

# Synthesis, IR and Raman Spectroscopic Studies of (Ba,Sr)TiO<sub>3</sub> Borosilicate Glasses with Addition of La<sub>2</sub>O<sub>3</sub>

Chandkiram Gautam<sup>1\*</sup>, Avadhesh Kumar Yadav<sup>1</sup>, Vijay Kumar Mishra<sup>2</sup>, Kunwar Vikram<sup>2</sup>

<sup>1</sup>Department of Physics University of Lucknow, Lucknow, India

<sup>2</sup>Department of Physics, Banaras Hindu University, Varanasi, India

Email: \*gautam\_ceramic@yahoo.com

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## ABSTRACT

A series of glasses were prepared by rapid melt quench method in the glass system  $(65 - x)[(\text{Ba}_{0.6}\text{Sr}_{0.4})\text{TiO}_3] - 30[2\text{SiO}_2 - \text{B}_2\text{O}_3] - 5[\text{K}_2\text{O}] - x[\text{La}_2\text{O}_3]$  ( $x = 0, 1, 2, 5$  and  $10$ ). X-ray diffraction of glass samples were carried to check its amorphousness. Density of glass samples were measured using Archimedes principle. The refractive index of these glass samples lies between 2.39 to 2.80. Optical properties of these glass samples were studied using Infrared (IR) and Raman spectroscopic techniques. IR measurements were done over a continuous spectral range  $450 - 4000 \text{ cm}^{-1}$  to study their structure networking systematically while Raman spectra were recorded over a continuous spectral range  $200 - 2000 \text{ cm}^{-1}$ . IR spectra of all glass samples showed number of absorption peaks. These absorption peaks occurs due to asymmetric vibrational stretching of borate by relaxation of the bond B-O of trigonal  $\text{BO}_3$ . The Raman spectra of all glass samples exhibited different spectral bands and intensity of these bands changes drastically. The network structure of these glass samples is mainly based on  $\text{BO}_3$  and  $\text{BO}_4$  units placed in different structural groups.

**Keywords:** Glasses; X-Ray Diffraction; Infrared Spectroscopy and Raman Spectroscopy

## 1. Introduction

Glasses in the system  $\text{PbO} - \text{B}_2\text{O}_3 - \text{SiO}_2$  and  $\text{PbO} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$  have different applications, such as thick film technology ink constituents, mixed oxide dielectrics (MODs) and host for fluorescence centers in optical devices. These glasses are chemically stable over a wide composition range and have a desirable electrical resistivity. The lead borosilicate glasses are used as radiation hard glasses [1]. Vibrational spectroscopy has been used for long time to investigate the structure of glasses and the identification of the main structural groups [2-4]. Infrared spectroscopy has very useful technique because it provides a means to determine local structure of building units which constitutes the glassy network [5]. Borates and borosilicate glasses containing boron oxide have been widely used for optical lenses with high refractive index and low dispersion characteristics [6]. The oxide glasses have wide applications in the fields of electronics, nuclear and solar energy technologies and acoustic-optic devices [7-11]. Glasses based on boron oxide exhibit structural chemistry of structure. Boron is commonly found in the glasses in the form of triborate and tetraborate units [12]. Alkali borate glasses are best glass forming systems for demonstrating the effectiveness of the spectroscopic technique in the glass science

[13]. IR spectra of  $(\text{Pb,Sr})\text{TiO}_3$  borosilicate glass system show sharp and diffuse absorption peaks. These peaks occur due to different vibrational mode of the borate network and asymmetric stretching relaxation of the B-O bond of trigonal  $\text{BO}_3$  units. Vibrational spectra of  $\text{PbO} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$  glasses show the formation of broad bands. IR studies of  $\text{ZnO} - \text{PbO} - \text{B}_2\text{O}_3 - \text{SiO}_2$  glasses shows absorption bands due to bond breaking between the trigonal elements  $\text{BO}_3$  and allowing the formation of  $\text{BO}_4$  units. The structure of Zn-doped borate glass consists of randomly connected  $\text{BO}_3$  and  $\text{BO}_4$  groups. The IR spectra of  $\text{ZnO} - \text{PbO} - \text{B}_2\text{O}_3$  glasses show eight to nine absorption peaks [14,15]. Low frequency bands in the IR spectra of these glasses can be attributed to vibration of metal cation such as  $\text{Pb}^{2+}$ . The broad bands are exhibited in the oxide spectra due to the combination of high degeneracy of vibrational states [16,17]. IR spectra of lead silicate glasses were exhibited due to bending modes Si-O-Si and O-Si-O as well as symmetric stretching of bridging oxygen between tetrahedra [18]. IR study of lithium borate glasses show cleared and disappearance of boroxol rings with the formation of  $\text{BO}_4$  groups [19]. Recently, IR studies of  $\text{B}_2\text{O}_3 - \text{ZnO} - \text{TeO}_2$  glass system gives absorption bands due to vibrational Te-O bond stretching. B-O linkages in the borate network of B-O-B bending vibrations in  $\text{BO}_4$  units and H-O-H or water groups are present in these glasses [20]. Raman spectroscopy is a very use-

