In Situ X-Ray Diffraction Studies of Crystallization Growth Behavior in ZnO-Bi2O3-B2O3 Glass as a Route to Functional Optical Devices

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ABSTRACT

Transparent optical ZnO–Bi_2O_3–B_2O_3 (ZBB) glass-ceramics were created by the melt quenching technique. In this work, a melt of the glass containing stoichiometric ratios of Zn/Bi/B and As was studied. Differential scanning calorimeter (DSC) measurements was used to measure the thermal behavior. VIS/NIR transmission measurements were used to determine the transmission window. X-ray diffraction (XRD) was used to determine crystal phase. In this study, we explore new techniques and report a detailed study of in-situ XRD of the ZBB composition in order to correlate nucleation temperature, heat treatment temperature, and heat treatment duration with induced crystal phase.

Introduction

Zinc Bismuth Borate (ZBB) glasses are known to have low glass transitional temperature, low melting temperature, large refractive index, and the ability to produce unique non-linear crystals with high structural stability upon thermal treatment [1-3]. Transparent glass-ceramics with nonlinear crystals are becoming increasingly important for photonic and optical technologies. These glasses have a potential for use as optical devices such as waveguides, microlenses, and photonic crystals [1-3].

In this work, we report the fundamental properties of the novel 31.6 ZnO-31.6 Bi_2O_3-31.6 B_2O_3-5.3 As_2O_3 ZBB glass composition including glass transition and crystallization temperature and transmission window. We also report a detailed study of *in-situ* temperature controlled XRD of the 31.6 ZnO-31.6 Bi_2O_3-31.6 B_2O_3-5.3 As_2O_3 ZBB composition in order to correlate nucleation temperature, heat treatment temperature, and heat treatment duration with induced crystal phase.

Experimental details

Glass samples were prepared using a conventional melt quenching procedure [1]. They were melted at 1000 ^oC for 1 hour, annealed at 330 ^oC, and cooled to room temperature at a rate of 1 ^oC/min. The final glass had a composition of 31.6 ZnO-31.6 Bi_2O_3-31.6 B_2O_3-5.3 As_2O_3 (figure 1(a)). Samples were cut and polished into coupons of 10.0 mm x 10.0 mm x 3.0 mm for characterization and heat treatments (HTs). Differential scanning calorimeter (DSC) measurements were used to determine the glass transition (T_g) and crystallization (T_c) temperatures (figure 1(b)). A JASCO UV-Vis-NIR spectrometer was used to measure the transmission of each polished sample (figure 1(c)). Temperature-controlled *in-situ* XRD measurements were conducted using an Empyrean diffractometer systems equipped with a AP HTK-2000N sample stage with a Pt heat strip. The anode material was Cu, the generator voltage was 45 kV, and the continuous scan range was 10^o to 80^o. As seen in figure 2, the bulk glass sample was loaded onto the hot stage installed in the temperature-controlled XRD system. Five XRD measurements were collected at temperatures of 25 ^oC, 460 ^oC, 500 ^oC, 540 ^oC and 580 ^oC after an anneal time of 20 min. These five temperatures were selected to include room temperature, two possible nucleation temperatures of below 500 ^oC, and two possible crystallization growth temperatures determined by the location of crystallization peaks from the DSC measurements. Each scan took 10 minutes.

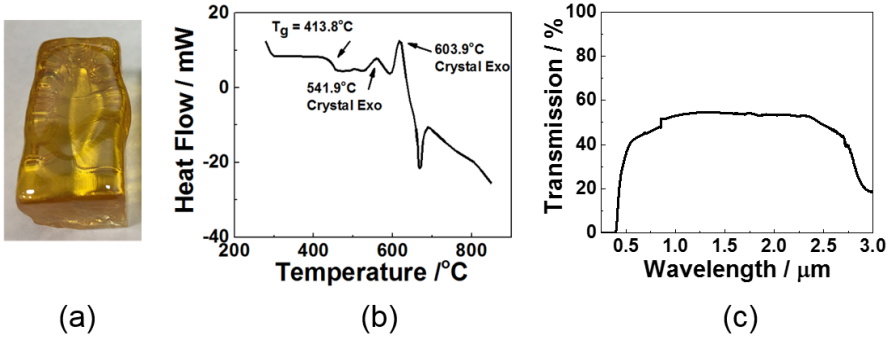

Figure 1. (**a**) 31.6 ZnO-31.6 Bi_2O_3-31.6 B_2O_3-5.3 As_2O_3 glass in bulk form. (**b**) Differential scanning calorimetry measurement showing glass transition temperature (T_g) and two crystallization temperatures. (**c**) UV-Vis-NIR base glass transmission.

