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, as in SiO$_2$, are again connected to two network-forming atoms, in case of boron. The radial distribution analysis describes the B$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$, 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$_2$O$_3$ 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$_2$O$_3$ glasses are shown in Figure 1. The nomenclature of these glasses has been listed in Table 1. IR spectra of pure B$_2$O$_3$ gives two absorption band at wavenumbers range of 1300–1700 cm$^{-1}$ 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$_2$O$_3$ and La$_2$O$_3$-B$_2$O$_3$ [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 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$_2$O$_3$ also affects the structural properties of these glasses.

2.2. Barium Lead Borate Glasses. IR studies of BaO-PbO-B$_2$O$_3$ 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$_2$O$_3$ 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-B₂O₃ of various glass samples [34].

<table>
<thead>
<tr>
<th>No.</th>
<th>PB-1</th>
<th>PB-2</th>
<th>PB-3</th>
<th>PB-4</th>
<th>PB-5</th>
<th>PB-6</th>
<th>PB-7</th>
<th>PB-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compositions</td>
<td>0.1PbO</td>
<td>0.2PbO</td>
<td>0.3PbO</td>
<td>0.4PbO</td>
<td>0.5PbO</td>
<td>0.6PbO</td>
<td>0.7PbO</td>
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</tr>
<tr>
<td></td>
<td>0.9B₂O₃</td>
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<td>0.7B₂O₃</td>
<td>0.6B₂O₃</td>
<td>0.5B₂O₃</td>
<td>0.4B₂O₃</td>
<td>0.3B₂O₃</td>
<td>0.2B₂O₃</td>
</tr>
</tbody>
</table>

Figure 2: Possible structural units of PbO-B₂O₃ glasses: (a) three coordinated boroxol rings modified by Pb²⁺; (b) formation of Pb–O–B covalent bands; (c) bridge networks between [BO₃] and [BO₄] units; (d) complex structures of Pb²⁺-modified boron–oxygen rings and chains [34].

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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\(_2\)O-B\(_2\)O\(_3\)-SiO\(_2\).

2.4. MoO\(_3\)-Doped Lead Borate Glasses. The structural studies of MoO\(_3\)-doped Pb\(_2\)O\(_3\)-B\(_2\)O\(_3\) 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\(_2\)O\(_3\). 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\(_3\) and PbO) [102, 103]. Pb\(_2\)O\(_3\)-B\(_2\)O\(_3\) glasses show the formation of BO\(_3\) 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\(_2\)O–B bonds is at 30% of PbO, which probably results from the replacement of B\(_2\)O–B\(_3\) 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\(_2\)O\(_3\):xTiO\(_2\) (0.0 ≤ x ≤ 2.0) [50], and its detailed description was given as

\[
\begin{align*}
T_0 &: 30\text{PbO}-4\text{MoO}_3-66.0\text{B}_2\text{O}_3, \\
T_2 &: 30\text{PbO}-4\text{MoO}_3-65.8\text{B}_2\text{O}_3:0.2\text{TiO}_2, \\
T_4 &: 30\text{PbO}-4\text{MoO}_3-65.6\text{B}_2\text{O}_3:0.4\text{TiO}_2, \\
T_6 &: 30\text{PbO}-4\text{MoO}_3-65.4\text{B}_2\text{O}_3:0.6\text{TiO}_2, \\
T_8 &: 30\text{PbO}-4\text{MoO}_3-65.2\text{B}_2\text{O}_3:0.8\text{TiO}_2, \\
T_{10} &: 30\text{PbO}-4\text{MoO}_3-65.0\text{B}_2\text{O}_3:1.0\text{TiO}_2, \\
T_{12} &: 30\text{PbO}-4\text{MoO}_3-64.5\text{B}_2\text{O}_3:1.5\text{TiO}_2, \\
T_{20} &: 30\text{PbO}-4\text{MoO}_3-64.0\text{B}_2\text{O}_3:2.0\text{TiO}_2.
\end{align*}
\]

