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Rare earth ion controlled crystallization of mica glass-ceramics

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ABSTRACT

In understanding the effects of rare earth ions to control the crystallization and microstructure of alkaline boroaluminosilicate system, the CeO_2, Nd_2O_3, Sm_2O_3 and Gd_2O_3 doped K_2O–MgO–B_2O_3–Al_2O_3–SiO_2–F glasses were synthesized by melt-quenching at 1550 °C. Higher density (2.82–3.06 g cm^{-3}) and thermal stability (glass phase) is experiential on addition of rare earth content, which also affects in increasing the glass transition temperature (T_g) and crystallization temperature (T_c). Decrease of thermal expansion in glasses with rare earth ion content is maintained by the stabilization of glass matrix owing to their large cationic field strength. A significant change in the non-isothermal DSC thermogram observed at 750–1050 °C is attributed to fluorophlogopite crystallization. Opaque glass-ceramics were prepared from such glasses by single step heat-treatment at 1050 °C; and the predominant crystalline phases are identified as fluorophlogopite mica, $KMg_3(AlSi_3O_{10})F_2$ by XRD and EDX analysis. The compact glass-ceramic microstructure by the agglomeration of fluorophlogopite mica crystallites (crystal size ~ 100–500 nm, FESEM) is achieved in attendance of rare earth ion; and such microstructure controlled the variation of density, thermal expansion and microhardness value. Higher thermal expansion (11.11–14.08 × 10^{-6}/K at 50–800 °C and 50–900 °C) of such glass-ceramics approve that these rare earth containing glasses can be useful for high temperature vacuum sealing application with metal or solid electrolyte. The increase of Vickers microhardness (5.27–5.61 GPa) in attendance of rare earth ions is attributed to the compact crystallinity of fluorophlogopite mica glass-ceramic microstructure.

1. Introduction

Mica based glasses have long been one of the hottest area to material science researchers in virtue of their superior properties, including large thermal shock resistivity, high thermal expansion coefficient, good mechanical behavior and long term sustainability, which could lead to potential applications such as materials for high temperature sealing, transparent and opaque cooking ware, cooking top panels, heat resistant windows and telescope mirror blanks [1–3]. K_2O–MgO–B_2O_3–Al_2O_3–SiO_2–F (KMBAS) is a type of silicate based glass system, is converted to mica glass-ceramic at temperature over 800 °C, and is largely used for high temperature sealing material [3]. Achievement of good thermal shock resistivity and better mechanical behavior on controlled crystallization makes this glass system so much elegant for solid oxide fuel cell (SOFC) sealing application in this decade [3]. To facilitate the crystallization in silicate based glasses, several transition metal oxides like TiO_2, ZrO_2, V_2O_5, Ta_2O_5, Cr_2O_3, MoO_3, WO_3, Fe_2O_3, MnO_2, CoO, NiO, CuO, ZnO etc. and other oxides like P_2O_5, MgF_2 etc. are extensively used for controlling the nucleation mechanism [2–7]. Small amount addition of these nucleants allows the development of fine randomly oriented crystalline grains without voids, micro-cracks or porosity by efficient internal nucleation; and it is the basis of controlled crystallization [2–4]. In silicate based glass-ceramics, the ability of rare-earth (RE) ions has been premeditated to tune the crystallization phenomena and microstructural morphology [4,5]. Now, the question arises that how the crystallization is controlled by these doping agents (nucleants)? During the crystallization process, nucleating agent like RE ions can either support the heterogeneous phase separation or these can cause the accumulation in a specific microphase or nanophase of the phase-separated glass [8–11]. The rare-earth (RE) ions having large cationic field strength, tend to form 'cluster', which makes a minority of oxide ions involved in RE-O linkages, and hence, isolated from silicate glass network. So, these can form heterogeneous nuclei for phase separation to affect the crystallization behavior of Si–O–Si based glass [9]. Chen et al. [10] synthesized Yb^{3+}/Ho^{3+} activated nano glass-ceramics by heat-treatment at 670 °C in

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cerium doped aluminosilicate glass of SiO_2–Al_2O_3–NaF–YF_3–YbF_3–HoF_3 system. Small extent of these rare earth additives significantly affected the microstructural morphology as well as thermo-mechanical properties of glass-ceramics. Mica glass-ceramics with dense nanocrystalline grained microstructure are highly desired for improving thermal and mechanical properties. Additionally, the fluorophlogopite mica glass-ceramic having tendency to form interlocked type microstructure, shows excellent capability to avert the generation and growth of micro-crack in a thermal recycling operation performed in high temperature application.

