Research Article

Synthesis, Structural and Optical Investigations of (Pb, Bi)TiO₃ Borosilicate Glasses

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A new series of lead bismuth titanate borosilicate glasses with addition of one percent lanthanum oxide have been synthesized using melt-quench technique. X-ray diffraction patterns have been recorded to confirm the amorphous nature of the prepared glass samples. The synthesized glasses have been characterized by using various spectroscopic techniques such as UV-visible, infrared, and Raman spectroscopy. UV-visible measurements were recorded in the wavelength range from 200 to 1100 nm whereas IR and Raman spectroscopic measurements were recorded over a continuous wavenumber range from 400 to 5000 cm⁻¹ and 1000 to 2000 cm⁻¹ respectively. The different absorption peaks/bands were formed in IR spectral patterns. The spectral bands appear towards the lower wavenumber sides due to the Bi and Pb content while the bands appear towards the higher wavenumber sides due to the formation of diborate and triborate network units.

1. Introduction

Glass and glass ceramics are very important materials for their device making applications such as cryogenic temperature sensors which include a capacitance thermometer, a dielectric bolometer, and capacitive energy storage capacitors. The application of Aurivillius family of bismuth based ferroelectric compounds with a layered structure in capacitors, sensors, and piezoelectric and electrooptic devices is strongly influenced by the method of preparation [1–4]. The melt-quench method gives possibility of doping with different cations to enhance their optical and electrical properties. Apart from this, these glasses were known to exhibit large third-order nonlinear optical properties [5]. Heavy metal containing glasses are the most suitable for the nonlinear applications because of their cubic nonlinearity. Particularly, Bi and Pb based glasses show higher refractive index, due to their higher hyperpolarizable nature. Since these glasses exhibit nonlinear phenomenon, they are useful in optical fibers and in optical switches [6–10]. The demonstration of electrooptic effect in transparent glasses containing ferroelectric crystalline phases has enhanced the prospects of using electrooptic glasses and glass ceramics for various nonlinear optical (NLO) applications [11–13]. The Pb based glasses are popular as commercial, low temperature, and sinterable glasses due to their desirable application properties such as low softening temperature, low dielectric constant (<15), and high reflectivity [14]. The structural properties of borosilicate glasses can be modified within a wide range by the introduction of oxides of bivalent or monovalent metals that modify the network structure of the boron [15]. Glasses based on Bi₂O₃ and PBO were intensely investigated in the last decade because of their interesting technological applications such as thermal and mechanical sensors, waveguides in nonlinear optics, scintillation detectors in high-energy physics, optoelectronic circuits as ultrafast switches, infrared windows, and optical isolators and also in advanced computer [16, 17]. More recently, (Pb, Sr)TiO₃ and (Ba, Sr)TiO₃ borosilicate glasses were prepared successfully by Gautam et al. to explore the optical and electrical properties of these glasses [18, 19]. Such type glasses are used for shielding of X-rays radiation.

The optical properties of (Pb, Bi)TiO₃ (lead bismuth titanate) doped with 1 mole percent La₂O₃ (lanthanum oxide)
glasses are presented in this work. This is, to our knowledge, the first time that this host is doped with rare-earth oxides. Now, the focuses are on the structural and optical properties evaluation of the glasses and these properties are correlated with their compositions.

2. Experimental Methods

The AR grade chemicals, PbO (Fisher Scientific 99%), Bi₂O₃ (Himedia 99.9%), TiO₂ (Himedia 99%), SiO₂ (Himedia 99.5%), H₃BO₃ (Himedia 99.8%), and La₂O₃ (Himedia 99.9%), were mixed for 3.0 hours in acetone media using agate mortar and pestle to obtain desired homogeneity of the powder. The well mixed and dried powders were kept in a platinum crucible and then crucible is placed inside the high temperature SiC programmable electric furnace in the temperature range from 1200 to 1300°C. The melt was poured into an aluminum mould and pressed by a thick aluminum plate and then immediately transferred into a preheated programmable muffle furnace for annealing at temperature 450°C up to 4 hours. The XRD of powder glass samples was carried out using a Rigaku Miniflex-II X-ray diffractometer using Cu-Kα radiation to check the amorphous state of the prepared glass samples. The structures of the prepared glass samples were analyzed using analytical tools such as UV-Visible, IR, and Raman spectroscopy and XRD. The UV-Visible spectroscopic measurements are carried out on (Labtronics LT-2900) double beam spectrometer in the wavelength range from 200 to 1100 nm at room temperature. The powdered samples were dissolved in double distilled water; reference sample was taken as double distilled water of various prepared glass samples in the system UV-visible absorption spectra.

