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Review Article

A Review on Infrared Spectroscopy of Borate Glasses with Effects of Different Additives

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Borate glasses are the technologically important class of glasses and play a significant role in various applications. Borate glasses contain planar BO_3 groups as structural units, rather than tetrahedral SiO_4 groups. The oxygen atoms are, as in SiO_2, again connected to two network-forming atoms, in case of boron. The radial distribution analysis describes the B_2O_3 glass structure as consisting of boroxol rings, that is, planar rings containing three boron atoms and three oxygen atoms. The network forming of the B_2O_3 and the SiO_4 is affected with the addition of some metal cation additives Pb, Zn, Cd, and so forth. These additives also work as a network modifier and a nucleating agent for crystallization of glass. Therefore, the optical properties of the borate glasses have been changed significantly.

1. Introduction

Glasses are supercooled liquids, transparent, and amorphous in nature. They are inorganic product of fusion which has cooled to a rigid condition without any crystallization. The main distinction between glass and crystals is the presence of long-range order in the crystal structure [1]. The optimization of such properties as a function of composition and other processing parameters requires a good knowledge of the microscopic glassy structure. For many years, glasses containing transition metal ions have attracted attention because of their potential applications in electrochemical, electronic, and electro-optic devices. A host of borate rich glasses containing alkaline earth oxides along with ZnO, PbO, TeO_2 Bi_2O_3, MgO, CaO, SrO, and BaO as glass modifiers are optimistic materials for their probable applications in the fields of optical communications (optical fibers), laser hosts, optical filters, X- and γ-ray absorbers, photonic devices, and so forth [2–8]. Infrared spectroscopy (IR) is an important tool for understanding the structure and dynamics of amorphous materials. It is also used to assign the observed absorption peaks to the proper vibration of the atoms in geometric grouping. The spectra of many solids variables can affect the absorption peaks, and the assignment of vibration peaks of the atoms is very difficult. Usually, the method of repeated occurrence is followed in analysing the IR spectrum of solid materials [9, 10]. In this spectroscopy, the nature of the light matter interaction is not same as in Raman spectroscopy, and the fundamental differences of the two processes determine the selection rules, which control Raman or IR activity of normal mode of vibrations. Interaction of IR radiation with a normal mode of vibration only occurs when the electric field of radiation oscillates with same frequency as instant dipoles caused by atomic vibrations. A normal vibration is therefore, IR active only if a change in the dipole moment of the vibration occurs and is a one photon process, as only photon is absorbed [11]. Therefore, IR spectra give additional information rather than Raman spectra by which the symmetries of normal modes of vibration of molecules and crystal lattices are determined [12–15]. The spectrum of a sample is compared with the spectrum of a large number of compounds containing a common atom group or groups. Certain absorption peaks are common to certain groups and are assigned the vibration characteristics of these atom groups. Borate glasses have been the subject of numerous infrared studies because of their

structural peculiarities [16–23]. A widespread set of very different borate glasses with optical, magnetic, superionic conductivity, and other technologically interesting properties are currently produced [24, 25].

2. Infrared Spectroscopy

2.1. Lead Borate Glasses. During the past five decades, many efforts have been taken to realize the roles of PbO in glass networks using different techniques [26–30]. PbO-B_2O_3 glasses are of technological interests owing to their unique properties such as their low melting temperatures, wide glass formation regions, and good radiation shielding properties, [31–34]. IR spectra of the various PbO-B_2O_3 glasses are shown in Figure 1. The nomenclature of these glasses has been listed in Table 1. IR spectra of pure B_2O_3 gives two absorption band at wavenumbers 1300–1700 and 720 cm^{-1}. The absorption bands at wavenumbers range of 1300–1700 cm^{-1} are attributed to the bending vibration and stretching vibration of B–O–B in [BO_3] triangles [35, 36]. The addition of 10–20 mol% PbO does not affect borate network. The absorption bands below 620 cm^{-1} are attributed to vibration of PbO [37]. Therefore, PbO acts as a network participant filled in the interspaces of [BO_3] units in the form of Pb^{2+} ions (Figure 2(a)). The electrostatic fields of the strongly polarizing Pb^{2+} ions are affected with increase of PbO content, which might serve to increase the wavenumber of B–O–B bending vibrations [38]. Absorption band between 900 and 950 cm^{-1} was observed due to the stretching vibration of [BO_4] units [39]. This indicates that the addition of PbO leads to the conversion of [BO_3] units to [BO_4] units in borate glass, which is also confirmed in glass system of CeO_2-B_2O_3 and La_2O_3-B_2O_3 [39–41]. Moreover, with increase of the content of PbO from 30 to 50 mol%, the frequency of [BO_4] unit shifts from 945 cm^{-1} to a lower wavenumber 931 cm^{-1}. This may be due to the formation of bridging bonds of Pb–O–B (Figure 2(b)). Since the stretching force constant of Pb–O bonding is substantially lower than that of the B–O, the stretching frequency of Pb–O–B might tend to be lower. Another dominant shift in the glass (30 PbO 50 mol%) is the sharp decreasing trend from 1360 to 1315 cm^{-1}. Lorösch et al. [42] attribute the broad bond of about 1300 cm^{-1} to the vibration of B–O rings composed by [BO_3] and [BO_4] units. Therefore, the presumption that B–O rings are formed in the glasses by the connection of the bridge oxygen ions between [BO_3] triangles and [BO_4] tetrahedrons can be made (Figure 2(c)), due to the decreasing frequency of the stretching vibration of B–O–B. Subsequent additions of PbO (60–80 mol%) have the same effect on the structure of glasses. The biggest shift of 916–876 cm^{-1}, observed in PB-8 sample, indicates that when the content of PbO is up to 80 mol%, the content of Pb–O–B becomes dominant in the glass network structure. It can be presumed that the increasing polarization of Pb^{2+} with the increase content of PbO contributes to the formation of Pb^{2+}-modified boron–oxygen rings and their chains. New bands at 1016 and 1020 cm^{-1} of PB-6 and PB-7 glasses can be attributed to

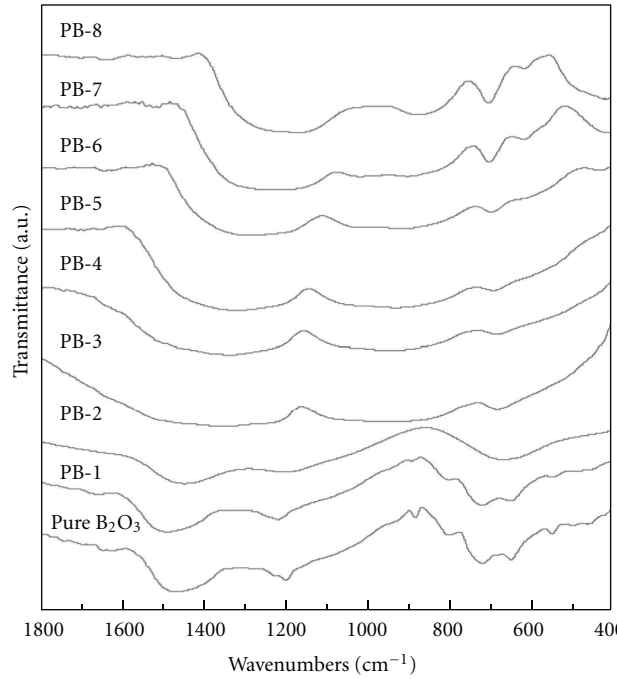

Figure 1: Infrared absorption spectra of PbO-B_2O_3 glasses [34].

the absorption vibration of [BO_4] units [43], indicating the increasing content of [BO_4] units in glassy networks. The absorptions of PbO (below 620 cm^{-1}) show that PbO is one of the good network former of glasses in this region. Apart from the above discussions, it can be concluded that as PbO content exceeds 60 mol%; five bridging oxygens may be involved in glass networks: B–O–B in [BO_3] and [BO_4] units, the bridging oxygen ions between [BO_3] and [BO_4] units, Pb–O–B in bridge connection of [BO_3] and [BO_4] units, and Pb–O in covalent bonds (Figure 2(d)). Molecular dynamics represented that the radial distribution pattern is consistent with structures having a low concentration of such rings [40]. Although borate glass forms a three-dimensional network, its viscosity is substantially lower than that of silicate glass. Again, addition of alkali lowers the viscosity of the melt, but the effect is by no means as dramatic as for silicate glass [44, 45]. Introduction of alkali or moisture to alkali metal borate glasses causes some of the three-coordinate boron atoms to become four coordinate [46, 47]. The addition of various constituents in PbO-B_2O_3 also affects the structural properties of these glasses.

