CHAPTER 2

FTIR SPECTROSCOPIC STUDY of 60B₂O₃-(40-x)PbO-xMCl₂ and 50B₂O₃-(50-x)PbO-xMCl₂ (M=Pb, Cd) GLASSES

2.1. Introduction

Infrared spectroscopy is an important tool for understanding the structure and dynamics of amorphous materials. IR spectroscopy is used to assign the observed absorption peaks to the proper vibration of the atoms in geometric grouping. But in the spectra of solids many 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 solids. 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 characteristic of these atom groups. Infrared spectroscopy has been extensively employed over the years to investigate the structure of glasses. Borate glasses, in particular, have been the subject of numerous infrared studies because of their structural peculiarities.

X-ray analysis shows that long-range translational symmetry is absent in glasses. But many glasses retain key structural features of the corresponding crystals in a disordered fashion. Two different basic approaches are proposed for the description of disordered structures. The random network hypothesis assumes that fundamental polyhedra present in crystals are also present in the corresponding glasses. They are connected by allowing some degree of bond angle distortion, and more or less complete freedom for values of dihedral angles. On the other hand, the crystalline
model\textsuperscript{12} considers glasses to consist of sub-microscopically ordered regions, which are connected to one other by a disordered structure.

Krogh-Moe's\textsuperscript{13} postulated a hypothesis to study the structure of borate glasses using Raman and IR spectroscopy. This hypothesis was based on the supposition that structural units or groups present in oxide melt and oxide glasses, resemble the units or groups present in corresponding crystalline compounds. This procedure had considerable success\textsuperscript{14,15} in identifying the specific groups in borate glasses. Krogh-Moe and co-workers\textsuperscript{13,16}, by a systematic study and comparison of the IR spectra of crystalline borate compounds and the corresponding borate glasses, demonstrated that remarkable similarity exists between the two series of spectra, and this was taken to indicate the presence of the same type of borate groups in the glassy state and in corresponding crystals. Subsequently, many investigators have extensively made use of infrared spectroscopy to explain the structure of borate glasses\textsuperscript{3-10}.

The structural groups which are found in borate compounds are shown in Figure 2.1. Many of these structural groups are present in borate glasses and a detailed interpretation of the infrared spectra of borate glasses is not an easy task. The situation becomes more complicated when more than one group gives rise to vibrational peaks in the same region and the identification of the peaks corresponding to the individual groups is rather difficult. In spite of these drawbacks IR spectroscopy has been used to develop a comprehensive model for borate glasses.
Figure 2. 1. Different structural groups found in Borate glasses

The important results of IR spectroscopic studies of borate glasses reported in the literature and which are used for the interpretation of the spectra of glasses in the present study are given in the following paragraphs.
According to Krogh-Moe the structure of boron-oxide glass consists of a random network of planar BO$_3$ triangles, with a certain fraction of six numbered boroxol rings. But according to Mozzi and Warren, boroxol rings build up the major part of glass. Guha and Walrafen postulate that the structure of vitreous B$_2$O$_3$ is made up of an equal portion of boroxol rings and BO$_3$ triangles.

Pure boron oxide glasses are characterized by IR reflection maxima at 656, 1276 and 1492 cm$^{-1}$. The strong band around 1276 cm$^{-1}$, and shoulder at 1492 cm$^{-1}$, are assigned to the B-O stretching vibrations. The weak band at 656 cm$^{-1}$ was attributed to the bending vibrations of B-O-B linkage within the glass network.

With the addition of alkali oxide, several changes occur in the borate glass network, due to the formation of poly borate groups. The spectra of alkali borate glasses containing different alkali ions are similar for low concentration of the alkali oxides. According to Konijnendijk for a concentration of alkali oxide up to 20-mole percentage, boroxol groups and tetra borate groups are predominant in the glass structure. Above 20-mole percentage of alkali oxide, the tetraborate groups are converted into diborate groups. Krogh Moe proposed that alkali borate glasses containing 33.3-mole percentage or less alkali oxide, consists of four different structural units linked together in various proportions. These four units are boroxol group, penta borate group, triborate group and diborate group. Griscom pointed out that the structure of glasses with composition (B$_2$O$_3$)$_{1-x}$-(K$_2$O)$_x$ (R=Li, Na, K, Rb, Cs) consists of B-O network built up from planar three co-ordinates and tetrahedral four co-ordinated boron atoms.

