CHIN.PHYS.LETT. Vol. 25, No. 12 (2008) 4421

Optical Transmittance and Band Gap of Ferroelectric $BaTi_2O_5$ Bulk Glass

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(Received 24 September 2008)

Optical transmittance and reflectance on ferroelectric $BaTi_2O_5$ glasses prepared recently by a containerless synthesis technique are measured at room temperature in the wavelength range 190–800 nm. The fundamental absorption edge located around 340 nm demonstrates the colourless and transparent character of the glass. The optical band gap of 3.32 eV has been estimated. The tail of the optical absorption near the fundamental absorption edge is found to follow the Urbach rule. Our analysis of the experimental spectra supports an indirect allowed interband transition between the valence band formed by O-2p orbitals and the conduction band formed by Ti-3d orbitals.

PACS: 78. 55. Qr, 78. 40. −q, 78. 20. Ci

Glasses and ferroelectric materials are among the most popular materials owing to their wide-spread technological applications. The conventional glasses are usually prepared using a glass forming network. However, very recently, Yu and Arai[1] have reported a new glass of ferroelectric $BaTi_2O_5$ (BTO), which has been prepared without using any glass forming network. The glass phase remains stable up to glass transition temperature $T_g = 972$ K. Above T_g, three successive phase transitions, from glass to a metastable α phase at 972 K, then to a metastable β phase at 1038 K, and finally to a stable γ phase above 1100 K, have been observed.[1] The crystal structure of the final γ phase has been identified as monoclinic similar to that reported for the ferroelectric BTO crystals.[2,3] The structure of both α- and β-phases is not yet known. In the metastable α phase, a pronounced response of real part of permittivity ϵ_r has been observed with its magnitude increased to 10^6 at 100 Hz on increasing temperature to 994 K, at which ϵ_r displays a very sharp peak with its maximum magnitude reached from 10^6 to 1.5×10^7 and then dropped to 1×10^7 within a temperature interval of 1 K and a time interval of 20 s. Very recently, Taniguchi *et al.*[5] have revealed using Raman scattering experiment that the glass phase present in the metastable phases acts as a matrix in which nano-scaled crystals are dispersed when the material undergoes a successive crystallization phases suggesting an important role of the base material, i.e. glass, in forming and controlling the size of these nano-crystals. Thus it is quite interesting to investigate the properties of ferroelectric BTO glass at first stage in order to understand the mechanism of controlling the physical properties of the nano-scaled crystals dispersed in metastable phases.

In this Letter, we report the optical properties of three newly synthesized ferroelectric BTO glasses of different thickness by measuring their optical transmittance T and reflectance R spectra at room temperature in the wavelength range 190–800 nm. We have calculated the optical energy gap and discussed the nature of the optical transition in the BTO glass. The results reported here are new and not published elsewhere to the best of our knowledge.

The BTO glass spheres of 2 mm diameter were synthesized in an aerodynamic levitation furnace (ALF) by a new containerless synthesis technique, which solidifies the undercooled liquid into a selected phase and is considered suitable for synthesizing the material of desired structure and novel properties.[6,7] The detail of sample preparation can be found elsewhere.[1] Briefly, high purity commercial powders of $BaTiO_3$ and TiO_2 were mixed keeping mole ratio as 1:1 and compressed into rods under a hydrostatic pressure of 200 MPa. The rods were sintered at 1427 K for ten hours. Bulk samples with a mass of about 10 mg were cut from the rods, which were later on levitated with the ALF and then melted by a continuous-wave CO_2 laser beam. During the process of melting, the temperature of the sample was measured by a pyrometer. For obtaining a magnified view of the sample, a high-resolution CCD video camera equipped with a telephoto objective lens was used. Prior to quenching, the sample was carefully brought to the desired temperature employing the laser power. After quenching at a cooling rate of about 1000 K/s, the glass spheres of approximately 2 mm diameter were obtained.

For optical measurements, three samples of thickness (diameter) 0.236 mm (1.352 mm), 0.315 mm (1.321 mm), and 0.454 mm (1.508 mm) named here-

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after as S-1, S-2, and S-3 respectively, were used. The optical T and R measurements were carried out at room temperature using a UV-VIS (V-570, JASCO) dual beam scanning spectrophotometer in the wavelength range 190–800 nm (in fact, the T and R spectra were also measured from 2000 nm to 190 nm; above 800 nm, both the T and R spectra are flat and featureless and therefore not important). Since the samples were of small size, a specially designed sample holder with a central hole of diameter slightly smaller than that of the respective sample was used to measure the optical T and R. During the measurements, only the sample was exposed to incident light and rest of the sample holder was carefully masked by a black paper. It was checked that R of the sample holder masked with black paper was zero in the absence of sample. For the R measurements, aluminium film deposited on glass was used as a reference. Further detail of the R measurement can be seen elsewhere.[8–10]

