Optical properties of $(1 - x - y)\text{B}_2\text{O}_3\text{-}x\text{Li}_2\text{O-}y\text{MCl}_2$ ($\text{M} = \text{Cd, Zn}$) glasses

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Abstract. Optical absorption and transmission spectra of $(1 - x - y)\text{B}_2\text{O}_3\text{-}x\text{Li}_2\text{O-}y\text{MCl}_2$ ($\text{M} = \text{Cd, Zn}$) glasses of varying compositions were recorded in the UV-visible region. From the spectra, various optical parameters such as optical energy gap (E_{opt}), refractive index (n), optical dielectric constant (ϵ'), width of the tail of localized states in the forbidden gap (ΔE), ratio of carrier concentration to the effective mass (N/m^*) and the constant B were evaluated. The effects of composition of glasses on these parameters are discussed.

Keywords. Borate glasses; optical energy gap; refractive index.

1. Introduction

There has been interest in recent years on halide glasses because of the possibility of developing low loss IR waveguide (Jiang *et al* 1990). Szukwei *et al* (1982) reported a systematic investigation of the optical and electrical properties of Ge–Se–Te glass system in order to find out the relationship between the glass composition and band gaps. Morsi *et al* (1986) investigated the addition of Ti^{4+} and Co^{2+} ions to borate glasses which introduced an intense charge transfer band in the UV region that shifts towards longer wavelength. Kh Shokr (1992) explained the increase of optical gap with increase of Se content and thickness of film in terms of decrease in the percentage of tellurium and elimination of defects in the amorphous film. Refractive index measurements (Ma *et al* 1993) had been performed on different tellurium halide based glasses. Banfi *et al* (1995) investigated the non linear response of semiconductor doped glasses at a photon energy of 1.17 eV. They found that the third-order nonlinearity is overshadowed by a fifth-order one when the band gap of the semiconductor crystallites become smaller than twice the photon energy. The fifth-order nonlinearity is due to the refraction of the free carriers generated by two-photon absorption (TPA). The effect of composition of lead–bismuth–titanate glasses on various optical parameters had been reported by Burghate *et al* (1995). The influence of composition and film thickness on the optical band gap and width of the band tail of thin solid films of chalcogenide glass system As–Ge–Se were investigated by Abd

El-Rahman *et al* (1998). Sedeek (1998) investigated the optical and electrical properties of amorphous GeSe and $\text{Ge}_{0.97}\text{Se}_2\text{Cd}_{0.03}$ films. Cd^{2+} incorporation in these systems affects greatly the thermal activation energy but has little effect on the optical gap. The optical energy gap of a number of amorphous oxide glasses (Rashed and Abd El-Ghani Salem 1984; Al-Ani and Higazy 1991; Sabry and El-samanoudy 1995; Sharma *et al* 1995) have been analysed on the basis of the theory suggested by Davis and Mott (1970) and Tauc *et al* (1966). Values of the optical energy gap of $\text{ZnO-P}_2\text{O}_5$ glasses were reported and were found to decrease linearly with the ZnO concentration (Rashed and Abd El-Ghani Salem 1984). A series of glass specimens were prepared from the binary glasses ($\text{MgO-P}_2\text{O}_5$), and their densities and optical absorption edges in the UV-visible range were measured by Al-Ani and Higazy (1991). Sabry and El-samanoudy (1995) reported that the optical band gap increases as the B_2O_3 content in the $\text{TeO}_2\text{-B}_2\text{O}_3$ system increases from 5–30 mole percentage. Sharma *et al* (1995) reported the optical absorption spectra and energy band gap in praseodymium borophosphate glasses. Studies on the optical properties of borate glasses had also been reported by Terashima *et al* (1995). But information available on the optical properties of glasses containing a mixture of an oxide and a halide is very limited (Dalba *et al* 1983). It has been reported that the optical absorption of the $(\text{AgI})_x(\text{Ag}_2\text{O-B}_2\text{O}_3)_{1-x}$ glasses shifts linearly on increasing the AgI content, x . We report here the results of a systematic study of the optical properties of $(1 - x - y)\text{B}_2\text{O}_3\text{-}x\text{Li}_2\text{O-}y\text{MCl}_2$ ($\text{M} = \text{Cd, Zn}$) glasses and the variation of these properties with composition.

