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Glass-ceramics based on spodumene–enstatite system from natural raw materials

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ABSTRACT

Glasses of compositions (wt%) corresponding to 50–90 spodumene and 50–10 enstatite were prepared depending on natural raw materials and Li_2CO_3 as small ingredient. The crystallization behavior was studied using DTA and XRD. The effect of addition of the nucleating agents (LiF) to a selected glass was also examined. Polarizing microscope and dilatometeric techniques were used to study the microstructures and the thermal expansion coefficient, respectively. XRD showed that the crystalline materials are mainly enstatite, clinoenstatite, β-eucryptite ss and β-spodumene ss. The shift of the glass composition to that of enstatite results in increased bulk crystallization. The presence of LiF does not greatly affect the mineral assemblages yet it improves the thermal expansion coefficients (TEC) of the crystalline samples and promotes the initial crystallization. Low and even negative values, ranging from -5.91×10^{-7}/K to 2.48×10^{-7}/K in the temperature range 293–573 K and 300–737 K, respectively, could be obtained, which make such materials applicable for thermally stable articles.

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1. Introduction

Extensive investigation has been made on the crystallization of glasses and/or melts based on natural rocks and waste material to obtain new crystalline glass materials (glass-ceramics) from cheap resources. Glass-ceramics are used in a wide range of technical applications, for example, in construction and for domestic purposes, and in the microelectronics industry [1] particularly low expansion glass ceramics which form the most important class of glass ceramics commercially for cook top panels and precision optical applications [2]. Refractory glass-ceramics containing at least 90% by volume enstatite and exhibiting a high modulus of rupture and a use temperature of at least 1200 °C, were developed [3]. Glass-ceramics from local raw materials in the Li_2O–MgO–Al_2O_3–SiO_2 system were prepared and the effects of nucleating agents TiO_2, Cr_2O_3, and P_2O_5 and heat treatment temperature (800 °C, 900 °C, 1000 °C and 1100 °C) on crystallization and morphology were studied [4]. The major phases formed were β-eucryptite and β-spodumene ($LiAlSi_2O_6$), in addition to enstatite and a little anorthite and hematite. Locsei [5] obtained glass-ceramic materials characterized by high wear resistance and chemical durability from glasses based on blast furnace slag, sand and clay with some additions of crystallization catalysts. Khater and Idris [6] studied the crystallization of glasses based on clay, silica sand and some chemical reagents. They obtained crystalline materials composed mainly of spodumene and celsian. Glass-ceramic materials from glasses based on slag, quartz sand, limestone, dolomite, talc, natural raw materials, industrial mining and industrial wastes have also been obtained [7–10]. The nature of the crystalline phases and microstructure of the glass ceramic materials were reported to most important factors affecting the technical properties of the glass-ceramics [11].

Crystal nucleation is a fundamental process of phase formation in glass melts based on molecular level fluctuations under a regime of super saturation. The time and temperature dependent kinetics of crystal nucleation are of crucial importance in determining the glass forming abilities of melts and play an important role in their wide ranging technological applications as glass ceramic materials. Whereas for most devetrifications the composition differ for glass and crystal, a limited number of glass compositions crystallise isochemically, i.e. without changes in composition [12]. Nucleation can occur in such glasses on pre-existing surfaces and in the absence of any initial surface [13]. The nucleation kinetics of the latter process (homogeneous volume nucleation) has been described using the results of the classical nucleation theory [14–17].

Glass ceramics based on the enstatite–spodumene has been chosen for the present study because of, the easy of obtaining their components from natural raw materials that reduce the costs of its preparation. Furthermore, the effect of the nucleating agent LiF has not been studied for such system. The outstanding strength, excellent abrasion, chemical resistance and low thermal

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Table 1
Chemical compositions (wt%) of the raw materials used.

Oxides	Silica sand	Clay	Magnesite
SiO_2	99.50	54.40	3.12
Al_2O_3	0.52	28.20	0.05
Fe_2O_3	0.04	2.33	0.06
TiO_2	–	1.35	0.02
MgO	0.05	0.27	44.60
CaO	0.05	0.26	2.45
Na_2O	0.05	0.58	0.08
K_2O	0.05	0.18	0.02
L.O.I.[a]	–	12.37	49.12

[a] Loss on ignition.

expansion are of the most valuable features of the phases formed in the chosen glasses. Beta-spodumene was considered as a candidate structural material for use in fusion reactor environments, where it has good thermal shock resistance and a very low coefficient of thermal expansion [18]. Beta-spodumene has also exceptional long time dimensional stability at high temperature [19]. Enstatite ceramics are important for its very high melting point, mechanical and electrical properties [20]. The aim of this work is to study the crystallization behavior of some glasses of compositions (wt%) corresponding to 50–90 spodumene and 10–50 enstatite. The effect of the nucleating agent LiF, on the phase assemblages and microstructures and thermal expansion characteristics will also be explored.

