

Optical properties of $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{MCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{MCl}_2$ ($\text{M} = \text{Pb}, \text{Cd}$) glasses

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Abstract. Optical absorption and transmittance spectra of $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{MCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{MCl}_2$ ($\text{M} = \text{Pb}, \text{Cd}$) ($10 \leq x \leq 20$) glasses of varying composition were recorded in the UV-visible region. Various optical parameters such as optical energy gap (E_{opt}), Urbach energy (E_c), refractive index (n_0), optical dielectric constant (ϵ_∞), and ratio of carrier concentration to the effective mass (N/m^*) were determined. The variation of optical energy gap with increase in the concentration of PbCl_2 or CdCl_2 is discussed.

Keywords. Borate glasses; optical energy gap; Urbach energy.

1. Introduction

Study of optical absorption has been one of the most productive methods in understanding the band structure and energy gap of both crystalline and amorphous materials. The measurement of optical absorption coefficient, particularly near the fundamental absorption edge, is a standard method for the investigation of optically induced electronic transitions. There is neither grain boundary nor interface within a glass structure and so the intrinsic scattering loss in a glass is very small. Hence, a glass is transparent to light in the wavelength region where intrinsic absorption does not occur, and on the short wavelength side of the UV-visible spectrum the electronic fundamental absorption bands limit the transparency. Strong absorption bands arising from electron excitations produce essentially a UV cut-off causing most glasses to appear opaque in the UV (Varshneya 1994).

The optical energy gap of a number of amorphous binary oxide glasses (Edirisinghe and Hogarth 1989; Al-Ani and Higazy 1991; Kentaro Terashima *et al* 1995; Sabry and El-Samanoudy 1995) has been analysed on the basis of the theory suggested by Tauc *et al* (1966), and Davis and Mott (1970). They reported that values of the optical energy gap are affected by the addition of modifier ions in the glass structure. The optical properties of glasses containing oxides of metals like lead were reported (Khanna *et al* 1996; Khanna 2000; Stentz *et al* 2000). A survey of literature indicates that reports on the optical properties of borate glasses containing an oxide and a halide are very limited. The present article reports the opti-

cal properties of borate glasses containing a heavy metal oxide (PbO) and a halide, PbCl_2 or CdCl_2 . The optical energy gap (E_{opt}), Urbach energy (E_c), other optical parameters such as refractive index (n_0), optical dielectric constant at infinitely high frequency (ϵ_∞), and ratio of carrier concentration to the effective mass (N/m^*) were evaluated from the absorption and transmission spectra. The variation of optical energy gap (E_{opt}) with increase in mole percentage of PbCl_2 or CdCl_2 is discussed.

2. Experimental

$60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{MCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{MCl}_2$ ($\text{M} = \text{Cd}, \text{Pb}$) glasses of different compositions ($x = 10, 12.5, 15, 17.5$ and 20) were prepared from appropriate amounts of analar grade H_3BO_3 , PbO , and PbCl_2 or CdCl_2 . The composition of the glass samples along with sample codes are given in tables 1 and 2. Calculated quantities of the chemicals were mixed thoroughly in an agate mortar. While preparing glasses containing PbCl_2 or CdCl_2 , 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 the charge in a closed porcelain crucible in an electric furnace for 1 h at 500°C and then transferring the closed crucible to another furnace kept at $850\text{--}950^\circ\text{C}$ depending on the composition of the glasses. The melting process was continued for 15 min. The melt was then quenched by pouring it into a brass mould and pressing by another brass disc to obtain glass discs of diameter 2 cm and thickness ~ 1 mm. The samples were then annealed for 3 h in a furnace preheated to 300°C and then allowed to cool to room temperature. The samples were polished to obtain glass discs of thickness about 0.75 mm.

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The optical absorption (figures 1 and 2) and transmission (figures 3 and 4) spectra of the glass samples were recorded using Shimadzu 160A spectrophotometer in the wavelength region 200–900 nm at normal incidence. All the spectra were recorded at room temperature. It is clear from these figures that there are no sharp absorption edges, which is a characteristic of the glassy nature of the sample and which was verified by X-ray diffraction analysis.