The far infrared spectra of alkali borate glasses $x$M$_2$O- $(1-x)$ B$_2$O$_3$ (M= Li, Na, K, Rb, Cs) have been studied by Kamitsos et al. The spectra were analysed to study the cation network interactions and their compositional dependence. Activation energies for the ion transport were also calculated.
from the absorption maximum in the far IR spectra. The structure of fused B\textsubscript{2}O\textsubscript{3} and a series of sodium borate glasses, are reported by Anderson et al.\textsuperscript{1} It was shown that hydrogen bond played an important role in the atomic arrangement in glasses of zero and low sodium content. The glass systems Na\textsubscript{2}O- (1-x) B\textsubscript{2}O\textsubscript{3} (0.35\leq x \leq 0.75) containing high concentration of Na\textsubscript{2}O were studied by Kamitsos et al\textsuperscript{22} using Raman and far infrared spectroscopy. Increasing Na\textsubscript{2}O content was found to induce the formation and subsequent destruction of diborate groups, loose diborate, loose BO\textsubscript{4} and nonbridging oxygens. High sodium contents (x > 0.60) cause the formation of highly charged pyroborate and orthoborate units. The far infrared spectra of these glasses were used to probe the localized vibrations of the alkali cations at the network sites.

Detailed study of the glass system B\textsubscript{2}O\textsubscript{3}-xLi\textsubscript{2}O-yLiCl using IR and Raman spectroscopy has established\textsuperscript{23,24} that addition of LiCl to B\textsubscript{2}O\textsubscript{3}-Li\textsubscript{2}O glass does not induce drastic changes in the structure. Comparing the infrared reflection spectra of B\textsubscript{2}O\textsubscript{3}-xLi\textsubscript{2}O-yLiCl and B\textsubscript{2}O\textsubscript{3}-xLi\textsubscript{2}O glasses, Irion et al\textsuperscript{23} observed remarkable similarity in the IR reflection spectra of these two glass systems. The authors concluded that the covalent boron-oxygen network in the structure depends only on the relative concentration of B\textsubscript{2}O\textsubscript{3} and Li\textsubscript{2}O, and even 55-percentage concentration of LiCl in the glass system did not produced any interaction in the network.

The infrared spectra of AgX-Ag\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3} (X= I, Br) glasses were reported\textsuperscript{25} and it was found that the glass structure consists of BO\textsubscript{3}, BO\textsubscript{4} and B-O-B groups regardless of the chemical composition of the glass. In addition to the above-mentioned groups, BO\textsubscript{3}X groups were also present in the glasses when the Ag\textsubscript{2}O/B\textsubscript{2}O\textsubscript{3} mole ratio was larger than unity.

The structure of the ternary glass system xMgO-yNa\textsubscript{2}O- B\textsubscript{2}O\textsubscript{3} were analysed by Kamitsos et al\textsuperscript{26}, in order to study the role of MgO in such glasses. It was shown that for the compositions x + y = 0.33, 0.53 and 0.67,
the presence of Mg\[^{2+}\] cations caused the destruction of diborate groups in favour of boroxol rings, tetrahedral groups, pyroborate, and metaborate units.

Doweidar et al\(^{27}\) studied the structure of ZnO-PbO-B\(_2\)O\(_3\) glasses of different compositions, by using the infrared spectroscopy. The IR spectra of glass systems of different compositions were compared and found that the basic glass structure was not affected by varying the composition of constituents. In this glass system ZnO was found to enter the structure both as glass modifier and as a glass former.

The infrared absorption spectra of the glass system Li\(_2\)O-B\(_2\)O\(_3\)-Al\(_2\)O\(_3\) have been reported by Khalifa et al\(^{28}\). The absorption spectra have been analyses and compared with the data obtained from crystalline borates. The effect of changing the glass composition on structure of the glasses has also been investigated\(^{28}\).