\*Corresponding author.

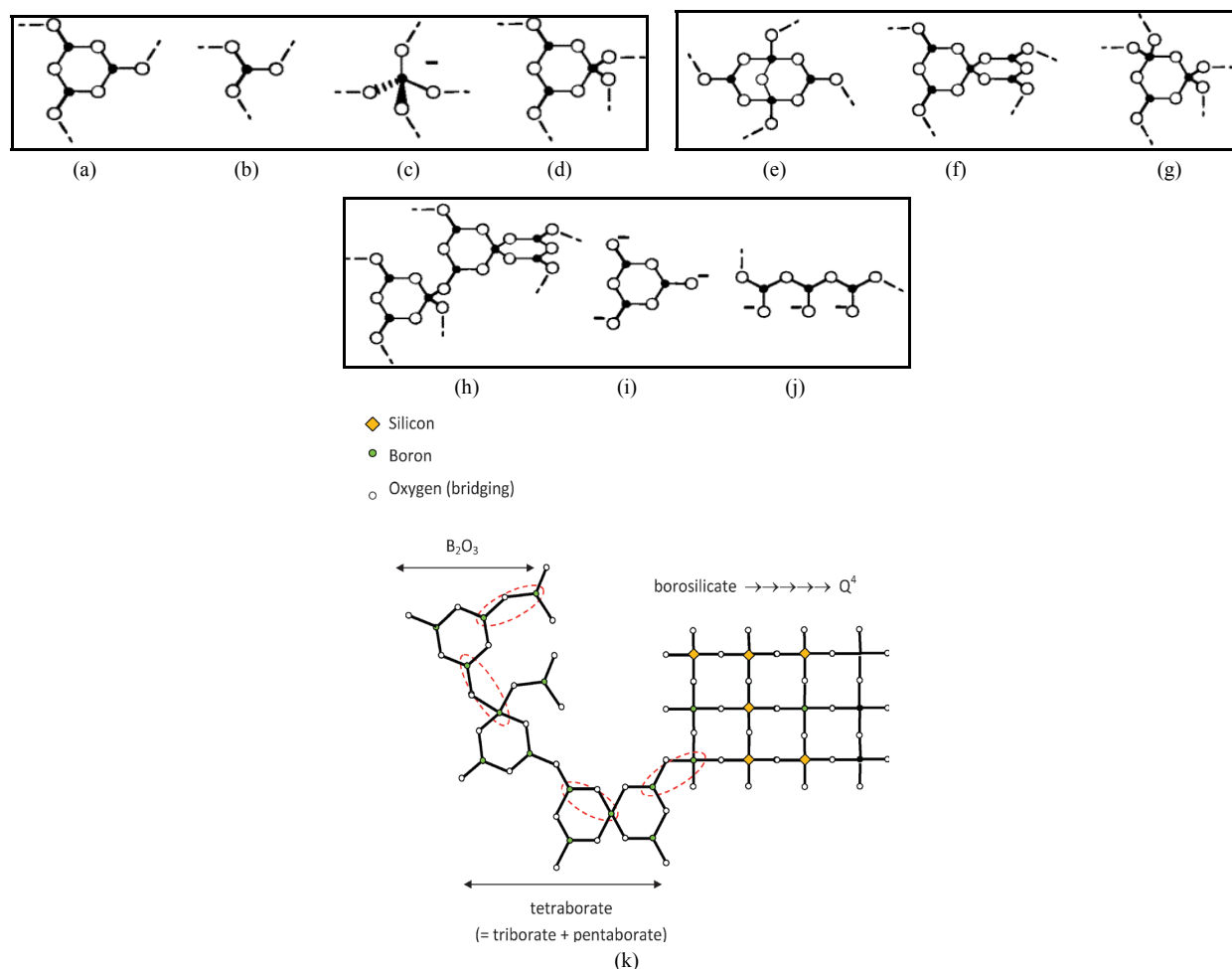
ful tool to provide valuable information about impurities, internal stress, crystal symmetry and bond nature [21-26]. IR and Raman studies on lithium-potassium-borate glasses exhibited due to vibrational stretching of borate network of the  $\text{BO}_3$  and  $\text{BO}_4$  units placed in different structural groups [27]. The various structural groups of borate network are shown in **Figure 1** [27,28].