2.2. Barium Lead Borate Glasses. IR studies of BaO-PbO-B_2O_3 glasses were reported by Schwarz and Ticha. In this study, it is seen that structural groups BO_3 and BO_4 can form borate networks [48]. These structural groups makes the complexity due to extensively overlapping bands, and they cover the spectral range from 600 cm^{-1} to 1500 cm^{-1} [56]. Figure 3 (1, 2–9) show the IR spectra of various BaO-PbO-B_2O_3 glass samples. The compositional distribution of these glasses has been listed in Table 2. B–O stretching of trigonal BO_3 units of vibrations 1200–1500 cm^{-1} and 850–1200 cm^{-1}

Table 1: The molar compositions of PbO-B_2O_3 of various glass samples [34].

No.	PB-1	PB-2	PB-3	PB-4	PB-5	PB-6	PB-7	PB-8
Compositions	0.1PbO $0.9B_2O_3$	0.2PbO $0.8B_2O_3$	0.3PbO $0.7B_2O_3$	0.4PbO $0.6B_2O_3$	0.5PbO $0.5B_2O_3$	0.6PbO $0.4B_2O_3$	0.7PbO $0.3B_2O_3$	0.8PbO $0.2B_2O_3$

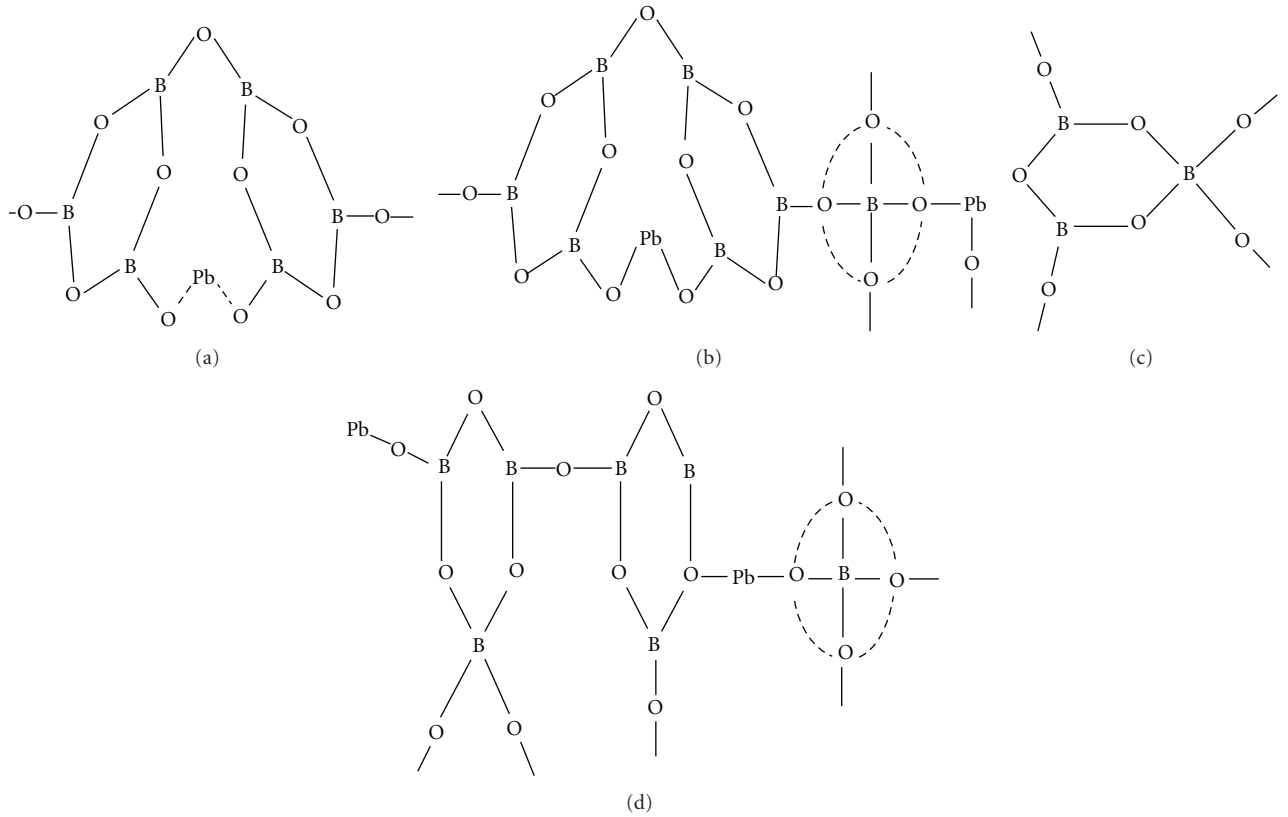

Figure 2: Possible structural units of PbO-B_2O_3 glasses: (a) three coordinated boroxol rings modified by Pb^{2+}; (b) formation of Pb–O–B covalent bands; (c) bridge networks between $[BO_3]$ and $[BO_4]$ units; (d) complex structures of Pb^{2+}-modified boron–oxygen rings and chains [34].

is due to B–O stretching of tetrahedral BO_4^- units, while 600–800 cm^{-1} is due to bonding vibrations of B–O–B groups in various borate segments [57–59]. The IR response in the other two spectral regions changes significantly with the increase of PbO content. The intensity of two broad IR features, 850–1200 cm^{-1}, due to BO_4^- units decreases with increase of PbO content. Thus, PbO enters to the network as a network former. A spectral band at 806 cm^{-1} occurred due to boroxol ring formation in the glassy matrix [60].

2.3. Cadmium Lead Borate Glasses. Alemi et al. give investigations of Cd-doped Pb_2O_3-B_2O_3 glasses by IR spectra in the range of 400–4000 cm^{-1} and show their structures in Figure 4 [49]. In this study, the formation of boroxol ring and tetrahedral coordination inside the glassy matrix was not observed in IR spectra of these glasses, while the conversion of threefold to fourfold coordination of boron atoms in the structure of glasses was observed. The progressive substitution of boroxol rings by triborate and tetraborate groups is observed. In pure B_2O_3 glass, the frequency 806 cm^{-1} is a characteristic of boroxol ring. The vanishing of 806 cm^{-1} means no boroxol ring in the glass structure. This type of behavior is also observed in B_2O_3-Li_2O glasses [67–69]. The IR spectra show the number of spectral bands which occurs due to various vibrational modes (symmetric $(BO_3)^{3-}$ triangles, $(BO_4)^{4-}$ tetrahedral and asymmetric $(BO_3)^{3-}$ units (nonbridging oxygen). A broad spectral band between the ranges from 3200 to 3600 cm^{-1} is attributed to hydroxyl or water groups [70, 71]. The structure of boron oxide glass consists of a random network of planar BO_3 triangles with a certain fraction of six-membered (boroxol) rings (Krogh Moe's model) [72]. These spectral bands are also seen in the borate glasses studied by Ghoneim et al. [73]. The spectral band in range from 1200 to 1600 cm^{-1} is due to the asymmetric stretching relaxation of the B–O band of trigonal BO_3 units, while the spectral bands lies between 800 and 1200 cm^{-1}, and around 700 cm^{-1} is occurred due to the B–O bond stretching of the tetrahedral BO_4 units and bending of B–O–B linkages, respectively. The

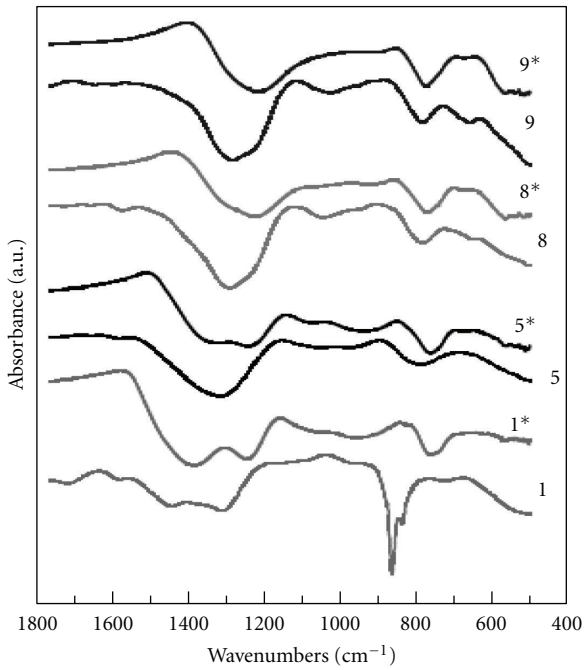

Figure 3: Raman and infrared reflectivity spectra of glass samples (*represents the Raman spectra which are not considered here) [48].

Table 2: Compositional distribution of BaO-PbO-B_2O_3 glasses [48].