3. Results and discussion

The optical absorption spectra of the glass samples in the wavelength region 200–400 nm are shown in figures 1 and 2. The absorption coefficient, $a(n)$, in amorphous materials, in the optical region near the absorption edge, at a particular temperature, obeys an empirical relation known as Urbach rule (Urbach 1953) given by

$$a(n) = a_0 \exp(hn/E_e), \quad (1)$$

where hn is the photon energy, a_0 a constant, and E_e an energy which is interpreted as the width of the localized state in the normally forbidden band gap and which is also

known as the Urbach energy. Urbach plots are shown as insets to figures 1 and 2. The absorption coefficient (a) for amorphous materials is given by Tauc (1969) equation

$$a(n) = \text{const} \left[\frac{(hn - E_{\text{opt}})^2}{hn} \right], \quad (2)$$

where hn is the photon energy and E_{opt} the optical energy gap. The $(ahn)^{1/2}$ vs hn plot for the samples are given in figures 5 and 6. The values of optical energy gap (E_{opt}) which is the extrapolation of the linear region of the plots of $(ahn)^{1/2}$ against hn to $(ahn)^{1/2} = 0$ and Urbach energy (E_e) is the slope of the Urbach plots, are given in tables 1 and 2. The optical transmittance spectra are shown in figures 3 and 4. The calculated optical parameters obtained from transmittance spectra are also given in tables 1 and 2.

It is seen from figures 1 and 2 that the glass samples show strong absorption in the UV region. The tail of the band is trailing into the visible region. Optical absorption in solids occurs by a mechanism that involves the coupling of the electric field of the incident radiation to the dipole moment in the material and the consequent transfer of energy (Hogarth 1983). According to Stevals (1953), the absorption edge in oxide glasses corresponds to the transi-

Table 1. Glass composition, optical energy gap (E_{opt}), Urbach energy (E_e), refractive index (n_0), dielectric constant (ϵ_∞) and ratio of carrier concentration to effective mass (N/m^*) of $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{PbCl}_2$ and $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{CdCl}_2$ glasses of different compositions.

Glass composition	Sample code	Optical energy gap, E_{opt} (eV)	Urbach energy, E_e (eV)	Refractive index (n_0)	ϵ_∞	$(N/m^*) \times 10^{21}$ (cm^{-3})
$60\text{B}_2\text{O}_3-30\text{PbO}-10\text{PbCl}_2$	BPP1	3.21	0.41	1.84	4.03	2.00
$60\text{B}_2\text{O}_3-27.5\text{PbO}-12.5\text{PbCl}_2$	BPP2	3.24	0.37	2.00	4.48	2.29
$60\text{B}_2\text{O}_3-25\text{PbO}-15\text{PbCl}_2$	BPP3	3.25	0.48	1.71	3.53	1.71
$60\text{B}_2\text{O}_3-22.5\text{PbO}-17.5\text{PbCl}_2$	BPP4	3.22	0.41	1.65	3.30	2.07
$60\text{B}_2\text{O}_3-20\text{PbO}-20\text{PbCl}_2$	BPP5	3.23	0.48	1.57	2.90	1.31
$60\text{B}_2\text{O}_3-30\text{PbO}-10\text{CdCl}_2$	BPC1	3.28	0.45	2.01	4.53	1.46
$60\text{B}_2\text{O}_3-27.5\text{PbO}-12.5\text{CdCl}_2$	BPC2	3.34	0.50	1.91	4.03	1.90
$60\text{B}_2\text{O}_3-25\text{PbO}-15\text{CdCl}_2$	BPC3	3.44	0.57	1.76	3.71	1.94
$60\text{B}_2\text{O}_3-22.5\text{PbO}-17.5\text{CdCl}_2$	BPC4	3.42	0.50	1.64	3.23	2.02
$60\text{B}_2\text{O}_3-20\text{PbO}-20\text{CdCl}_2$	BPC5	3.40	0.37	1.55	3.86	1.64

Table 2. Glass composition, optical energy gap (E_{opt}), Urbach energy (E_e), refractive index (n_0), dielectric constant (ϵ_∞) and ratio of carrier concentration to effective mass (N/m^*) of $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{PbCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{CdCl}_2$ glasses of different compositions.

