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Optical and structural properties of ZnO–PbO–B₂O₃ and ZnO–PbO–B₂O₃–SiO₂ glasses

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Abstract

Borate and borosilicate glasses with compositions of $x\text{ZnO}-2x\text{PbO}-(1-3x)\text{B}_2\text{O}_3$ and $x\text{ZnO}-2x\text{PbO}-1/2(1-3x)\text{B}_2\text{O}_3-1/2(1-3x)\text{SiO}_2$ with x varying from 0.1 to 0.26 mole fraction were prepared by the conventional melt quench technique. Optical and structural properties have been determined by using ultraviolet–visible (UV/vis) and Fourier transform infrared (FTIR) spectroscopic techniques. Decreases in the band gap from 3.57 to 2.62 eV for borate glasses and from 3.00 to 2.35 eV for borosilicate glasses with an increase in the metal oxide content is observed. The density and molar volume has also been measured. Increases in density from 3.994 to 6.339 g cm⁻³ for borate and from 4.221 to 6.548 g cm⁻³ for borosilicate glasses are observed with an increase in metal oxide (PbO, ZnO or PbO + ZnO) content. Changes in the atomic structure with composition are observed due to the formation of BO₄⁻ units.

1. Introduction

The study of oxide glasses has received considerable attention due to their structural peculiarities [1, 2]. These glasses have wide applications in the fields of electronics, nuclear and solar energy technologies and acoustic-optic devices [3–7]. Borates and borosilicate glasses containing boron oxide have been widely used for optical lenses with high refractive index and low dispersion characteristics [8]. ZnO–PbO–B₂O₃ glasses have been characterized for a strong tendency for phase separation and are used in glass solders for sealing CTV bulbs, IC packages, glass discharge tubes etc [9, 10].

The structural and physical properties of PbO glasses have been described well by Worrel and Henshell [11]. PbO and ZnO can enter a glass network both as a network former and as a network modifier, which has been described well in [12]. At lower concentrations, PbO modifies the network through forming BO₄ tetrahedra at the rate of two BO₄ groups per PbO molecule [13] and, at higher concentrations, PbO can partly

play the role of a glass-forming oxide in the form of PbO₄ pyramids with Pb²⁺ at the apex of the pyramid [14].

In the present work, an attempt has been made to undertake an optical and structural investigation of ZnO–PbO–B₂O₃ and ZnO–PbO–B₂O₃–SiO₂ glasses with the help of density/molar volume, UV/vis, and FTIR spectroscopy.

2. Experimental procedure

2.1. Sample preparation

Glass samples of compositions $x\text{ZnO}-2x\text{PbO}-(1-3x)\text{B}_2\text{O}_3$ and $x\text{ZnO}-2x\text{PbO}-1/2(1-3x)\text{B}_2\text{O}_3-1/2(1-3x)\text{SiO}_2$ with $x = 0.1-0.26$ mole fraction were prepared (see table 1). The raw materials lead oxide, zinc oxide, boric oxide, and silicon oxide of analar grade were obtained from Aldrich Chemical Company. Appropriate amounts of chemicals were weighed by using an electric balance with an accuracy of 0.001 g. The weighed samples were thoroughly mixed and melted in a Pt crucible in a temperature range of 800–1000 °C for 30 min until a bubble-free liquid was formed. The melt was then poured

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Table 1. Nominal composition (mole fraction) of the glass samples used in this work.

Sample code	ZnO	PbO	B ₂ O ₃	SiO ₂
PbB1	0.100	0.200	0.70	
PbB2	0.130	0.260	0.610	
PbB3	0.210	0.420	0.370	
PbB4	0.240	0.480	0.280	
PbB5	0.260	0.520	0.220	
PbBSi1	0.100	0.200	0.350	0.350
PbBSi2	0.130	0.260	0.305	0.305
PbBSi3	0.210	0.420	0.185	0.185
PbBSi4	0.240	0.480	0.140	0.140
PbBSi5	0.260	0.520	0.110	0.110

into a preheated graphite mold of dimensions $10 \times 10 \times 1 \text{ mm}^3$. The mold was then moved into an annealing furnace at an annealing temperature of 300°C to avoid breaking the sample through residual internal strain. The obtained samples were polished with cerium oxide to obtain maximum flatness.

