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Impact of Yb^{3+}/Er^{3+} ions on crystallization of phosphosilicate glass melts

LU Qiang (鲁 强)[1], LIU Shujiang (刘树江)[1,*], CAO Wanqiang (曹万强)[2,*], ZHAO Ping (赵 萍)[1]

(1. Key Laboratory of Processing and Testing Technology of Glass & Functional Ceramics of Shandong Province, Qilu University of Technology, Jinan 250353, China; 2. Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, School of Materials Science and Engineering, Hubei University, Wuhan 430062, China)

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Abstract: Transparent glass ceramics were prepared from the phosphosilicate system by melt-quenching devitrification (MQD) method, i.e., nanocrystals spontaneously form during cooling of the melts. Introduction of 2.5 wt.% Yb_2O_3 and 0.5 wt.% Er_2O_3 into the glass melt induced the change of type and concentration of crystals. The comparison of rheological and thermodynamic properties of both undoped and Yb^{3+}/Er^{3+} doped melts showed that addition of Yb^{3+}/Er^{3+} oxides caused increase of liquid fragility, and degree of medium-range order. In addition, the thermodynamic barriers for nucleation ΔG^* as a function of reduced temperature T/T_m were calculated with an assumption of wetting angle θ=90º, Yb^{3+}/Er^{3+} doped melt tended to firstly nucleate as compared to undoped melt at small undercooling.

Keywords: crystallization; transparent glass ceramics; Yb^{3+}/Er^{3+} ions; rare earths

Nowadays, transparent glass ceramic (TGC) have been applied in various fields such as fireplace protection, vehicle windows, substrates for LCD devices, printed optical circuits and telescope mirrors due to much improved properties, e.g., mechanical, thermal and optical properties[1–6]. Generally, glass melts show a tendency of spontaneous crystallization with decreasing temperature due to lower energy of TGCs than corresponding amorphous glasses from the thermodynamic viewpoint, however, devitrification could cause opalescence due to uncontrolled crystal growth during cooling[7]. Therefore, post heat-treatment on parent glasses becomes the main way to obtain TGCs. To realize controlled crystallization, two-stage treatment is usually performed on the parent glasses corresponding to nucleation and growth of crystals, respectively. However, if the crystals could form spontaneously in a controlled way during cooling of the glass melts, it is more energy-saving and efficient to obtain TGCs compared to the conventional post heat-treatment on parent glasses at an elevated temperature above glass transition temperature (T_g). Commercial opal glasses of fluosilicate system were obtained by such melt-quenching devitrification (MQD) method[8,9], however, the uncontrolled crystallization behavior of glass melts during cooling leads to large particle size (>100 nm) of fluoride, which is responsible for the loss of transparency. Our recent work showed that nanocrystals with a diameter less than 30 nm could precipitate spontaneously during slow cooling of MgO-bearing phosphosilicate glass melts[10,11].

For the MQD method to obtain TGCs, different from the traditional post heat-treatment way, the whole crystallization behavior takes place in very short duration, e.g., several minutes or even seconds. Thus, there are still some questions needed to be answered in terms of the thermodynamics and dynamics of transformation from liquid to crystal, e.g., the dependence of crystal types on chemical compositions, the link between crystal size and concentration with crystal type. This is also very important in the aspect of technical application. In general, rare earth oxides are introduced into TGCs for optical applications, and the effect of rare earth ions on crystallization behavior has been widely studied by post heat-treatment on parent glasses[12–15]. However, the reports on how rare earth ions affect crystallization behavior during cooling of glass melts are very rare to the best of our knowledge.

In the present work, we attempted to investigate the correlation between chemical compositions with crystal type and concentration. The focus was placed on how rare earth oxides (Yb_2O_3 and Er_2O_3) influence crystallization behavior of ZnO-bearing phosphosilicate glass melts during cooling, by comparing the configurational entropies and nucleation rates of both undoped and Yb^{3+}/Er^{3+} doped glass melts.

1 Experimental

In this work, the phosphosilicate glasses have the fol-

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* **Corresponding authors:** LIU Shujiang, CAO Wanqiang (**E-mail:** lsj-24@163.com, caowanq@163.com; **Tel.:** +86-531-89631232, +86-27-88661729)

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lowing compositions (wt.%): (100–x) (53SiO_2-4.5Al_2O_3-7.3P_2O_5-19ZnO-16.2Na_2O)·x(2.5Yb_2O_3-0.5Er_2O_3) (with x=0, 1). The mixtures of reagent grade chemicals (SiO_2, Al_2O_3, $(NH_4)_2HPO_4$, ZnO, Na_2CO_3, Yb_2O_3 and Er_2O_3) were preheated at 673 K for 12 h and at 1273 K for 2 h to remove NH_3 and CO_2, and then completely melted in a lidded platinum crucible placed in an electric furnace at 1753 K for 2 h. Subsequently the homogeneous melts were cast onto a cold stainless steel mold to obtain bulk samples with a thickness of 7.0 mm and naturally cooled to room temperature in air.

