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By G. Ramadevudu, S.Lakshmi Srinivasa Rao, Md. Shareeffuddin, M.Narasimha Chary & M.Lakshmipathi Rao
Osmania University, Hyderabad, India

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G. Ramadevudu[α], S.Lakshmi Srinivasa Rao[σ], Md. Shareeffuddin[ρ], M.Narasimha Chary[ρ]
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I. INTRODUCTION

Borate glasses constitute an interesting system in which the charged network building units can be either borate triangles with non-bridging oxygen atoms or borate tetrahedrons with all bridging oxygen atoms. Many studies were reported to elucidate the presence of different structural units in various borate glasses. Based on structure-property relationship many studies on properties such as electrical and optical were reported in these glasses [1-3]. Optical energy band gaps, Urbach energies, refractive indices, broad band emission of various borate glasses like alkali borate, lead borate, and bismuth borate glasses have been reported by several workers [4-6]. Alkaline earth borate glasses containing rare earth dopants are some of the promising candidates for optoelectronic devices such as optical fiber amplifiers and tunable lasers [4].

Borate glasses containing PbO, ZnO, MgO form chemically stable glasses. In addition, these glasses exhibit challenging electrical, optical and thermal properties [7]. Glasses containing heavy metal oxides such as PbO can be used for laser hosts, high refractive index materials, linear and non-linear photonic materials etc [8]. Lead borate glasses are of research interest, because PBO greatly improves the non-linear optical properties of the glass [4, 9, 10]. Addition of MgO also improves stability of the borate glasses.

Infrared spectroscopy is the most advantageous and extremely used tool over the years to investigate the structure of glasses. Optical absorption is another useful spectroscopic technique to get the band structure and optical energy band gap in glasses [11]. Optical basicity, an important property of glasses, is the average electron donor power of the individual oxides in the glass matrix [12]. Optical basicity refers to the state of the oxygen atoms and how they would react to solute metal ions.

The survey of literature shows that studies on the infrared and optical properties of magnesium lead borate glasses is limited. Therefore, in this paper, studies on infrared spectra, optical energy band gap and optical basicity studies in the new and novel magnesium lead borate glasses with general formula (10-x) MgO-xMgCl$_2$-40PbO-50B$_2$O$_3$ are reported. The studies on electrical conduction through Mg^{2+} ion in these glasses and their possible application as electrolytes in the fabrication of solid state batteries are going on in our laboratory. The advantages of magnesium based glasses are (i) Mg is less hygroscopic compared to lithium, potassium and sodium (ii) Mg has diagonal symmetry with lithium (iii) magnesium is eco-friendly and (iv) MgO act as a glass network modifier (GNM) at low concentrations and as a glass network former (GNF) at higher composition in the glass matrix.

II. EXPERIMENTAL

Glasses with the general formula (10-x) MgO-xMgCl$_2$-40PbO-50B$_2$O$_3$ (x = 0, 1, 2, 3, 4, 5, 6, 7, 8 and 10 mole %) were prepared by the conventional melt quenching technique. Analar grades H$_3$BO$_3$, MgCl$_2$.6H$_2$O, lead monoxide (PbO) and magnesium oxide (MgO) were the starting materials. These materials were mixed in the appropriate mole percent to get required composition. The ingredients after thorough mixing were taken in a porcelain crucible and melted in an electrical furnace maintained at 1000^{0}C for about 30-40 minutes. To obtain homogeneity, the molten melt was shaken frequently. The melt was quickly poured onto a stainless steel plate (containing cuboids- 30mm x 7mm x 2mm and circular groves of 1cm diameter of 1mm thickness) and pressed with a steel rod, both being

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Author α : Department of Physics, Vasavi College of Engineering, Ibrahimbagh, Hyderabad-31, India. E-mail : dr.ramdev@gmail.com
Author σ : Department of Physics, Bhavan's New Science College, Narayanaguda, Hyderabad, India.
Author ρ : Department of Physics, Osmania University, Hyderabad - 500 007, India.

maintained at 373K. The glass samples thus obtained were clear, transparent and bubble free. Grinding and polishing are employed to get samples with uniform thickness of about 0.3 – 0.7 mm. Table.1 gives the glass compositions studied in the present investigation.