No.	Chemical composition		
	PbO	BaO	B_2O_3
1	10	10	80
5	30	10	60
8	50	10	40
9	60	10	30

absorption peak at 1307 cm^{-1} is the characteristic of B(III)–O–B(IV) stretching vibrations. B–O stretching vibrations of trigonal $(BO_3)^{3-}$ units in metaborates, pyroborates, and orthoborates are assigned at around 1357 cm^{-1} [74]. In these glasses, the boron is tetrahedrally surrounded by four oxygen atoms [75]. The band around 1292 cm^{-1} is due to B–O asymmetric stretching of BO_3 unit. The band at 1234 cm^{-1} was found to be B–O stretching vibrations of $(BO_3)^{3-}$ unit in metaborate chains and orthoborates. Nonbridging oxygen in the form of BO_4 vibrations was observed at 1005 cm^{-1} [76]. The absorption around 1000 cm^{-1} indicates the formation of diborate groups in the glassy matrix. The band at about 995 cm^{-1} is attributed to a stretching vibration of B–O–Si linkage in the glass system Na_2O-B_2O_3-SiO_2.

2.4. MoO_3-Doped Lead Borate Glasses. The structural studies of MoO_3-doped Pb_2O_3-B_2O_3 glasses by IR spectra show various absorption bands which are characteristics of different vibrational modes. The absorption band is at 700 cm^{-1} which indicates the presence of BO_3 or boroxol groups in glass system containing 80% PbO and 20% B_2O_3. The absorption bands ranges from 740 to 1120 cm^{-1} and from 1130 to 1520 cm^{-1} which are attributed to the abundance of BO_4 groups and BO_3 groups [76, 98–101]. The presence of water in glassy matrix was confirmed by the IR study in this system, and these bands lies in the range from 3200 to 3640 cm^{-1}, which is related to the vibrations of hydrogen bonding, molecular water, BOH, or hydroxyl groups [77–79]. Thus, PbO may act as a network modifier in the same way as alkali oxide disrupting the bonds connecting neighboring SiO_4, BO_3, and BO_4 groups. The ionic cross-links provided by lead ions (Pb^{2+}) are stronger than those provided by alkali ions. On the other hand, PbO can be incorporated into the glass as network forming Pb–O groups (PbO_4 and PbO_3) [102, 103]. Pb_2O_3-B_2O_3 glasses show the formation of BO_4 groups proceeds at the rate of two tetrahedral added oxygen. This formation of tetrahedral is reduced with increasing the content of PbO above 20% because some of the lead atoms now participate in the network as PbO_4 pyramids with the Pb atom forming the apex of the pyramid. These pyramids are assumed to preferentially bridge to BO_3 rather than BO_4 units [6, 104]. The change in electron distribution in the B_3–O bonds is at 30% of PbO, which probably results from the replacement of B_3–O–B_4 by B_3–O–Pb bonds. The effect of the increase in the MoO_3 content is specifically reflected first in the far-infrared spectra [105, 106].

Various glasses were synthesized in the glass system 30PbO-4MoO_3-$(66-x)B_2O_3 : xTiO_2$ $(0.0 \leq x \geq 2.0)$ [50], and its detailed description was given as

T_0: 30PbO-4MoO_3-66.0B_2O_3,

T_2: 30PbO-4MoO_3-65.8B_2O_3 : 0.2TiO_2,

T_4: 30PbO-4MoO_3-65.6B2O3 : 0.4TiO_2,

T_6: 30PbO-4MoO3-65.4B_2O_3 : 0.6TiO_2,

T_8: 30PbO-4MoO_3-65.2B_2O_3 : 0.8TiO_2,

T_{10}: 30PbO-4MoO_3-65.0B_2O_3 : 1.0TiO_2,

T_{15}: 30PbO-4MoO_3-64.5B_2O_3 : 1.5TiO_2,

T_{20}: 30PbO-4MoO_3-64.0B_2O_3 : 2.0TiO_2.

The IR spectra of these glasses were recorded in the wavenumber range of 400–1600 cm^{-1} as shown in Figure 5. The absorption bands in the range lie from 1300 to 1400 cm^{-1}, 1000–1200 cm^{-1}, and another band lies at about 710 cm^{-1}. These bands were assigned due to stretching relaxations of B–O bonds of the trigonal BO_3 units, vibrations of the BO_4 structural units, and bending vibrations of B–O–B linkages, respectively [107]. An absorption band near 470 cm^{-1} associated with vibrations of PbO_4 structural units in IR spectra of all the glasses. Two new bands were observed due to υ_1 and υ_3 vibrational modes of MoO_4^{2-} tetrahedral units near 890 and 836 cm^{-1} [108, 109]. The intensity of the absorption bands due to MoO_4^{2-} tetrahedral units was observed to decrease and the band at 890 cm^{-1} was found to be shifted slightly towards the higher frequency side, whereas the band at 836 cm^{-1} was observed and to be shifted towards lower frequency with increasing the concentration

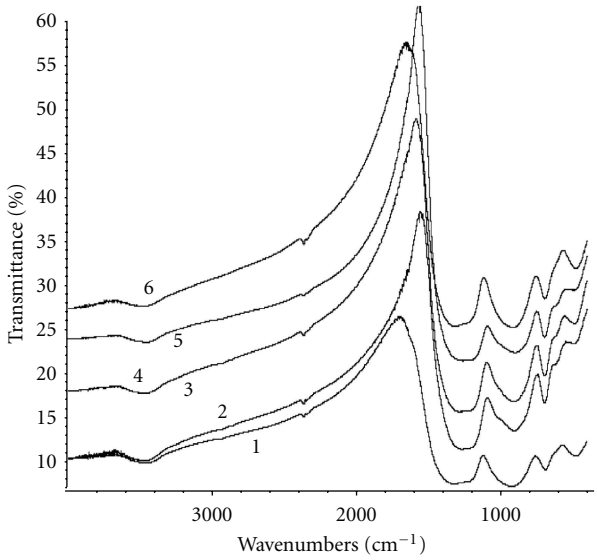

FIGURE 4: IR spectra of CdO doped lead borate (xPbO$_2$-(50-x)CdO-50B$_2$O$_3$) glasses (1: $x = 10$, 2: $x = 15$, 3: $x = 20$, 4: $x = 25$, 5: $x = 30$, and 6: $x = 35$) [49].

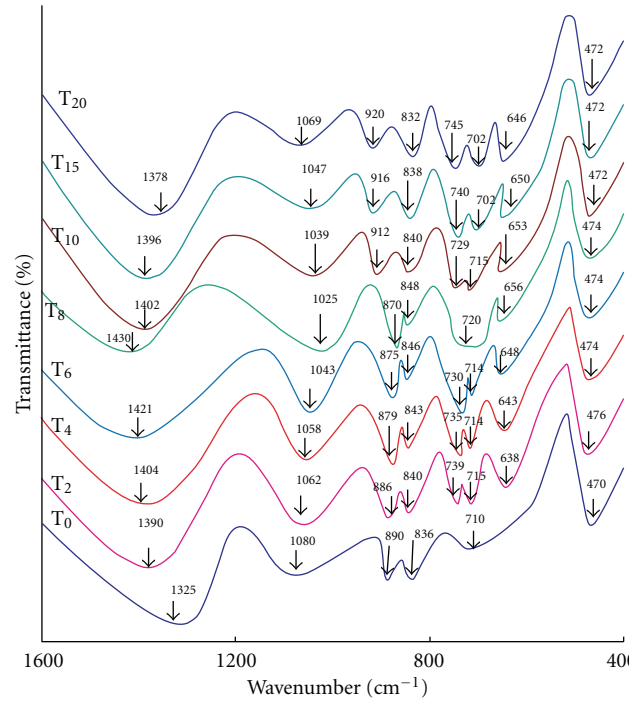

FIGURE 5: IR spectra of PbO-MoO$_3$-B$_2$O$_3$:TiO$_2$ glasses [50].

of the dopant TiO$_2$ beyond 0.8 mol%. The intensity of the band associated with BO$_3$ structural units was observed to increase at the expense of the band arising from BO$_4$ units. The IR spectrum of glass T$_2$ exhibited two additional prominent bands at 739 and 638 cm^{-1}. With increasing the concentration of TiO$_2$ up to 0.8 mol%, the intensity of the band at 739 was observed to increase and shifted towards low-frequency region. With further increase in the concentration of TiO$_2$, a reversal trend in the intensity of these two bands has been observed.