2.2. Density and molar volume

The density of glass samples at room temperature was measured by the standard principle of Archimedes using a sensitive microbalance with pure benzene as the immersion fluid. The density was calculated according to the known formula

$$D = W_a / (W_a - W_b) \times d \quad (1)$$

where W_a is the weight of the sample in air, W_b is the weight of the sample in benzene, and d is the density of buoyancy at room temperature. All the measurements were made using a digital balance (M/s Sartorius, model BP221S, USA). The accuracy in the measurement of weight was $\pm 0.1 \text{ mg}$. The experiment was repeated five times to get an accurate value of density. The overall accuracy in the density measurement was $\pm 0.5 \text{ kg m}^{-3}$ and, hence, the percentage error in the measurement of density was $\pm 0.006 \text{ g cm}^{-3}$.

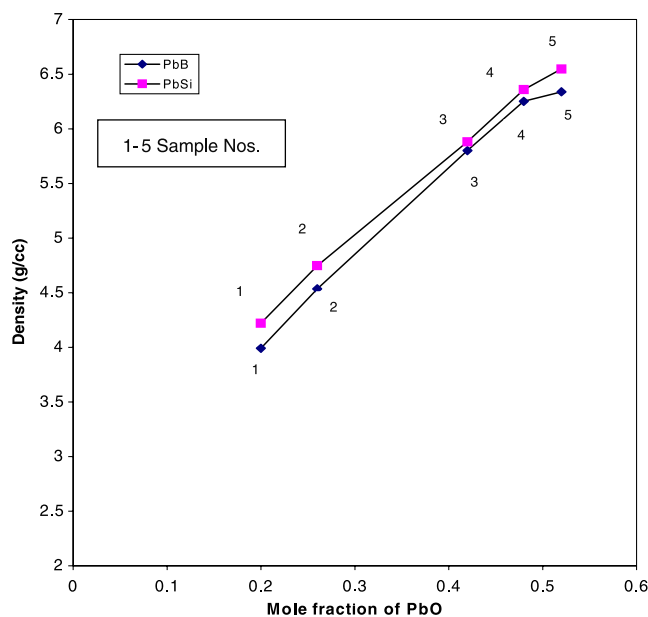
The molar volume is calculated as:

$$V_m = \sum_i M_i / D. \quad (2)$$

M_i denotes the molar mass of the glass, where $M_i = C_i A_i$. Here C_i and A_i are the molar concentrations and molecular weight of the i th component, respectively, and D is the calculated density.

2.3. UV/vis spectroscopy

The optical absorption spectra of these glasses were recorded by using a UV/vis spectrometer (Shimadzu, Japan), in the wavelength range 200–1100 nm at normal incidence. The optical absorption coefficient $\alpha(\omega)$ was calculated for each of the specimens at various photon energies $\hbar(\omega)$ by using the Lambert–Beer relation $I_t = I_0 e^{-\alpha(\omega)d}$, where d is the thickness of the sample; I_0 and I_t are the incident and transmitted photon intensity, respectively. The optical bandgap energy E_g was calculated by interpolation of the linear region to meet the $\hbar\omega$ axis at $(\alpha\hbar\omega) = 0$ [15].

**Figure 1.** Variation in density with mole fraction of PbO.

(This figure is in colour only in the electronic version)

2.4. Infrared spectroscopy

Infrared spectroscopy was carried out at room temperature in the region $400\text{--}4000 \text{ cm}^{-1}$ using a spectrometer of type Shimadzu FTIR-8700. 4.0 mg of each sample was mixed with 20 mg of KBr in an agate mortar and then pressed to a pressure of 100 kg cm^{-2} , and the resulting pellets of 13 mm diameter were used for recording the absorption spectra. For each sample the spectrum represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet.