Ganguli and Rao\(^{29}\) have carried out the thermal and spectroscopic studies on a number of glasses in the glass system Li\(_2\)O-PbO-B\(_2\)O\(_3\) over a wide range of compositions. They have reported that PbO behaves as a network former in these glasses probably as (PbO\(_{4}\))\(^{2-}\) units. The formation of (PbO\(_{4}\))\(^{2-}\) units leads to the creation of neutral three coordinated borons, which in turn leads to the formation of four coordinated and singly coordinated boron atoms.

Recently, Varsamis et al\(^{30}\) reported infrared reflectance and transmission spectroscopy studies in the super ionic borate glass xAgI -(1-x) [Ag\(_2\)O-nB\(_2\)O\(_3\)] (n=2,0.5) in bulk and thin film forms. They have shown that the network structure of diborate glasses (n = 2) consists of B\(_2\)O\(_7\)\(^-\), B\(_3\)O\(_4\) triangles and B\(_4\)O\(_4\) tetrahedra (O and O' represent bridging oxygen and nonbridging oxygen respectively), and pyroborate glasses (n = 0.5) contain orthoborate triangles BO\(_3\)\(^-\), pyroborate dimmers B\(_2\)O\(_5\)\(^4+\), and B\(_4\)O\(_4\) tetrahedra.
They have also reported that substitution of AgI directly affected short-range order of the network.

In this chapter (chapter2) of the thesis FTIR spectroscopic studies of the glass systems 60B₂O₃-(40-x)PbO-xMCl₂ and 50B₂O₃-(50-x)PbO-xMCl₂ (M = Pb, Cd) of different compositions (x = 10, 15 and 20 mole percentage) are presented. The effects of substituting PbCl₂ or CdCl₂ for PbO on the structure of glass systems are discussed in comparison with reported IR spectra of binary and ternary systems of borate glasses. From the absorption spectra of the glass systems, the fraction of tetrahedrally coordinated boron atoms (N₄) was calculated. The variations of N₄ with the substitution of PbCl₂ or CdCl₂ for PbO in the glass systems are also discussed.

2.2. Experimental

In the present study, 60(B₂O₃)-(40-x)(PbO)-x(MCl₂) (M = Cd,Pb) and 50(B₂O₃)-(50-x)(PbO)-x(MCl₂) (M = Pb,Cd) glasses of different compositions (x = 10, 15 and 20) were prepared from appropriate amounts of analar grade H₃BO₃, PbO, and PbCl₂ or CdCl₂. The composition of the glass samples along with sample codes are given in table 2.1 and 2.2. Calculated quantities of the chemicals were mixed thoroughly in an agate mortar. While preparing glasses containing PbCl₂ or CdCl₂, considerable amount of vapour loss (Chlorine) may occur during the melting process. To minimize such a loss, the melting of the charge was done first by heating in an electric furnace for 1 hr at 500°C and then transferring the closed crucible in to another furnace kept at 850 to 950°C depending on the composition of the glasses. The melting process was continued for 15 minute. The melt was then poured in to a brass mould and pressed by another brass disc to quench the melt and to obtain glass discs of diameter 1cm and thickness approximately 1mm. The samples were then annealed below the glass transition temperature³¹ in a furnace preheated to 300°C for 3hrs and then allowed to cool to room temperature. The amorphous
nature of the glass samples was verified by x-ray diffraction analysis. The x-ray diffraction pattern of two typical samples is shown in figure 2.2.

![X-ray diffraction pattern](image)

**Figure 2.2.** X-ray diffraction pattern of (a) 60B₂O₃-25PbO-15PbCl₂ and (b) 60B₂O₃-25PbO-15CdCl₂ glass samples

The familiar KBr pellet technique was used for recording the IR spectra of the samples. The spectra were recorded at room temperature in the range 400-4000 cm⁻¹. A BRUKER IFS 66V FTIR SPECTROMETER was used for recording the IR spectra of the glass samples.

