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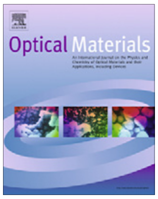

Preparation, phase formation and photoluminescence properties of $ZnO–SiO_2–B_2O_3$ glasses with different ZnO/B_2O_3 ratios

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ABSTRACT

Glasses in $ZnO–SiO_2–B_2O_3$ ternary system with different ZnO/B_2O_3 ratios were studied as scintillating materials. Differential thermal analysis and X-ray diffraction patterns showed that nucleation of willemite and zinc oxide was considerably facilitated with increasing the ZnO/B_2O_3 ratio. Photoluminescence spectra showed a reduction in intensity over the UV region upon this increment prior to the formation of crystalline phases. Optical basicity as a measure of nonbridging oxygens (NBOs) is elaborated in this study as a major cause of this effect. However, near band edge emission (NBE) after crystallization implied an increase in intensity upon the increment of the ZnO/B_2O_3 ratio which proved the key role of willemite and zinc oxide as UV emission centers.

1. Introduction

ZnO is a wide band gap (E_g = 3.37 eV) donor semiconductor with two photoluminescence emission bands: one at the UV-region which is due to near-band edge excitons of electrons and holes recombination and another at the visible region from transition of trapped electrons [1,2]. The narrow UV emission band around 380 nm (3.25 eV) has a short lifetime (10–100 ps) which makes it favorable for superfast scintillators, whereas that of the wider and more intense band over the visible region at 500–530 nm (2.35–2.50 eV) is in the μs range [3]. While initial investigations on ZnO were predominantly done on photo electrochemistry and photo catalysis, recent research interests have been attracted to ZnO's potential applicability in optoelectrical devices [1] such as gamma ray detectors [4] and vacuum fluorescent displays [3].

ZnO is well known as a nonstoichiometric oxide due to existence of oxygen vacancies which together with other structural defects leads to the visible emission band in ZnO. Intrinsic structural defects in ZnO are eliminated considerably when it is embedded in a glass. Moreover, scintillating glasses are produced more easily at a lower expense and have higher durability and thermal shock resistance compared to single crystals [5]. However, only a few studies have so far been conducted on photoluminescence properties of ZnO embedded in a glass matrix. Glass ceramics have both advantages of glasses and single crystals at the same time and thus attract research interests in optical applications such as light emitting and laser diodes.

In this work, 60–63 mol ZnO was added to borosilicate glass compositions ranging from $25SiO_2–15B_2O_3$ to $25SiO_2–12B_2O_3$ to investigate the influence of embedding ZnO within a glass matrix on its PL characteristics after excitation. SiO_2 as a main component of all samples acts as the glass former while B_2O_3 plays its role as an efficient flux due to the weak bonds between $[BO_n]$ structural units [6]. ZnO as PL emission centers is included in all samples with the largest proportion of glass compositions. The influence of different nucleating agents such as TiO_2 and V_2O_5 on thermal and photoluminescence properties of this glass system was investigated in a previous work [7]. In the present study, we probed the effect of increasing the ZnO/B_2O_3 ratio on phase formation, microstructure and PL properties of $SiO_2–ZnO–B_2O_3$ glass systems prepared by melt quenching method in order to optimize preparation conditions including time and temperature of heat treatment as well as composition of the glass.

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2. Material and methods

Chemically pure reagents SiO_2, H_3BO_3, ZnO were chosen as raw materials to prepare glass samples using conventional melt quenching method. Glass composition of $(60 + x)ZnO–25SiO_2–(15 - x)B_2O_3$ was used for the four glass samples with $x = 0, 1, 2, 3$ noted as G0, G1, G2, G3, respectively. This composition range was chosen according to a separate study conducted by Roth et al. [8] in order to facilitate the nucleation of willemite crystals as prominent emission centers. The 100-g batches were melted in high alumina crucibles in an electric furnace at 1400 °C for 3 h in air. The melt was poured onto a preheated steel mold and was annealed at about 600 °C to release the internal stresses formed during quenching. Then the furnace was turned off to allow the specimens to cool down spontaneously to room temperature. Differential thermal analysis was run on powdered glass specimens of $\leqslant 45$ µm and 75–225 µm particle size by means of a STA apparatus (1500-Rheometric scientific) to characterize thermal behavior and peak crystallization temperatures of glass samples. Accordingly, glass specimens were heat treated at nucleating temperature range and at peak crystallization temperature for 3 h. Crystalline phases and microstructure were investigated by X-ray diffractometry (Philips-PW1800) and scanning electron microscopy (PHILIPS-XL30), respectively. Photoluminescence measurements were run on glass specimens heat treated at 610 °C/3 h and at their peak crystallization temperature for 0.5 and 3 h. They were tested over the UV and visible region (250–550 nm) by means of a fluorescence spectrophotometer (Perkin Elmer LS-5) using excitation light at different wavelengths at room temperature in air.

