Second-harmonic generation in transparent surface crystallized glasses in the $BaO-B_2O_3-TeO_2$ system

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A transparent glass–ceramic containing borate crystallites in tellurite glass is reported. Controlled heat treatment resulted in surface crystallization of BaB_4O_7 in the $BaO-B_2O_3-TeO_2$ glass system. The second-order optical nonlinearities observed in these surface crystallized glasses were attributed to the distortion present in the BaB_4O_7 unit cell as evidenced by x-ray powder diffraction studies. A d_{33} value of 0.08 pm/V was obtained from the Maker fringe analysis for a surface crystallized glass. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1808873]

Recently, there has been an increasing interest in the transparent glass-ceramics containing nonlinear optical/ferroelectric materials in view of their application as nonlinear photonic materials.[1–3] Transparent glass-ceramic in the system $BaO-B_2O_3$ was first reported by Kao and co-workers.[3] The controlled heat treatment of this glass yielded submicron crystallites of β-BaB_2O_4 in the glass matrix. However, the transparent samples could contain only low crystallite content and produced less efficient second-harmonic generation (SHG). The attempts to increase the crystallite content lead to the loss of transparency. It was also reported that the crystallites are mostly accumulated toward the surface of the glass. Later, Ding and co-workers fabricated transparent glass-ceramic with a β-BaB_2O_4 surface crystalline layer in $40BaO-15TiO_2-45B_2O_3$ and $47.5BaO-47.5B_2O_3-5Al_2O_3$ glasses.[4,5] The surface nucleation was enhanced using ultrasonic surface treatment with aqueous suspension that contained β-BaB_2O_4 particles. Transparent glass-ceramic containing β-BaB_2O_4 was also prepared by the incorporation method.[6]

On the other hand, there have been a considerable amount of studies on the tellurite glasses containing ferroelectric oxides viz. $LiNbO_3$, $KNbO_3$, and $BaTiO_3$ which show efficient SHG.[7,1,8] However, the crystallization of borate in a tellurite glass is a concept which has not yet been attempted. We systematically studied the crystallization behavior of many glass compositions in the system $BaO-B_2O_3-TeO_2$. It was found that $15BaO-15B_2O_3-70TeO_2$ (in mol%) was one of the best compositions in this system, which lead to the fabrication of transparent glass ceramics with large optical nonlinearities. The details of which will be presented in this letter.

The glasses under investigation were prepared from reagent grade $BaCO_3$, B_2O_3, and TeO_2 as starting materials. The stoichiometric compositions of these raw materials were mixed thoroughly and melted in a covered platinum crucible at about 900 °C for 20 min in an electric furnace. Transparent glasses were made by quenching the melts onto a copper plate. These glasses were sufficiently annealed at a temperature (T_g-40) °C for 12 h and cooled slowly to release the thermal stress associated with these glasses during the quenching process. Differential scanning calorimetry (DSC) (Rigaku ThermoPlus DSC 8270) was employed to ascertain the glassy nature of the as-quenched samples and to find out the glass transition (T_g), crystallization (T_x), and melting (T_m) temperatures.

The amorphous nature of the as-quenched glass and crystalline phase formation of the heat-treated samples (plate and crushed powder) were studied by x-ray powder diffraction (XRD) (Rigaku RINT 2000) using Cu Kα radiation. Scanning electron microscopy (SEM) and optical microscopy were employed to study the microstructure of the heat-treated samples. The transmission spectra of the as-quenched and heat-treated glasses were recorded with an ultraviolet–visible-near-infrared (NIR) (UV) spectrophotometer (Perkin–Elmer Lamda 900) in the spectral range 175–3300 nm. Second-harmonic (SH) intensities were measured using a fundamental wave of a Q-switched Nd:YAG laser operating at a wavelength of 1064 nm as incident light. The absolute calibration of the SH intensities was carried out using a Z-cut quartz single crystal taking $d_{11}=0.503$ pm/V as reference. Combination of p-excitation and p-detection (pp-polarization) was used during the SHG measurements. d_{33} values of the surface crystallized glasses were obtained via Maker fringe analysis. The details of the Maker fringe analysis were reported elsewhere.[9]