2.3. Results and Discussion

The FTIR transmittance spectra of the glass systems 60B₂O₃-(40-x) PbO-xMCl₂ and 50B₂O₃-(50-x)PbO-xMCl₂ (M = Pb, Cd) containing different concentrations (x = 10, 15 and 20 mole percentage) of PbCl₂ and CdCl₂ recorded in the present study are given in figures 2.3 - 2.14. Usually the IR spectra of borate glasses are active in 600-750, 750-1150, and 1150-1600 cm⁻¹ regions. It is widely accepted that the broad band in borate glasses observed between 600-750 cm⁻¹ is the result of band bending vibrations of B-O-B linkage of boron-oxygen network. The region 800-1100 cm⁻¹ is attributed to the B-O stretching of tetrahedral BO₄ units while that in the region 1150-1600 cm⁻¹ is due to the B-O band stretching of BO₃ units. It is observed from
the figures 2.3-2.14 that the spectra of the samples in the present study contain bands in all the three regions.

The various spectral features observed in the spectra of the samples in the present study are discussed, based on the composition of the glasses, in the following sections.

2.3.a. 60B$_2$O$_3$-(40-x)PbO-xPbCl$_2$ and 50B$_2$O$_3$-(50-x)PbO-xPbCl$_2$ (x= 10,15,20) glass system

FTIR transmission spectra of 60B$_2$O$_3$-(40-x)PbO-xPbCl$_2$ and 50B$_2$O$_3$-(50-x)PbO-xPbCl$_2$ (x = 10,15 and 20, sample codes P1 to P3 and P4 to P6 respectively) glass samples are shown in figures 2.3- 2.8.

![Figure 2.3. FTIR spectra of 60B$_2$O$_3$-30PbO-10PbCl$_2$ glass sample](image)

**Figure 2.3.** FTIR spectra of 60B$_2$O$_3$-30PbO-10PbCl$_2$ glass sample
Figure 2.4. FTIR spectra of $60B_2O_3-25PbO-15PbCl_2$ glass sample

Figure 2.5. FTIR spectra of $60B_2O_3-20PbO-20PbCl_2$ glass sample
Figure 2.6. FTIR spectra of $50B_2O_3-40PbO-10PbCl_2$ glass sample

Figure 2.7. FTIR spectra of $50B_2O_3-35PbO-15PbCl_2$ glass sample
Figure 2.8. FTIR spectra of 50B₂O₃-30PbO-20PbCl₂ glass sample

Table 2.1 shows the dominant peaks observed in the spectra along with glass compositions and sample codes used. In the spectra of 60B₂O₃-(40-x) PbO-xPbCl₂ glass system (P1 to P3), the dominant peaks were observed around 1348, 1023, 990, 675 cm⁻¹, weak bands occurred around 1392, 744 cm⁻¹, and shoulders were observed around 1235 and 860 cm⁻¹. The dominant peaks in 50B₂O₃-(50-x)PbO-xPbCl₂ glasses (P4 to P6) were observed around 1345, 950 and 680 cm⁻¹ and a shoulder was observed at 1235 cm⁻¹. When PbCl₂ was progressively substituted for PbO in both glass systems, three broad bands appeared around 1325, 950, and 675 cm⁻¹.

The IR spectra of 60B₂O₃-(40-x) PbO-x PbCl₂ and 50B₂O₃-(50-x) PbO-xPbCl₂ glasses showed a band near 1340 cm⁻¹ for all the six concentrations of PbCl₂. In the case of ZnO-PbO-B₂O₃ glasses, the IR absorption band at 1340 cm⁻¹ was assigned to the B-O stretching vibration of trigonal BO₃⁻³ units in metaborate, pyroborate and orthoborates. In comparison with the reported spectra of ZnO-PbO-B₂O₃ glasses, the band observed near 1340 cm⁻¹ in the
present study was assigned to B-O stretching vibration of trigonal $BO_3^{3-}$ units in meta borate, pyroborates and orthoborates.