Raman spectroscopy of epitaxial barium titanate, BT, thin film shows both paraelectric to ferroelectric phase transformations. The diffuse phase transition is confirmed by the gradual decrease of the intensities of the overdamped soft mode and the tetragonal Raman shift [29]. Raman spectra of hetero-epitaxial BST prepared on MgO substrates were obtained in side-view backscattering geometry and causes local distortions of the Ti-O-Ti chains [30]. Vibrational spectra of BT single crystals have been studied and give displacive order-disorder crossover [31-36]. Recently, IR and Raman spe-

ctroscopic studies have been done on alkaline-earth silicate glasses by Angelos G Kalampounias [37]. This study shows the vibrational spectra due to vibrational stretching of Si-O in (Si-OH) silanol groups. BST borosilicate glasses have potential applications in making high refractive index glasses for optical devices and their glass ceramics are used for making electronic devices, such as barrier layer capacitor. In this research paper we are reporting our results on optical properties of BST borosilicate glasses with doping effect of  $\text{La}_2\text{O}_3$ .

## 2. Experimental Procedure

The high purity of AR grade chemicals  $\text{BaCO}_3$  (Himedia 99%),  $\text{SrCO}_3$  (Himedia 99%),  $\text{TiO}_2$  (Himedia 99%),  $\text{SiO}_2$  (Himedia 99.5%),  $\text{H}_3\text{BO}_3$  (Himedia 99.8%),  $\text{K}_2\text{CO}_3$  (Himedia 99.9%) and  $\text{La}_2\text{O}_3$  (Himedia 99.9%) were mixed for 1.0 hour in acetone media using mortar and pestle.



**Figure 1. Structural groups found in glassy and crystalline potassium borates: (a) boroxol ring; (b) nonring  $\text{BO}_3$ ; (c) nonring  $\text{BO}_3^-$ ; (d) triborate; (e) diborate; (f) pentaborate; (g) di-triborate; (h) tetraborate; (i) ring-type metaborate; (j) chain-type metaborate; (k) combination of triborate and pentaborate units. Filled circles and open circles represent boron and oxygen atoms, respectively. Dashed lines in the structures denote connections to the network, and charges are shown for the non-bridging oxygen (NBO) in the metaborate groups [27,28].**

The well mixed and dried powder were transferred in to a high alumina content crucible and then crucible is replaced inside the high temperature SiC electric furnace in the temperature range 1200°C - 1350°C. The melt was poured into an aluminum mould and pressed by a thick aluminum plate then immediately transferred in to a pre-heated muffle furnace for annealing at temperature 450°C up to 3 hours. XRD patterns of glass samples were recorded using a Rigaku Miniflex-II X-ray diffractometer using Cu-K $\alpha$  radiation for checking amorphous nature glass samples. The glass samples were prepared for measurement of refractive index. The five glass samples were designed of having equal thickness (0.7 mm) along with equal area (25 mm<sup>2</sup>). These samples were polished with different mesh of SiC powder to get the smooth surfaces. Electroding has been done on the both polished surfaces of all glass samples with silver palladium paste and then electroded samples were dried in a preheated oven at 200°C. Finally, well dried glass samples were carried out for their capacitance measurement at room temperature. The density of glass samples depends upon doping concentration of La<sub>2</sub>O<sub>3</sub>. Therefore, it is worth-while to calculate the density of the prepared glass samples. The density of all glass samples were calculated by using Archimedes Principle [40]. Distilled water was used as the liquid medium. The density of these glass samples were listed in **Table 1**. The following formula was used for determination of the density of glass samples.