Among all the compositions studied in the $BaO-B_2O_3-TeO_2$ system, $15BaO-15B_2O_3-70TeO_2$ (in mol%) (hereafter referred to as BBT15) was chosen to be the best one with large optical nonlinearities. The glass transition, crystallization, and melting temperatures of BBT15 were found to be 360, 515, and 600 °C, respectively. The heat treatment of BBT15 glass sample was undertaken at various temperatures above *Tg*. Figures 1(a) and 1(b) show the XRD patterns of BBT15 heat treated at 375 °C/24 h for powder and plate, respectively. The crushed powder did not show any XRD peaks except a halo pattern. Interestingly, the plate showed very intense XRD peaks, which are the characteristics of surface crystallization. All the Bragg peaks in Fig. 1(b) could be indexed to a monoclinic cell of BaB_4O_7 with mean cell parameters $a=10.627$, $b=8.128$, c

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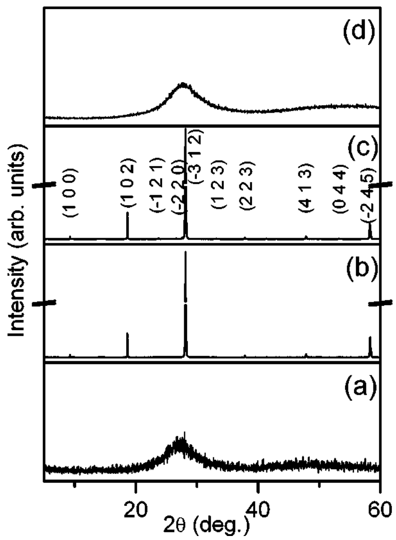

FIG. 1. XRD patterns of the BBT15 glass (a) heat treated at 375 °C/24 h (powder), (b) heat treated at 375 °C/24 h (plate), (c) heat treated at 390 °C/24 h (plate), and (d) heat treated at 390 °C/24 h and polished to remove the surface layer to about 1 μm (plate).

=13.034 Å, and β=105.70°. However, the calculated lattice parameters are slightly different from the values reported in the literature for BaB_4O_7 (a=10.586, b=8.194, c=13.045 Å, and β=105.1°),[10] indicating that there is some distortion in the surface crystallized BaB_4O_7 in the present investigation. The sample heat treated at 390 °C/24 h also showed a similar surface crystallized pattern with a very few additional peaks [Fig. 1(c)]. It is interesting to note that the samples heat treated at 375 and 390 °C/24 h were quite transparent. Samples heat treated beyond these temperatures turned out to be translucent. The depth of the surface crystallinity was evaluated by performing XRD on samples whose surface layers were removed by polishing. Figure 1(d) shows the XRD pattern of the 390 °C/24 h heat-treated sample polished to about 1 μm. Almost all of the crystalline features disappeared by removing the surface layer. This confirms that uniform surface crystallized layers of BaB_4O_7 with a thickness of less than 1 μm were produced upon heat treatment at 390 °C/24 h. It was reported that the crystallization of glasses containing BaO and B_2O_3 always produces surface crystallization, and attempts to form bulk nuclei by heat treatment near the glass transition temperature failed.[11] It was also shown from the literature that for a few glass compositions with BaO and B_2O_3, only BaB_4O_7 crystals were nucleated during the heat treatment.[11]

Figure 2(a) shows the optical micrograph of BBT15 sample heat treated at 390 °C/24 h and confirms the formation of a homogeneous crystalline layer. The surface of this sample was polished to about 1 μm and again subjected to optical microscopy, which displayed a smooth texture-less surface similar to that of the as-quenched sample (not shown in Fig. 2). This substantiates the results of XRD measurements that the surface crystallized layer is restricted only to a thickness less than 1 μm. Figure 2(b) depicts the cross-sectional SEM image of 390 °C/24 h heat-treated sample. It is very clear from the SEM image that uniform crystalline layer is formed only at the surface of the heat-treated sample. The average crystalline layer thickness was obtained to be 0.65±0.10 μm. This value was used for the quantitative evaluation of the d_{33} value.

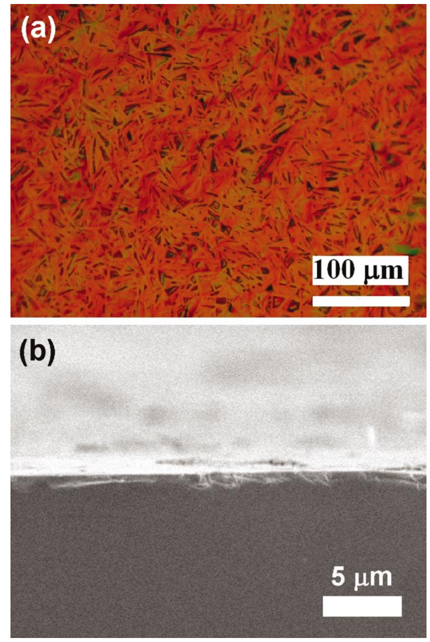

FIG. 2. (color) (a) Optical micrograph and (b) cross-sectional SEM image for 390 °C/24 h heat–treated BBT15 glass.