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\(_3\) structural units in IR spectra of all the glasses. Two new bands were observed due to \(\nu_1\) and \(\nu_2\) 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.
of the dopant TiO\textsubscript{2} beyond 0.8 mol\%. The intensity of the band associated with BO\textsubscript{3} structural units was observed to increase at the expense of the band arising from BO\textsubscript{4} units. The IR spectrum of glass T\textsubscript{2} exhibited two additional prominent bands at 739 and 638 cm\textsuperscript{-1}. With increasing the concentration of TiO\textsubscript{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\textsubscript{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\textsuperscript{-1} (Figure 6). (A) 20PbO\textsubscript{2}–30ZnO–50B\textsubscript{2}O\textsubscript{3}; (B) 25PbO\textsubscript{2}–25ZnO–50B\textsubscript{2}O\textsubscript{3}; (C) 30PbO\textsubscript{2}–20ZnO–50B\textsubscript{2}O\textsubscript{3}; (D) 35PbO\textsubscript{2}–15ZnO–50B\textsubscript{2}O\textsubscript{3}; (E) 40PbO\textsubscript{2}–10ZnO–50B\textsubscript{2}O\textsubscript{3}. This study reaches to conclusion of various vibration groups which are responsible for making their structure. An absorption band at 3450 cm\textsuperscript{-1} was occurred due to O–H stretching vibration [110–112]. The presence of structural units such as symmetric (BO\textsubscript{3})\textsuperscript{3–} triangles, BO\textsubscript{4} tetrahedral, and asymmetric (BO\textsubscript{3})\textsuperscript{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\textsuperscript{-1} which occurred due to the asymmetric stretching relaxation of the B–O band of trigonal BO\textsubscript{3} units and the vibrational group from 800 to 1200 cm\textsuperscript{-1}. This vibrational group assigned is due to the B–O bond stretching of the tetrahedral BO\textsubscript{4} units [116, 117]. The third group was observed at around 700 cm\textsuperscript{-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\textsubscript{2}O\textsubscript{3} glasses consist of BO\textsubscript{3} and BO\textsubscript{4} groups. These groups may be attached in the form of random network. This corresponds to the progressive substitution of boroxol ring by BO\textsubscript{3} and BO\textsubscript{4} groups [120–122]. The absorption band near 1357 cm\textsuperscript{-1} in 40 mol\% glass was assigned to B–O stretching vibrations of trigonal (BO\textsubscript{3})\textsuperscript{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\textsuperscript{-1} is due to B–O asymmetric stretching of BO\textsubscript{3} unit [125], and bands around 1234 cm\textsuperscript{-1} was arisen by B–O stretching vibrations of (BO\textsubscript{3})\textsuperscript{3–} unit in metaborate chains and orthoborates [126]. Vibrations of some boron atoms attached to nonbridging oxygen in the form of BO\textsubscript{4} vibration were assigned band at 1004 cm\textsuperscript{-1} [36]. The formation of diborate group in present glasses had been represented by absorption around 1000 cm\textsuperscript{-1}. IR spectra showed the band at about 995 cm\textsuperscript{-1} was attributed to a stretching vibration of B–O–Si linkage [82]. The absorption band is at 993 cm\textsuperscript{-1} which occurred due to O–H stretches of BO\textsubscript{4} and PbO\textsubscript{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\textsuperscript{-1} is due to
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 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\(_2\)O\(_3\) works as glass former, but still B\(_2\)O\(_3\) is required for the formation of well-transparent glasses. Figure 7 shows the IR spectra of ZnO-Bi\(_2\)O\(_3\)-B\(_2\)O\(_3\) glasses with Bi\(_2\)O\(_3\) 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 \(\gamma\)-B\(_2\)O\(_3\) 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...
When glass sample was radiated with IR radiation, then significant change in their IR spectra. A prominent band at different wavenumbers of 710, 1260, and 1420 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 rise to the B–O bond stretch- ing 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 1200 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.

2.8. Lithium-Potassium Borate Glasses. IR studies of lithium-potassium borate glass system (30-x)Li\(_2\)O-xK\(_2\)O-10CdO-59B\(_2\)O\(_3\) (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 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\(_2\)O\(_3\) 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 1200 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.

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\(_3\) units. Absence of peak around 806 cm\(^{-1}\) indicates that borate network does not contain any boroxol ring. Generally, in pure B\(_2\)O\(_3\) glass, most of the boron is involved in B\(_3\)O\(_5\) 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 in our samples also [97].

2.10. Lead Strontium Titanate Borosilicate Glasses. IR study of lead strontium titanate borosilicate glasses in glass system [(Pb\(_2\)O\(_{2}\))\(_2\)(TiO\(_2\))]\(_{-1}\)–[2SiO\(_2\)–B\(_2\)O\(_3\)]–[BaO–K\(_2\)O–La\(_2\)O\(_3\)] was studied by Srivastava [62] and Gautam et al. [63]. Five letters...
Table 3: The FTIR peaks positions of the (90-x)H2BO3-xLi2CO3-10K2CO3 glasses system [55].

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Composition (mol%)</th>
<th>Absorption peak (cm⁻¹)</th>
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<td>Li2CO3</td>
</tr>
<tr>
<td>S1</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>S2</td>
<td>75</td>
<td>15</td>
</tr>
<tr>
<td>S3</td>
<td>70</td>
<td>20</td>
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<td>25</td>
</tr>
<tr>
<td>S5</td>
<td>60</td>
<td>30</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Band</th>
<th>Position of Band (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>425</td>
<td>Vibration of metal cations such as Zn²⁺/Mn²⁺</td>
</tr>
<tr>
<td>B</td>
<td>700</td>
<td>Bending of B-O-B linkages</td>
</tr>
<tr>
<td>C</td>
<td>1020</td>
<td>B-O stretching of BO₄ tetrahedra</td>
</tr>
<tr>
<td>D</td>
<td>1280</td>
<td>Asymmetric stretching of B-O of trigonal BO₃</td>
</tr>
</tbody>
</table>

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 La₂O₃ 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 \([\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3]\)-\([2\text{SiO}_2\cdot\text{B}_2\text{O}_3]\)-\([\text{BaO}\cdot\text{K}_2\text{O}]\)-\([\text{La}_2\text{O}_3]\)$ [62].