2.5. Zinc Lead Borate Glasses. Motke et al. [51] reported the IR study of zinc lead borate glasses in wavenumber range of 400–4000 cm^{-1}(Figure 6). (A) 20PbO$_2$-30ZnO-50B$_2$O$_3$; (B) 25PbO$_2$-25ZnO-50B$_2$O$_3$; (C) 30PbO$_2$-20ZnO-50B$_2$O$_3$; (D) 35PbO$_2$-15ZnO-50B$_2$O$_3$; (E) 40PbO$_2$-10ZnO-50B$_2$O$_3$. This study reaches to conclusion of various vibration groups which are responsible for making their structure. An absorption band at 3450 cm^{-1} was occurred due to O–H stretching vibration [110–112]. The presence of structural units such as symmetric $(BO_3)^{3-}$ triangles, BO_4^- tetrahedral, and asymmetric $(BO_3)^{3-}$ units (i.e., nonbridging oxygen) were also confirmed in each glass samples, but ZnO does not affect the structure [103]. Similar vibrational studies had been also reported by Kamitsos et al., Ezz-Eldin et al., and Davis and Mott [113–115]. In these studies, it was found that the first structural group of bands lies within wavenumber range of 1200–1600 cm^{-1} which occurred due to the asymmetric stretching relaxation of the B–O band of trigonal BO$_3$ units and the vibrational group from 800 to 1200 cm^{-1}. This vibrational group assigned is due to the B–O bond stretching of the tetrahedral BO$_4$ units [116, 117]. The third group was observed at around 700 cm^{-1} and is due to bending of B–O–B linkages in the borate networks [118, 119]. This glass system shows the absence of boroxol ring formation. But the successive substitution of boroxol rings by triborate and tetraborate groups is observed. The pure B$_2$O$_3$ glasses consist of BO$_3$ and BO$_4$ groups. These groups may be attached in the form of random network. This corresponds to the progressive substitution of boroxol ring by BO$_3$ and BO$_4$ groups [120–122]. The absorption band near 1357 cm^{-1} in 40 mol% glass was assigned to B–O stretching vibrations of trigonal $(BO_3)^{3-}$ units in metaborates, pyroborates, and orthoborates [123]. There was a change in the coordination number of boron with addition of boron trioxide to borate glasses. In these glasses, the boron is tetrahedrally surrounded by four oxygen atoms [124]. The band around 1292 cm^{-1} is due to B–O asymmetric stretching of BO$_3$ unit [125], and bands around 1234 cm^{-1} was arisen by B–O stretching vibrations of $(BO_3)^{3-}$ unit in metaborate chains and orthoborates [126]. Vibrations of some boron atoms attached to nonbridging oxygen in the form of BO$_4$ vibration were assigned band at 1004 cm^{-1} [36]. The formation of diborate group in present glasses had been represented by absorption around 1000 cm^{-1}. IR spectra showed the band at about 995 cm^{-1} was attributed to a stretching vibration of B–O–Si linkage [82]. The absorption band is at 993 cm^{-1} in the IR spectra; these glasses may be attributed to a stretching vibration of B–O–M (B–O–Pb) linkage, where M represents a metal ion, while band at 694 cm^{-1} was due to combined vibrations of BO$_4$ and PbO$_4$ groups [83–85]. The structure of the borate glasses was also affected by the different rates of cooling of the melt and quenching temperature [127]. In 40 mol% PbO content glass, the absorption at 616 cm^{-1} is due to

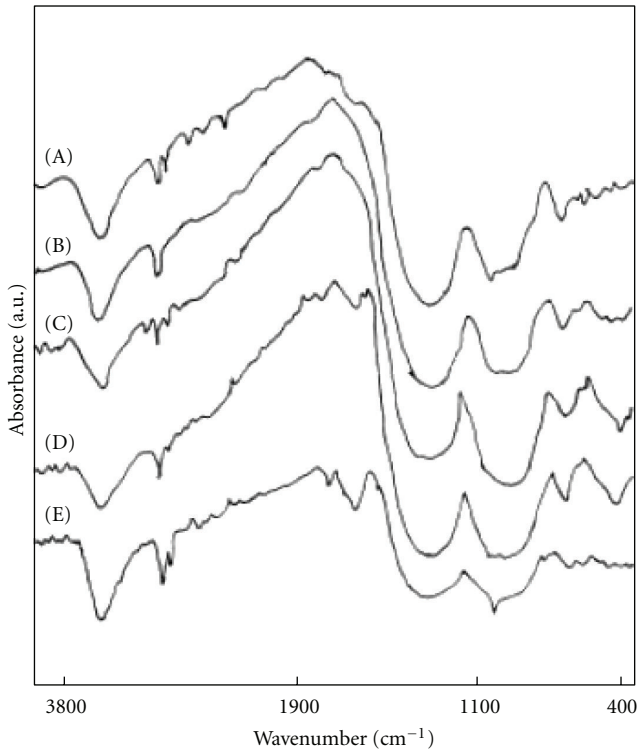

Figure 6: IR spectra of glass series X PbO_2-(50-X) ZnO-50B_2O_3 [51].

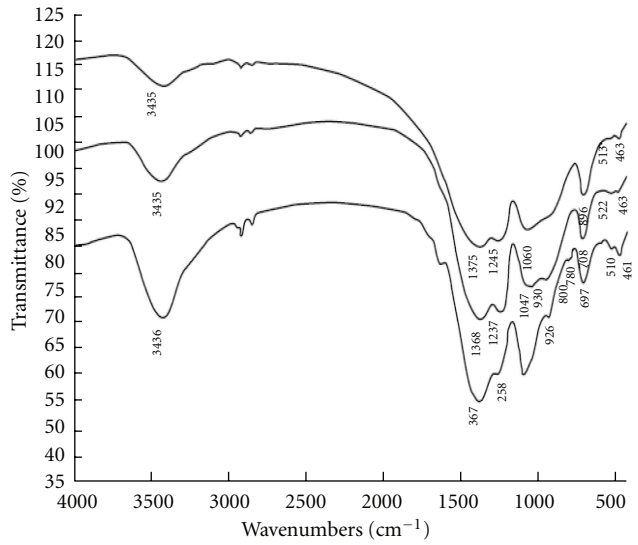

Figure 7: IR spectra of the ZnO-Bi_2O_3-B_2O_3 glasses with Bi_2O_3 content of (1) 25, (2) 35, and (3) 45 wt% [52].

bending of O–B–O. The lead plays dual role of Pb^{2+} cations in glass structure. First, it acts as a network modifier in the glassy matrix when these cations are ionically bonded, and secondly, if Pb–O bond is covalent, Pb^{2+} cation will act as glass former [89]. Because of this dual role, lead ions may disrupt the glass network and form BO_4 tetrahedral. The low-frequency bands near 453 cm^{-1} in IR spectra of borate

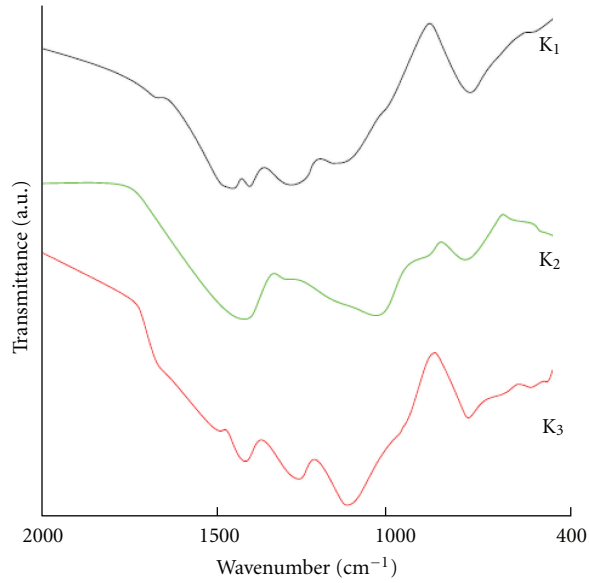

Figure 8: IR spectra of potassium borate glasses [53].

glasses can be attributed to vibration of metal cations such as Pb^{2+} or Zn^{2+} [46, 91–93].

2.6. Bismuth Borate and Lead Bismuth Borate Glasses. Bobkova's studies on bismuth borate and lead bismuth borate glasses by IR spectroscopy show extensive report that Bi_2O_3 works as glass former, but still B_2O_3 is required for the formation of well-transparent glasses. Figure 7 shows the IR spectra of ZnO-Bi_2O_3-B_2O_3 glasses with Bi_2O_3 in the wavenumber range of 450–4000 cm^{-1}. A continuous network of octahedral [BiO_6] groups connected through atoms of oxygen and the high polarizability of Bi^{3+} cations leads to an increase in the covalent bonding between bismuth and oxygen. IR studies of pure γ-B_2O_3 show a broad absorption band wavenumber range of 400–550 cm^{-1}, while the adsorption bands in the range of 150–500 cm^{-1} occur due to the oscillations of the Bi–O bond. BiO_6, BiO_4 and BiO_3 are the basic structural units associated in the bismuth borate glasses, but most widely BiO_6 group was found in these glasses [128–131].

