Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 35 (2009) 3221–3227

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of some rare-earth oxides on structure, devitrification and properties of diopside based glasses

Ishu Kansal [a], Ashutosh Goel [a], Dilshat U. Tulyaganov [a,b], José M.F. Ferreira [a,*]

[a] Department of Ceramics and Glass Engineering, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal
[b] State Committee of Geology and Mineral Resources, Centre of remote sensing and GIS technologies, 11-A, Shevchenko str., 100060 Tashkent, Uzbekistan

Received 3 March 2009; received in revised form 8 April 2009; accepted 18 May 2009

Abstract

Four diopside based glasses containing an equimolar concentration of different rare-earth oxides (La_2O_3, Nd_2O_3, Gd_2O_3 and Yb_2O_3) respectively, were obtained by melt-quenching technique. Structural and thermal behaviour of the glasses was investigated by density and molar volume, infrared spectroscopy (FTIR), dilatometry, and scanning electron microscopy (SEM). All the glasses exhibited amorphous phase separation. The crystallization behaviour of the glasses was investigated by using differential thermal analysis (DTA). Sintering, crystallization, microstructure, and properties of the glass-ceramics were investigated under non-isothermal heating conditions in the temperature range of 800–900 °C.

Keywords: A. Sintering; D. Glass; D. Glass-ceramics; Rare-earth oxides

1. Introduction

Glass-ceramics (GCs) offer the possibility of combining the special properties of conventional sintered ceramics with the distinctive characteristics of glasses. It is, however, possible to develop modern GC materials with features unknown so far either in glasses or ceramics or in other materials such as metals or organic polymers. Furthermore, developing GCs demonstrates the advantage of combining various remarkable properties in one material.

GCs based on pyroxenes attract interest in several advanced fields [1–4] as they offer an excellent opportunity to control their properties, thus leading to the possibility of achieving the desired physical properties and high chemical durability. Diopside (here after briefly designated as Di) belongs to the group of inosilicates and is an important member of clinopyroxene group, with composition $CaMgSi_2O_6$. It forms complete solid solution series with hedenbergite ($CaFeSi_2O_6$) and augite, and partial solid solutions with orthopyroxenes, pigeonite and Ca–Al-bearing monoclinic pyroxene, known as Ca-Tschermak ($CaAl_2SiO_6$).

The present study is an attempt to investigate the influence of different rare-earth oxides (RE_2O_3) on the structure and crystallization behaviour of diopside based glasses with general composition $Ca_{0.8}Ba_{0.1}Mg_{0.9}Zn_{0.1}Al_{0.1}RE_{0.1}Si_{1.9}O_6$ (RE corresponds to La, Nd, Gd and Yb, respectively). Since, it has already been shown that substitution of ZnO for MgO improves the sintering behaviour of diopside-Ca-Tschermak GCs [6], therefore, a substitution 0.1MgO ↔ 0.1ZnO was attempted in the present investigation. B_2O_3 (1.75 mol%) was introduced in all the investigated glass compositions in order to be consistent with our previous study [5]. Table 1 presents the detailed compositions of all the investigated glasses.

2. Experimental procedure

High purity powders of SiO_2, $CaCO_3$, $BaCO_3$, $MgCO_3$, Al_2O_3, ZnO, H_3BO_3, La_2O_3, Nd_2O_3, Gd_2O_3 and Yb_2O_3 were used. Homogeneous mixtures of batches (~100 g), obtained by ball milling, were calcined at 900 °C and then melted in Al_2O_3-crucibles at 1580 °C for 1 h.

Glasses in bulk form were produced by pouring the melts on preheated bronze moulds followed by annealing at 550 °C for

---

* Corresponding author. Tel.: +351 234 370242; fax: +351 234 370204.
E-mail address: jmf@ua.pt (J.M.F. Ferreira).

0272-8842/$36.00 © 2009 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2009.05.023

Table 1
Composition of glasses.

Glass	MgO	CaO	BaO	ZnO	SiO_2	B_2O_3	Al_2O_3	Ln_2O_3
S–La (wt.%)	14.80	18.31	6.26	3.32	46.58	2.00	2.08	6.65
Ln=La (mol.%)	22.67	20.15	2.52	2.52	47.85	1.77	1.26	1.26
S–Nd (wt.%)	14.77	18.27	6.24	3.32	46.48	2.00	2.08	6.85
Ln=Nd (mol.%)	22.67	20.15	2.52	2.52	47.85	1.78	1.26	1.26
S–Gd (wt.%)	14.69	18.17	6.21	3.30	46.23	2.00	2.06	7.34
Ln=Gd (mol.%)	22.66	20.15	2.52	2.52	47.85	1.79	1.26	1.26
S–Yb (wt.%)	14.59	18.05	6.17	3.28	45.93	2.00	2.05	7.93
Ln=Yb (mol.%)	22.66	20.14	2.52	2.52	47.85	1.80	1.26	1.26