**Table 1**

Sample code, Glass composition and observed IR bands of 60B$_2$O$_3$-(40-x) PbO-xPbCl$_2$ and 50B$_2$O$_3$-(50-x) PbO-xPbCl$_2$ glass system.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Glass composition</th>
<th>Band Positions</th>
<th>←600-750→</th>
<th>←750-1150→</th>
<th>←1150→</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>60B$_2$O$_3$-30PbO-10PbCl$_2$</td>
<td></td>
<td>479</td>
<td>680</td>
<td>744</td>
</tr>
<tr>
<td>P2</td>
<td>60B$_2$O$_3$-25PbO-15PbCl$_2$</td>
<td></td>
<td>675</td>
<td>753</td>
<td>930</td>
</tr>
<tr>
<td>P3</td>
<td>60B$_2$O$_3$-20PbO-20PbCl$_2$</td>
<td></td>
<td>435</td>
<td>687</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>50B$_2$O$_3$-40PbO-10PbCl$_2$</td>
<td></td>
<td>442</td>
<td>683</td>
<td></td>
</tr>
<tr>
<td>P5</td>
<td>50B$_2$O$_3$-35PbO-15PbCl$_2$</td>
<td></td>
<td>439</td>
<td>693</td>
<td></td>
</tr>
<tr>
<td>P6</td>
<td>50B$_2$O$_3$-30PbO-20PbCl$_2$</td>
<td></td>
<td>680</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the present study, the glass sample P1 showed a band at 1392 cm$^{-1}$ which shifted to 1383 cm$^{-1}$ in spectrum of sample P2. In glass sample P3 this band was not observed. In the case of magnesium sodium borate glasses with the glass composition xMgO-yNa$_2$O-B$_2$O$_3$, a band at 1400 cm$^{-1}$ that showed a systematic frequency down shift on increasing the modifier concentration was assigned the ring stretching vibrations by Kamitsos et al$^{26}$. Also in lithium borate glasses$^{13}$ the high frequency envelope around 1380 cm$^{-1}$ showed a compositional dependence and was attributed to the stretching of B-O bonds of rings of various borate arrangements. The band observed at 1392 cm$^{-1}$ in the spectrum of sample P1 was found to be shifted to 1383 cm$^{-1}$ in the case of P2, exhibiting a compositional dependence and this band could be assigned to the ring stretching vibrations. The intensity of band at 1383 cm$^{-1}$ in the spectrum of the sample P2 was lower than that of the band around 1392 cm$^{-1}$
shown by sample P1 and such a band was not observed in the case of the samples P3 to P6 indicating that boron-oxygen rings were progressively destroyed as PbCl$_2$ was substituted for PbO.

Krogh-Moe$^{32}$ observed a band around 1250 cm$^{-1}$ in the IR spectrum of glassy B$_2$O$_3$ and assigned this band to the B-O stretching vibrations that involve the linkage of different groups. In the spectrum of xMgO-yNa$_2$O-B$_2$O$_3$ glasses, Kamitsos et al$^{26}$ assigned a band at 1250 cm$^{-1}$ to the B-O stretching vibration involving mainly boroxol and tetraborate groups. The band that appeared at 1260 cm$^{-1}$ in lithium borate glasses was also assigned$^{32}$ to the B-O stretching of B-O-B linkage involving boroxol and tetraborate groups. The shoulder observed around 1235 cm$^{-1}$ in the spectra of all the samples containing different concentrations of PbCl$_2$ in 60B$_2$O$_3$-(40-x)PbO-xPbCl$_2$ and 50B$_2$O$_3$-(50-x)PbO-xPbCl$_2$ glass samples in the present study can be assigned to the B-O stretching vibrations of B-O-B linkage that involves mainly boroxol and tetraborate groups.

The band around 1130 cm$^{-1}$ in lithium borate glasses was identified as the asymmetric stretching vibrations of B-O-B linkage in the pyroborate units$^{33}$. The band shown by the glass sample P1 around 1160 cm$^{-1}$ may be assigned to pyroborate units. This band was absent in the spectra of the glass samples P2, P3, and P4 to P6 indicating that pyroborate units were absent in these samples.

The bands in the region 850-1100 cm$^{-1}$ in the IR spectra of borate glasses were attributed to the B-O stretching vibrations of BO$_4$ units$^{26}$. In the absorption region of BO$_4$ units (850-1100 cm$^{-1}$), usually three bands are evident around 880, between 900-1000 and around 1056 cm$^{-1}$. In the 850-1100 cm$^{-1}$ region, crystalline tetraborate compounds show strong bands around 1020 and 880 cm$^{-1}$ while lithium borate absorbs strongly around 970 cm$^{-1}$.$^{30}$ Kamitoss et al$^{26}$ assigned the 1050 and 880 cm$^{-1}$ bands to BO$_4$ vibration in triborate and pentaborate groups respectively. The BO$_4$
tetrahedral vibrations in diborate groups give rise to the absorption in the 900-
1000 cm\(^{-1}\) region\(^{26}\). In the present study the band observed in the sample P1
around 1025 cm\(^{-1}\) was attributed to the vibration of borate arrangements
containing BO\(_4\) tetrahedra in triborate groups. The broad band observed in all
the six samples (sample code P1 to P6) in the 900-1000 cm\(^{-1}\) region could be
due to the vibrations of the BO\(_4\) tetrahedra in diborate groups. The shoulder
around 860 cm\(^{-1}\) present in the spectrum of sample P1 was assigned to the
vibration of borate arrangements containing BO\(_4\) tetrahedra in pentaborate
group. This band was not observed in the spectra of glass samples P2-P6.

