Nd_2O_3$ were prepared by melt-quench technique and converted to glass-ceramics. In glass samples, addition of Nd_2O_3 showed an increase in the glass transition temperature (T_g) and crystallization temperature. Thermo-mechanical analysis (TMA) showed that crystallized samples have very low thermal expansion coefficient (α) of value around 2.5×10^{-6}/°C (30–300). The microhardness and density values of crystallized samples were found to be higher than the base glasses. XRD and SEM techniques were employed to see nature of phases and their microstructures in glass/glass ceramic samples. From XRD formation of β-spodumene ($LiAlSi_2O_6$) as major crystalline phase while Berlinite ($AlPO_4$)and Srilankite ($TiZrO_4$) were identified as minor crystalline phases after heat treatment at 850 °C.· The microstructure of LASa and LASb samples heat treated at 675 °C showed formation of nanocrystals (size < 50 nm) of $TiZrO_4$ within the glass matrix, whereas samples heat treated at maximum 850 °C showed formation of shell type/spherical particles structure which support the three dimensional or bulk crystallization in these samples. Micro-laser Raman spectroscopy was carried out to confirm presence of $TiZrO_4$ phase after heat treatment at 675 °C. Crystallization kinetics study was carried out by recording DTA traces at different scanning rate. Activation energy (E) and Avrami parameter (n) were calculated by using Kissinger and Marotta methods and Augis-Bennett equation. Activation energy of crystallization for LASa and LASb were found to be 263 kJ/mol and 270 kJ/mol, respectively whereas the Avrami parameter (n) for LASa and LASb glass was found to be greater than 2 and greater than 4, respectively. Avrami parameter greater than 2 indicates near three dimensional growth of spodumene phase, which is also confirmed by microstructural analysis and parameter greater than 4 indicated interfacial controlled growth.

1. Introduction

Glass-ceramics are polycrystalline materials prepared by controlled nucleation and crystallization of glasses with suitable nucleants [1]. Glass-ceramic materials share many properties with both glass and traditional ceramics. They have an amorphous phase and one or more crystalline phases. The crystallinity varies between 0.5 and 99.5%.

The β-spodumene ($LiAlSi_2O_6$) ceramics have low thermal expansion, high strength, good corrosion resistance e.g., sulphur and salt corrosion, thermal stability and good resistance to mechanical and thermal shock [2–6]. Such properties enable these materials to be used in heat regenerators of gas turbine engines, cookware, industrial furnaces, cooktop panels, IC substrate and telescope mirror supports [7]. The β-spodumene ceramic can be prepared either by controlled crystallization of LAS based glass or by powder sintering route which is a conventional method for production of different ceramics.

Preparation of spodumene through sintering route requires a fine, homogenous powder as the precursor material. One of the drawbacks of the sintering route is the possible agglomeration of powder precursor during storage that may lead to variation in green density and heterogeneity in sintered body. The other drawback is the occurrence of coarsening during sintering, which is deleterious to mechanical strength of a material. Though coarsening can be addressed by addition of sintering aids and through pressure sintering, it also results in additional issues. Controlled crystallization of glasses yields a variety of materials with interesting combinations of properties. Unlike sintered ceramics, glass-ceramics are inherently free from porosity because there is usually no pressing and sintering, they are much stronger than the sintered ceramics. The glass-ceramic route has several advantages over powder sintering route [8], such that they can be mass produced by any glass forming technique, it is possible to design its microstructure or nanostructure in a way as to combine and tune the thermo-physical properties. For example coefficient of thermal expansion can be controlled by the type of morphology of crystalline phase. Glass-ceramics can be made of any sizes and shapes. For glass-ceramic preparation, it is

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necessary to add nucleating agents e.g., P_2O_5, TiO_2, ZrO_2, V_2O_5, Ta_2O_5, CaF_2, MgF_2, to the batch to promote phase separation and bulk nucleation [9]. The study of kinetics of nucleation/crystallization is very important to prepare transparent glass-ceramics suitable for optical applications. The literature survey showed that TiO_2, ZrO_2 and P_2O_5 are more effective nucleating agents for crystallization of LAS glass-ceramics [10]. Many crystallization and microstructural studies have been done on Li_2O-Al_2O_3-SiO_2 glass-ceramics with different nucleating agents [11–16]. Sung et al. [13] studied the effect of TiO_2 nucleating agent on crystallization of LAS glass-ceramic system with 3.85 wt% TiO_2. The activation energy and Avrami parameter were found to be 290 kJ/mol and 2, respectively. The effect of combination of TiO_2 and ZrO_2 nuclei on LAS glasses were investigated by M. Guedes et al. [14] and results showed the activation energy in between the 195.8 kJ/mol and 113.2 kJ/mol and Avrami parameter varying between 1 and 3, which showed surface and volume crystallization occurring simultaneously. Thomas Hoche et al. [17] have studied the crystallization of nucleating agent ($TiZrO_4$) in low thermal expansion LAS glass-ceramics.

There are only a few publications available on effect of rare earth addition on kinetics of evolution of spodumene derived from LAS glass. Uk Kang et al. [18] have reported optical properties of Nd doped transparent LAS glass-ceramics nucleated with either ZrO_2 or TiO_2. Result showed Nd enters in structure of β-spodumene which decreases concentration quenching of Nd^{3+} fluorescence. Dymnikov et al. [19] have studied structure of luminescence centers of Nd^{3+} in LAS glasses nucleated with 3 mol% ZrO_2. Result showed change in structural states of Nd^{3+} ions during phase transformation. F·Gabel et al. [20] have studied the nucleation processes in TiO_2 and ZrO_2 doped LAS glass-ceramics. They proved Raman spectroscopy is a powerful and non destructive technique to investigate this. Xingzhong et al. have [15] reported crystallization, microstructure and colorization effect of Nd_2O_3 in LAS glasses with 10 wt% Li_2O and 4 wt% TiO_2 and results showed activation energy varying between 252.06 and 243.43 kJ/mol and Avrami parameter in between 1.3 and 3.45 with variation of Nd^{3+} concentration from 0 to 2 wt%. This study was done with single nucleating agent (TiO_2).