Glass composition	Sample code	Optical energy gap, E_{opt} (eV)	Urbach energy, E_e (eV)	Refractive index (n_0)	ϵ_∞	$(N/m^*) \times 10^{21}$ (cm^{-3})
$50\text{B}_2\text{O}_3-40\text{PbO}-10\text{PbCl}_2$	BPP6	3.32	0.43	1.99	3.98	3.48
$50\text{B}_2\text{O}_3-37.5\text{PbO}-12.5\text{PbCl}_2$	BPP7	3.35	0.34	1.85	2.87	2.49
$50\text{B}_2\text{O}_3-35\text{PbO}-15\text{PbCl}_2$	BPP8	3.39	0.47	1.55	4.65	1.99
$50\text{B}_2\text{O}_3-32.5\text{PbO}-17.5\text{PbCl}_2$	BPP9	3.35	0.44	1.52	2.74	1.18
$50\text{B}_2\text{O}_3-30\text{PbO}-20\text{PbCl}_2$	BPP10	3.32	0.43	1.45	2.72	2.02
$50\text{B}_2\text{O}_3-40\text{PbO}-10\text{CdCl}_2$	BPC6	3.32	0.35	1.73	3.70	2.28
$50\text{B}_2\text{O}_3-37.5\text{PbO}-12.5\text{CdCl}_2$	BPC7	3.40	0.43	1.60	3.13	1.60
$50\text{B}_2\text{O}_3-35\text{PbO}-15\text{CdCl}_2$	BPC8	3.44	0.50	1.47	2.57	1.29
$50\text{B}_2\text{O}_3-32.5\text{PbO}-17.5\text{CdCl}_2$	BPC9	3.37	0.42	1.58	3.02	1.93
$50\text{B}_2\text{O}_3-30\text{PbO}-20\text{CdCl}_2$	BPC10	3.35	0.35	1.47	2.67	1.50

tion of an electron belonging to an oxygen ion to an excited state. The more weakly these electrons are bound, the more easily absorption occurs (Stevels 1953).

The variations of the optical energy gap (E_{opt}) with increase in mole percentage of PbCl_2 in $60\text{B}_2\text{O}_3-(40-x)$

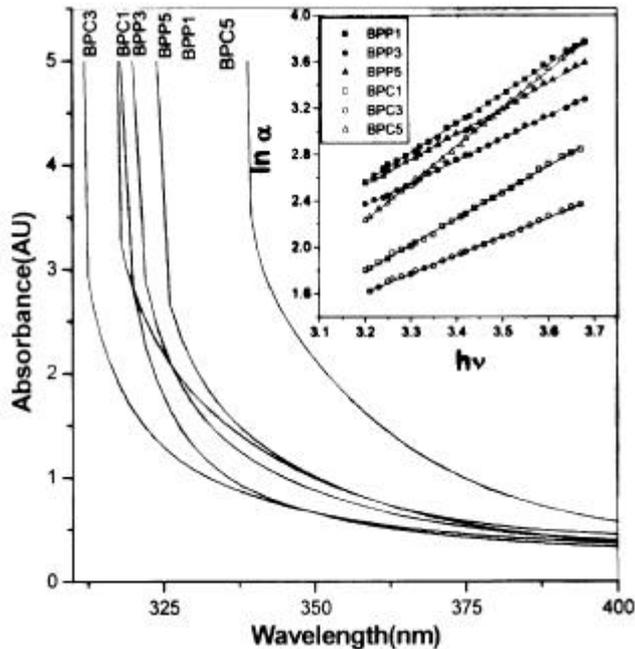


Figure 1. Optical absorption as a function of wavelength for $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{PbCl}_2$ and $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{CdCl}_2$ glasses. Inset: Urbach plots of same glass samples.

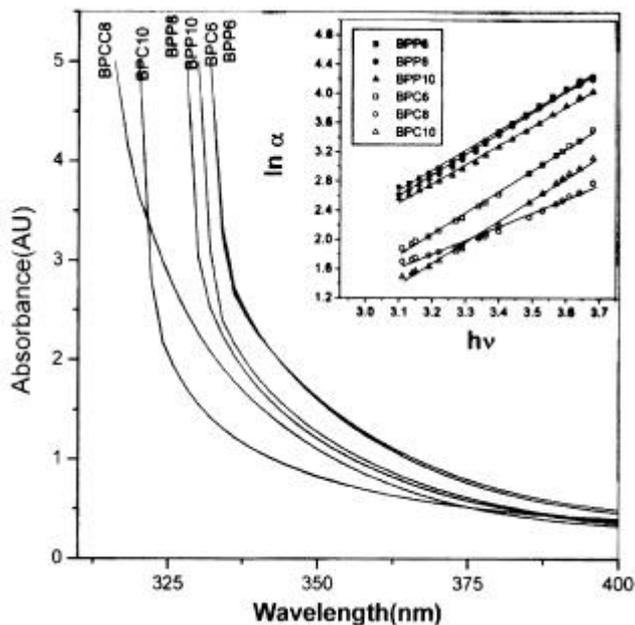


Figure 2. Optical absorption as a function of wavelength for $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{PbCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{CdCl}_2$ glasses. Inset: Urbach plots of same glass samples.