Philips Xpert PRO XRD (PanAnalytic) model powder X-ray diffractometer with copper K_α tube was used to record the X-ray diffractograms. All the X-ray diffractograms are recorded at room temperature. All the recorded peak free X-ray diffractograms confirmed the amorphous nature of the samples, used in the present studies. Figure.1 shows the X-ray diffractograms of the glass samples G4 and G5.

Finely powdered glass samples were used to record infrared spectra at room temperature by KBr pellet method at room temperature. Perkin Elmer FTIR spectrometer model Spectrum BX was used to record IR spectra. The samples were scanned in the wave number range 4400-400cm^{-1}. The resolution of the instrument is 8cm^{-1}.

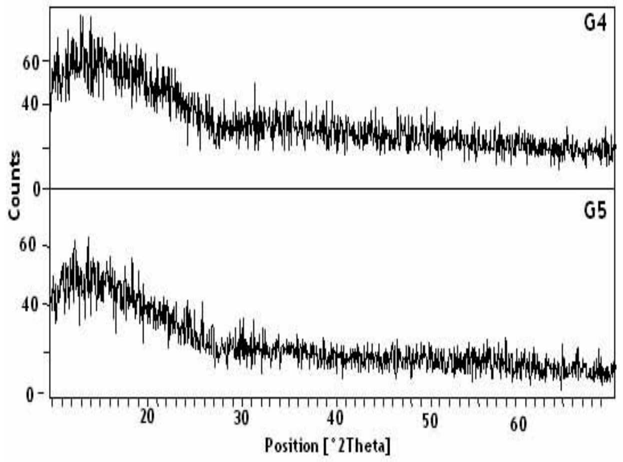


Fig.1: X-ray diffractograms of the glass samples G4 and G5.

Finely polished glass pieces of uniform thickness were used to record optical absorption spectra on Shimadzu UV-VIS-NR-3100 spectrophoto - meter in the wavelength range 300nm to 500nm at room temperature.

III. RESULTS AND DISCUSSION

a) FTIR Studies

Figure.2 shows the infrared spectra of the present glass samples. The FTIR spectra exhibited seven to eight peaks. These peaks can be divided as sharp, medium and broad. Similar to other borate glasses, the present samples also exhibited the following three main characteristic active vibrational modes of borate network (i)1200-1600 cm^{-1} group of bands which are due to the asymmetric stretching relaxation of B-O bond of trigonal BO_3 units (ii)Bands in the range 800-1200 cm^{-1} due to B-O bond stretching of tetraghedral BO_4 units and (iii) Peaks around 700 cm^{-1} due to bending of B-O-B linkages in the borate networks [13-16].