A weak band was observed around 750 cm\(^{-1}\) in the spectra of the
samples P1 and P2. Such a band could be assigned to the B-O-B bending of
bridges containing one trigonal and one tetrahedral boron\(^{4}\).

In the case of lithium borate glasses with low Li\(_2\)O content\(^{34}\), a broad
band around 700 cm\(^{-1}\) was assigned to the bending of B-O-B linkage of B-O
network. In the infrared spectroscopic study of lithium borate glasses with
high Li\(_2\)O content, Kamitsos et al\(^{33}\) observed a band at 660 cm\(^{-1}\) which was
assigned as due to B-O-B bending of B\(_2\)O\(_4\)\(^{4-}\) units. In comparison with the
reported spectra\(^{33}\) the band observed around 680 cm\(^{-1}\) in the present study was
assigned to the B-O-B bending vibrations of B\(_2\)O\(_4\)\(^{-}\) units.

2.3.b. \(60\text{B}_2\text{O}_3-(40-x)\text{PbO-xCdCl}_2\) and \(50\text{B}_2\text{O}_3-(50-x)\text{PbO-xCdCl}_2\) (x = 10, 15, 20) glass system

The FTIR transmission spectra of \(60\text{B}_2\text{O}_3-(40-x)\text{PbO-xCdCl}_2\) and
\(50\text{B}_2\text{O}_3-(50-x)\text{PbO-xCdCl}_2\) (x = 10, 15, 20 with sample codes C1 to C3 and C4
to C6 respectively) glass samples are shown in figures 2.9-2.14.
Figure 2.9. FTIR spectra of 60H2O3-30PbO-10CdCl2 glass sample

Figure 2.10. FTIR spectra of 60B2O3-25PbO-15CdCl2 glass sample
**Figure 2.11.** FTIR spectra of $60\text{B}_2\text{O}_3-20\text{PbO}-20\text{CdCl}_2$ glass sample

**Figure 2.12.** FTIR spectra of $50\text{B}_2\text{O}_3-40\text{PbO}-10\text{CdCl}_2$ glass sample
Figure 2.13. FTIR spectra of $50\text{B}_2\text{O}_3\text{-35PbO-15CdCl}_2$ glass sample

Figure 2.14. FTIR spectra of $50\text{B}_2\text{O}_3\text{-30PbO-20CdCl}_2$ glass sample
The positions of the observed bands along with the sample codes are shown in table 2.2. The dominant peaks were observed around 1345 cm\(^{-1}\), between 900 to 1000 and around 680 cm\(^{-1}\). Also a shoulders was observed around 1235 cm\(^{-1}\) in the spectra of all the samples.

### Table 2.2

Sample code, Glass composition and observed IR bands of 60B\(_2\)O\(_3\)-(40-\(x\)PbO-xCdCl\(_2\) and 50B\(_2\)O\(_3\)-(50-\(x\))PbO-xCdCl\(_2\) glass system.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Glass composition</th>
<th>Band Positions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(-600,\text{-}750)</td>
</tr>
<tr>
<td>C1</td>
<td>60B(_2)O(_3)-30PbO-10CdCl(_2)</td>
<td>683</td>
</tr>
<tr>
<td>C2</td>
<td>60B(_2)O(_3)-25PbO-15CdCl(_2)</td>
<td>429 680</td>
</tr>
<tr>
<td>C3</td>
<td>60B(_2)O(_3)-20PbO-20CdCl(_2)</td>
<td>681</td>
</tr>
<tr>
<td>C4</td>
<td>50B(_2)O(_3)-40PbO-10CdCl(_2)</td>
<td>687</td>
</tr>
<tr>
<td>C5</td>
<td>50B(_2)O(_3)-35PbO-15CdCl(_2)</td>
<td>440 690</td>
</tr>
<tr>
<td>C6</td>
<td>50B(_2)O(_3)-30PbO-20CdCl(_2)</td>
<td>475 677</td>
</tr>
</tbody>
</table>