$\text{PbO}-x\text{PbCl}_2$ ($x = 10, 12.5, 15, 17.5$ and 20 mole percentage, sample codes BPP1 to BPP5) and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{PbCl}_2$ ($x = 10, 12.5, 15, 17.5$ and 20 mole percentage, sample codes BPP6 to BPP10) glasses are shown in figure 7. The energy gap increases with increase in the concentration of PbCl_2 up to 15 -mole percentage and then decreases. Arbutov (1996), Stevels (1953) and Mcswain *et al* (1963) suggested that in oxide glasses (like alkali or alkaline-earth borate, silicate or phosphate glasses) the shift of energy gap to lower energies could be related to the formation of non-bridging oxygen which binds excited electrons less tightly than bridging oxygen. Duffy (2001) explained the ultraviolet transparency of oxide glasses in terms of electronegativity of the constituent oxygen atoms. In glasses, negative charges on the non-bridging oxygens have larger magnitude than that on the bridging oxygens. Increasing the ionicity of oxygen ions, by converting them from bridging to non-bridging oxygen (NBO) ions, raises the top of the valence band resulting in the reduction of band gap energy (E_g). Hence ultraviolet absorption occurs at lower photon energies, as the oxygen atom becomes NBO (Duffy 2001).

Vitreous boron oxide glass features high UV transparency. Addition of alkali and alkaline earth elements above 15 -mole percentage brings about a shift in the fundamental absorption edge towards the longer wavelength region. In sodium borate glasses, on increasing Na_2O concentration, boron transforms from three-fold to four-fold coordinated state and Na^+ ions provide the electroneutrality of the four-coordinated boron (Zagar 1971). After the completion of the four coordination rearrangements, further addition

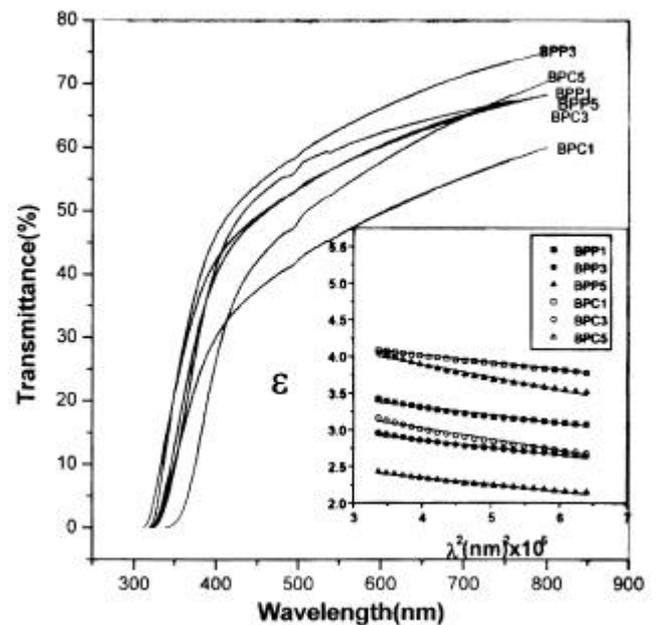


Figure 3. Optical transmittance as a function of wavelength for $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{PbCl}_2$ and $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{CdCl}_2$ glasses. Inset: ϵ vs λ^2 of same glass samples.

of alkali oxide leads to the breaking of bridging bonds and the formation of non-bridging oxygen ions. Gressler and Shelby (1989) proposed a similar change in the structure of lead oxy borate glasses with Pb^{2+} ions acting as