3. Results

According to Fig. 1 which presents DTA curves of the glass samples, one main exothermic peak is observed in thermograms of all four samples which decreased from 775 °C to 765 °C with increasing the ZnO/B_2O_3 ratio from G0 to G3. Meanwhile, the sharpness of the exothermic peak increased slightly and glass transition temperature increased from 580 °C to 615 °C.

DTA analysis was run on both fine ($\geqslant 45$ µm) and coarse ($\leqslant 225$ µm) particle size of the base glass composition G0 in order to determine the effect of particle size on thermal behavior of the glass. The result is presented in Fig. 2. It is seen that the peak crystallization temperature is shifted up from 775 °C to 840 °C and meanwhile increased noticeably in intensity upon replacing the fine particles by the coarse ones. Therefore, it seems reasonable to conclude that the main crystallization mechanism in the present system is by the surface rather than bulk.

Fig. 3 presents XRD patterns of G0, G1, G2 and G3 heat treated at different temperatures for 3 h. It is seen that samples heat treated at 610 °C/3 h and 650 °C/3 h, had amorphous structure. Willemite (JCPDS no. 8-0492) and zinc oxide (JCPDS no. 3-0808) with different intensities appeared after heat treating the samples at the exothermic peak temperature for 3 h except for G0. More-

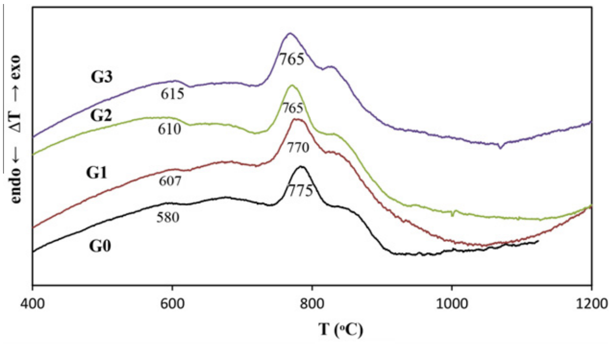

Fig. 1. DTA analysis of the glass specimens.

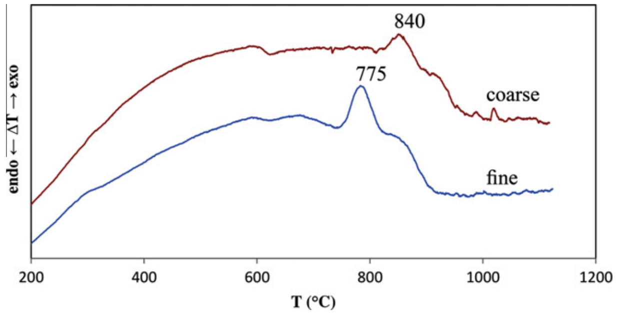

Fig. 2. DTA curves of fine and coarse particle size of the base glass G0.

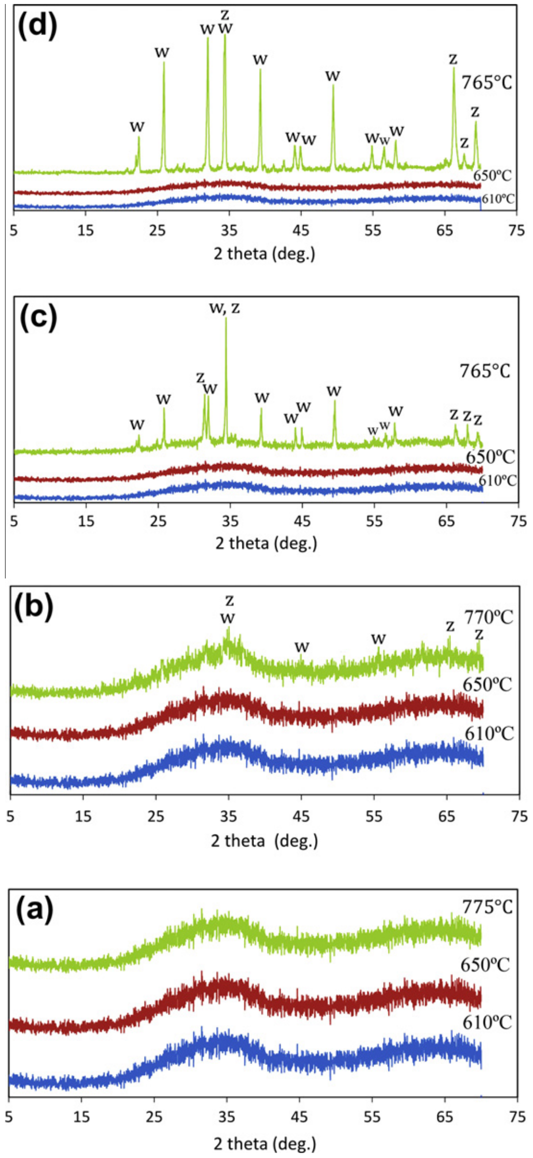

Fig. 3. XRD patterns of (a) G0, (b) G1, (c) G2 and (d) G3 heat treated at different temperatures for 3 h in accordance to the DTA curves (w: willemite, z: zinc oxide).