2.7. Potassium Borate Glasses. The structural information in potassium borate glasses was extensively studied by Singh et al. [53]. This study of these glass systems gives the information not only about structure, but also about the coordination number of the compound with respect to oxygen, network formers, and change in oxygen bonds of the framework which also is induced by the cations modifiers [132, 133]. IR studies of potassium borate glasses in the wavenumber range of 450–2000 cm^{-1} are shown in the Figure 8. Due to small mass as other network forming elements, the main vibrational modes associated with the glass network appear well above 500 cm^{-1} (in the mid-infrared region), and these networking modes are well separated from the metal ion site vibrational modes which are active

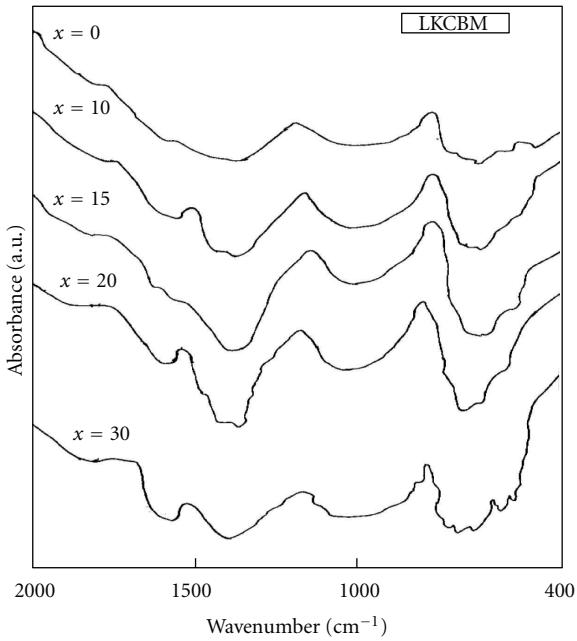

Figure 9: IR transmission spectra of LKCBM glasses [54].

in the far infrared region [94–96]. Boron has an ability to change its coordination number with oxygen between three and four providing a range of anionic environment that can coordinate the modifying metal ions. The main IR-absorption peaks in B_2O_3 containing glasses lie at different wavenumbers of 710, 1260, and 1420 cm^{-1}. The absorption peak near 1420 cm^{-1} occurred due to the ring stretching of the boroxol groups, and the 1260 cm^{-1} vibration is due to the B–O–B bond constituting the linkage of boroxol groups to neighbouring groups [134]. The absorption bands near 680 and 1350 cm^{-1} can be attributed to bending vibrations of BO_3 triangles and stretching vibrations of BO_3 units with nonbridging oxygens (NBOs), respectively [135–138]. The band near 1066 cm^{-1} was observed due to B–O bond stretching vibrations from triborate, tetraborate, and pentaborate groups. This indicates that there is a formation of four-coordinated boron units with the addition of heavy metal oxide. The broad absorption peaks at around 1210 cm^{-1} can be attributed to asymmetric stretching vibrations of B–O bond in metaborates, pyroborates, and orthoborates. With the addition of fly ash, potassium borate glasses give significant change in their IR spectra. A prominent band at 950 cm^{-1} attributed to the stretching vibrations of B–O–Si linkage, as the main content of fly ash is silica. A shoulder band at 816 cm^{-1} can be assigned due to combined effect of stretching vibrations of Si–O–Si and B–O–B network [87].

2.8. Lithium-Potassium Borate Glasses. IR studies of lithium-potassium borate glass system $(30\text{-}x)Li_2O\text{-}xK_2O\text{-}10CdO\text{-}59B_2O_3$ ($x = 0, 10, 15, 20$, and 30) doped with $1MnO_2$ in the wavenumber range of 400–2000 cm^{-1} show different transmission bands at different wavenumber positions (Figure 9). When glass sample was radiated with IR radiation, then portions of the incident radiation are absorbed at particular wavelengths. This characterizes the functional groups comprising the molecule and the overall configuration of the atoms as well. The IR transmission spectra of LKCBM glasses are given in Figure 9. IR spectra of these glasses show a band in the range of 400–1600 cm^{-1}. The band in the wavenumber range of 400–780 cm^{-1} was formed due to the bending vibrations of various borate arrangements, vibrations of Li cations through glass network, and deformation modes of network structures as well as vibrations of some MnO_4 groups [36, 54, 139, 140]. The spectral band in the region 780–1100 cm^{-1} is due to the B–O asymmetric stretching of tetrahedral BO_4 units and vibrations of diborates bridging to pentaborate groups; while the dominating transmission bands in the range of 1100–1600 cm^{-1} were assigned due to the stretching vibrations of borate units in which boron atoms are connected to the three oxygens (BO_3 and B_3O_6 units) [141, 142]. Recently, Aboud et al. reported the IR studies of these glasses in the wavenumber range of 600–2000 cm^{-1} as shown in Figure 10. The compositional distribution and assignment of IR spectra have been listed in Table 3 [55]. In this study, it was observed that the vibrational modes of the borate network are mainly active in three infrared spectral regions from 1200 to 1500 cm^{-1} (B–O stretching of trigonal BO_3^- units), from 800 to 1200 cm^{-1} (B–O stretching of tetrahedral BO_4^- units), and from 600 to 800 cm^{-1} (bending vibrations of various borate segments).

2.9. Zinc and Manganese-Doped Borate Glasses. The vibration spectra of the zinc and manganese oxides containing borate glasses were obtained using KBr pellet technique in the range of 400–4000 cm^{-1}. FTIR spectrum of manganese oxides containing borate glasses is shown in Figure 11. IR spectra exhibit broad absorption bands as a consequence of the general disorder in the network, mainly due to a wide distribution of structural units occurring in these glasses. The band in low wavenumber side marked as "A" attributed to the presence of transition metal ions in bivalent state (Zn^{2+}, Mn^{2+}). The absorption bands marked as "B," "C" and "D" are due to borate matrix. Details classifications of the appeared peaks have been presented in Table 4. The absorption peak near 700 cm^{-1} was assigned due to bending of B–O–B linkage, and peaks about at 1020 cm^{-1} were occurred due to B–O stretching of BO_4 tetrahedra, while peaks at wavenumber 1280 cm^{-1} attributed to asymmetric stretching of B–O of trigonal BO_3. Absence of peak around 806 cm^{-1} indicates that borate network does not contain any boroxol ring. Generally, in pure B_2O_3 glass, most of the boron is involved in B_3O_6 boroxol rings [143–145]. The addition of transition metal ion breaks these rings, and increasingly BO_3 and BO_4 units are formed, which is reflected in Inset: magnified version of FTIR curves to prove the absence of boroxol rings our samples also [97].

2.10. Lead Strontium Titanate Borosilicate Glasses. IR study of lead strontium titanate borosilicate glasses in glass system $[(Pb_xSr_{1-x})TiO_3]\text{-}[2SiO_2\cdot B_2O_3]\text{-}[BaO\cdot K_2O]\text{-}[La_2O_3]$ was studied by Srivastava [62] and Gautam et al. [63]. Five letters

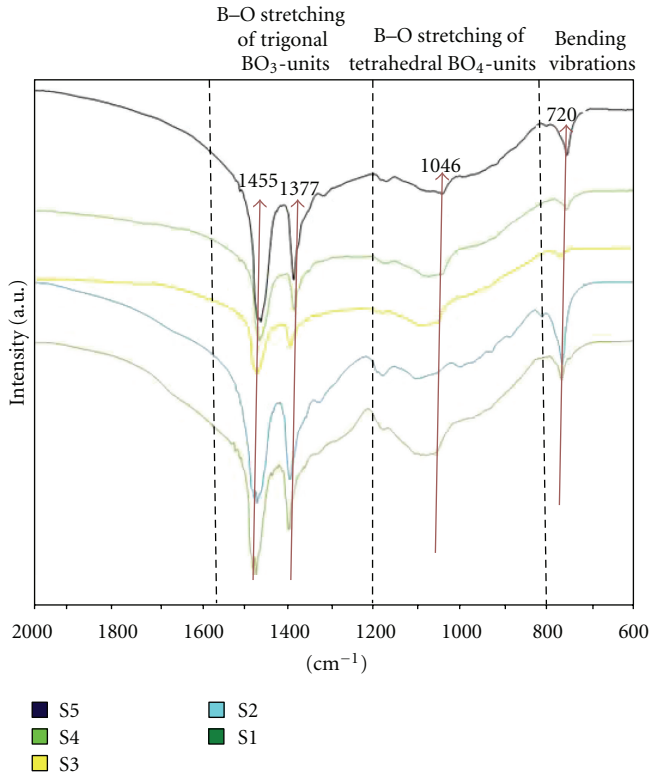

Figure 10: FTIR spectra of lithium potassium borate glasses [55].

