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Crystal growth in zinc borosilicate glasses

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ABSTRACT

Glass samples with a molar composition $(64+x)$ZnO–$(16-x)B_2O_3$–$20SiO_2$, where $x=0$ or 1, were successfully synthesized using a melt-quenching technique. Based on differential thermal analysis data, the produced glass samples were submitted to controlled heat-treatments at selected temperatures (610, 615 and 620 °C) during various times ranging from 8 to 30 h. The crystallization of willemite (Zn_2SiO_4) within the glass matrix was confirmed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Under specific heat-treatment conditions, transparent nanocomposite glass-ceramics were obtained, as confirmed by UV–vis spectroscopy. The influence of temperature, holding time and glass composition on crystal growth was investigated. The mean crystallite size was determined by image analysis on SEM micrographs. The results indicated an increase on the crystallite size and density with time and temperature. The change of crystallite size with time for the heat-treatments at 615 and 620 °C depended on the glass composition. Under fixed heat-treatment conditions, the crystallite density was comparatively higher for the glass composition with higher ZnO content.

1. Introduction

Glass materials are crucial nowadays, being used in a wide range of applications, from the most primitive purposes such as windows and kitchen glassware, to high-tech products like optical fibres. Regarding the optoelectronics field, glasses are particularly interesting due to their versatility of application in devices such as sensors or light emitting and laser diodes [1,2].

Glass-ceramics, polycrystalline materials that can be obtained by controlled heat treatment of a glass, usually offer superior properties than the precursor glass in terms of strength, heat resistance and thermal shock resistance [3–5]. Glass crystallization includes two individual stages: the first corresponds to nucleation, when nuclei form, and the second one, called crystal growth, in which the previously formed nuclei grow in size [5,6]. Recently, glass-ceramics have attracted numerous research interests in the functional materials field as a consequence of associating the advantages of both glasses and single crystals [3,7]. Glass-ceramics can effortlessly provide the optical efficiency of crystals, along with the shaping versatility and high physical and chemical stability of the glasses, at a more reasonable cost [8,9].

Recently, some authors [1,7,9] reported the photoluminescence characteristics of glasses from the ZnO–B_2O_3–SiO_2 system, where controlled heat treatments lead to the formation of willemite and zinc oxide crystals, which act as UV emission centres. Moreover, it has been reported that transparent crystallized glasses based on this glass system can be of great use for hosting optically active transition or rare-earth elements, which provide luminescence and fluorescence to the glass-ceramic [8,10]. Having in mind optical-related applications, glass-ceramic transparency is one of the most important requirements, being directly related with the size of the embedded crystals present in the glass matrix. The main hindrance is to maintain transparency in the glasses when growing nanocrystals, therefore, the investigation on the effect of the heat treatment conditions on crystal growth is of great importance.

This study is part of a more general work where the synthesis and characterization of glasses from the ternary ZnO–B_2O_3–SiO_2 system with a ZnO content higher than 60 mol% are being investigated. To the authors' knowledge, no data concerning the influence of the composition and heat treatment conditions on crystal growth, for this particular glass system, can be found in literature. In the present work, two different glass compositions were prepared, and the effect of the heat treatment temperature and time on crystal growth and on optical transparency was investigated.

2. Experimental details

Two different glass samples were studied having the following compositions: i) 64ZnO–$16B_2O_3-20SiO_2$, named as 64Z and ii) 65ZnO–$15B_2O_3-20SiO_2$, named as 65Z. Chemically pure ZnO

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(Merck), H_3BO_3 (Sigma-Aldrich) and SiO_2 (BDH) powders were chosen as raw materials to prepare the glass samples using the conventional melt quenching method. All raw materials were weighed in 10 g batches, mixed for 1 h (WAB Turbula T2F mixer) to ensure a homogeneous mixture, and placed in a platinum crucible. The crucible was then introduced in an electric furnace operating at 1350 °C for 2 h in air. The melt was poured into a preheated steel mould, and annealed at 560 °C for 1 h in a furnace, to release the internal stresses arising from the quenching process.

Differential thermal analysis (DTA) was performed in order to evaluate the characteristic temperatures of the glass samples: the glass transition temperature (T_g), the onset crystallization temperature (T_x) and the peak crystallization temperature (T_p). A DTA apparatus (Linseis STA PT1600) was used, where powdered specimens with a particle size bellow 65 μm were heated under non-isothermal conditions with a 10 °C/min heating rate.

Small sized specimens (approximately 5 mm × 6 mm × 2 mm) were cut off from the glasses and heat treated in an electric furnace during various times (from 8 to 30 h) at 610, 615 and 620 °C, temperatures that were selected on the basis of DTA results. The presence of crystalline phases was investigated by X-ray diffraction (DMAX – IIIC diffractometer – Rigaku Industrial Corporation), which was performed in powdered samples placed in a Si (100) substrate, using Cu Kα radiation and scanning from 20° to 60° (2θ). The microstructure of the heat-treated glasses was investigated by Scanning Electron Microscopy. SEM images of the fracture surfaces were acquired with an acceleration voltage of 5 kV and aperture size of 30 μm (Carl Zeiss Auriga crossbeam station). Samples were previously etched in a solution of 10% hydrofluoric acid (Merck) in water, for 5 s. To reduce charge effects, the samples were attached to aluminium holders using a double-sided carbon tape and coated with a thin iridium layer using a sputter coater (Q300T D Quorum) before SEM observation. Crystal size was evaluated using ImageJ Software on SEM images.