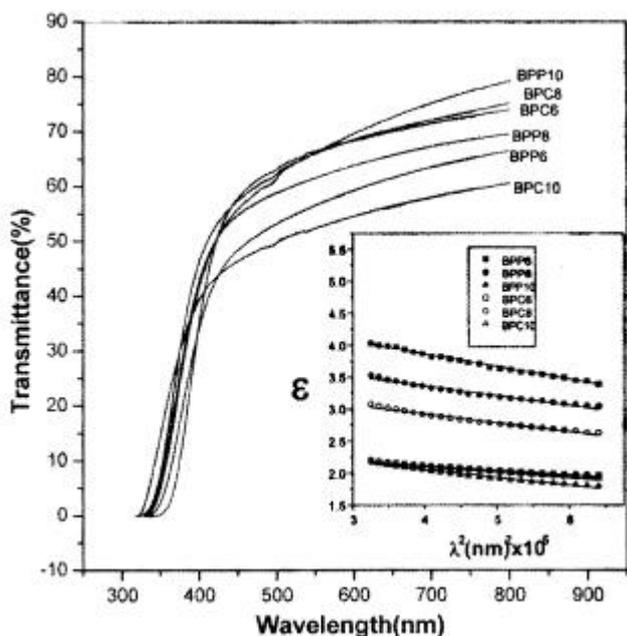


Figure 4. Optical transmittance as a function of wavelength for $50B_2O_3-(50-x)PbO-xPbCl_2$ and $50B_2O_3-(50-x)PbO-xCdCl_2$ glasses. Inset: ϵ vs λ^2 of same glass samples.

charge compensators for negatively charged BO_4^- units. Usually, for the lower concentration of modifier ions in the glass network, a four-coordination of boron takes place and the percentage of non-bridging oxygen present in the glass structure is limited. As the concentration of modifier ions is increased, four-coordination of boron reaches a saturation point and the network begins to break up producing non-bridging oxygens (Mcswain *et al* 1963).

El-Damravi (1994, 1995) studied the influence of $PbCl_2$ on the physical properties of $xPbCl_2-(40-x)PbO-60B_2O_3$ and $xPbCl_2-(30-x)PbO-40B_2O_3-30P_2O_5$ glasses. A change in glass structure due to an expansion of the network in lead chloroborate glasses was observed when $PbCl_2$ was substituted for PbO . For lower concentration of $PbCl_2$ in the glass system, the Cl^- ions did not enter the boron oxygen network but were inserted interstitially in the glass matrix without the destruction of the network. As more and more $PbCl_2$ was substituted for PbO , direct replacement of one O^{2-} ion by two Cl^- ions took place and correspondingly the oxygen to boron ratio (O/B) decreased. This decrease in O/B ratio results in the gradual replacement of three dimensionally linked BO_4^- tetrahedra by planar BO_3 triangles (El-Damravi 1994). Since ionic radii of Cl^- ion is larger than O^{2-} (Cl , 0.183 nm and O , 0.132 nm), an open, less rigid structure could be formed upon Cl^- addition which favoured expansion of the network (El-Damravi 1994). A random introduction of halogen ions (F, Cl, Br, I) into the interstices of the borate and silicate network results in the decrease of continuity of the vitreous network (Coon *et al* 1988; Gressler

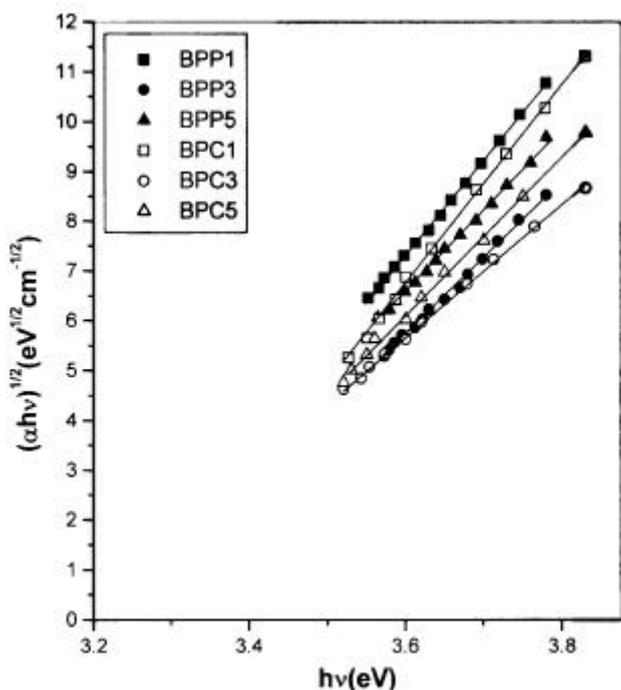


Figure 5. $(\alpha hv)^{1/2}$ vs hv plots of $60B_2O_3-(40-x)PbO-xPbCl_2$ and $60B_2O_3-(40-x)PbO-xCdCl_2$ glasses.