Table 3: The FTIR peaks positions of the (90-x)H_2BO_3-xLi_2CO_3-10K_2CO_3 glasses system [55].

Sample number	Composition (mol%)			Absorption peak (cm^{-1})		
	H_3BO_3	Li_2CO_3	K_2CO_3	B–O stretching of trigonal BO_3^- units	B–O stretching of tetrahedral BO_4^- units	Bending vibrations
S1	80	10	10	1455–1377	1046	720
S2	75	15	10	1455–1377	1046	720
S3	70	20	10	1455–1377	1046	722
S4	65	25	10	1458–1376	1045	722
S5	60	30	10	1455–1376	1045	720

Table 4: Various absorption peak positions obtained from FTIR spectra [61].

Band	Position of Band (cm^{-1})	Assignment
A	425	Vibration of metal cations such as Zn^{2+}/Mn^{2+}
B	700	Bending of B–O–B linkages
C	1020	B–O stretching of BO_4 tetrahedra
D	1280	Asymmetric stretching of B–O of trigonal BO_3

glass code refers to the composition of the glass. First two letters PT, 9P, and so forth designate the fraction of lead, that is, x in the glass. PT refers to $x = 1.0$, that is, 100% lead (Pb) and 0% strontium. 9P, 8P, and so forth, refer to $x = 0.9, 0.8$, respectively. The third letter L indicates that La_2O_3 is used as an additive. The last two letters 5B refer to fraction of modifier oxides BaO in the parent glass compositions. These spectra consist of broad and sharp bands in different regions of 400–4000 cm^{-1} as shown in Figures 12 and 13. The compositional changes in IR spectra are strongly influenced. These IR spectra of these glasses show ten absorption peaks. Absorption peaks in the range of 3425–3501 cm^{-1} are attributed to stretching of $–OH^-$ bond inside the glassy network, and it form at nonbridging oxygen sites. Two absorption bands in the range of 1200–1750 cm^{-1} were found in all the glass samples. A single-broad absorption peak was observed in the glass lead rich glass composition, while the same peak splitted into two peaks in all Sr rich glass compositions. These spectral bands were observed due to the vibrational mode of the borate network, and these vibrational modes of the

Table 5: Wavelengths of different absorption peaks in FTIR spectra of the glasses in the system $[(Pb_xSr_{1-x})TiO_3]$-$[2SiO_2 \cdot B_2O_3]$-$[BaO \cdot K_2O]$-$[La_2O_3]$ [62].

Glass codes	x	Wave length of different absorption peaks (cm^{-1})																	
		1	2		3		4	5	6	7		8		9	10				
			a	b	a	b						a	b		a	b			
PTL5B	1.0	3483	2915	2890	—		1730	1650	—	1280		995		715	420				
9PL5B	0.9	3472	2991	2860	—		1730	1630	—	1250		1000		725	430				
8PL5B	0.8	3500	2990	2890	—		1730	1630	—	1290		995		730	450				
7PL5B	0.7	3480	2925	2865	—		1750	1645	—	1300		990		705	460				
6PL5B	0.6	3490	2915	2840	—		1740	1638	—	1230		990		701	480				
5PL5B	0.5	3450	2925	2840	2410	2290	1740	1640	—	1310	1210	1000		703	550	480			
4PL5B	0.4	3485	2940	2850	2420	2300	1740	1650	1575	1340	1210	1030	940	703	550	480			
3PL5B	0.3	3500	2922	2850	2500	2300	1750	1680	—	1375	1225	1000	960	720	555	440			

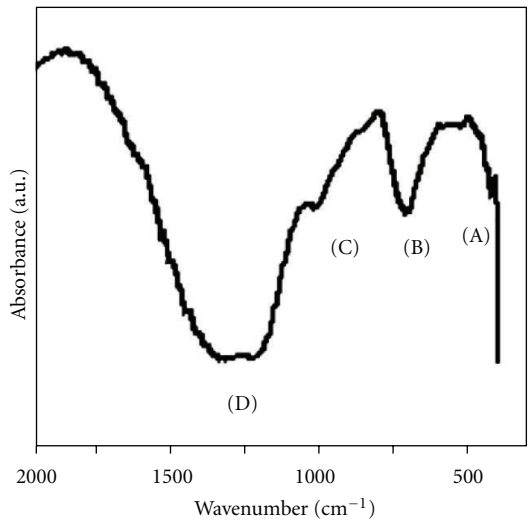

Figure 11: FTIR spectra of zinc manganese borate glasses for 50 mol% B_2O_3 [61].

borate network are mainly due to the asymmetric stretching relaxation of the B–O bond of trigonal BO_3 units. These vibrational modes occur at 1200–1600 cm^{-1}. The bands at around 1000 cm^{-1} are attributed to a stretching vibration of B–O–Si linkage. A broad absorption peak lies between 685 and 709 cm^{-1} and was due to the bending of B–O–B linkages in the borate glassy network [86, 146]. The low-frequency bands in the IR spectra of these glasses can be attributed to vibration of metal cation such as Pb^{2+} and was attributed to the vibrations of Pb^{2+} cations. Absorption peaks in FTIR spectra of the (Pb Sr)TiO_3 borosilicate glasses have been listed in Table 5.

2.11. Barium Strontium Titanate Borosilicate Glasses. More recently, our research group reported the IR studies of barium strontium titanate borosilicate glasses in wavenumber range of 450–4000 cm^{-1} and shown in Figure 14. The first sharp and broad absorption peak at 3440 cm^{-1} was assigned due to stretching mode of O–H bonds inside the glassy network [64]. These O–H bond groups are formed at nonbridging oxygen sites. An absorption band at wavenumber 2372 cm^{-1} (peak no. 2) was observed in the IR spectra. IR spectra show a sharp absorption at 1632 cm^{-1} (peak no. 3). A doublet absorption band occurs at wavenumbers 1351–1398 cm^{-1} (peak no. 4 a, b). The absorption peak no. 5 was observed at wavenumber 1276 cm^{-1}. These absorption bands occurred due to the vibrational mode of the borate network in borate containing glass systems and asymmetric stretching relaxation of the B–O bonds of trigonal BO_3 units. This band lies between wavenumber range of 1200–1750 cm^{-1} [80, 81]. An absorption peak at 1025 cm^{-1} is attributed to stretching vibrations of B–O–Si linkage. Absorption band at 714 cm^{-1} occurred 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. An absorption peak at 519 cm^{-1} at low wavenumber side was also observed due to vibration of metal cation such as Ba^{2+} and Sr^{2+}.

2.12. Sodium Borosilicate Glasses. IR studies of sodium borosilicate glasses show various absorption bands in the wavenumber ranges of 400–2000 cm^{-1}; it has been given in the Figures 15 and 16. The bands near 900–1100 cm^{-1} dominate over all bands. The absorption band around 970 cm^{-1} and a line near 1065 cm^{-1} were identified. Three additional weaker bands peaking near 460, 780, and 1420 cm^{-1} can be identified in the IR spectrum. When Ca and Ba are substituted for sodium, the shape of the dominant absorption band changes, and the band peak shifts into the high-frequency side [65]. In addition, the intensity of the band peaking at 1420 cm^{-1} increases, while a small bands near 715 cm^{-1} and 780 cm^{-1} shifts by approximately 20 cm^{-1} into the high-frequency region. The low-frequency sideband peaking near 460 cm^{-1} is due to deformation vibrations of the Si–O–Si bridges, and bands in the region of 780–800 cm^{-1} were formed due to deformation vibrations of the Si–O– end groupings, while the band near 970 cm^{-1} attests to the presence of BO_4 tetrahedra in the structure of the glass [147]. The band at 1065 cm^{-1} IR spectra of the sodium glass is related with the asymmetric stretching vibrations of the

