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 Bi$_2$O$_3$ 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)TiO$_3$ and (Ba, Sr)TiO$_3$ 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)TiO$_3$ (lead bismuth titanate) doped with 1 mole percent La$_2$O$_3$ (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; reference sample was taken as double distilled water. 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.

2.1. 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 I(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.

2.2. UV-Vis Spectroscopy.

UV-visible absorption spectra of various prepared glass samples in the system range from 450 to 4000 cm⁻¹. The UV-visible absorption spectra of lead-free glass samples 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. 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)TiO₃ 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.

| Glass sample code | Composition \( x \) | Weight % | \((2\text{SiO}_2\cdot\text{B}_2\text{O}_3)\) | \(\text{La}_2\text{O}_3\) | Glass transition temperature, \(T_g\) (°C) |
|------------------|------------------|---------|------------------|------------------|------------------|
| BTIL0.0          | 0.0              | 55      | 44               | 1                | 558              |
| PBTIL0.1         | 0.1              | 55      | 44               | 1                | 541              |
| PBTIL0.3         | 0.3              | 55      | 44               | 1                | 532              |
| PBTIL0.5         | 0.5              | 55      | 44               | 1                | 530              |
| PBTIL0.7         | 0.7              | 55      | 44               | 1                | 514              |
| PBTIL0.9         | 0.9              | 55      | 44               | 1                | 500              |

Figure 1: XRD patterns of glass samples (a) 55BTIL0.0, (b) 55PBTIL0.1, (c) 55PBTIL0.3, (d) 55BTIL0.5, and (e) 55PBTIL0.7.

\[20\text{ cm}^{-1} \text{ to } 700\text{ cm}^{-1}, \text{ and } 700 \text{ to } 400\text{ cm}^{-1}, \text{ respectively. It is known that boron exhibits more than one stable configuration. The addition of alkali or alkaline earth oxides to the borate network changes the boron coordination from three to four. This results in the formation of di-, tri-, tetra-, and pentaborate groupings. Due to the boron anomaly, addition of modifier oxides forms } \text{BO}_4 \text{ units. The IR spectra of the present glass samples have exhibited similar spectral features of ternary borate glasses containing PbO, SrO, ZnO, Bi}_2\text{O}_3, \text{ and TeO}_2 \text{ reported in the literature [21–27]. The first absorption peak lies in the wavenumber range from 3325 to 3400 cm}^{-1} \text{ which is mainly due to hydroxyl or water groups present in the glass samples and attributed to the O–H stretching vibration [28]. Weak peaks and some shoulders are observed in Bi rich glass samples in the range from 2700 to 3000 cm}^{-1} \text{, while these weak peaks were found absent in the Pb rich IR patterns (Figures 3(e) and 3(f)) which are attributed to the presence of hydrogen bonding in the glass samples. The peak number 3 in between 2265 and 2343 cm}^{-1} \text{ is attributed to \(–\text{OH group present in the glass samples [29]. Only two doublet degeneracies have been observed in all the La-doped glass samples at different wavenumbers, represented by peak numbers 4 and 5 (a and b). These peaks were present due to the asymmetric stretching relaxation of the B–O bond of trigonal \text{BO}_3 \text{ units. A very strong and sharp absorption peak number 7 is present at wavenumber 1106–1121 cm}^{-1} \text{ and was found due to the stretching vibration of } \text{BO}_4 \text{ tetrahe...} \]
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.

| Glass code | Wavelength of different absorption peaks (cm⁻¹) |
|------------|-----------------------------------------------|
|            | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 |
| BT1L0.0    | 3396 | 2928 | 2265 | 1631 | 1596 | 1384 | 1350 | 1190 | 1121 | 987 | 753 | 656 | 612 | 437 | 418 |
| PBT1L0.1   | 3325/3384 | 2928 | 2343 | 1631 | 1600 | 1384 | 1350 | 1190 | 1121 | 987 | 753 | 656 | 612 | 437 | 418 |
| PBT1L0.3   | 3393 | 2925 | 2343 | 1631 | 1596 | 1400 | 1350 | 1190 | 1121 | 987 | 753 | 656 | 612 | 437 | 418 |
| PBT1L0.5   | 3400 | —   | —   | 1631 | 1600 | 1384 | 1350 | 1190 | 1109 | 987 | 753 | 656 | 612 | 437 | 418 |
| PBT1L0.7   | 3387 | —   | —   | 1631 | 1587 | 1384 | 1350 | 1190 | 1106 | 987 | 750 | 656 | 609 | 437 | 418 |
| PBT1L0.9   | 3387 | —   | —   | 1631 | 1596 | 1384 | 1350 | 1190 | 1109 | 987 | 753 | 656 | 612 | 437 | 418 |

Table 2: Peak position of IR spectra of different glass samples in the system 55[(PbₓBi₁−ₓ)TiO₃]-44[2SiO₂·B₂O₃]-1[La₂O₃].
Figure 3: IR spectra of glass samples (a) BTIL0.0, (b) PBTIL0.1, (c) PBTIL0.3, (d) BTIL0.5, (e) PBTIL0.7, and (f) PBTIL0.9.

Table 3: Assignment of infrared and Raman bands in the spectra of different glass samples.

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

Conflict of Interests

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

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