Bulk samples for optical spectroscopy were prepared in the form of polished plates (thickness: 2.0 mm). UV-VIS-NIR spectra were recorded over the wavelength range of 300–1100 nm using a UV-VIS-NIR Specord 200 spectrophotometer (Analytik Jena AG) at a resolution of 1 nm.

To determine the glass transition temperature, amorphous frits were prepared by pouring the melts into cold water. Then isobaric heat capacity (C_p) measurements were performed on the obtained amorphous glasses by using synchronous thermal analyser (STA) (Setaram Labsys evo). A platinum crucible containing the samples and an empty platinum crucible were heated at a rate of 10 K/min to the maximum temperature. Two upscan runs were conducted on each amorphous sample, and the glass transition temperature (T_g) values were acquired on C_p curve of the second upscan run by using tangent method[16,17].

The high temperature viscosity was measured using a concentric cylinder viscometer (model SRV-1600, Orton Company, USA) under atmospheric condition. The standard glass NIST SRM 717A was used for calibration of the viscometer[18]. Good agreement was achieved between the measured and the standard viscosity values. The error range of the viscosity measurements is $\Delta\lg\eta$ (η in Pas)=0.05.

In order to identify the crystalline phases in all samples, X-ray powder diffraction (XRD) measurements were performed using X-ray diffractometer (BRUKER AXS D8-Advance) with graphite monochromatized Cu $K\alpha_1$ radiation.

To verify whether liquid-liquid phase separation occurs in melts before quenching, slice sample with a thickness of about 2.5 mm was obtained based on press forming, i.e. the homogeneous melt was cast onto a cold steel plate, and then pressed by another cold steel plate with a pressure of 0.78 MPa. A field emission scanning electron microscope (FE-SEM) (FEI Quanta 200) was used to observe the morphology of both slice and bulk samples. The FE-SEM measurements were made on fresh fracture surfaces of the samples, which had been etched in 5 wt.% HNO_3 for 15 s.

2 Results

After cooling in air, both undoped and Yb^{3+}/Er^{3+} doped bulk samples are still transparent, and the latter shows slight pink color due to existence of Yb_2O_3 and Er_2O_3. Fig. 1 shows the UV-VIS-NIR spectra and optical images of undoped and Yb^{3+}/Er^{3+} doped bulk samples, which are 2.0 mm in thickness. For undoped sample, the transmittance over the wavelength range of visible light is around 80%, however, it increases to 90% for Yb^{3+}/Er^{3+} doped sample. In addition, there exist several absorption bands in the transmittance curve of Yb^{3+}/Er^{3+} doped sample, these absorption bands are attributed to the 4f–4f transitions of Er^{3+} ions, i.e., the transitions from the ground state ($^4I_{15/2}$) to the excited states.

Fig. 2 presents the XRD patterns of frits and bulk samples, which correspond to different thermal history during cooling. It is observed that the frits show typical amorphous character (see Fig. 2(a)), meaning that fast

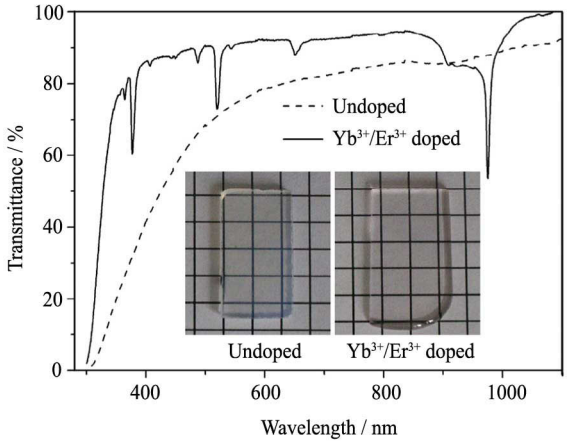

Fig. 1 Transmittance curves and optical images of undoped and Yb^{3+}/Er^{3+} doped bulk samples, which were obtained by casting glass melts onto a cold stainless steel mold (the sample thickness is 2 mm for both samples)

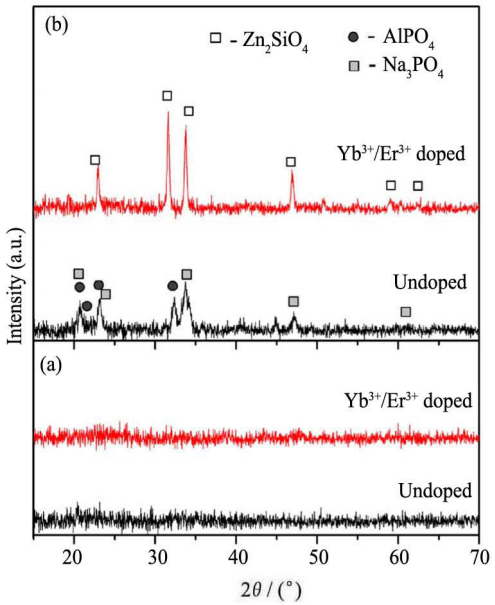

Fig. 2 XRD patterns of undoped and Yb^{3+}/Er^{3+} doped samples (a) Frits which were obtained by pouring glass melts into cold water; (b) Bulk samples which were obtained by casting glass melts onto a cold stainless steel mold