3. Results and Discussions

3.1. X-Ray Diffraction Analysis of Glass Samples. The XRD patterns of various glass samples BT1L0.0, PBT1L0.1, PBT1L0.3, BT1L0.5, and PBT1L0.7 are shown in Figure 1(a–e). These XRD patterns exhibit a broad diffuse scattering at different angles instead of crystalline peaks and confirm a long range structural disorder characteristic of amorphous glassy network.

3.2. UV-Vis Spectroscopy. UV-visible absorption spectra of various prepared glass samples in the system 55[(Pb,Bi)₂OTiO₂]·44[(2SiO₂B₂O₃)]·1La₂O₃ were shown in Figures 2(a)–2(g). All UV patterns show nonlinear behavior and there is a no sharp increase in absorption peak at energies close to the band gap that manifests itself as an absorption edge in the UV-visible absorption spectra except UV spectrum of glass samples PBT1L0.3. This indicates the amorphous nature of glass samples, which is also confirmed by XRD results of the same glass samples. Figure 2(a) showed the UV spectrum of lead-free glass sample BT1L0.0 and it is found different in comparison to the rest of UV samples. This indicates only two absorption edges near wavelengths 286 and 338 nm. After this, it is found constant up to certain value of the wavelength and then gradually decreases with increasing the value of the wavelength. (Bi)TiO₃ demonstrates an obvious photoabsorption in the visible-light region, and its absorption edge shifts to the visible-light region, which is consistent with the yellowish color of the samples [20]. The band gap absorption edge of the prepared glass sample is determined to be 286 nm, corresponding to the band gap energy value of 6.94 eV. Figure 2(b) depicts the UV pattern of the glass sample PBT1L0.1 showing two absorption bands at different wavelengths, 292 and 344 nm. The first absorption band is present due to the content of the Bi, while the second is due to lead content. The value of absorbance continuously decreases with increasing in the value of wavelength. Figures 2(c) and 2(d) show the UV pattern of glass samples PBT1L 0.3 and PBT1L 0.4; three absorption peaks were observed in these samples at different wavelengths. At higher wavelength side two absorption peaks were observed at 918 and 1012 nm, while in Figure 2(d) only a soider of an absorption peak is observed at 950 nm. Figures 2(e)–2(g) show the UV spectrum of the three different glass samples. The UV pattern of glass sample PBT1L0.5 was found to be similar to UV pattern of glass sample PBT1L0.4 (Figure 2(d)). The UV patterns of glass samples PBT1L0.7 and PBT1L0.9 are almost similar and only a single absorption peak is observed at lower wavelength side. It might be due to the increasing concentration of Pb for Bi.

3.3. Infrared Spectroscopy. The IR spectra occur due to change in the dipole moment of the molecule. It involves the twisting, bending, rotating, and vibrational motions in a molecule. IR spectra of various (PbBi)₂TiO₃ borosilicate glass samples doped with La₂O₃ are shown in Figures 3(a), 3(b), 3(c), 3(d), 3(e), and 3(f). IR spectra of all glass samples consist of broad and sharp bands in different regions lying between the wavenumbers 400 and 4000 cm⁻¹. These absorption bands are strongly affected due to variation of compositional changes. Wavenumbers of various absorption peaks for all glass samples are listed in Table 2. These absorption peaks have been marked as numbers 1, 2, 3, ...,12, starting from high wavenumber side to low wavenumber side. The broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of the vibrational states, thermal broadening of the lattice dispersion bands, and mechanical scattering from powder samples. The absorption peaks in IR spectra can be divided into four main groups in the ranges from 3400 to 2300 cm⁻¹, 1600 to 1200 cm⁻¹, 900
Table 1: Nomenclature of glass samples and their compositional distributions.