$$\text{Density} = \frac{(W_2 - W_1)}{(W_4 - W_1) - (W_3 - W_2)} \quad (1)$$

where, W<sub>1</sub> = weight of empty specific gravity bottle (in gram);

W<sub>2</sub> = weight of specific gravity bottle with sample (in gram);

W<sub>3</sub> = weight of specific gravity of bottle with sample and distilled water (in gram);

W<sub>4</sub> = weight of specific gravity bottle with distilled water (in gram).

Density of distilled water = 1.0 gm/cm<sup>3</sup>

The powdered glass samples were mixed with KBr

powder and pressed as pellets. These pellets are carried out for the recording of IR spectra using JASCO FT/IR-5300 in the wave number range 450 - 4000 cm<sup>-1</sup> at room temperature. Micro Raman setup, Renishaw, UK, equipped with a grating of 1800 lines/mm and Olymapus (model MX-50) A/T was attached with spectrometer which focuses laser light into sample and collect the scattered at 180° by scattering geometry. The 15.4 nm Ar<sup>+</sup> laser was used as an excitation source and GRAM-32 software for data collection. Raman spectra of powdered glass samples were also recorded in the wave number range 200 - 2000 cm<sup>-1</sup>.

### 3. Results and Discussion

#### 3.1. X-Ray Diffraction Analysis

The XRD patterns of all glass samples are shown in **Figure 2**. These figures exhibit a broad diffuse scattering at different angles instead of crystalline peaks, confirming a long range structural disorder characteristic of amorphous network.

#### 3.2. Density Analysis of Glass Samples

The density of BST borosilicate glass samples doped with La<sub>2</sub>O<sub>3</sub> is listed in **Table 1**. The variation of density Vs doping concentration of La<sub>2</sub>O<sub>3</sub> is shown in **Figure 3**. With increasing doping concentration of La<sub>2</sub>O<sub>3</sub> increases the density of the glass samples. The density of BST borosilicate glass without doping of La<sub>2</sub>O<sub>3</sub> was calculated 2.67 gm/cc. This is because of high density of La is 6.17 gm/cc whereas density of Ba and Sr are 3.5 and 2.6 gm/cc.

#### 3.3. Dielectric Constant and Refractive Index

The dielectric constant for all glass samples are measured, by measuring their capacitance measurement at room temperature and 50 Hz frequency, using the relation

$$C = \epsilon_0 A/d \quad (2)$$

where “ $\epsilon_0$ ” denotes the permittivity in air, “A” denotes the area of samples and “d” denotes the thickness of samples.

**Table 1. Glass samples code, compositional distribution of different constituents, density, dielectric constant and refractive index of glass samples.**

Glass samples code	(Ba <sub>0.6</sub> Sr <sub>0.4</sub> )TiO <sub>3</sub>				Density (gm/cc)	Dielectric constant		Refractive index	
	weight %	(2SiO <sub>2</sub> -B <sub>2</sub> O <sub>3</sub> )	K <sub>2</sub> O	La <sub>2</sub> O <sub>3</sub>		Dielectric constant = 2.2 × ε <sub>r</sub> = ε/ε <sub>0</sub>	Calculated	Experimental	
BST5K0.4	65	30	5	0	2.67	5.87	5.71	2.42	2.39
BST5K1L0.4	64	30	5	1	2.69	5.92	5.76	2.43	2.40
BST5K2L0.4	63	30	5	2	2.85	6.27	6.15	2.50	2.48
BST5K5L0.4	60	30	5	5	2.98	6.56	6.50	2.56	2.55
BST5K10L0.4	55	30	5	10	3.10	6.82	7.80	2.61	2.80

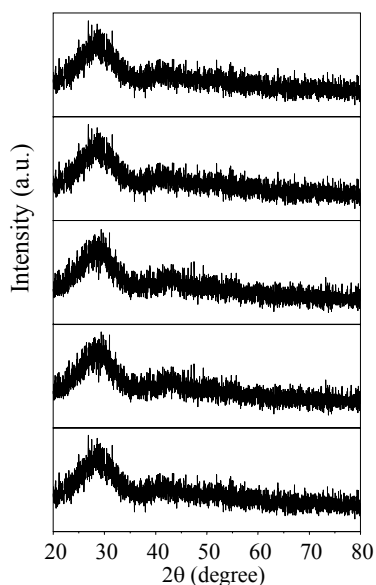


Figure 2. XRD pattern of BST borosilicate glass samples.