The RE ion can affect not only the crystallization process, but also the density, glass transition temperature, softening point, mechanical and chemical stability of glass phase [11,12]. In the study of Eu^{3+} and Er^{3+} doped transparent glass-ceramics containing cubic $K(Y_{1-x}Yb_x)_3F_{10}$ solid-solution nanocomposite from SiO_2–Al_2O_3–K_2O–KF–YF_3–YbF_3-Ln^{3+} system, Chen and his co-authors [13] argued the formation of glass-ceramic by self-crystallization pact owing to the segregation of lanthanide activators during melt-quenching temperature. In another study, Chen et al. [14] reported the orthorhombic YF_3 nanocrystals embedded oxyfluoride glass-ceramics by controlled heat-treatment at 670 °C in SiO_2–Al_2O_3–NaF–YF_3–Eu^{3+}/Eu^{2+} matrix. Based on optical basicity model, they [14] optimized that both Eu^{3+} and Eu^{2+} ions co-exist in synthesized glass; where Eu^{3+} ions incorporated into the β–YF_3 nanophase but Eu^{2+} ions remained in glass phase. Although the RE ions appear to influence the coloration of aluminosilicate glass, they affects the thermal properties, melting temperature and nanocrystal formation in the glasses [4,5,11,15]. However, a precise role and comparative study of the rare earth ions to affect the microstructural properties after crystallization still remains unclear.

This work is concerned to demonstrate the development of fluorophlogopite mica [$KMg_3AlSi_3O_{10}F_2$] nanocrystalline microstructure by single-step heat-treatment (at 1050 °C) in K_2O–MgO–B_2O_3–Al_2O_3–SiO_2–F (KMBAS) glass, controlled by CeO_2, Nd_2O_3, Sm_2O_3 and Gd_2O_3. We report their comparative effect on thermal and mechanical properties correlating from crystallization and microstructural morphology.

2. Experimental

2.1. Synthesis of glass and heat-treatment

A series of boroaluminosilicate glasses with K_2O–MgO–B_2O_3–Al_2O_3–SiO_2–F (KMBAS) system (composition shown in Table 1) with different rare earth (RE) oxides were prepared using high purity powders of SiO_2 (Quartz Powder), $Mg(OH)_2$ (97%, Loba Chemie, Mumbai, India), $Al(OH)_3$ (97%, Loba Chemie, Mumbai, India), K_2CO_3 (98%, Loba Chemie, Mumbai, India), H_3BO_3 (99.5%, Loba Chemie, Mumbai, India), MgF_2 (99.9%, Loba Chemie, Mumbai, India), CeO_2 (99.99%, Indian Rare Earths Ltd., Udyogamandal, India), Nd_2O_3 (99.99%, Indian Rare Earths Ltd., Udyogamandal, India), Sm_2O_3 (99.99%, Indian Rare Earths Ltd., Udyogamandal, India) and Gd_2O_3 (99.99%, Indian Rare Earths Ltd., Udyogamandal, India). Homogeneously mixed batches were allowed to melt at 1550 °C (2 h) using an electric furnace (Kanthal) followed by a stirring for 0.5 min with a silica glass rod in an open platinum crucible. Molten glasses were then cast into a carbon plate and properly annealed at about 20 °C below the glass transition temperature. The annealed glasses were then heat-treated at 1050 °C for nucleation and crystallization.

Table 1
Composition (mol%) of the studied K_2O–MgO–B_2O_3–Al_2O_3–SiO_2–F glasses doped with and without rare earth content.