3. Results and discussion

3.1. Density and molar volume

The change in geometrical configuration, co-ordination number, cross-link density and the dimensions of the interstitial space in the glass decide the density, and therefore the density is a tool in revealing the degree of change in the structure with the glass composition. In borate glasses, the trend in density is controlled by the fraction of four-coordinated borons [16]. It is an established fact that boron can have a coordination number of three and/or four [17–20]. Consequently, boron can have its structure in a triangular and/or tetrahedral form. Tetrahedral groups are more rigid compared to triangular groups. In pure B_2O_3 glasses most of the boron is involved in $[\text{B}_3\text{O}_6]$ boroxol rings [21]. In our present system of $\text{ZnO}\text{--}\text{PbO}\text{--}\text{B}_2\text{O}_3$ glasses, an increase in density with increased modifier content of ZnO and PbO is observed and is shown in figure 1. As more PbO and ZnO is added, more boron atoms go into four-coordination. The separation between BO_4 tetrahedra and a neighboring BO_3 should be less than the separation between two adjacent BO_3 triangles, i.e. the conversion of three-coordinated boron to a four-coordinated boron is the cause of network contraction [22]. With the addition of ZnO and PbO,

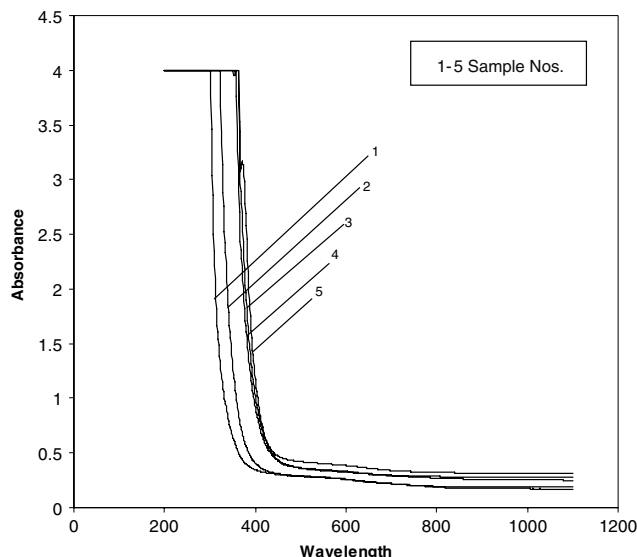


Figure 2. Optical absorption as a function of wavelength for ZnO–PbO–B₂O₃ glasses.

breaking of these rings and an increase in the formation of [BO₄] units was observed. Moreover, the maximum amount of [BO₄] units at about 50 mol% of PbO and a decrease for higher PbO content was observed [23]. Singh and Bhatti [24] also observed an increase in the fraction of [BO₄] units at the expense of [BO₃] units with an increase in the mole fraction of ZnO in zinc oxide borate glasses.

In ZnO–PbO–B₂O₃–SiO₂ glasses, an increase in density with increased modifier content is observed. It is interesting to note that, as silica is added to zinc lead borate glasses, the density increases even though the density of silica (2.20 g cm⁻³) is less than that of the borate glasses (2.38 g cm⁻³). Similar results have been seen for the addition of silicon to sodium borate glasses [25]. It was observed that, as silica is added to the glasses, f_2 is able to achieve a higher value. The f_2 borate tetrahedron is denser than any of the other borate units. This may also be the case in our system, which accounts for the increase in [BO₄] units and hence the density.

3.2. Bandgap energy

The optical absorption spectra recorded as a function of ZnO–PbO–B₂O₃ and ZnO–PbO–B₂O₃–SiO₂ glasses are shown in figures 2 and 3, respectively. These figures show that the absorption edges are not sharp, which is an indication of the glassy or amorphous nature of our samples.