Optical transmittance measurements were performed in glass plates (approximately 10 mm × 10 mm × 1 mm) in a wavelength ranging from 200 to 900 nm, using a UV–vis double-beam spectrophotometer (T90+PG Instruments).

3. Results and discussion

After melt-quenching and annealing, it was found that the listed compositions originate transparent glasses that were fully amorphous as confirmed by powder XRD analysis [11].

The DTA curves obtained for both glasses are presented in Fig. 1. From these results, it was observed that for sample 64Z, T_g = 576 °C, T_x = 656 °C, T_{p1} = 675 °C and T_{p2} = 715 °C, while for sample 65Z, T_g = 580 °C, T_x = 660 °C, T_{p1} = 685 °C and T_{p2} = 726 °C. The results show a high influence of the composition in the glass characteristic temperatures. It is noticeable an increment of these temperature values for the sample with the highest ZnO content (65Z). The sharpness of the exothermic crystallization peak also increases with ZnO increment. Taking into account the DTA results, the temperatures of 610 °C, 615 °C and 620 °C, between T_g and T_x for both samples 64Z and 65Z, were selected to investigate crystal growth with time for both glass compositions. These temperatures were selected in order to induce nucleation and to avoid uncontrolled crystal growth.

Structural analysis of heat-treated glasses was performed by XRD. Fig. 2 presents the XRD patterns obtained for samples 64Z and 65Z heated at 615 °C for various times. At this temperature, an amorphous halo was observed for samples heated for 8 h, but the presence of willemite, a zinc orthosilicate phase, Zn_2SiO_4 (PDF-00-037-1485) [12] was clearly identified in the glasses heated for longer times. Some XRD data showed a peak of the Si 200

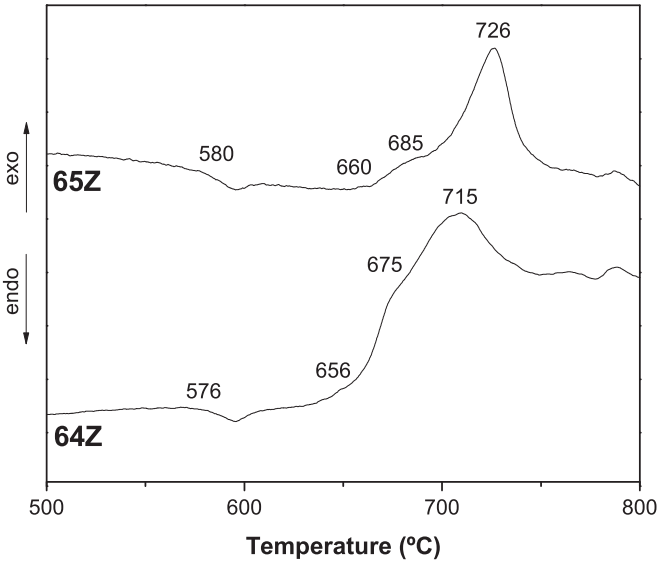

Fig. 1. DTA curves of the produced glasses obtained at 10 °C/min.

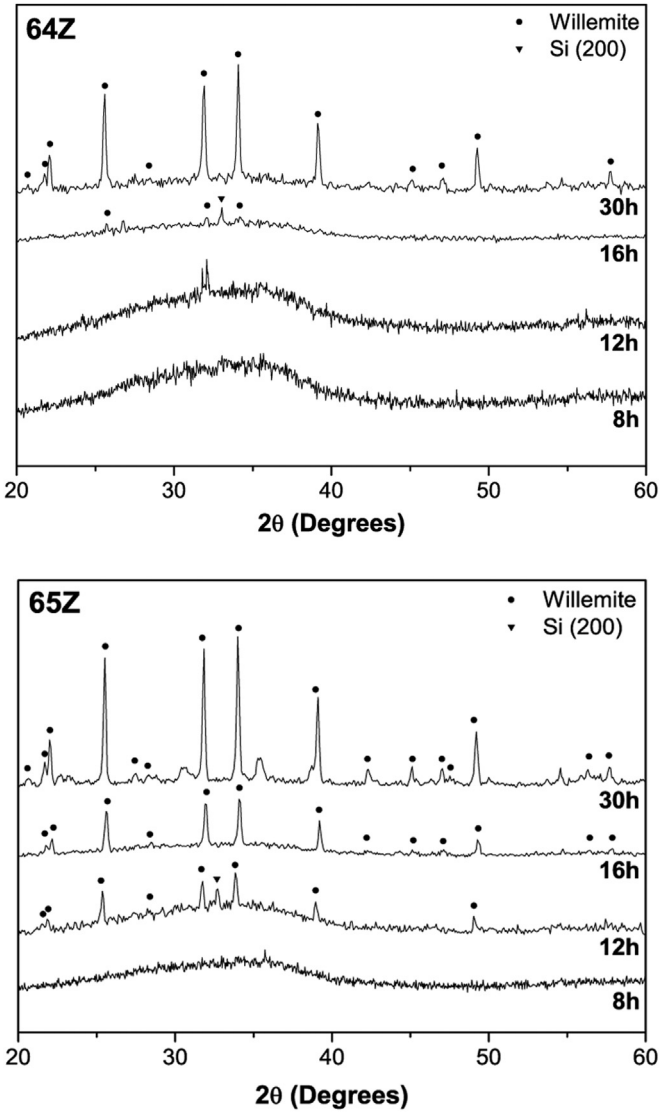

Fig. 2. XRD results for the glasses heat-treated at 615 °C for various times.