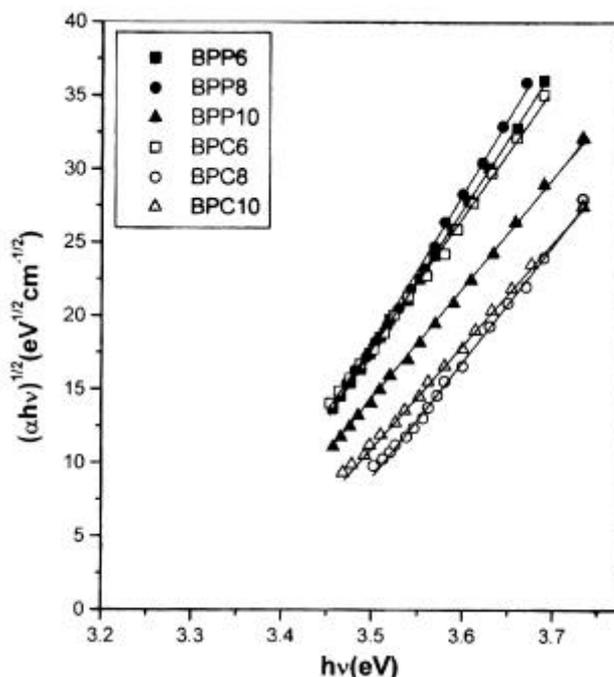


Figure 6. $(\alpha hv)^{1/2}$ vs hv plots for $50B_2O_3-(50-x)PbO-xPbCl_2$ and $50B_2O_3-(50-x)PbO-xCdCl_2$ glasses.

and Shelby 1988). Gressler and Shelby (1988, 1989) observed an increase in molar volume in $\text{B}_2\text{O}_3\text{-PbO-PbF}_2$ glass system when PbF_2 was substituted for PbO , indicating expansion of the glass structure.

The observed variation in the optical energy gap (E_{opt}) with increase in mole percentage of PbCl_2 in the present study can be explained by considering the changes in the glass structure because of expansion of the glass network. The substitution of PbCl_2 for PbO decreased the O/B ratio and consequently the percentage of non-bridging oxygens were limited. Since optical energy gap depends on the percentage of non-bridging oxygens, E_{opt} shifted to the shorter wavelength side, as the mole percentage of PbCl_2 increased from 10 to 15. As more and more PbCl_2 was substituted for PbO , Cl^- ion in the network increased. As a result the network became systematically weakened and a more open network with non-bridging oxygens was formed. Non-bridging oxygens in the glass network shifted the fundamental absorption edge towards the long wavelength side. The above reasoning may be held valid for $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{CdCl}_2$ (samples BPC1 to BPC5) and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{CdCl}_2$ (samples BPC6 to BPC10) glasses in which CdCl_2 was substituted for PbO similar to the substitution of PbCl_2 for PbO in BPP glasses. The variation in the optical energy gap in BPC glasses was similar to that in BPP glasses (figure 7). For lower concentration of CdCl_2 (< 15 mole percentage), as CdCl_2 was substituted for PbO , Cl^- ions would have been inserted

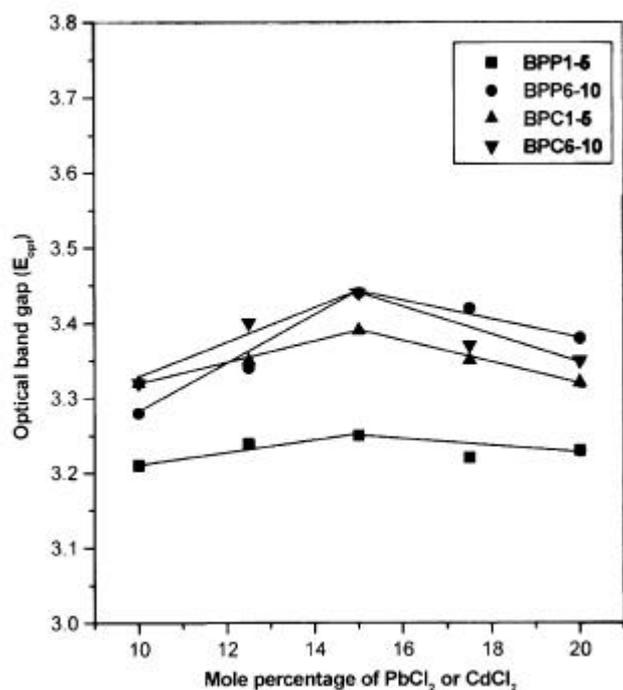


Figure 7. Variation of absorption edge (E_{opt}) with increase in mole percentage of PbCl_2 or CdCl_2 in $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{MCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{MCl}_2$ ($\text{M} = \text{Cd}, \text{Pb}$) glasses.