1 h. The annealing temperature was decided in accordance with our previous study [5]. The glass-powder compacts were produced from glass frits, which were obtained by quenching of glass melts in cold water. The dry frits were milled in high-speed agate mill resulting in fine glass powders with mean particle sizes of 10–15 μm (Coulter LS 230, Beckman Coulter, Fullerton CA; Fraunhofer optical model). Circular disc shaped pellets with Ø 20 mm and thickness ~3 mm were prepared from glass powders by uniaxial pressing (80 MPa). The pellets were sintered under non-isothermal conditions for 1 h at 800 °C, 850 °C and 900 °C, respectively at a slow heating rate of 2 K min^{-1}. The possibility of occurrence of phase separation in the glasses was examined by heating the bulk glasses at 700 °C for 1 h at heating rate of 5 K min^{-1}.

Infrared spectra of the glasses were obtained using an Infrared Fourier spectrometer (FTIR, model Mattson Galaxy S-7000, USA). For this purpose samples were crushed to powder form, mixed with KBr in the proportion of 1/150 (by weight) and pressed into a pellet using a hand press.

Dilatometry measurements were done on prismatic samples with a cross section of 4 mm × 5 mm (Bahr Thermo Analyze DIL 801 L, Hüllhorst, Germany; heating rate 5 K min^{-1}). The glass transition temperature (T_g), onset of crystallization (T_c) and peak temperature of crystallization (T_p) were obtained from differential thermal analysis of fine powders which was carried out in air (DTA-TG, Setaram Labsys, Setaram Instrumentation, Caluire, France) at heating rate (β) of 5 K min^{-1}.

The linear shrinkage during sintering was calculated from the difference of the diameter between the green and the sintered pellets. Archimedes' method (i.e. immersion in diethyl phthalate) was employed to measure the apparent density of the bulk annealed glasses and sintered GCs. The mean values and the standard deviations presented for linear shrinkage and density have been obtained from (at least) 10 different samples.

The amorphous nature of the glasses and presence of crystalline phases in the GCs were determined by X-ray diffraction (XRD) analysis (Rigaku Geigerflex D/Max, C Series, Tokyo, Japan; CuK$_\alpha$ radiation; 2θ angle range 10–80°; step 0.02°/s). Microstructure observations were done on polished (and etched) glasses and GCs using scanning electron microscopy (SEM, Hitachi SU-70, Tokyo, Japan) under secondary electron mode. The etching was performed by immersion of samples in 2 vol.% HF solution for 5 s (glasses) and 2 min (GCs), respectively.

3. Results and discussion

3.1. Characterization of glasses

3.1.1. Casting ability, physical appearance and microstructural features

Melting at 1580 °C for 1 h was adequate to obtain highly homogenous molten glasses for all the investigated compositions, which, after casting, resulted in bubble-free, homogenous, transparent glasses. All the glasses except S–Nd were yellow while this particular glass (S–Nd) was purple in colour. In general, the appearance of different colours in RE^{3+}-doped glasses is due to splitting of 4f levels and can be explained on the basis of *crystal field theory*. The study pertaining to investigate the local environment of Nd^{3+} and its structural role in the glass network has already been attempted [7]. In this regard it has been documented that presence of neodymium results in clustering effect and affects the optical properties of glasses [8]. The different colour of glass S–Nd in the present case may be due to the following reasons: (i) a change in the oxidation state resulting in a change in number of 4f electrons and thus, leading to a different number of possible electronic transitions for otherwise identical conditions (apart from its well known +3 oxidation state, Nd also exhibits +2 and +4 oxidation states [9]); (ii) a change in coordination number, thus resulting in a difference in splitting energy. Previously, Corradi et al. [10] studied the local environment of neodymium in Na_2O–SiO_2–Nd_2O_3 glass system through molecular dynamic simulations and concluded that Nd^{3+} exists preferentially in octahedral coordination in alkali silicate glasses while Loiseau et al. [11], with the help of spectroscopic techniques, showed that Nd occupies a highly distorted 8–9-fold coordinated site in the glass system SiO_2–Al_2O_3–CaO–ZrO_2–TiO_2. Therefore, from the physical appearance of glasses, it can be judged that the structure of glass S–Nd differs from the rest of the three investigated glasses. The SEM images of all bulk glasses (heated at 700 °C for 1 h) (Fig. 1) evidenced spinodal decomposition phase separation [12]. The change in type of RE^{3+} had no significant effect on the phase separation in the investigated glasses.

3.1.2. Density and molar volume

The density of the glasses varied between 3.06 and 3.11 g cm^{-3} (Table 2) and increased with an increase in the molecular weight of the RE-oxide present in the glass.