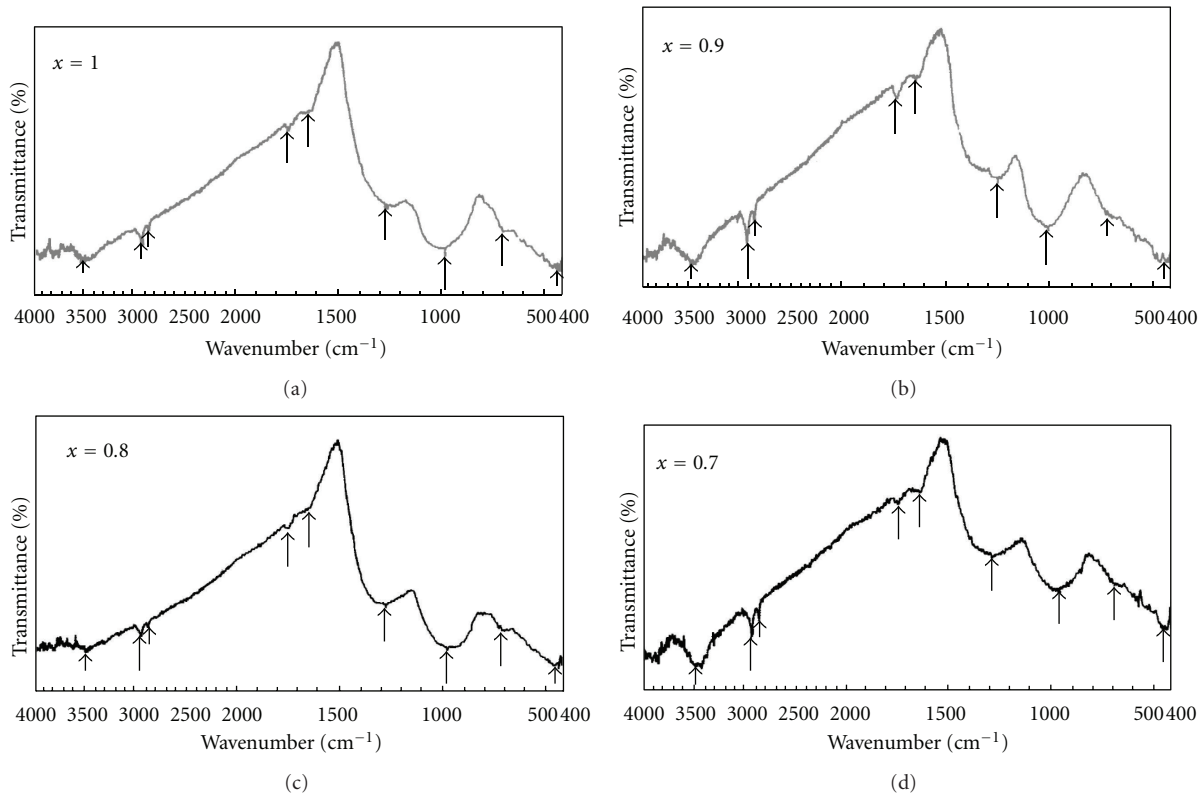

Figure 12: Infrared spectra of glasses (a) PTL5B, $x = 1.0$, (b) 9PL5B, $x = 0.9$, (c) 8PL5B, $x = 0.8$, and (d) 7PL5B, $x = 0.7$ [62, 63].

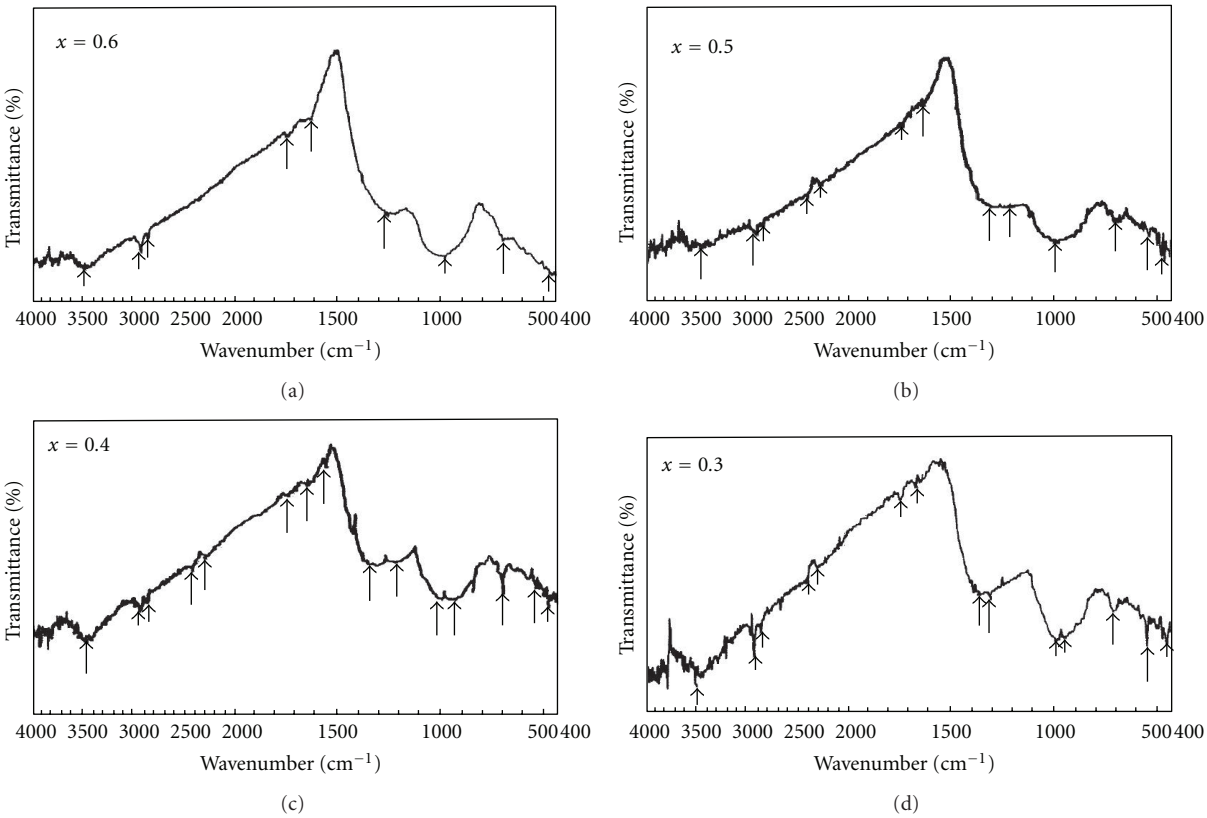

Figure 13: Infrared spectra of glasses (a) 6PL5B, $x = 0.6$, (b) 5PL5B, $x = 0.5$, (c) 4PL5B, $x = 0.4$, and (d) 3PL5B, $x = 0.3$ [62, 63].

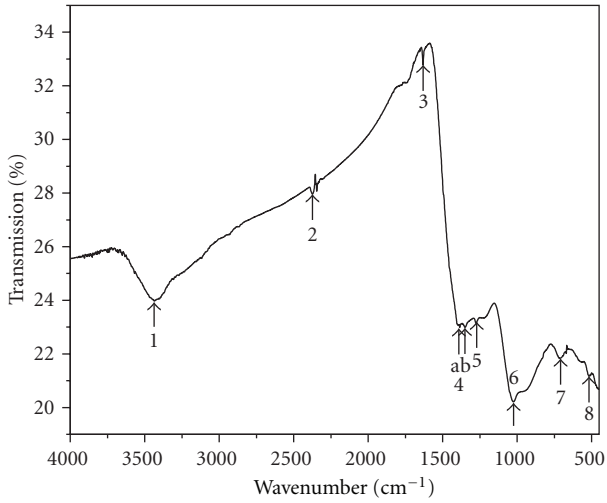

Figure 14: IR studies of barium strontium titanate borosilicate glasses [64].

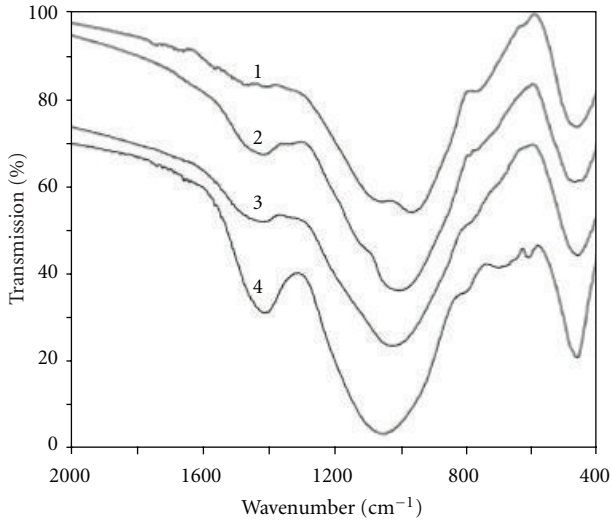

Figure 15: IR spectra of calcium containing sodium borosilicate glasses [65].