It is clear from the spectra (figures 2 and 3) that the region of high absorption of all the glass samples for both series in the ultraviolet range seems to move to longer wavelengths. Such a change has already been reported for the (PbO–Bi₂O₃–B₂O₃) [26] glass series. A soft fall in absorption spectra (in figure 3) of sample 5 at a wavelength of about 475 nm is observed, which can be attributed to defects. As for the studied glass compositions, a pronounced increase in absorption in the wavelength region from 400 to 700 nm indicates the formation of hole centers (HC) like an OHC (oxygen hole center) or a BOHC (boron oxygen hole center) [27].

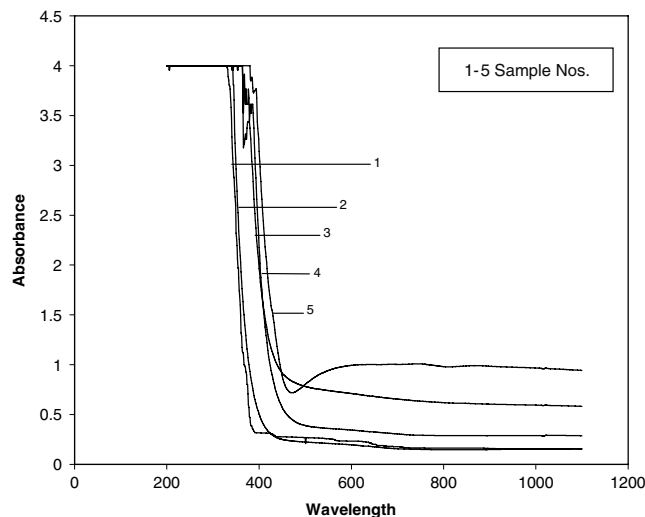


Figure 3. Optical absorption as a function of wavelength for ZnO–PbO–B₂O₃–SiO₂ glasses.

Measurement of the optical absorption and particularly the absorption edge is important, especially in connection with the theory of the electronic structure of amorphous materials. The absorption edge in disordered materials at a higher level of absorption ($\alpha > 10^4$ cm⁻¹) is usually interpreted in terms of indirect transitions across an optical gap. For many amorphous and glassy materials in which the optical transitions are indirect, this is found to obey the relation suggested by Davis and Mott [28]:

$$\alpha\omega = \beta(\hbar\omega - E_{\text{opt}})^2/\hbar\omega$$

where $\hbar\omega$ is the absorption coefficient, β is a constant, E_{opt} is the optical gap and $\hbar\omega$ is the photon energy of the incident radiation. The values of E_{opt} (determined by plotting $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ and extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = 0$) for the glass samples are listed in table 2. It is clear from table 2 that the values of E_{opt} for the glass samples of both series decreased with an increase in PbO and ZnO content. It is obvious from the above observation that the value of the optical bandgap energy is dependent on the glass composition. Similar results have been reported by other workers for (PbO–Bi₂O₃–B₂O₃) [26, 29, 30].

The absorption characteristics of these glasses may be described with the generally accepted qualitative understanding that the absorption edge is determined by the oxygen bond strength in the glass-forming network; for instance, the formation of bridging oxygen changes the absorption characteristics.

In our present system of glasses, the possible explanation for the shift of the absorption edge to a higher wavelength with increasing PbO and ZnO content is the increase in the oxygen environment, and hence an increase in the formation of bridging oxygen (BO₄ units) is expected.

3.3. Fourier transform infrared spectroscopy

3.3.1. FTIR spectra of ZnO–PbO–B₂O₃ glasses. The infrared absorption spectra of the glasses under investigation

Table 2. Thickness, density, molar volume and energy band gap, along with standard deviation of the studied glass samples. The errors in the measurement of thickness, density and absorption coefficient are estimated to be $a \pm 10 \mu\text{m}$, $\pm 0.006 \text{ g cm}^{-3}$ and ± 0.0089 , respectively.