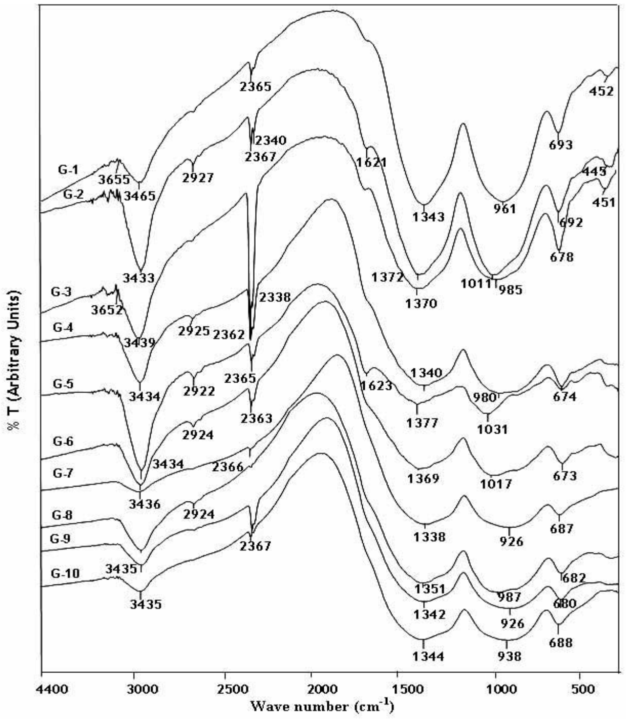


Fig.2 : FTIR spectra of the present glass samples

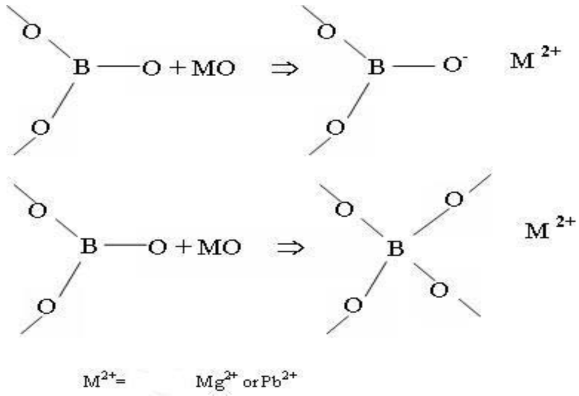
The bands in the range 3200-3600cm^{-1} in the IR spectra are attributed to the hydroxyl or water groups originating from molecular water [9, 13]. The broad band around 3434cm^{-1} corresponds to OH stretching vibration [17]. The presence of hydrogen bending in all the glass samples is ascertained due to the band at 2924cm^{-1}. The peaks around 2338-2367 cm^{-1} are attributed to –OH groups [18, 9].

The weak band around 1622cm^{-1} indicates presence of crystal water with H-O-H bending mode in the samples. The IR bands in the range 1321-1376cm^{-1} can be assigned to B-O asymmetric stretching vibrations of $(BO_3)^{3-}$ units in meta, pyro and ortho borates [19]. The peaks around 1011-1031 cm^{-1} may be assigned to asymmetric stretching of (B4)-O. The presence of diborate, formation of non-bridging oxygens (NBOs) and existence of MgO_4 tetrahedra can be confirmed from the bands 926-987 cm^{-1} [14]. Absorption peaks around 950-1050cm^{-1} may also be due to stretching vibrations of tetrahedral BO_4 group [8]. The absorption bands in the range 672-692 cm^{-1} indicates bending of B-O-B linkages in the borate network. The bands 446-453cm^{-1} show the existence of vibration of Pb^{2+} and/or Mg^{2+} ions in the network vacancies. The occurrence of these bands corresponds to Mg and Pb cations in glass network modifier (GNM) positions. However as the mole percent of PbO is greater (40 mole %), in the glass network it should act as glass former along with B_2O_3. At lower concentrations MgO acts as GNM [8] and hence in the present case MgO plays a role of network modifier. The existence of Mg^{2+} and formation of NBOs create channels for Mg^{2+} ion migration.

Hydroxyl or water groups presence is not only due to absorption of moisture in KBr pellet techniques of recording IR spectra, but also because borate glasses contain water traces and strongly dependent on OH content. The presence of crystal water and OH groups in the present glasses are due to retention of traces of water both due to H_3BO_3 and $MgO.6H_2O$ along with the capture of moisture by KBr.

It can be seen from the FTIR spectra that the effect of composition on the types of structural groups present in the glass matrix is almost negligible. This is because of small compositional variation (MgO and $MgCl_2$ concentration is limited to x = 10 mole %). The lead-borate network remains the same. This can also be attributed to the presence of symmetric triangles of $(BO_3)^{3-}$, asymmetric units of $(BO_3)^{3-}$, and formation of BO_4 tetrahedral units.

Infrared spectroscopy provides insights into the interaction between alkali/alkaline metal ions and B-O network. Addition of alkali or alkaline earth oxides (M_2O) to borate glasses changes the coordination of boron from three to four. In addition, complicated structures containing BO_3 and BO_4 units like di, tri, meta, penta borates are formed without changing B-O bond distance i.e short range order [20, 21]. Introduction of halogens (Cl, Br, I) into the interstices of borate network create disorder of BO_3 units. This disorder is due to the expansion of B-O network [20]. The presence Cl^- ions can produce path ways for Mg^{2+} by B-O network expansion further with formation of NBOs. The following structural units may be present in the present glass networks.



Borate glasses consist of random network of planar BO_3 triangle units with boroxol rings [22]. In the present glass samples the characteristic frequency of boroxol ring at 806cm^{-1} in the IR spectra is not observed. Hence no boroxol rings are present in the glass samples.