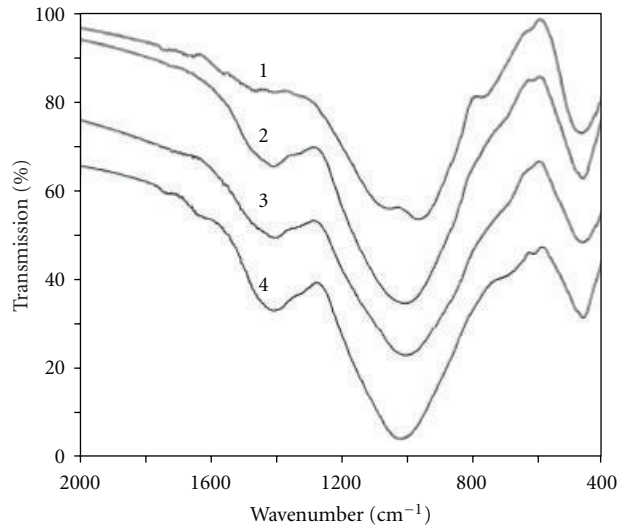

Figure 16: IR spectra of barium containing sodium borosilicate glasses [65].

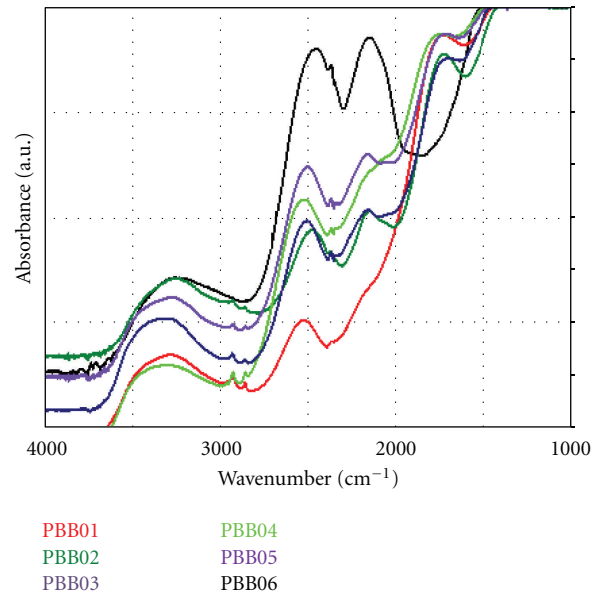

Figure 17: IR spectra of PbO-Bi_2O_3-B_2O_3 glass samples [66].

Si–O–Si bonds, and the shift of its peak is due to a change of the degree of polymerization of the glass structure [148]. The absorption bands near 715 and 1420 cm^{-1} are associated with different vibrational modes of the planar BO_3 triangles [36].

2.13. Lead Bismuth Borosilicate Glasses. The IR studies of lead bismuth borate glasses had been reported by Chen et al. and shown in Figure 17. The glass compositions have been given as PBB01(50-40-10), PBB2 (40-50-10), PBB03 (20-70-10), PBB4 (35-45-20), PBB5 (15-65-20), and PBB06 (25-35-40). This absorption band occurs due to stretching mode of O–H bonds inside the glassy network. With addition of lead oxide, the band shifted towards higher wavenumber side. An absorption band between wavenumber 2867 and 2943 cm^{-1}, and it occurs due to hydrogen bonding [81]. This absorption band disappears in IR spectra when lead content increased to 40%. The vibrational mode of the borate network exhibited an absorption band between wavenumbers 1522 and 1483 cm^{-1} due to the asymmetric stretching relaxation in B–O bonds of trigonal BO_3 units. Such types of vibrational modes occur within the wavenumbers range of 1200–1750 cm^{-1} [88]. The broad absorption band at around 1120–1153 cm^{-1} was occurred due to a stretching vibration of B–O–Si linkage [149]. IR spectra of all glass samples exhibited an absorption band within the wavenumber range of 816–833 cm^{-1} due to the diborate linkage, B–O–B, in the borate glassy network. In this linkage, both boron atoms are tetrahedrally coordinated with triborate superstructural units [150]. An absorption peaks at lower wavenumber

Table 6: Assignment of infrared bands in the spectra.

Peak Positions (cm^{-1})	IR Assignments	References
3600–3750	OH group	[70, 71]
3200–3500	Molecular water	[70, 71, 77–79]
2700–3000	Hydrogen bonding	[36]
1200–1750	Asymmetric stretching relaxation of B–O bonds of trigonal BO_3 units	
	Detailed Classification of group 1200–1750	
~1480	Asymmetric stretching modes of borate triangles BO_3 units	[57–59, 64, 74–76, 80, 81]
~1345	Presence of pyroborate, orthoborate groups containing BO_3^-	
1200–1300	B–O bond stretching vibrations and B–O bridging between B_3O_6 and BO_3 triangles	
~1235	Asymmetric stretching vibrations of B–O bonds from orthoborate groups	
700–1200	Composite of two silicate chains and borate phases	
	Detailed Classification of groups 700–1200	
~1015	Pentaborate group	
992	B–O–M, M means metal ion	
~965	B–O–B linkages	
950–1050	Stretching vibrations of B–O–Si linkage	[38, 39, 49, 60, 63, 67, 68, 82–88]
~875	Stretching vibrations of tetrahedral BO_4^- units	
816–833	Diborate linkage, B–O–B networks	
~815	Si–O–Si network	
806	Boroxol rings	
760	BO_3–O–BO_4 bond-bending vibrations	
700	Bending of B–O–B linkage	
~694	Combined vibrations of BO_4 and PbO_4 groups	[83–85]
680	B–O–B bond-bending vibrations from pentaborate group or bending vibrations of BO_3 triangles	[80]
~616	Bending of O–B–O	[89]
<600	Pb^{2+}, Zn^{2+}, Mn^{2+}, Bi^{3+}, Li^+, and Ba^{2+} or any metallic cations	[55, 80, 90–97]

side attributed to vibration of metal cation such as Pb^{2+} and Bi^{3+}. The assignment of various vibrations groups in IR spectra have been listed in Table 6. FTIR spectra of these glasses many absorption bands at different wavelengths region which may attributed attribute to OH-group and other borate groups. PBB01 showed more than 70% of transmittance from 2000 nm to 4000 nm. The peak around 3300 nm is due to the OH absorption. With the increase of PbO and Bi_2O_3 content, the spectrum exhibits a shift to longer wavelength [66].

3. Summary

In this paper, we have discussed the infrared spectroscopy of borate glasses and the effects of various additives on structural properties of these glasses. The borate glasses contain the molecular water, hydroxyl group along with hydrogen bonding which was confirmed by absorption bands in wavenumber range of 2700–3750 cm^{-1} in the IR spectra of these glasses. The amount of molecular water content affected with variation of different metallic additives. 10–20 mol% addition of PbO does not affect the borate network in lead borate glasses, while with increasing the concentration of PbO, the absorption bands below 620 cm^{-1} are attributed. Moreover, with in content from 30 to 50 mol% of PbO, bands related to the [BO_4] unit shifts from 945 cm^{-1} to a lower wavenumber 931 cm^{-1}. Boroxol ring formation in the glassy matrix at wavenumber 806 cm^{-1} in lead borate glasses was observed while its formation inside the glassy matrix of Cd-doped PbO-B_2O_3 glasses was not observed in IR spectra. This may be lead to the conclusion that the addition of Cd in glassy matrix deformed the boroxol ring. The conversion of three-fold to four-fold coordination of boron atoms in the structure of glasses was also observed in Cd-doped PbO-B_2O_3 glasses. Similarly, the presence of a stretching vibration of B–O–M (B–O–Pb) linkage, where "M" represents a metal ion in the glassy matrix of Cd, Pb, Ba, Mo, and so forth, doped borate glasses also confirmed by IR spectra and assigned near 992 cm^{-1}. The absorption

band at 696 cm^{-1} is due to combined vibration of BO_4 and PbO_4 groups. The addition of lead in borate glass system modified the network of glassy matrix. Asymmetric stretching relaxation of B–O bonds of trigonal BO_3 units and composite of two silicate chain and borate phases have been presented in various vibration modes such as diborate, triborate, tetraborate, orthoborate, and pyroborate in the wavenumber regions of 1200–1750 cm^{-1} and 700–1200 cm^{-1}. These networks significantly affected by additives in borate glasses. In borosilicate glasses, the addition vibrations due to presence of silica were also observed, and these vibrations present basically two forms. Firstly, the stretching vibration of B–O–Si linkages, and secondly, they may be found as stretching vibrations of Si–O–Si. The metallic cations vibrations in glassy matrix may be attributed in low wavenumber sides (<600 cm^{-1}).

Acknowledgments

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