<table>
<thead>
<tr>
<th>Glass sample code</th>
<th>(Pb_{x}Bi_{1-x})TiO_{3} Composition x</th>
<th>Weight %</th>
<th>(2SiO_{2}-B_{2}O_{3})</th>
<th>La_{2}O_{3}</th>
<th>Glass transition temperature, $T_{g}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTL0.0</td>
<td>0.0</td>
<td>55</td>
<td>44</td>
<td>1</td>
<td>558</td>
</tr>
<tr>
<td>PBTL0.1</td>
<td>0.1</td>
<td>55</td>
<td>44</td>
<td>1</td>
<td>541</td>
</tr>
<tr>
<td>PBTL0.3</td>
<td>0.3</td>
<td>55</td>
<td>44</td>
<td>1</td>
<td>532</td>
</tr>
<tr>
<td>PBTL0.5</td>
<td>0.5</td>
<td>55</td>
<td>44</td>
<td>1</td>
<td>530</td>
</tr>
<tr>
<td>PBTL0.7</td>
<td>0.7</td>
<td>55</td>
<td>44</td>
<td>1</td>
<td>514</td>
</tr>
<tr>
<td>PBTL0.9</td>
<td>0.9</td>
<td>55</td>
<td>44</td>
<td>1</td>
<td>500</td>
</tr>
</tbody>
</table>

3.4. Raman Spectroscopy. Raman spectrums of the representative (Pb, Bi)TiO_{3} borosilicate glass samples doped with La_{2}O_{3} are shown in Figures 4(a)–4(e). Each RS spectrum indicates more than two peaks. Figure 4(a) shows the RS spectra of glass sample BTL0.0 without lead content ($x = 0.0$). Band formation at lower wavenumber side range from 400 to 900 cm$^{-1}$ in all Raman spectra of the glass samples is attributed to metaborate groups and symmetric breathing vibrations of six-member rings with one or two BO$_3$ triangles replaced by BO$_4$ tetrahedra [33]. These bands also occurred due to bending vibrations of planar BO$_3$ triangles in random network [34]. The positions of the bands are a little bit changed with variation of the compositions. Two separate peaks were observed at different wavenumbers 2656 and 2694 cm$^{-1}$ in the Raman spectra of lead-free glass sample, while the peak positions are shifted towards the higher
Figure 2: UV-Visible spectrum of glass samples (a) BT1L0.0, (b) PBT1L0.1, (c) PBT1L0.3, (d) PBT1L0.4, (e) PBT1L0.5, (f) PBT1L0.7, and (g) PBT1L0.9.

Table 2: Peak position of IR spectra of different glass samples in the system \(55[(\text{Pb},\text{Bi}_{1-x})\text{TiO}_3] - 44[\text{2SiO}_2 \cdot \text{B}_2\text{O}_3] - 1[\text{La}_2\text{O}_3]\).