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2. Experimental

$(1-x-y)\text{B}_2\text{O}_3-x\text{Li}_2\text{O}-y\text{MCl}_2$ ($\text{M} = \text{Cd}, \text{Zn}$) glasses of different compositions were prepared from appropriate amounts of analar grade H_3BO_3 , Li_2CO_3 , and CdCl_2 or ZnCl_2 (table 1). Calculated quantities of the chemicals were mixed thoroughly in an agate mortar and heated to 950°C in a crucible so that a homogeneously mixed melt was obtained. Glass discs of ~ 0.90 mm thickness, and diameter ~ 2 cm were made using melt quenching technique. The glass samples were annealed at a temperature of about 450°C for 4 h. The samples were cooled to room temperature and were then polished. The grinding and polishing of the glass samples are only possible with those glasses annealed at 450°C . If the annealing temperature is below 450°C it will break during polishing. The transmission and absorption spectra of glasses were recorded using Shimadzu 160A spectrophotometer in the wave-

length range 200–1000 nm (figures 1 and 2). All the spectra were recorded at room temperature. The glassy nature of the samples was confirmed by recording the X-ray diffraction pattern.

3. Theory

For absorption coefficient $\alpha \geq 10^4 \text{ cm}^{-1}$, the following relation is obeyed (Tauc *et al* 1966; Davis and Mott 1970; Tauc and Menth 1972)

$$\alpha(\omega)\hbar\omega = B(\hbar\omega - E_{\text{opt}})^r, \quad (1)$$

where $\hbar\omega$ is the photon energy, B a constant, E_{opt} the optical gap and r a number which characterizes the transition process. The exponent r can take the values 2, 3, $1/2$, and $3/2$ for indirect allowed, indirect forbidden, direct allowed, and direct forbidden transitions, respec-

Table 1. Variation of optical energy gap (E_{opt}), infinitely high frequency dielectric constant (ϵ_∞), refractive index (n_0), constant (B), ratio of carrier concentration to the effective mass (N/m^*), and the extent of band tailing (ΔE) with different glass compositions.

Glass composition	Sample code	E_{opt} (eV)	ϵ_∞	n_0	B ($\text{cm}^{-1} \text{ eV}^{-1/2}$)	$(N/m^*) \times 10^{22}$ (cm^{-3})	ΔE ($\text{cm}^{-1} \text{ eV}^{-1/2}$) $\times 10^{-3}$
0.75B ₂ O ₃ -0.05Li ₂ O-0.20ZnCl ₂	BZL1	2.97	3.241	1.65	394.5	1.645	1.540
0.70B ₂ O ₃ -0.10Li ₂ O-0.20ZnCl ₂	BZL2	3.32	3.063	1.83	481.8	0.944	1.130
0.65B ₂ O ₃ -0.15Li ₂ O-0.20ZnCl ₂	BZL3	3.21	4.387	2.01	872.8	1.181	0.570
0.60B ₂ O ₃ -0.20Li ₂ O-0.20ZnCl ₂	BZL4	3.53	12.92	3.63	2276	0.391	0.121
0.75B ₂ O ₃ -0.20Li ₂ O-0.05ZnCl ₂	BZL5	3.18	2.374	1.54	788.8	1.385	0.823
0.70B ₂ O ₃ -0.20Li ₂ O-0.10ZnCl ₂	BZL6	3.26	2.815	1.87	1266	1.995	0.422
0.65B ₂ O ₃ -0.20Li ₂ O-0.15ZnCl ₂	BZL7	3.15	5.023	2.13	768.8	1.540	0.611
0.75B ₂ O ₃ -0.05Li ₂ O-0.20CdCl ₂	BCL1	3.16	3.073	1.66	812.8	0.963	0.742
0.70B ₂ O ₃ -0.10Li ₂ O-0.20CdCl ₂	BCL2	3.27	1.773	1.25	1205	0.559	0.664
0.65B ₂ O ₃ -0.15Li ₂ O-0.20CdCl ₂	BCL3	3.12	3.091	1.75	903.8	0.671	0.632
0.60B ₂ O ₃ -0.20Li ₂ O-0.20CdCl ₂	BCL4	3.24	2.926	1.74	301.6	0.376	1.910
0.75B ₂ O ₃ -0.20Li ₂ O-0.05CdCl ₂	BCL5	3.48	2.310	2.06	1165	0.388	0.417
0.70B ₂ O ₃ -0.20Li ₂ O-0.10CdCl ₂	BCL6	3.35	2.745	1.42	513.8	2.137	1.370
0.65B ₂ O ₃ -0.20Li ₂ O-0.15CdCl ₂	BCL7	2.83	3.492	1.88	66.54	0.126	7.990