Despite the intense XRD peaks observed for the surface crystallized samples heat treated at 375 and 390 °C/24 h, they were quite transparent as confirmed via optical transmission studies. Figure 3 shows the optical transmission spectra (uncorrected for reflection and scattering losses) of the as-quenched, 375, and 390 °C/24 h heat-treated BBT15 samples. All of these samples were found to have a wide transmission window starting from the NIR to UV (down to about 350 nm).

The surface crystallized samples were found to exhibit SHG, and the SH coefficient (d_{33}) was evaluated using the Maker fringe analysis.[9] Figure 4 shows the variation of the SH intensity with angle for the BBT15 sample heat treated at 390 °C/24 h. The open circle represents the experimentally observed Maker fringes, whereas the solid line is the fitted one obtained using the thickness of the crystallized layer found via SEM studies and the refractive indices (n) measured at ω and 2ω (n_{ω}=2.009 and $n_{2\omega}$=2.095). As a result of fitting, the d_{33} value was estimated to be 0.08±0.02 pm/V for the surface crystallized glass heat treated at 390 °C/24 h. The low value of the d_{33} is ascribed to the presence of large contents of glass forming oxides.[9] The sample heat treated at

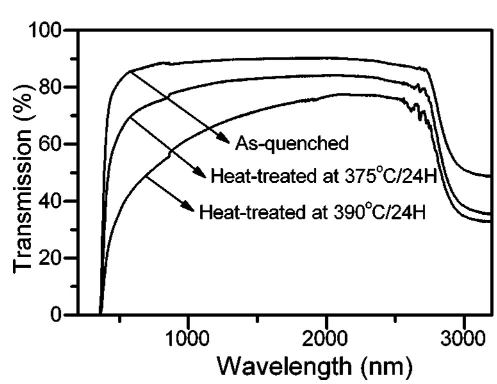

FIG. 3. The optical transmission spectra (uncorrected for reflection and scattering losses) for the as-quenched BBT15 glass and BBT15 glass heat treated at 375 and 390 °C/24 h.

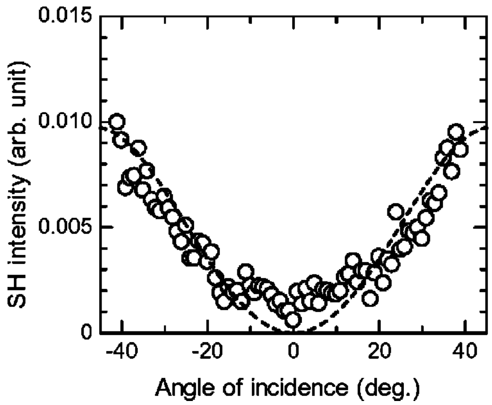

FIG. 4. Experimental (open circles) and fitted (solid line) Maker fringe patterns for transparent surface crystallized glass.

375 °C/24 h also exhibited intense SHG and similar Maker fringe pattern (not shown in Fig. 4). The Maker fringe patterns obtained for the present surface crystallized glasses are similar to that of electrically poled glasses.[12] This is because the structure of the surface crystallized glasses is the same as that of electrically poled glasses. Though BaB_4O_7 is reported to belong to the centrosymmetric crystal class, the optical nonlinearity associated with these surface crystallized samples is attributed to the large distortions in their unit cells. Similar studies were reported for the transparent surface crystallized glass in the systems $15K_2O-15Nb_2O_5-70TeO_2$ (Refs. 13 and 14) and $15BaO-15TiO_2-70TeO_2$.[8]

In conclusion, transparent surface crystallized glasses containing BaB_4O_7 crystallites in the $BaO-B_2O_3-TeO_2$ glass system have been fabricated. The XRD and optical microscopic studies on a heat-treated sample before and after polishing (to remove the surface layer) confirmed the presence of surface crystalline layer, confined only to about 1 μm thick or less. The cross-sectional SEM was used to find out that the thickness of the crystalline layer was 0.65 μm. The surface crystallized glasses exhibited intense SHG and the d_{33} value obtained using the Maker fringe analysis was 0.08 ± 0.02 pm/V.

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