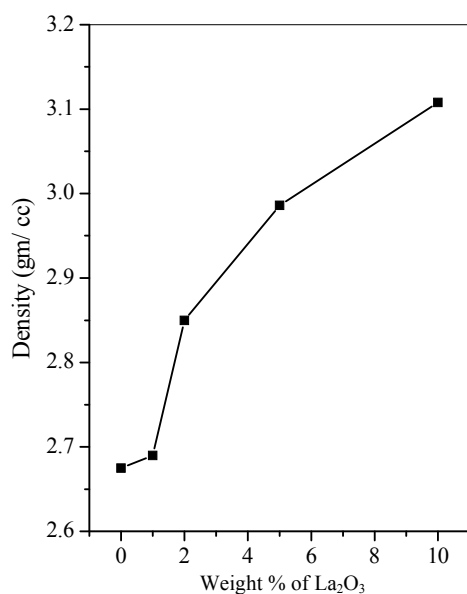


Figure 3. Density of glass samples vs doping concentration of La<sub>2</sub>O<sub>3</sub>.

The numerical value of dielectric constant can be estimated for most industrial glasses by using the empirical formula [38]:

$$\text{Dielectric constant} = 2.2 \times \text{density} \quad (3)$$

The dielectric constants calculated by both methods are comparable which are listed in **Table 1**. The refractive index of BST borosilicate glass samples were calculated by using the relation between refractive index and dielectric constant.

$$n = (\epsilon_r)^{1/2} \quad (4)$$

where  $n$  is the refractive index of the material and  $\epsilon_r$  is

the relative dielectric constant.

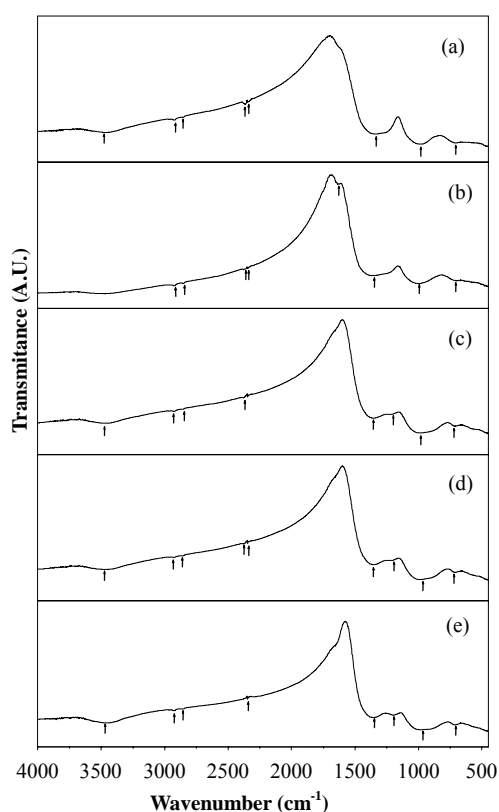
The refractive index of these glass samples are listed in **Table 1**. The measured refractive indices are of same order, which are calculated by two methods. The refractive of glass sample BST5K1L0.4 is found to be 2.43 whereas for glass sample BST5K2L0.4 is 2.50. It is observed from **Table 1** the refractive index of glass samples are increases with increasing the concentration of La<sub>2</sub>O<sub>3</sub>. It is because of the refractive index of La<sub>2</sub>O<sub>3</sub> is very high. The refractive indices of all glass samples were found to be more than 2. Therefore, these glass samples are useful for making lenses application in small optical devices such as smart phones with a digital camera, endoscopes, and next-generation optical disk systems [39]. These results indicate that the La<sub>2</sub>O<sub>3</sub> doped BST borosilicate glass system would be useful for optical applications in the visible to infrared region.