Figure 1. Transmission and absorption spectra of BCL glasses.

Figure 2. Transmission and absorption spectra of BZL glasses.

tively. The constant B is related to the parameter ΔE , which is a measure of extent of band tailing, by the following equation (Mott and Davis 1979),

$$B = 4\pi\sigma_{\min}/nC\Delta E, \quad (2)$$

where $\sigma_{\min}$ is the extrapolated dc-conductivity at $T = \infty$, n the refractive index and C the velocity of light. Ignoring the variation of n with $\hbar\omega$ and taking n_0 as the average value of n , it follows that $(n_0B)^{-1} \sim \Delta E$ is a measure of extent of band tailing. The reflectance of glass samples was calculated using the equation

$$t = (1-R)^2 \exp(-A), \quad (3)$$

where R is the reflectance, t the transmittance and A the absorbance. Absorption coefficient α is obtained from the absorbance (A) with an accuracy ± 0.02 through the relation

$$A = \alpha d,$$

where d is the thickness of the sample (measured with an accuracy of ± 0.005 mm). The optical dielectric constant (ϵ') and the square of wavelength (λ^2) are related (Spitzer and Fan 1957) through the following equation

$$\begin{aligned} \epsilon' &= n^2 = [(1 + \sqrt{R}) / (1 - \sqrt{R})]^2 \\ &= \epsilon'_\infty - e^2 N \lambda^2 / \pi c^2 m^*, \end{aligned} \quad (4)$$

where ϵ'_∞ is the infinitely high frequency dielectric constant, e the electronic charge, and (N/m^*) the ratio of carrier concentration to the effective mass.

Figure 3. Plot of $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ for different mole% of ZnCl_2 and Li_2O in BZL glasses.

Figure 4. Plot of $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ for different mole% of CdCl_2 and Li_2O in BCL glasses.

4. Results and discussion

The various optical parameters of the glass samples were calculated and the results are given in table 1.

The nature of plots (figures 3 and 4) is found to consist of two linear regions (a) and (b); in the region (b), $r = 2$, suggesting the absorption process to be due to an indirect allowed transition. The optical energy gap (E_{opt}) of the glass samples and the constant B were obtained from the extrapolation of the linear region (b) and from the slopes of the above-derived curves, respectively. The values of E_{opt} (determined with an accuracy of 0.008 eV), as a func-