The assignment of high frequency bands (1350-1500 cm\(^{-1}\)) to specific borate groups is not easy, because most of the borate groups absorb in this region. The spectra of all the glass samples 60B\(_2\)O\(_3\)-(40-\(x\))PbO-xCdCl\(_2\) and 50B\(_2\)O\(_3\)-(50-\(x\))PbO-xCdCl\(_2\) containing different concentrations of CdCl\(_2\) showed a band around 1345 and a shoulder at 1235 cm\(^{-1}\). As mentioned earlier in section 2.3(a) the band around 1345 cm\(^{-1}\) could be assigned to the B-O stretching vibration of trigonal \(BO_3^2\) units and the shoulder observed around 1235 cm\(^{-1}\) could be assigned to B-O stretching vibrations of B-O-B linkage that involved mainly boroxol and tetraborate groups.
The absorption band observed around 1025 cm^{-1} in the spectra of samples C4 and C5 was assigned to BO_4 vibration in triborate groups\textsuperscript{26}. Such a band was not observed in the spectra of the samples C6 and C1 to C3. But the spectra of all the six samples containing different concentrations of CdCl_2 showed a broad band between 900-1000 cm^{-1}. As mentioned earlier in the discussion of FTIR spectra of 60B_2O_3-(40-x) PbO-xPbCl_2 and 50B_2O_3-(50-x) PbO-xPbCl_2 glass systems, the band between 900-1000 cm^{-1} was assigned to the vibration of borate arrangements contained in BO_4 tetrahedra\textsuperscript{27} in diborate groups.

The absorption in the low frequency region of the mid infrared (550-800 cm^{-1}) is due to the bending vibration of various borate units\textsuperscript{33,34}. The band observed around 680 cm^{-1} in the spectra of all the samples (C1 to C6) was assigned to the B-O-B bending of B_2O_4\textsuperscript{4+} units.

The absorption band around 3500 cm^{-1} in the spectra of all glass samples in the present study could be attributed to the O-H stretching vibration\textsuperscript{35} of absorbed water in the samples.

A shoulder around 450 cm^{-1} in the spectra of ZnO-PbO-B_2O_3 glasses was assigned\textsuperscript{27} to the vibration of metal cation such as Pb\textsuperscript{2+} or Zn\textsuperscript{2+}. In comparison with this report, the band observed around 450 cm^{-1} in the spectra of the samples P1 to P6 was assigned to the vibration of Pb\textsuperscript{2+} metal cations.

The similarity of the FTIR spectra of 60B_2O_3-(40-x)PbO-x MCl_2 and 50B_2O_3-(50-x)PbO-xMCl_2 (M = Pb, Cd) glass samples in the present study indicated that the basic borate glass structure was not affected by the substitution of CdCl_2 for PbCl_2.
2.4. Determination of the Fraction of Tetrahedrally Coordinated Boron Atom

It is well known from infrared spectroscopic studies that stretching vibrations of B-O groups are active above 800 cm$^{-1}$. It is also known that, 1600-1100 cm$^{-1}$ absorption band observed in borate glasses is due to the stretching vibrations of trianguly co-ordinated boron atoms, B$_3$, in BO$_3$ triangles and BO$_2$O$^-$ units (where O represents bridging oxygen and O$^-$ represents a non-bridging oxygen), and absorption band in 1100-800 cm$^{-1}$ region is due to the stretching vibrations of tetrahedrally co-ordinated boron atoms B$_4$ in BO$_4^-$ units. The concentration of the borate units (B$_3$ and B$_4$) is proportional to the area of the characteristic component bands. The area of the absorption bands between 1600- 1100 cm$^{-1}$ ($A_3$) and 1100-800 cm$^{-1}$ ($A_4$) is respectively proportional to the total concentration of triangular and tetrahedral boron groups in the borate glass structure. The area $A_4$ normalized with respect to total infrared absorption area ($A_3+ A_4$) from 800-1650 cm$^{-1}$ is a measure of the fraction of tetrahedrally co-ordinated boron atoms $N_4$. The absorbance spectra of P1 to P6 and C1 to C6 glass samples in the 800 to 1650 cm$^{-1}$ wave number region are shown in figures 2.14 and 2.15 respectively.
Figure 2.14. Infrared absorption spectra of of $60\text{B}_2\text{O}_3-(40-x)\text{PbO-x PbCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO-x PbCl}_2$ glasses of different composition.