2. Experimental procedure

Five glass compositions within the spodumene ($LiAlSi_2O_6$)–enstatite ($MgSiO_3$) system were selected for the present work. These compositions are based on the spodumene composition with successive additions of enstatite up to 50 wt% at 10% intervals of the enstatite component. Natural raw materials (clay, magnesite and silica sand) in addition to some technical chemical reagents such as Li_2CO_3 as a source of Li_2O were used. Table 1 lists the compositions of the used natural raw materials. The details of glass compositions in oxide percentages and percentages of raw materials are given in Table 2. A selected glass (G3) was chosen to add the nucleating agent (LiF). This glass (G3) has an average content of enstatite (30%) in the range of compositions studied (10–50%).

The batches of the compositions under consideration were thoroughly mixed, melted in Pt crucibles in a Globar furnace at temperatures ranging from 1400 to 1450 °C for 2–3 h depending upon the composition. The melts become more viscous for glasses of compositions with high wt% enstatite. The homogeneity of the melts was achieved by swirling the crucible several times at about 20 min intervals. After melting and refining the bubble-free melt was cast onto a steel marver into buttons and rods and transferred to a preheated muffle furnace for stress release.

DTA scans were carried out to determine the crystallization temperatures using a Shimadzu DTG60 microdifferential thermoanalyzer. 40 mg of powdered glass sample, of grain size less than 0.60 mm and larger than 0.2 mm, was used against Al_2O_3 powder as a reference material. A heating rate of 20 °C/min and sensitivity setting of 20 μv/inch were maintained for all the runs.

To induce crystallization using the pre-determined DTA crystallization temperatures, the glass samples were subjected to two different controlled heat treatment processes. The first, was carried out in a muffle furnace from room temperature to the required temperatures (850 or 950 °C) and kept at the intended temperature for 2 h, after which the furnace was switched off and the samples were allowed to cool inside it to room temperature. The second heat treatment processes is a double-stage heat-treatment schedule where glass samples were first soaked at 700 °C for 1 h and then at 950 °C for 2 h.

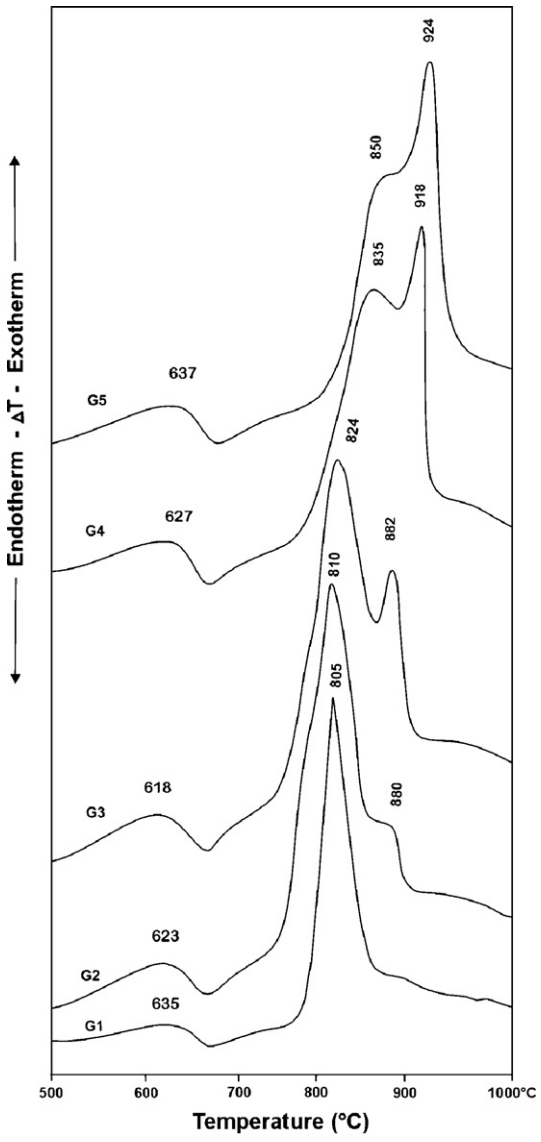

Fig. 1. DTA scans of glasses G1–G5.

The microstructure of almost all the heat treated specimens were examined optically in thin sections using a polarizing Carl Zeiss research microscope.

The crystalline phases precipitated in the course of crystallization was identified by the X-ray diffraction analysis using powdered samples. The X-ray diffraction patterns were obtained using a Bruker D8 Advance, Germany, adopting Ni-filtered CuKα radiation. All the instrument settings were maintained for all the analyses using a Si disk as an external standard.

Measurements of linear thermal expansion coefficients (TEC) of the nucleated glass and corresponding glass-ceramics were carried out using a thermo-dilatometeric analyzer of Netzsch Dil 402 PC, using a fused silica bar as a standard. The thermal expansion of annealed glass rod specimens was measured from room temperature up to temperatures slightly exceeding their dilatometeric softening points. The glass rods were then subjected to thermal treatment and their TEC was measured again from room temperature up to the maximum heat-treatment temperatures. The expansion coefficient (α) was calculated using 5.4×10^{-7} as the correction factor of the quartz tube. The transition temperature (T_g)

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