### 3.4. Infrared Spectroscopy

The IR absorption spectra gives significant information about molecular vibrations as well as rotation associated with a covalent bond. 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 BST borosilicate glasses doped with La<sub>2</sub>O<sub>3</sub> are shown in **Figure 4**. IR spectra of all glass samples consist of broad and sharp bands in different regions lies between wavenumbers 450 - 4000 cm<sup>-1</sup>. These bands are strongly influenced by doping of La<sub>2</sub>O<sub>3</sub>. Wavenumbers of different absorption peaks for all the glass samples are listed in **Table 2**. All the absorption peaks have been marked as numbered 1, 2, 3,... 8 starting from high wave number side to low wave number side. The broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion bands and mechanical scattering from powder samples [40]. The first absorption peak lies in the wavenumber range 3467 - 3479 cm<sup>-1</sup>. This absorption peak is sharp in glass sample BT5K10L0.4 in comparison to other glass samples. The sharpness of this peak increases by increasing the doping concentration of La<sub>2</sub>O<sub>3</sub>. This band occurs due to molecular water inside the glassy network [41]. The absorption peaks 2 and 3 were found in all glass samples and lies within wavenumber 2852 - 2925 cm<sup>-1</sup>. The absorption band of this wavenumber range occurs due to hydrogen bonding in the glassy matrix [42]. IR spectra of various glass samples show sharp and diffuse absorption peaks in wavenumbers range 2346 - 2380 cm<sup>-1</sup> (peak no. 4 a, b). This peak shows a splitting into two closed doublet peaks with different peak position in their IR spectra. The sharpness of the peaks decreases by increasing the doping concentration of La<sub>2</sub>O<sub>3</sub>. This absorption band attributed to O-H

**Table 2. Peak positions in IR spectra of glass samples in the system  $(65 - x)[(\text{Ba}_{0.6}\text{Sr}_{0.4})\text{TiO}_3] - 30[2\text{SiO}_2 \cdot \text{B}_2\text{O}_3] - 5[\text{K}_2\text{O}] - x[\text{La}_2\text{O}_3]$ .**

Glass samples code	Wave length of different absorption peaks ( $\text{cm}^{-1}$ )								
	1	2	3	4		5	6	7	8
				a	b				
BST5K0.4	3479	2924	2853	2365	2346	1328	-	988	707
BST5K1L0.4	3467	2923	2852	2366	2346	1351	-	991	704
BST5K2L0.4	3467	2925	2854	2380	-	1355	1204	983	715
BST5K5L0.4	3467	2925	2854	2380	2346	1348	1208	960	715
BST5K10L0.4	3468	2925	2854	-	2346	1352	1196	971	712

**Figure 4. IR spectra of BST borosilicate glass samples (a) BST5K0.4; (b) BST5K1L0.4; (c) BST5K2L0.4; (d) BST5K5L0.4 and (e) BST5K10L0.4.**

bond groups. These O-H bond groups are formed at non-bridging oxygen sites. A broad peak no. 5 is observed with wavenumbers range  $1196 - 1296 \text{ cm}^{-1}$  in the IR spectra of glass samples containing amount of  $\text{La}_2\text{O}_3$  ( $x = 2, 5$  and  $10$ ) while this peak is absent for glass samples BST5K0.4 and BST5K1L0.4. Generally absorption bands occur due to the vibrational mode of the borate network in such type glass system. The vibrational modes of the borate network are mainly due to the asymmetric stretching relaxation of the B-O bonds of trigonal  $\text{BO}_3$  units. Such type of vibrational modes occurs within the wavenumbers range  $1200 - 1750 \text{ cm}^{-1}$  [43,44]. The broad absorption band around wavenumbers,  $960 - 991 \text{ cm}^{-1}$