interstitially. Increasing the CdCl_2 content caused the glass structure to become progressively crowded with Cl^- ions that played a role for weakening and expanding the network. Thus the optical energy gap first increased and then decreased with the substitution of CdCl_2 .

The relation between absorption coefficient (α) and the photon energy is given by the Urbach rule (1). The Urbach plots are shown in the insets of figures 1 and 2. The origin of the exponential absorption is still a matter of debate but it is generally agreed that random fluctuations in the potential associated with any lattice distortions, like thermal vibrations, dislocations, electric fields of defects, etc can affect the energy bands and cause tailing of energy states into the forbidden gap. The Urbach rule for absorption coefficient is an attempt to explain the observed exponential tail in terms of internal electric fields generated within a solid. This internal electric field leads to the exponential broadening of the energy states. Dexter (1958) and Redfield (1963) have qualitatively shown that such a tailing off of states could modify the direct band transition and cause an exponential energy dependence on the intrinsic edge. The value of band tailing energy (E_c) varied from 0.34–0.57 eV (tables 1 and 2) for the glass samples in the present study.

The calculated optical parameters obtained from transmittance and absorption spectra are given in tables 1 and 2. Spitzer and Fan (1957) have shown that the real part of dielectric constant, ϵ , and the square of wavelength (I^2) are related through the following equation

$$\epsilon = \epsilon_{\mu} - e^2 / pc^2 (N/m^*) I^2, \quad (3)$$

where ϵ_{μ} is the infinitely high frequency dielectric constant, e the electronic charge and (N/m^*) the ratio of the carrier concentration to the effective mass. The plots of dielectric constant, ϵ vs I^2 plots, given in the insets of figures 3 and 4 are linear verifying (3). The value of ϵ_a is determined from the extrapolation of these plots to $I^2 = 0$. The values of refractive index (n_0) were calculated using $T = 2n/(1 + n^2)$ (Moss 1959) over the wavelength region 500–800 nm. Refractive index was more or less constant over this region and the average values are given in tables 1 and 2.

The ratio of carrier concentration to effective mass (N/m^*) has been calculated from the slope of the plots of ϵ vs I^2 (insets of figures 3 and 4) using (3). The value of N/m^* for different glass samples are tabulated in tables 1 and 2. The values of N/m^* are found to be of the order of 10^{21} cm^{-3} in agreement with the values reported for oxide glasses (Ghosh and Chaudhuri 1986) and amorphous chalcogenide thin films (Wakkad 1990; Eh Shoker and Wakkad 1992; Eh Shoker *et al* 2000).

4. Conclusions

Optical absorption and transmittance spectra of $60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{MCl}_2$ and $50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{MCl}_2$ ($\text{M} = \text{Pb}$,

Cd) ($10 \leq x \leq 20$) glasses of varying composition were recorded in the UV-visible region and various optical parameters such as optical energy gap (E_{opt}), Urbach energy (E_u), optical dielectric constant (ϵ_{∞}), and ratio of carrier concentration to the effective mass (N/m^*) were determined. Optical energy gap was found to increase as the mole percentage of $PbCl_2$ was increased from 10 to 15. Beyond 15-mole percentage, optical energy gap was found to decrease. The variation in the optical energy gap with increase in mole percentage of $PbCl_2$ is discussed on the basis of the expansion of the glass network and the formation of non-bridging oxygen. When $CdCl_2$ was substituted for PbO in B_2O_3 - PbO - $CdCl_2$ glass systems, the optical properties showed similar variations as in the case of B_2O_3 - PbO - $PbCl_2$ glasses. The Urbach plots were linear for all the glass samples studied verifying Urbach law. The value of Urbach energy varied from 0.34–0.57 eV for different glass samples. The value (N/m^*) is of the order of 10^{21} cm^{-3} which is in agreement with values reported for oxide glasses and amorphous chalcogenide thin films.

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