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

Figure 11: FTIR spectra of zinc manganese borate glasses for 50 mol% $\text{B}_2\text{O}_3$ [61].

The low-frequency bands in the IR spectra of these glasses can be attributed to vibration of metal cation such as $\text{Pb}^{2+}$ and was attributed to the vibrations of $\text{Pb}^{2+}$ cations. Absorption peaks in FTIR spectra of the ($\text{Pb}$ $\text{Sr}$)$\text{TiO}_3$ 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 $\text{O}–\text{H}$ bonds inside the glassy network [64]. These $\text{O}–\text{H}$ bond groups are formed at non-bridging 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 $\text{B–O}$ bonds of trigonal $\text{BO}_3$ 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 $\text{B–O–Si}$ linkage. Absorption band at 714 cm$^{-1}$ occurred due to the diborate linkage of $\text{B–O}$–$\text{B}$, 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 $\text{Ba}^{2+}$ and $\text{Sr}^{2+}$.

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 $\text{Ca}$ and $\text{Ba}$ 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 $\text{Si}–\text{O}–\text{Si}$ bridges, and bands in the region of 780–800 cm$^{-1}$ were formed due to deformation vibrations of the $\text{Si}–\text{O}–$ end groupings, while the band near 970 cm$^{-1}$ attests to the presence of $\text{BO}_3$ 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) 9PL55B, $x = 0.9$, (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].
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), PBB3 (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.

<table>
<thead>
<tr>
<th>Peak Positions (cm(^{-1}))</th>
<th>IR Assignments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600–3750</td>
<td>OH group</td>
<td>[70, 71]</td>
</tr>
<tr>
<td>3200–3500</td>
<td>Molecular water</td>
<td>[70, 71, 77–79]</td>
</tr>
<tr>
<td>2700–3000</td>
<td>Hydrogen bonding</td>
<td>[36]</td>
</tr>
<tr>
<td>1200–1750</td>
<td>Asymmetric stretching relaxation of B–O bonds of trigonal BO(_3) units</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detailed Classification of group 1200–1750</td>
<td></td>
</tr>
<tr>
<td>~1480</td>
<td>Asymmetric stretching modes of borate triangles BO(_3) units</td>
<td>[57–59, 64–76, 80, 81]</td>
</tr>
<tr>
<td>~1345</td>
<td>Presence of pyroborate, orthoborate groups containing BO(_3)(^-)</td>
<td></td>
</tr>
<tr>
<td>1200–1300</td>
<td>B–O bond stretching vibrations and B–O bridging between B(_2)O(_6) and BO(_3) triangles</td>
<td></td>
</tr>
<tr>
<td>~1235</td>
<td>Asymmetric stretching vibrations of B–O bonds from orthoborate groups</td>
<td></td>
</tr>
<tr>
<td>700–1200</td>
<td>Composite of two silicate chains and borate phases</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detailed Classification of groups 700–1200</td>
<td></td>
</tr>
<tr>
<td>~1015</td>
<td>Pentaborate group</td>
<td></td>
</tr>
<tr>
<td>992</td>
<td>B–O–M, M means metal ion</td>
<td>[38, 39, 49, 60, 63, 67, 68, 82–88]</td>
</tr>
<tr>
<td>~965</td>
<td>B–O–B linkages</td>
<td></td>
</tr>
<tr>
<td>950–1050</td>
<td>Stretching vibrations of B–O–Si linkage</td>
<td></td>
</tr>
<tr>
<td>~875</td>
<td>Stretching vibrations of tetrahedral BO(_4)(^-) units</td>
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</tr>
<tr>
<td>816–833</td>
<td>Diborate linkage, B–O–B networks</td>
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</tr>
<tr>
<td>~815</td>
<td>Si–O–Si network</td>
<td></td>
</tr>
<tr>
<td>806</td>
<td>Boroxol rings</td>
<td></td>
</tr>
<tr>
<td>760</td>
<td>BO(_3)–BO(_4) bond-bending vibrations</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>Bending of B–O–B linkage</td>
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</tr>
<tr>
<td>~694</td>
<td>Combined vibrations of BO(_4) and PbO(_4) groups</td>
<td>[83–85]</td>
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<tr>
<td>680</td>
<td>B–O–B bond-bending vibrations from pentaborate group or bending vibrations of BO(_3) triangles</td>
<td>[80]</td>
</tr>
<tr>
<td>~616</td>
<td>Bending of O–B–O</td>
<td>[89]</td>
</tr>
<tr>
<td>&lt;600</td>
<td>Pb(^{2+}), Zn(^{2+}), Mn(^{2+}), Bi(^{3+}), Li(^+), and Ba(^{2+}) or any metallic cations</td>
<td>[55, 80, 90–97]</td>
</tr>
</tbody>
</table>


dside 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\(_2\)O\(_3\) 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\(_3\)] 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\(_2\)O\(_3\) 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\(_2\)O\(_3\) 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\(^{-1}\)).

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