Figure 2.15. Infrared absorption spectra of of $60\text{B}_2\text{O}_3-(40-x)\text{PbO-x CdCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO-x CdCl}_2$ glasses of different composition.

The fractions of the tetrahedrally coordinated boron ($N_4$), calculated from the absorption spectra of the glass samples in the present study are given in table 2.3.
Table 2.3.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Fraction of tetrahedrally coordinated boron atoms (N₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.428</td>
</tr>
<tr>
<td>P2</td>
<td>0.416</td>
</tr>
<tr>
<td>P3</td>
<td>0.404</td>
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<tr>
<td>P4</td>
<td>0.470</td>
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<tr>
<td>P5</td>
<td>0.443</td>
</tr>
<tr>
<td>P6</td>
<td>0.442</td>
</tr>
<tr>
<td>C1</td>
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</tr>
<tr>
<td>C2</td>
<td>0.415</td>
</tr>
<tr>
<td>C3</td>
<td>0.414</td>
</tr>
<tr>
<td>C4</td>
<td>0.450</td>
</tr>
<tr>
<td>C5</td>
<td>0.432</td>
</tr>
<tr>
<td>C6</td>
<td>0.420</td>
</tr>
</tbody>
</table>

It can be seen that N₄ decreases with increase in mole percentage of PbCl₂ in 60B₂O₃-(40-x)PbO-xPbCl₂ and 50B₂O₃-(50-x)PbO-xPbCl₂ glass systems.

Substituting PbCl₂ for PbO resulted in replacement of one O²⁻ by two Cl⁻ ions, maintaining the lead (Pb) concentration constant. As more and more PbCl₂ was substituted for PbO, the oxygen to boron (O/B) ratio decreased. This decrease corresponds to gradual replacement of three dimensionally linked B₃O₄ tetrahedra by planar BO₃ triangles.

In 60B₂O₃-(40-x)PbO-xCdCl₂ and 50B₂O₃-(50-x)PbO-xCdCl₂ glass samples, CdCl₂ was substituted for PbO in a similar fashion as PbCl₂ was-
substituted for PbO in 60B₂O₃-(40-x)PbO-xPbCl₂ and 50B₂O₃-(50-x)PbO-xPbCl₂ glasses. The variation in the calculated tetrahedrally co-ordinated boron atoms N₄, in CdCl₂ substituted glasses showed a variation similar to that of PbCl₂ substituted glasses indicating that the substitution of CdCl₂ for PbCl₂ did not affected the basic borate glass structure in the present study.

2.5 Conclusion

The FTIR transmission spectra of ternary glasses systems 60B₂O₃-(40-x) PbO-xMCl₂ and 50B₂O₃-(50-x)PbO-xMCl₂ (M= Pb,Cd) with x = 10,15 and 20 mole percentage were recorded. The features of the spectra were discussed in the light of reported spectra of binary and ternary glasses. The addition of PbCl₂ for PbO was seen to affect a little on the structure of the ternary glasses in the present study. The structure of the glasses is build up of random network of BO₃⁺ bearing metaborate, pyroborate and orthoborate groups, BO₄ tetrahedra containing diborate, triborate and pentaborate groups, and a fewer number of other groups like boroxol rings. Tetrahedrally co-ordinated boron atoms (N₄) decrease with increase in mole percentage of PbCl₂ or CdCl₂ indicates that three dimensionally linked B₂O₄ tetrahedra are gradually replaced by planar BO₃ triangles.

References


32. J. Korogh-Moe, Phys. Chem. Glasses, 6 (1965) 46