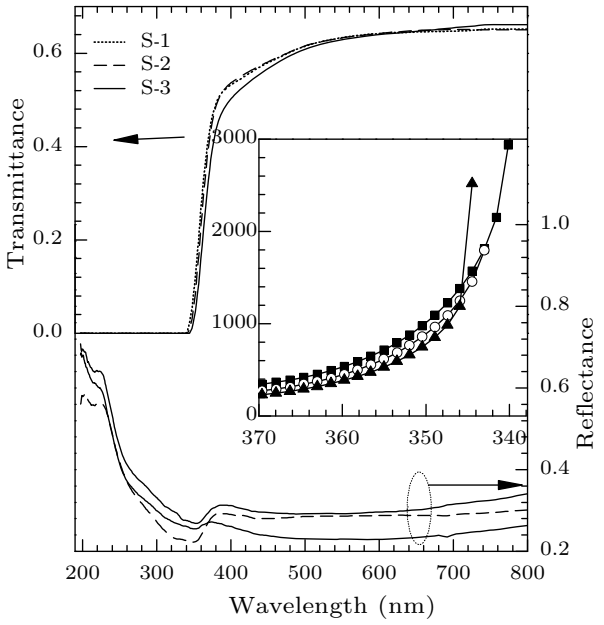


Fig. 1. Optical transmittance and reflectance of BTO glass of thickness 0.236 mm (S-1), 0.315 mm (S-2) and 0.426 mm (S-3). The inset shows the absorption coefficient α (cm^{-1}) along vertical axis versus wavelength (nm) along horizontal axis as estimated from the T and R spectra (see text). The α near the absorption edge is plotted only.

The optical T and R spectra for BTO glass are shown in Fig. 1. A sharp absorption edge at 340 nm in the T spectrum and a peak at a slightly longer wavelength in the R spectrum indicating a reflection band are observed for the S-1. Both the absorption edge and the reflection band, within our spectral measurement uncertainty, are found to be nearly overlapping for samples of different thicknesses. The appearance of the absorption edge in the UV wavelength region demonstrates the colourless and transparent character of the BTO glass. This colourless and transparent feature of the glass is similar to what is reported for the crystalline BTO, in which the absorption-edge wavelength defined at T becoming less than 0.01 is located at somewhat longer wavelength, i.e., 365 nm.[2] Above the reflection band, an intense R can be seen between 340 nm and 190 nm, i.e. UV region of wavelength, where T is zero.

From the experimental T and R spectra, we have determined the absorption coefficient (α) using the relation: $T = \dfrac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}}$, where d is the thickness of the sample. Here α near the absorption edge is shown in Fig. 1 (inset). However, we have noticed that α exhibits a long tail in the long wavelength region, almost up to about 370 nm. Below 370 nm, the α starts to increase slowly first followed by a steep rise down to 340 nm. Since the measurement of α near the fundamental absorption edge provides a standard method for the investigation of optically-induced electronic transitions and provide some ideas about the band structure and energy gap in both crystalline and non-crystalline materials, this later increase in absorption can be regarded as due to the onset of optical interband transition. The optical transitions, either direct or indirect, occur at the fundamental absorption edge and involve the interaction of an electromagnetic wave with an electron in the valence band of the solid which is raised across the energy gap to the conduction band.[11]

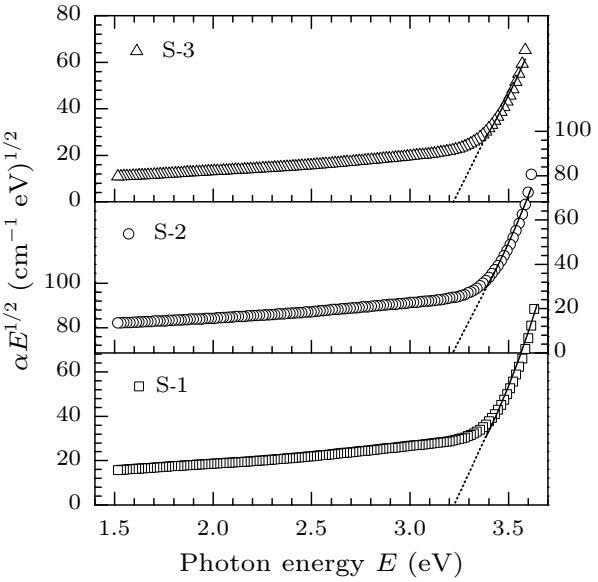


Fig. 2. Behaviour of $(\alpha E)^{1/2}$ as a function of photon energy for BTO glass. The solid lines are the best fit to Davis and Mott relation (see text), which are extrapolated to $(\alpha E)^{1/2} = 0$ (dotted lines) to estimate the band gap (E_g).