Glass identity	SiO_2	MgO	Al_2O_3	B_2O_3	K_2O	MgF_2	RE content
RE-0	41	20	10	10	7	12	–
Ce-5	41	20	10	10	7	12	CeO_2 = 5
Nd-5	41	20	10	10	7	12	Nd_2O_3 = 5
Sm-5	41	20	10	10	7	12	Sm_2O_3 = 5
Gd-5	41	20	10	10	7	12	Gd_2O_3 = 5

2.2. Characterization

The glass transition temperature (T_g), softening point (T_d) and thermal expansion coefficient (CTE) values were evaluated with cylinder shaped samples of length~25 mm and diameter~6 mm using a horizontal dilatometer, NETZSCH DIL 402 PC (NETZSCH-Gerätebau GmbH, Germany) at a heating rate of 5 °C/min (with an accuracy of ±1%). Density (d) value of glass and glass-ceramic was measured by the Archimedes method using distilled water as immersion liquid with an accuracy of ±0.7%. Finely Powdered (particle size < 60 μm) BAS glass samples were subjected to DSC study (DSC, Setaram Labsys, Setaram Instrumentation, Caluire, France) in open air from 30 to 1200 °C at 10 °C/min to obtain the phase transformation temperature. The standard deviation for the values of characteristic temperatures as obtained from DSC was in the range of ±5 °C. X-ray diffraction (XRD) analysis was recorded for the qualitative analyses of crystalline phases in BAS glass-ceramics (heat-treated at 1050 °C/4 h), using an XPERTPRO MPD diffractometer (PANalytical, Almelo, the Netherlands) operating with Ni-filtered CuKα = 1.5406 Å radiation as the X-ray source at 40 kV and 40 mA. Crystalline phases were analyzed in 2θ range of 5–90° with a step size of 0.05° at temperature 25 °C. The morphology of the KMBAS glass-ceramic was examined with a field-emission scanning electron microscope (FESEM model S430i, LEO, CEA, USA). Prior to the SEM investigations, the glass-ceramic samples were polished and chemically etched by 2 vol% aqueous HF solution for 10 min. To further confirm the existence of the desired elements (K, Mg, Al, Si, O and F) in the glass-ceramics, qualitative elemental composition analysis was performed using energy dispersive X-ray (EDX) analysis. Regarding EDX energy range, we have provided the

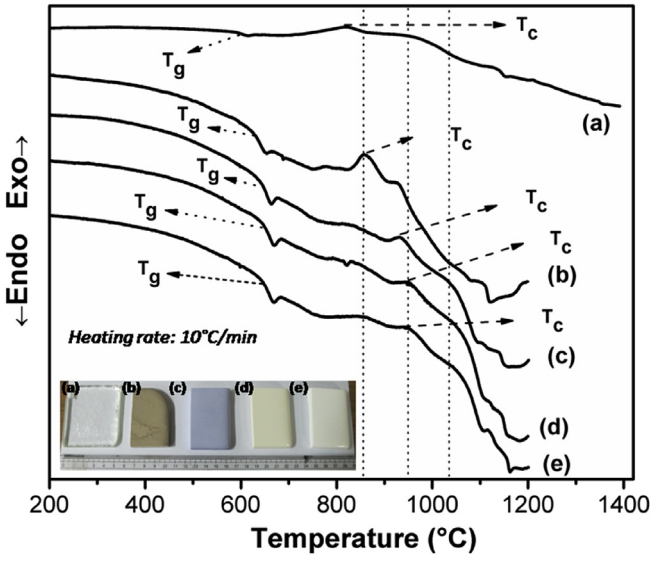

Fig. 1. Differential Scanning Calorimetric (DSC) thermogram of precursor (a) RE-0, (b) Ce-5, (c) Nd-5, (d) Sm-5 and (e) Gd-5 glasses (inset shows the photograph of melt-quenched K_2O–MgO–B_2O_3–Al_2O_3–SiO_2–F glasses).