Sample no.	Thickness (t) (cm)	Density (ρ) (g cm^{-3})	Molar volume (V_m) (cm^{-3})	Energy band gap (E_g) (eV)
PbB1	0.193	3.994	25.416	3.57 ± 0.013
PbB2	0.206	4.625	24.017	3.02 ± 0.020
PbB3	0.180	5.788	23.599	2.85 ± 0.016
PbB4	0.182	6.251	23.382	2.72 ± 0.015
PbB5	0.132	6.339	24.063	2.62 ± 0.018
PbBSi1	0.158	4.221	23.258	3.00 ± 0.012
PbBSi2	0.170	4.707	22.981	2.85 ± 0.008
PbBSi3	0.157	5.882	22.922	2.62 ± 0.017
PbBSi4	0.110	6.358	22.778	2.55 ± 0.019
PbBSi5	0.135	6.548	23.135	2.35 ± 0.016

Table 3. Assignment of the infrared absorption band of the studied glasses.

Peak position (cm^{-1})	Assignment
PbB glasses	
(1) 3600–3750	OH-group
(2) 3200–3500	Molecular water
(3) 2700–3000	Hydrogen bonding
(4) 1338, 1348	Presence of pyroborate, orthoborate and groups containing BO_3^- units
(5) 1150–1300	B–O bond stretching vibrations and B–O bridging b/w B_3O_6 rings and BO_3 triangles
(6) 964	B–O–B linkage
(7) 875	Stretching vibrations of tetrahedral BO_4^- units
(8) 420	Vibration of metal cations such as Pb^{2+} , Zn^{2+}
PbBSi glasses	
(1) 1250–1500	BO_3 stretching
(2) 700–1200	Composites of two silicate chains and borate phases (mainly BO_4)
(3) 708	BO_4 stretching
(4) 885	Stretching vibrations of BO_4^- units formation
(5) 420	Vibrations of metal cations such as Pb^{2+} , Zn^{2+}

have been recorded in order to obtain information about the possible changes of vibrational spectra due to the process of structural grouping rearrangements with a change in glass composition. Important changes in the properties of glass can occur as a result of structural transformations [31]. B_2O_3 is a well-known network former with BO_3 structural units. The presence of BO_4 units is evident in these glasses from the study of IR spectra. The infrared spectra of $\text{ZnO-PbO-B}_2\text{O}_3$ glasses (figure 4) show three main groups of absorption bands: in the mid-infrared region at 700 cm^{-1} , between 800 and 1200 cm^{-1} , and between 1200 and 1500 cm^{-1} (see table 3). Other weaker bands observed at various frequencies for these glasses are also present. It is generally accepted that the broad absorption region at $1200\text{--}1450 \text{ cm}^{-1}$ is attributed to B–O bond stretching of trigonal BO_3 units, and that the absorption region at $850\text{--}1100 \text{ cm}^{-1}$ originates from B–O bond stretching of tetrahedral BO_4 units [28, 29]. The band at 710 cm^{-1} is assigned to bond bending vibrations of B–O–B linkages of the boron–oxygen network [32–34].

The broad composition bands extending from 3200 to 3600 cm^{-1} are attributed to hydroxyl or water groups [35]. However, Doremns and co-workers [36, 37] have divided the broad water bands into:

- peak $2700\text{--}3000 \text{ cm}^{-1}$ —originating from hydrogen bonding;
- peak $3200\text{--}3500 \text{ cm}^{-1}$ —originating from molecular water; and
- peak $3600\text{--}3750 \text{ cm}^{-1}$ —originating from OH-groups.

In our system, closely lying peaks at $1338, 1348 \text{ cm}^{-1}$ show the presence of pyroborate, orthoborate and all borate groups containing BO_3^- units [12, 38].