The aim of the present work is to prepare low expansion spodumene based LAS glass-ceramics through the glass route and to study the effect of Nd_2O_3 on phase evolution, their microstructures and crystallization kinetics using multiple nucleating agents, TiO_2, ZrO_2 and P_2O_5. Minor amount of B_2O_3, ZnO, MgO were added to the glass to lower their melting point, to reduce viscosity and to increase the homogeneity [16,21].

2. Experimental

2.1. Preparation

Two Li_2O-Al_2O_3-SiO_2 (LAS) glasses of compositions (in wt%) (1) LASa: $59SiO_2$-$19Al_2O_3$-$3.5Li_2O$-$5B_2O_3$-1MgO-1.5ZnO-$2TiO_2$-$2ZrO_2$-$7P_2O_5$ and LASb: $58SiO_2$-$19Al_2O_3$-$3.5Li_2O$-$5B_2O_3$-1MgO-1.5ZnO-$2TiO_2$-$2ZrO_2$-$7P_2O_5$-$1Nd_2O_3$ were prepared by conventional melt quench technique. Li_2O is the third highest in glass if the compositions are expressed in mole percent. That's why this type of glass is labeled as LAS system. Analytical grade precursors i.e., Li_2CO_3, Al_2O_3, SiO_2, $NH_4H_2PO_4$, $MgCO_3$, ZnO, ZrO_2, TiO_2, B_2O_3 and Nd_2O_3 were mixed thoroughly and transferred to a high purity alumina crucible for calcination. The batch was subjected to calcination at maximum 740 °C in a predetermined heating schedule. Heating rate was 1–3 °C/min to the respective decomposition temperature (e.g., 220 °C for $NH_4H_2PO_4$, 350 °C for $MgCO_3$, 740 °C for Li_2CO_3). A dwell time ~5–12 h was provided at each decomposition temperature to allow complete calcinations. Subsequently batch was cooled in the furnace to room temperature. Calcination was done in a vertical tubular furnace with a programmable temperature controller and connected to exhaust system for removal of gases like NH_3, CO_2. To ensure complete decomposition of carbonates/phosphate to their corresponding oxides, the batch was weighed before and after calcinations to ascertain the weight loss. The calcined charge was melted in air ambient in a covered Pt-10% Rh crucible in the temperature range of 1600–1650 °C in a raising and lowering hearth electric furnace (Model: OKAYR-70 M/s Bysakh and Co.,·Kolkata) and held for 2–3 h for homogeneous mixing. The melt was poured into a preheated graphite mould and immediately transferred to an annealing furnace for removal of thermal stresses. Glass was annealed at the temperature 600 °C for 3–4 h followed by slow cooling to room temperature. All prepared glasses are transparent and bubble free.

2.2. Crystallization and characterization

The density measurement was carried out using Archimedes principle and water was used as immersing liquid. The measurements were carried out with an accuracy of ± 0.002 g/cm^3. Thermo-mechanical analysis (TMA) was employed for measurement of thermal expansion coefficient (TEC), glass transition temperature (T_g) and dilatometric softening temperature (T_{ds}). Glass and glass-ceramic samples in the form of flat circular discs of diameter 8–10 mm and thickness of 2–3 mm were used for thermo-mechanical analysis. The experiments were carried out at a heating rate of 10 K/min up to 800 °C in Ar ambient. Sample expansion was measured using a hemispherical silica probe under compressive load of 5 g. The TEC value calculated are in the range 30–300 °C with an accuracy of $\pm 5\%$ and values of T_{ds} are accurate to ± 2 °C. Microhardness measurements were performed on polished glass samples by a Vicker's microhardness tester (Model VMHT 30 M M/s Leica). An indentation load of 50 g for 5 s was employed. Average of about 10 reading was reported for hardness value, the error reported being the standard deviation in the measurements. Differential thermal measurements were performed on glass powders using Setaram 92-15 TG/DTA apparatus (Model: LABSYS). The non-isothermal experiments were carried out by heating approximately 40 mg of the sample in Pt crucible in Ar ambient. Measurements were carried out with the heating rate varying from 5 to 20 K/min in the range 30–1200 °C. DTA was used to determine glass transition temperature (T_g) and crystallization temperature (T_c). Values of T_g are accurate to ± 2 °C and T_c to ± 1 °C. Based on this information a two stage heat treatment was carried out on these glasses. In the first stage, the nucleation in which it is expected that $TiZrO_4$ nanocrystals form, was carried at 675 °C(5 h). In the second stage, where crystallization is expected to occur on $TiZrO_4$ nuclei, was carried at different temperatures between 750 and 850 °C for 1 h. The crystallization heat treatment schedules for LASa and LASb glass samples are listed in Table 1. The powder XRD measurements were carried out to confirm the amorphous nature of the annealed glasses and to identify the nature of crystalline phases in the glass-ceramic samples (using collimated CuKα radiation in the

Table 1
Heat treatment schedules for LASa and LASb glass samples.

Sample Name	T_1 (°C)	Dwell time at T_1(h)	T_2 (°C)	Dwell time at T_2(h)
LASa.1, LASb.1	675	5	–	–
LASa.2, LASb.2	675	5	750	1
LASa.3, LASb.3	675	5	800	1
LASa.4, LASb.4	675	5	850	1