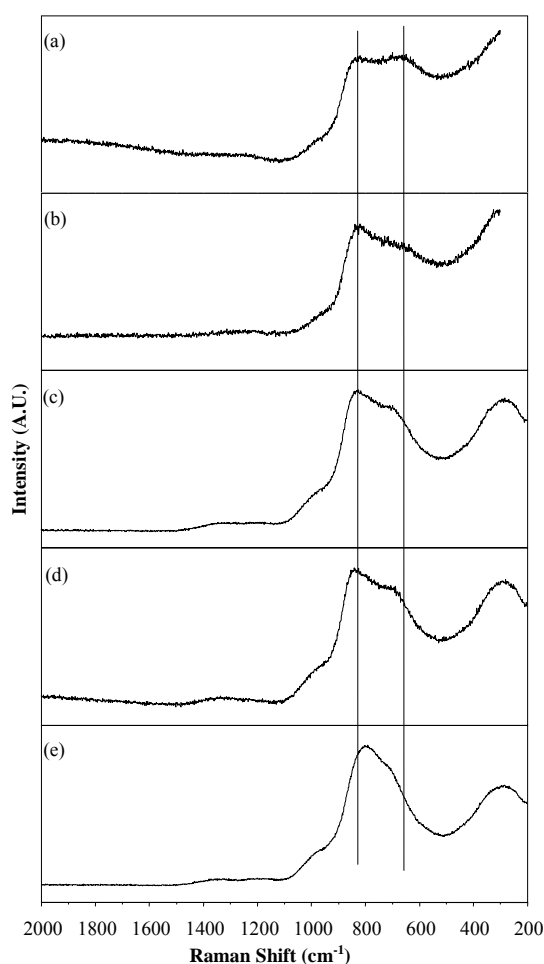
(peak no. 6) is attributed to stretching vibrations of B-O-Si linkage [45]. An absorption peak no.8 is observed with wavenumber range  $704 - 715 \text{ cm}^{-1}$  in the IR spectra of all glass samples. This peak was present due to the diborate linkage of B-O-B, in the borate glassy network. In this linkage both boron atoms are tetrahedrally coordinated with triborate superstructural units [46]. Assignment of Infrared bands in the spectra of different glass samples is listed in **Table 3**. The addition of  $\text{La}_2\text{O}_3$  increases the sharpness of the absorption peaks and decreases the broadness of absorption peaks.

### 3.5. Raman Spectroscopy

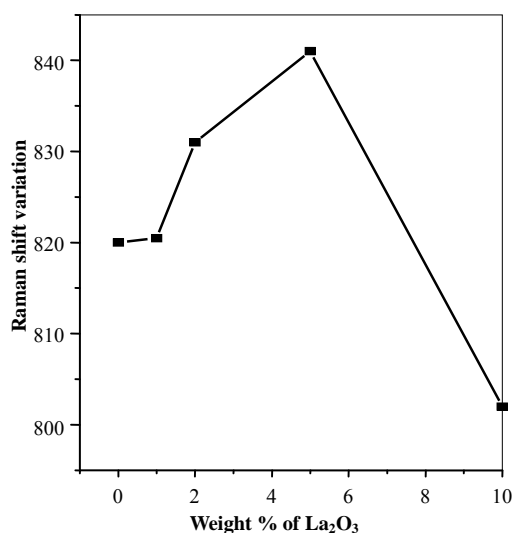
Raman spectroscopy is one of the powerful techniques to investigate the structure of a material. Raman spectra of various BST borosilicate glass samples doped with  $\text{La}_2\text{O}_3$  are shown in **Figures 5(a)-(e)**. Raman spectra of these glasses indicate two peaks at different position. **Figure 5(a)** shows Raman spectra of glass sample BST5K0.4 ( $x = 0$ ) without doping of  $\text{La}_2\text{O}_3$ . In this spectral pattern, two separate peaks were observed at wavenumbers  $675$  and  $820 \text{ cm}^{-1}$ . The peak at  $675 \text{ cm}^{-1}$  was attributed to metaborate groups while peak at wavenumber  $820 \text{ cm}^{-1}$  occurs due to symmetric breathing vibrations of six-member rings with one or two  $\text{BO}_3$  triangles replaced by  $\text{BO}_4$  tetrahedra [47]. The Raman spectra of glass sample BST5K1L0.4 doped with 1 wt% of  $\text{La}_2\text{O}_3$  is shown in **Figure 5(b)**. Raman spectra of glass sample BST5K2L0.4 doped with 2 wt%  $\text{La}_2\text{O}_3$  depict three peaks at wavenumbers  $283, 708$  and  $830 \text{ cm}^{-1}$  respectively (**Figure 5(c)**). The peak at  $708 \text{ cm}^{-1}$  is the characteristic of Symmetric breathing vibrations  $\text{BO}_3$  triangles replaced by  $\text{BO}_4$  tetrahedra. An extra peak at low wavenumber,  $283 \text{ cm}^{-1}$  was also observed. This peak occurs due to La-O and K-O (metallic cations) bonding vibrations. **Figure 5(d)** shows Raman spectra of glass sample BST5K5L0.4 doped with 5 wt% of  $\text{La}_2\text{O}_3$ . This spectra represents three peaks at wavenumbers  $288, 697$  and  $841 \text{ cm}^{-1}$  respectively. A shifting in the peak was also observed due to increase in doping concentration of  $\text{La}_2\text{O}_3$ . Raman spectra of glass sample BST5K10L0.4 doped with 10 wt% of  $\text{La}_2\text{O}_3$  are shown in **Figure 5(e)**. Three peaks were also