tion of the glass composition are shown in figure 6. There is a tendency for the optical band gap to become larger with increasing Li_2O or ZnCl_2 content for BZL glasses. But the values obtained for E_{opt} are found to exhibit a maximum at 10 mole per cent of Li_2O (BCL2) and minimum with 15 mole per cent of Li_2O (BCL3). Similarly for CdCl_2 variation, E_{opt} are found to exhibit a maximum at 5 mole per cent of CdCl_2 (BCL5) and minimum with 15 mole per cent of CdCl_2 (BCL7). The optical band gap of the glass system $\text{M}_2\text{O}-\text{B}_2\text{O}_3$ ($\text{M} = \text{Li, Na, K, Rb, Cs, Ag}$) was studied by Terashima *et al* (1995). There is a tendency for the optical band gap to become smaller with increasing M_2O content for each glass system. The compositional dependence of refractive index n_0 as shown in figure 5 reveals that n_0 is increasing with increasing concentration of Li_2O or ZnCl_2 in BZL glasses. For BCL glasses, n_0 shows a maximum at 15 mole per cent of Li_2O (BCL3) and a minimum value with 10 mole per cent of Li_2O (BCL2). While for CdCl_2 variation, n_0 shows a maximum at 5 mole per cent of CdCl_2 (BCL5) and a minimum value with 10 mole per cent of CdCl_2 (BCL6).

Figure 5. Variation of refractive index (n_0) with mole percentage of Li_2O (x) and CdCl_2 or ZnCl_2 (y).

Figure 6. Variation of optical bandgap (E_{opt}) with mole percentage of Li_2O (x) and CdCl_2 or ZnCl_2 (y).

Figure 7. Variation of dielectric constant (ϵ') with λ^2 .

Figure 8. Variation of dielectric constant (ϵ') with λ^2 .

Equation (4) is verified and the variation of ϵ' with λ^2 is shown in figures 7 and 8. The values of ϵ'_∞ and $e^2N/\pi c^2 m^*$ were determined from the extrapolation of the plot to $\lambda^2 = 0$ and their slopes, respectively. Then the quantity of (N/m^*) is computed and its values listed in table 1 as functions of glass composition. The derived values of $(n_0 B)^{-1}$, which is a measure of the extent of band tailing (ΔE), are found to decrease with increasing concentration of Li_2O or ZnCl_2 in BZL glass. But the values of ΔE show a maximum and minimum with increasing concentration of CdCl_2 or Li_2O content in BCL glasses (table 1). The small values of band tailing energy indicate the presence of sharp localized states in the band gap. The changes in the borate network produced by the addition of Li_2O may be the reason for the generation of localized states in the band gap. The introduction of oxygen from a modifier oxide to boric oxide glasses converts boron from a 3-coordinated state to a 4-coordinated state. In the BO_4 and BO_3 groups, the oxygens are fully bridging for small concentration of modifying oxygen and it will give more rigidity to the structure. Further addition of modifier oxide causes creation of non bridging oxygens in the structure and induces more disorder in the glass structure. From table 1 it is seen that there is almost a systematic variation in E_{opt} and ΔE

indicating that the degree of disorder is markedly influenced by the change in concentration of Li_2O , ZnCl_2 or CdCl_2 . The observation that the magnitude of the band tailing is small points to the generation of states in the band gap which are localized near the mobility edge. Variation of ΔE with composition of the glass also shows that the extent of the localized states is disorder dependent, which is in agreement with the theory of Mott and Davis (1979).

5. Conclusions

The optical gap (E_{opt}) and band tailing (ΔE) of the glass systems $(1-x-y)\text{B}_2\text{O}_3-x\text{Li}_2\text{O}-y\text{MCl}_2$ ($\text{M} = \text{Cd}, \text{Zn}$) were found to vary with the variation of Li_2O , CdCl_2 , and ZnCl_2 concentration in the glass composition. The refractive index (n_0) is found to increase with increasing concentration of Li_2O or ZnCl_2 content in the BZL glasses, while for BCL glasses, it shows a maximum and a minimum value for increasing concentration of Li_2O or CdCl_2 . It is observed that the transition in $(1-x-y)\text{B}_2\text{O}_3-x\text{Li}_2\text{O}-y\text{MCl}_2$ ($\text{M} = \text{Cd}, \text{Zn}$) glass system is indirect allowed in nature. The values of band tailing (ΔE) are found to be very small leading to large values of optical band gap.

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