The nature of the optical interband transition and value of the energy gap E_g can be determined using the relation derived independently by Tauc *et al.*[12]

and Davis and Mott[11] as $\alpha(E)E = C(E - E_g)^m$, where $m = 1/2$ and $3/2$ for allowed direct- and forbidden direct transitions, and $m = 2$ and 3 for allowed indirect- and forbidden indirect transitions respectively. C is a disorder parameter nearly independent of the photon energy E. E_g is approximately taken as the energy band gap. Thus the value of the optical band gap for BTO glass is obtained by plotting $(\alpha E)^{1/m}$ versus E in the high absorption range followed by extrapolating the linear region of the plots to $(\alpha E)^{1/m} = 0$. The analysis of our data shows that the plots of $(\alpha E)^{1/m}$ versus E give a linear relation which is best fitted by Davis and Mott relation with $m = 2$. This indicates that the nature of the fundamental interband transition in BTO glass may be indirect-allowed. We propose that this transition occurs between oxygen $2p$ valence band and the lowest conduction band derived from the d orbitals of the transition element Ti and is optically allowed. The plots of $(\alpha E)^{1/2}$ versus E are shown in Fig. 2. As predicted by Davis and Mott relation, these plots are linear at the higher value of the E but tend to deviate from linearity as the E approaches lower value. The linear region of these graphs extrapolated to E axis gives the value of the E_g. In taking the ambiguity of putting the straight line into account, the values of E_g are estimated to be around 3.32 eV. The values of the fit parameter C for S-1, S-2 and S-3 are respectively 934, 786 and 664 $\mathrm{cm^{-1}eV^{-1}}$.

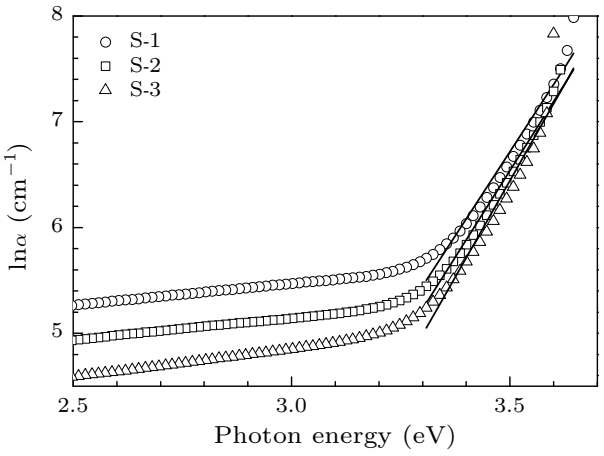


Fig. 3. Behaviour of $\ln(\alpha)$ versus photon energy E illustrating the validity of the Urbach rule for BTO glass.

As mentioned above, the absorption edge of the crystalline phase of BTO lies at longer wavelength as compared with that of the glass samples. Therefore, the value of E_g would definitely be smaller for the crystalline BTO than that of present glass system. This difference in E_g of both the crystalline BTO and BTO glass, and hence difference in the fundamental absorption edge, is due to the possibility that the valence and conduction bands, which are broad in crystalline phase resulting in a narrow band gap, become narrower, which hence results in widening of the band gap in the glass phase.

The optical absorption coefficient near the fundamental absorption edge is found to exponentially depend on the incident photon energy and obeys the empirical Urbach rule:[13] $\alpha(E) = \alpha_0 \exp \dfrac{\gamma(E - E_g)}{k_B T}$, where E is the energy of the incident radiation, k_B is the Boltzmann constant, and α_0 is a constant. The factor $\gamma/k_B T$ is a measure of the steepness of the absorption edge and is sometimes interpreted as the width of the tail of localized states in the band gap. Urbach relation at a particular temperature (URT) could be reduced to $\alpha(E) = \alpha_0 \exp(E/E_w)$, where E_w is the width of the tail of the localized states. The variation of $\ln(\alpha)$ as a function of E near the absorption edge for the BTO is presented in Fig. 3, which illustrates the validity of the Urbach rule for the present system. The values of E_w are 0.16, 0.15, and 0.14 eV for S-1, S-2 and S-3, respectively, which are extracted from fitting the data to the URT. Relatively larger value of E_w is found in the present glass. It is an established fact that the band tail in amorphous materials appears due to the presence of impurity and defect states within the band gap, which appear due to a variety of defects and dislocations present in these materials.[11] In the case of BTO glass, it is reported that the Ti and O atoms form highly distorted [TiO_5] polyhedra with each Ti atom coordinated by approximately five oxygen atoms on the average.[1] Since the distorted [TiO_5] polyhedra contributed mainly to the network former of the glassy state of the BTO it may possibly be responsible for the relatively large band tail observed in the BTO glass. Moreover, the fundamental absorption edges in non-crystalline materials arise from the interband transitions involving the band tails of the localized states where the density of the states falls exponentially.[14] Thus the absorption edge found in the BTO glass can be associated with the optical indirect interband transition. The refractive index of BTO glass is estimated to be around 3 (the refractive index n is calculated by $T = \dfrac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}$ and $R = \dfrac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$, where $k = \dfrac{\alpha\lambda}{4\pi}$ is the extinction coefficient).

In conclusion, we have measured the optical T and R spectra on a newly synthesized BTO glass at room temperature for wavelength range between 190–800 nm. The optical band gap of 3.32 eV has been estimated from the fundamental absorption edge located around 340 nm. The absorption edge in the T spectra or reflection band in the R spectra is possibly

associated to an indirect allowed interband transition, which takes place between the valence band formed by O $2p$ orbitals and the conduction band formed by Ti $3d$ orbitals. The relatively larger width of the band tail may be resulted from the highly distorted $[TiO_5]$ polyhedra.

JA acknowledges the VBL, University of Tsukuba, Japan for the award of postdoctoral fellowship.

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