A strong band between 1300 and 1150 cm^{-1} is attributed to B–O bond stretching vibrations involving mainly the linkages between oxygen and different groups, as well as the B–O bridging between B_3O_6 rings and BO_3 triangles [12, 38].

A broad weaker band appeared at 964 cm^{-1} in the sample PbB1. This band at 964 cm^{-1} is attributed to the B–O–B linkage (diborate linkage), in which both boron atoms are tetrahedrally coordinated and triborate superstructural units [39]. It is clearly observed from the spectra that, with addition of PbO modifying content, this band is growing; this clearly concludes an increase in BO_4 units with PbO content. Bands shifted to $892, 887$ and 875 cm^{-1} in samples PbB3, PbB4 and PbB5, respectively, are attributed to the stretching vibrations of tetrahedral BO_4^- units [40]. This is in accordance with our results for density and bandgap energy; that is, the

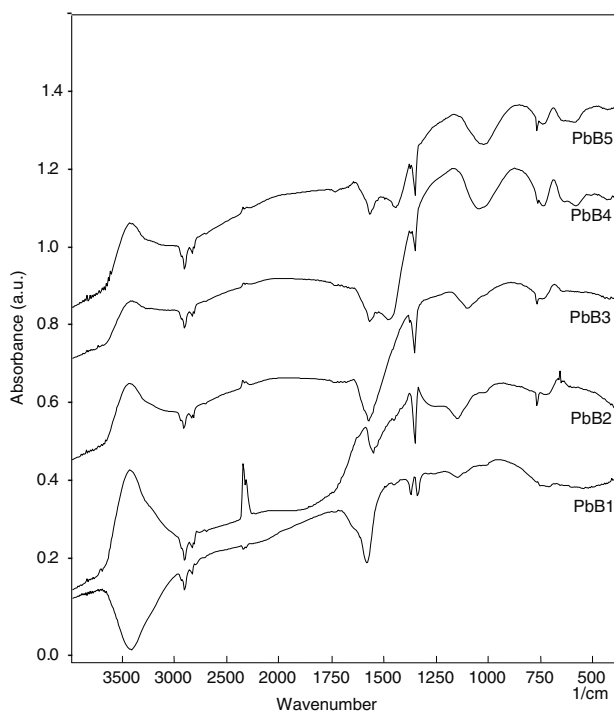


Figure 4. The infrared spectra of zinc lead borate glasses.

formation of BO_4 units at the expense of BO_3 units with an increase in ZnO and PbO content.

The absorption peaks around 420 cm^{-1} , which are more prominent in PbB4 and PbB5, are attributed to the vibration of metal cations such as Pb^{2+} and Zn^{2+} [12, 14].

3.3.2. IR spectra of ZnO–PbO– B_2O_3 – SiO_2 glasses. It is generally accepted that the building blocks of silicate glasses must be SiO_4 tetrahedra, and this view is supported by the general similarity of the IR spectra [41, 42] with the IR spectra of crystalline silicates.

In the glassy state, different units have somewhat different structures, and hence they vibrate at slightly different frequencies. When all the frequencies are superimposed on the spectrum, the peaks are observed to be broad. It is important to mention that the general nature of the normal mode is not altered greatly by the disorder, so that strong modes of vibration remain strong and weak modes remain weak [41, 42].

The detailed IR absorption spectra are shown in figure 5.