It may be evident from FTIR spectra that the present glasses consists of trigonal BO_3 and tetrahedral BO_4 structural units. The presence of tetrahedrally coordinated boron in the glass structure is evident from 1320-1376 cm^{-1} bands [23]. Hence the structure of present glasses, with absence of boroxol rings (806 cm^{-1}) consists of randomly connected trigonal BO_3 and tetrahedral BO_4 groups. It can be confirmed from the studies that MgO takes GNM positions. The glass matrix can be thought of consisting network of tri, tetra and penta borate (~1320-1376 cm^{-1}) units of BO_3 groups and tri, tetra, penta and diborate (~926-1031 cm^{-1}) units of BO_4 groups [13]. The broadening of the IR peaks can be attributed to the expansion of B-O network due to the presence of chlorine ions.

b) *Optical Energy band gap, refractive index and Optical basicity*

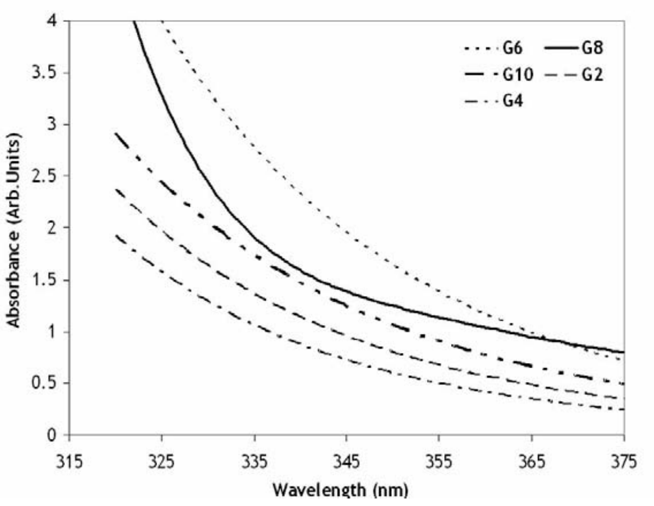


Fig.3 : Optical absorption spectra of few glass samples.

Figure.3 shows the optical absorption spectra of some of the glass samples. The optical absorption coefficient $\alpha(\nu)$ of a glass of thickness (t) near the absorption edge can be calculated from the relation [24].

$$\alpha(\nu) = \frac{1}{t}\ \ln(\frac{I_o}{I_t}) \qquad (1)$$

where $\ln(\frac{I_o}{I_t})$ is the absorbance, I_0 and I_t are the intensities of incident and transmitted light respectively. The optical absorption of disordered materials [$\alpha(\nu) \geq 10^4 cm^{-1}$] follows Davis and Mott power law [23]

$$\alpha(\nu) = B\ \frac{(h\nu - E_{opt})^r}{h\nu} \qquad (2)$$

where 'r' can take values ⅓, ½, 2, 3 for direct forbidden, direct allowed, indirect allowed, indirect forbidden transitions respectively. Here E_{opt} is the optical energy band gap, B is band tailing parameter (constant) and hν is the incident photon energy. Tauc's plot $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ for r = 2 which corresponds to indirect inter band optical transitions between conduction and valence bands are shown in figure.4. Extrapolation of the linear region of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$

plot to meet x-axis at $(\alpha\hbar\omega)^{1/2} = 0$ gives the optical energy band gap, E_{opt}. For absorption in lower incident photon energy [(υ) lying between 10^2-10^4 cm^{-1}] absorption coefficient α(υ) follows Urbach law given by

$$\alpha(\nu) = Cons\tan t\ \ X\ \ \frac{h\nu}{\Delta E} \qquad (3)$$

where ΔE is the Urbach's energy. Urbach's energy corresponds to the width of tail of localized states in the band gap. Hence it is a measure of disorder in amorphous solids [25]. The exponential tail is due to phonon assisted indirect electronic transitions [26]. Urbach energy values are calculated from the slopes of linear regions of the graphs lnα(ν) vs. hν. Theoretical energy band gap (E_{opt}) and Urbach energy values (ΔE) of (10-x) MgO-$xMgCl_2$-$40PbO$-$50B_2O_3$ glasses are given in Table.1, along with values reported in the literature.