<table>
<thead>
<tr>
<th>Glass code</th>
<th>Wavelength of different absorption peaks (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1  2  3  4  5  6  7  8  9  10  11  12</td>
</tr>
<tr>
<td>BT1L0.0</td>
<td>3396 2928 2265 1631 1596 1384 1350 1190 1121 987 753 656 612 437 418</td>
</tr>
<tr>
<td>PBT1L0.1</td>
<td>3325/3384 2928 2343 1631 1600 1384 1350 1190 1121 987 756 656 612 437 418</td>
</tr>
<tr>
<td>PBT1L0.3</td>
<td>3393 2925 2343 1631 1596 1400 1350 1190 1121 987 753 656 612 437 418</td>
</tr>
<tr>
<td>PBT1L0.5</td>
<td>3400 — — 1631 1600 1384 1350 1190 1109 987 912 753 656 612 437 418</td>
</tr>
<tr>
<td>PBT1L0.7</td>
<td>3387 — — 1631 1587 1384 1350 1190 1106 987 750 656 609 437 418</td>
</tr>
<tr>
<td>PBT1L0.9</td>
<td>3387 — — 1631 1596 1384 1350 1190 1109 987 753 656 612 437 418</td>
</tr>
</tbody>
</table>
Table 3: Assignment of infrared and Raman bands in the spectra of different glass samples.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>IR</th>
<th>Raman</th>
<th>IR assignments</th>
<th>Raman assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>418–437</td>
<td>400–900</td>
<td></td>
<td>Vibrations of metal cations such as Pb$^{2+}$ ions and doubly degenerate stretching vibration of BiO$_3$ groups</td>
<td>Metaborate groups and symmetric breathing vibrations of six-member rings with one or two BO$_3$ triangles replaced by BO$_4$ tetrahedra</td>
</tr>
<tr>
<td>612–656</td>
<td>—</td>
<td></td>
<td>Combined vibrations of BO$_4$ and PbO$_4$ groups</td>
<td>—</td>
</tr>
<tr>
<td>750–756</td>
<td>700–725</td>
<td></td>
<td>Bonding of B–O–B linkages (diborate linkage)</td>
<td>Symmetric breathing vibrations of BO$_3$ triangles replaced by BO$_4$ tetrahedra</td>
</tr>
<tr>
<td>1035</td>
<td>820–850</td>
<td></td>
<td>Stretching vibration of B–O–Si linkage</td>
<td>Symmetric breathing vibrations of six-member rings with one or two BO$_3$ triangles replaced by BO$_4$ tetrahedra</td>
</tr>
<tr>
<td>987</td>
<td>—</td>
<td></td>
<td>Stretching vibrations of B–O–Bi linkage</td>
<td>—</td>
</tr>
<tr>
<td>1106–1121</td>
<td>—</td>
<td></td>
<td>Stretching vibration of BO$_4$ tetrahedra groups</td>
<td>—</td>
</tr>
<tr>
<td>1200–1635</td>
<td>—</td>
<td></td>
<td>Asymmetric stretching relaxation of the B–O bond of trigonal BO$_3$ units</td>
<td>—</td>
</tr>
<tr>
<td>2265–2343</td>
<td>—</td>
<td>—</td>
<td>–OH bonding</td>
<td>—</td>
</tr>
<tr>
<td>2700–3000</td>
<td>2656–2694</td>
<td></td>
<td>Hydrogen bonding</td>
<td>Hydrogen and –OH bonding</td>
</tr>
<tr>
<td>3325–3400</td>
<td>—</td>
<td>Hydroxyl or water groups and O–H stretching vibrations</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3: IR spectra of glass samples (a) BT1L0.0, (b) PBT1L0.1, (c) PBT1L0.3, (d) BT1L0.5, (e) PBT1L0.7, and (f) PBT1L0.9.
Figure 4: Raman spectra of glass samples (a) BT1L0.0, (b) PBT1L0.1, (c) PBT1L0.3, (d) PBT1L0.5, and (e) PBT1L0.7.

wavenumber side for Raman spectra of the rest of glass samples. The shifting in their peak position is due to the replacement of the PbO with BiO. The presence of these peaks due to the hydrogen/OH bonding is also confirmed by their IR results. The assignment of IR and RS bands in the spectra of different glass samples is summarized in Table 3.

4. Conclusions

Bulk transparent and homogeneous (Pb, Bi)TiO$_3$ (PBT) borosilicate glasses doped with La$_2$O$_3$ were prepared by melt-quench technique. The addition of alkali or alkaline earth oxides to the borate network changes the boron coordination from three to four. UV patterns show nonlinear behavior and there is no sharp increase in absorption peak at energies close to the band gap values. The IR spectra were observed in four main groups, 3400–2300 cm$^{-1}$, 1600–1200 cm$^{-1}$, 900–700 cm$^{-1}$, and 700–400 cm$^{-1}$, respectively. This result concluded the formation of di-, tri-, tetra- and pentaborate groupings. IR spectra of PBT borosilicate glasses occur due to vibrational mode of the borate network of asymmetric stretching vibrations B–O bond of trigonal BO$_3$ units, molecular water, –OH bonding, and B–O–B and B–O–Si linkages. The low-frequency bands (peaks 12 a and b) are observed in all IR spectra of the glass samples and attributed to vibration of metal cation such as Pb$^{2+}$ ions in the glass and doubly degenerate stretching vibration of BiO$_3$ groups. The absorption bands are present due to the contents of Bi and Pb. Raman spectra of the glass samples are attributed to metaborate groups and symmetric breathing vibrations of six-member rings with one or two BO$_3$ triangles replaced by BO$_4$ tetrahedra which give the best agreement by IR spectra. Very high value of indirect optical band gap was found to be 6.94 eV which is reported first time for PBT borosilicate glasses. These glasses may be used for the protection of high-energy radiations such as X-rays and γ-rays.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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