Some of the borate groups, especially those due to BO_4 tetrahedra, gave absorption bands due to the silicate groups. The net result is that the absorption bands extending from 700 to about 1200 cm^{-1} are really composite ones of the two silicate chains and borate phase (mainly BO_4) groups. The absorption bands that are observed at 1250 – 1500 cm^{-1} are mainly due to BO_3 stretching, and this band is seen to shift towards 1200 cm^{-1} with an increase in ZnO and PbO content, which is attributed to the conversion of BO_3 units to BO_4 units (see table 3). The assumption regarding the vibrational frequencies of a borate chain can be supported by the work of Krongh-Moe [43] and Chryssikos *et al* [44]. It is observed that the frequencies of the borate chains are very close and

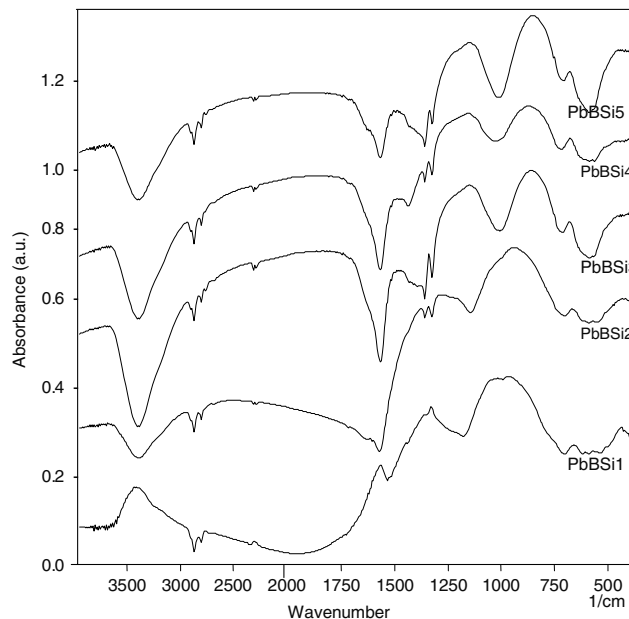


Figure 5. The IR spectra of zinc lead borosilicate glasses.

interfere with the frequencies of the silicate chains. It is thus expected that silicate glasses containing varying amounts of B_2O_3 should contain composite vibrational modes due to the combined presence of both silicate and borate chains to varying degrees.

A significant peak at 686 cm^{-1} in PbBSi1 shifts towards lower energy at 694 cm^{-1} in PbBSi2, 705 cm^{-1} in PbBSi3, 707 cm^{-1} in BS4 and 708 cm^{-1} in PbBSi5, which is attributed to the trigonal boron atoms and oxygen bridges between trigonal atoms (BO_4 stretching) [45, 46].

The comparison of spectra indicates that the main band around 972 cm^{-1} in the sample PbBSi1 is growing and shifts continuously towards lower wavenumber, reaching 885 cm^{-1} as more PbO and ZnO content is added. This clearly shows the formation of more BO_4 units with an increase in PbO and ZnO content. The lead ions are likely to form compact PbO_2 , pyramidal units taking on a more covalent arrangement [47].

The absorption peaks at around 420 cm^{-1} are due to the vibration of cations such as Pb^{2+} and Zn^{2+} [12, 16], and hence network-modifying behavior is observed in which these ions enter the interstices of the network. This supports our results, and network-modifying behavior of $\text{PbO} \leq 52\text{ mol}\%$ is observed.

4. Conclusions

An increase in Zn and Pb oxide causes compaction of B_2O_3 by breaking the bonds between the trigonal elements, allowing the formation of BO_4 units, and in this way increases the density and reduces the bandgap energy of ZnO–PbO– B_2O_3 glasses. By spectroscopic study it is concluded that, for ZnO–PbO– B_2O_3 glasses, the main groups such as BO_3 and BO_4 act as network structural groups, while PbO and ZnO appear in interstitial positions and BO_4 units increase with an increase in PbO and ZnO content. Similar trends for density

and bandgap energy are observed in ZnO–PbO–B₂O₃–SiO₂ glasses. A comparison of both series shows that the density of borosilicate glasses is greater and the bandgap energy is less than borate glasses with the same ZnO and PbO content, showing the more compact structure of borosilicate glasses than borate glasses. The results obtained from the density and bandgap energy measurements and FTIR spectroscopy are in agreement with each other and give approximately the similar information about the present glasses.

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