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

Wave number (cm <sup>-1</sup> )		IR assignments	Raman assignments
IR	Raman		
471 - 523	283 - 292	Vibrations of metal cations such as Ba <sup>2+</sup> , Sr <sup>2+</sup>	Metal cations bond vibrations
704 - 715	675	Bonding of B-O-B linkages (diborate linkage)	metaborate groups
960 - 991	700 - 725	Stretching vibration of B-O-Si linkage	Symmetric breathing vibrations BO <sub>3</sub> triangles replaced by BO <sub>4</sub> tetrahedral units
1196 - 1355	820 - 850	Asymmetric stretching relaxation of the B-O bond of trigonal BO <sub>3</sub> units	symmetric breathing vibrations of six-member rings with one or two BO <sub>3</sub> triangles replaced by BO <sub>4</sub> tetrahedra
2346 - 2380	-	-OH bonding	-
2852 - 2925	-	Hydrogen bonding	-
3467 - 3469	-	Molecular water	-

**Figure 5. Raman spectra of BST borosilicate glass samples (a) BST5K0.4; (b) BST5K1L0.4; (c) BST5K2L0.4; (d) BST-5K5L0.4 and (e) BST5K10L0.4.**

observed at different wavenumbers, 292, 720 and 796 cm<sup>-1</sup> in the Raman spectra of this glass sample. The second peak is closed to the first peak (796 cm<sup>-1</sup>). In other words, we can say that this peak is shifted towards higher wavenumber side because of high doping concentration

**Figure 6. Variation of raman shift with respect to doping concentration of La<sub>2</sub>O<sub>3</sub>.**

of La<sub>2</sub>O<sub>3</sub>. The Raman shifting was observed with increasing the doping concentration of La<sub>2</sub>O<sub>3</sub> which is shown by the two parallel lines in **Figure 5**. The variation of the peak position in Raman spectra was observed with varying concentration of La<sub>2</sub>O<sub>3</sub>. Variation of Raman shift with respect to doping concentration of La<sub>2</sub>O<sub>3</sub> is shown in **Figure 6**. Assignment of Raman bands in the spectra of different glass samples is also listed in **Table 3**. Raman spectra show a shifting in the peaks towards high wavenumber side from 0 to 5 wt% of La<sub>2</sub>O<sub>3</sub> while this shifting is going towards low wavenumber side for 10 wt% of La<sub>2</sub>O<sub>3</sub>.

#### 4. Conclusion

Bulk transparent glasses were prepared successfully in the BST borosilicate glass system with and without doping of La<sub>2</sub>O<sub>3</sub>. The absorption peaks occur in IR spectra is due to different vibrational modes of the borate network and asymmetric stretching relaxation of the B-O bond of

BO<sub>3</sub> units. The addition of La<sub>2</sub>O<sub>3</sub> decreases the sharpness of peaks and increases the broadness of absorption peaks in their IR spectra because La<sub>2</sub>O<sub>3</sub> acts as network modifier for this glass system. Raman spectra of all BST glass samples are observed in several spectral bands. These bands are attributed to symmetric breathing vibrations of six-member rings with one or two BO<sub>3</sub> triangles replaced by BO<sub>4</sub> tetrahedra, La-O and K-O bonding vibrations. As increasing the doping concentration of La<sub>2</sub>O<sub>3</sub> the intensity of the peaks are also increases. These results indicate that the La doped BST borosilicate glass system may be useful for optical applications in the visible to IR region.

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