The refractive index (n) of the samples is calculated theoretically from the optical energy band gap (E_{opt}) values using the relation proposed by Dimitrov and Sakka [27]

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_{opt}}{20}} \qquad (4)$$

Table 1 : Glass composition, energy band gap (E_{opt}) and Urbach energy values (ΔE) of (10-x)MgO-$xMgCl_2$-$40PbO$-$50B_2O_3$ glasses.

S.No	Glass	Composition	Optical bandgap E_{opt} (eV) (±0.01eV)	Urbach Energy (ΔE) eV (±0.001)	Reference
1	G1	$10MgO$-$40PbO$-$50B_2O_3$	3.34	0.074	Present
2	G2	$9MgO$-$1MgCl_2$-$40PbO$-$50B2O_3$	3.36	0.075	Present
3	G3	$8MgO$-$2MgCl_2$-$40PbO$-$50B2O_3$	3.37	0.081	Present
4	G4	$7MgO$-$3MgCl_2$-$40PbO$-$50B_2O_3$	3.29	0.101	Present
5	G5	$6MgO$-$4MgCl_2$-$40PbO$-$50B_2O_3$	3.30	0.117	Present
6	G6	$5MgO$-$5MgCl_2$-$40PbO$-$50B_2O_3$	3.31	0.105	Present
7	G7	$4MgO$-$6MgCl_2$-$40PbO$-$50B_2O_3$	3.32	0.101	Present
8	G8	$3MgO$-$7MgCl_2$-$40PbO$-$50B_2O_3$	3.33	0.096	Present
9	G9	$2MgO$-$8MgCl_2$-$40PbO$-$50B_2O_3$	3.34	0.090	Present
10	G10	$10MgCl_2$-$40PbO$-$50B_2O_3$	3.36	0.096	Present
11		$50B_2O_3$-$40PbO$-$10PbCl_2$	3.22	0.430	[30]
12		$70B_2O_3$-$15PbO$-$15Bi_2O_3$	2.16	0.429	[32]
13		$50B_2O_3$-$50PbO$	2.73	0.21	[33]

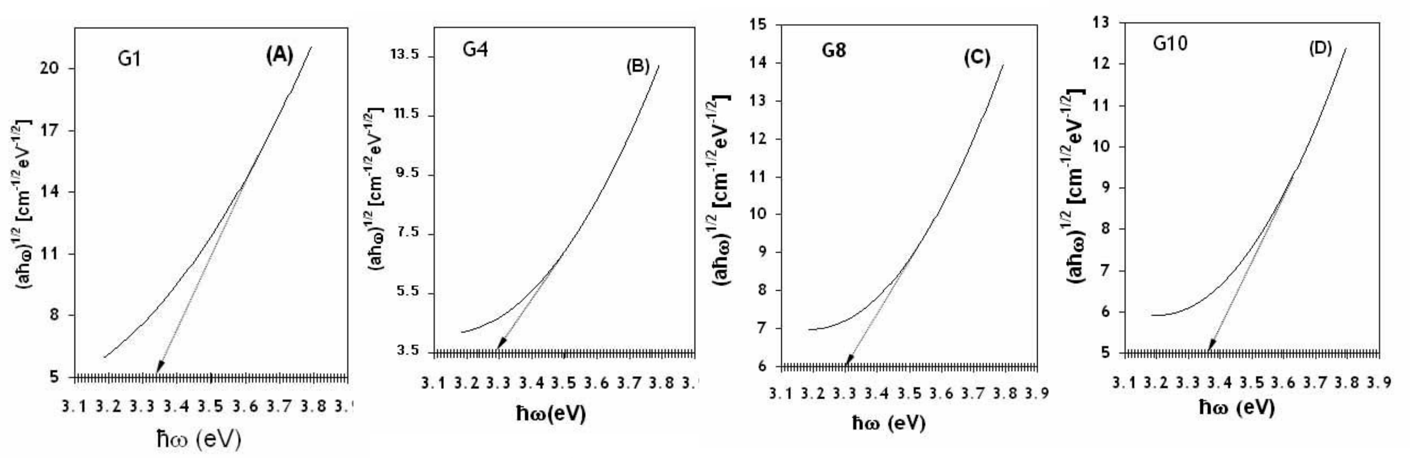


Fig.4 : Tauc's plot $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ for the glass samples G1,G4,G8 and G10.