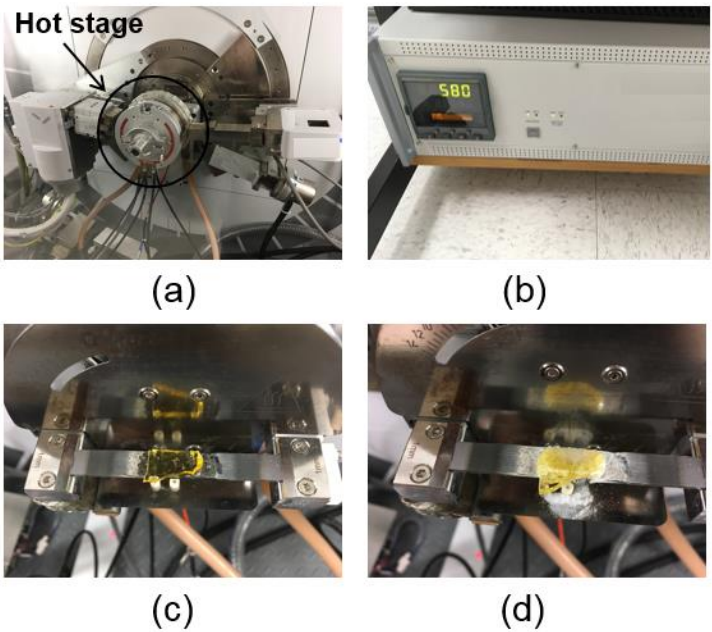

Figure 2. (a) XRD with hot stage. (**b**) XRD temperature controller. (**c**) ZBB sample on Pt hot stage before heat treatment. (**d**) ZBB sample on Pt hot stage after heat treatment.

Discussion

Figure 3(a) shows an example of the 31.6 ZnO-31.6 Bi_2O_3-31.6 B_2O_3-5.3 As_2O_3 glass after it was sliced and polished from the bulk melt seen in figure 1(a). The visible-

range transmission is apparent. Figure 3(b) shows a sample with surface crystallization after it has been through heat-treatment. A post heat-treatment polish is needed to remove surface crystals and re-measure transmission. The post heat-treatment re-polished sample is seen in figure 3(c).

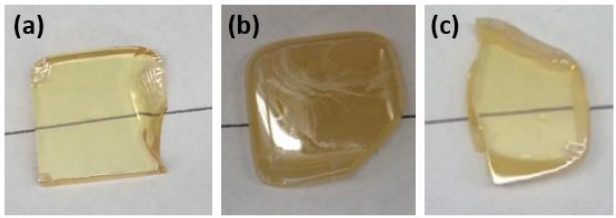

Figure 3. (**a**) Pristine glass sample. (**b**) Glass sample with surface crystallization. (**c**) Post heat-treatment and polished glass sample.

Figure 4 shows the results of the *in-situ* XRD measurements taken as a function of temperature. In figure 4 we see that the sample remains amorphous up to a temperature of 460 ºC, and at a temperature of 500 ºC, two peaks start emerging. The peaks become extremely narrow ($2\theta = 28^{o}$) at a temperature of 540 ºC, and the intensity of the major peak significantly increases. This trend continues further at a temperature of 580 ºC. Post-polishing peaks indicate $Bi_2ZnB_2O_7$ crystal formation remains. The emergence time and position of the peaks indicate that the glass may form additional surface crystal phases including ZnO and BiB_3O_6 [2].

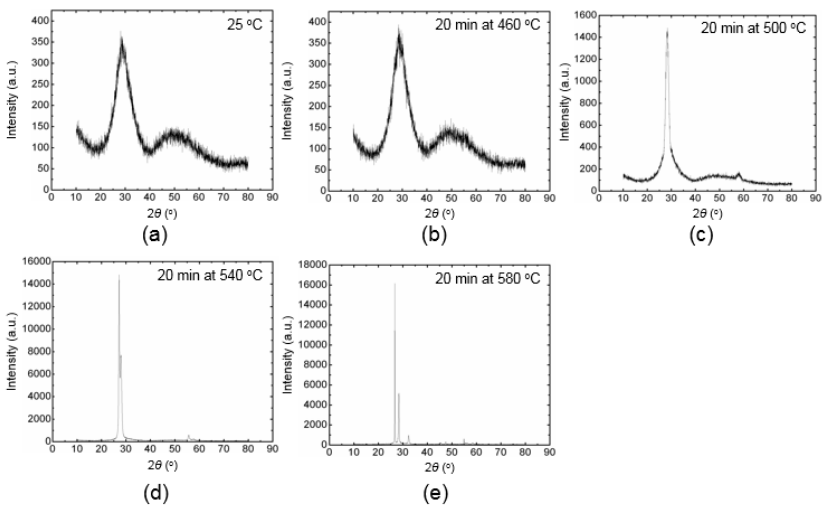

Figure 4. In-situ XRD measurements following the ramping-annealing procedure where five XRD measurements were collected at temperatures of (a) 25 ºC, (b) 460 ºC, (c) 500 ºC, (d) 540 ºC and (e) 580 ºC after an anneal time of 20 min.

Conclusions

Heat treatments were used to create transparent 31.6 ZnO-31.6 Bi_2O_3-31.6 B_2O_3-5.3 As_2O_3 glass ceramic containing $Bi_2ZnB_2O_7$ nanocrystals. Transmission was maintain for post heat treatment polished samples. For the first time *in-situ* XRD measurements revealed that the ZBB glass undergoes crystallization transitions relating to additional surface crystal phases. These measurements suggest that crystallization starts at the surface along with other possible crystal phases then extends into the bulk with increasing temperature.

Acknowledgments

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