Theoretical optical basicity values are calculated by the relation [28].

$$\Lambda_{th} = X_{MgO}\Lambda(MgO) + X_{PbO}\Lambda(PbO) + X_{B_2O_3}\Lambda(B_2O_3) \quad (5)$$

where X_{MgO}, X_{PbO} and $X_{B_2O_3}$ are the proportions of oxide atoms that each oxide in the composition contribute to the stoichiometry of the glass [29]. The optical basicity values of individual oxides are given by $\Lambda(B_2O_3) = 0.425$, $\Lambda(MgO) = 0.78$ and $\Lambda(PbO) = 1.19$ [30].

Theoretical refractive index (n), optical basicity (Λ_{th}) values along with cut-off wavelengths (λ_c) values are presented in Table.2

In the optical absorption spectra the fundamental absorption edges are not sharply defined. This is due to the amorphous nature of the glass samples. Figure.5 shows the variation of E_{opt} and refractive index (n) with $MgCl_2$ mole%. The E_{opt} values of the present glasses initially increased with increasing x mole % of $MgCl_2$ up to 2 mole% of and there is a sudden inflection. Afterwards E_{opt} value for the remaining samples increased lightly with $MgCl_2$ composition. Similar non-linear trends observed in other glass systems [31]. The variation in E_{opt} values with composition is very small. So these changes cannot be attributed to structural changes. The slightly variations may be due the change in the concentration of non-bridging oxygens (NBOs).

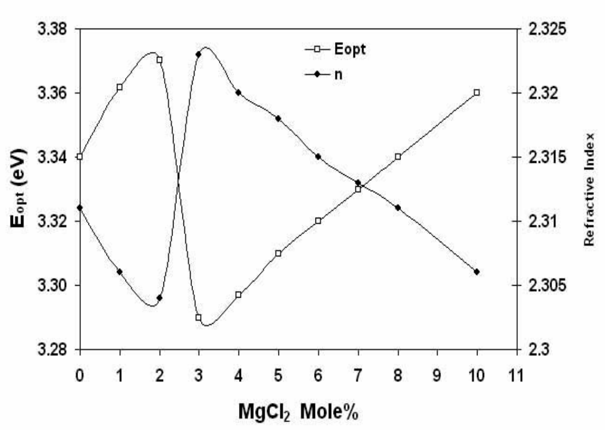


Fig.5 : Variation of E_{opt} and ref ractive index (n) with $MgCl_2$mole%.

Table 2 : Theoretical refractive index (n), Optical basicity values (Λ_{th}) and cut-off wavelengths of $(10\text{-}x)MgO\text{-}xMgCl_2\text{-}40PbO\text{-}50B_2O_3$ glasses.

Glass	Refractive Index (n) ± 0.01	Optical Basicity (Λ_{th})	Cut-off Wavelength (λ_c - nm) ± 2nm
G1	2.311	0.5770	317
G2	2.306	0.5787	316
G3	2.304	0.5797	312ss
G4	2.323	0.5807	335
G5	2.320	0.5817	332
G6	2.318	0.5828	325
G7	2.315	0.5838	323
G8	2.313	0.5848	320
G9	2.311	0.5857	322
G10	2.306	0.5877	321

Theoretical refractive index (n) values also have shown small variations with the composition of the glass which may also be due change in the concentration of non-bridging oxygens (NBOs) and expansion of B-O network with x mole %.

IV. CONCLUSIONS

The FTIR studies revealed that in the glass matrix various borate groups are randomly interconnected. Typical borate groups like other borate glasses were observed. The presence of BO_3 trigonal units, BO_4 tetrahedral units with complex borate groups like diborate, tri, tetra and penta borates units in the glass structure are confirmed from the IR absorption peaks at 1320-1376 cm^{-1} and 926-1031 cm^{-1}. The peaks around 680 cm^{-1} might be due to formation of bridges by oxygen between two trigonal atoms. MgO acted as a glass network modifier and PbO might be participated as glass network former. No considerable change in glass structure was observed with variation in composition. The variations in theoretical optical energy band gap values with $MgCl_2$ mole% are very small and these changes can be attributed to change in NBO concentration. The observed broadening of the IR peaks with increasing $MgCl_2$ mole % is attributed to B-O network expansion. The variations in theoretical refractive indices are also small.

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