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Effect of γ-irradiation on optical absorption of Al_2O_3–TeO_2–$Li_2B_4O_7$ glasses doped with MgF_2

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ABSTRACT

The effect of γ-radiation on the optical properties of the glassy system [$x$$MgF_2$–10$Al_2O_3$-(40-$x$) TeO_2–50$Li_2B_4O_7$], (x = 0, 15, 20 and 40 mol%) has been investigated. Samples were prepared by conventional melt-quench technique. The density and molar volume were estimated and found to decrease with increasing MgF_2 concentration. The obtained data indicate that the glass structure becomes less tightly packed with increasing the MgF_2 concentration. The effect of γ-irradiation (5, 20, 40 and 70 kGy) on optical absorption has been studied. It was observed that γ-radiation enhances the formation of NBOs. This leads to a decrease in the optical band gap energy. Radiation induced changes include hole trapping by bridging oxygen causing the increase of B–O bond length.

1. Introduction

Study of radiation effects on glass properties has been expanded recently due to its wide application in up to date technology such as optics on board space craft, optical fiber wave guiding and in mobilization of high level radio, active waste. Generally, exposure of high-energy radiation, X-rays, γ-rays, ultraviolet light and neutrons on materials produce interesting modifications in their properties, namely chemical, electrical, magnetic, mechanical as well as optical properties (Rai et al., 2010). The radiation damage processes, which take place in glass, are generally the same as those, which occur in crystalline systems. In the simplest purview, there are three basic processes: atomic displacement by momentum and energy transfer, ionization and charge trapping and radiolytic or photochemical changes.

In all the cases, what is defined as damage is the existence of post-irradiation local structure (either atomic or electronic) which differs from that present before irradiation (Singh et al., 2010; Ezz-Eldin et al., 1996). The investigation of radiation effects on transition metal (TM) doped glasses lead to a better understanding of the intrinsic defects due to the initial glass components as well as extrinsic defects related to the dopant TM ions (Singh et al., 2010).

The effect of irradiation on glasses usually depends on the type and energy of irradiation, glass composition and parameters such as temperature (Elalaily and Mahamed, 2002). It is well established that radiation damage in glass leads to active defects. Such defects can be introduced by ionization or atomic displacement mechanisms or via the activation of the preexisting defects (Rai et al., 2010; Elalaily and Mahamed, 2002).

Effects of gamma ray-irradiation on the optical properties of glasses are important, since they are related to the formation and accumulation of radiation – induced defects, which may lead to the occurrence of color centers. Similar to semiconductors, the defects are formed in pairs of negative electrons and positive holes. Electronic transition in color – centers may cause absorption in the UV and visible spectral ranges (Marzouk et al., 2006; Sharma et al., 2006b). Therefore, optical spectroscopy can be used to determine the amount of defects created during irradiation. It has been observed that the interaction of gamma-rays with glass results in profound structural changes affecting optical and other physical properties (Sharma et al., 2006b). The presence of impurities, such as alkali, alkaline earth and transition metals, in the glass increases radiation-induced defects (Elalaily and Mahamed, 2002). These defects may be either permanent or temporary. Defect recovery mechanisms, such as optical bleaching, control the rate of recovery during and after irradiation (Elalaily and Mahamed, 2002). Borate glasses containing transition metal (TM) oxides are very interesting materials for the radiation dosimetry applications because their effective atomic number is very close to that of human tissue (El Batal et al., 2008).

B_2O_3 is one of the best-known glass constituents and is present in varieties of commercial glasses. It is often used as a dielectric and insulating material, and it is known that borate glass is a good shield against IR radiation. It is also of academic interest because of the occurrence of the boron anomaly (Marzouk et al., 2006; El Batal et al., 2008). However, pure borate glasses have certain disadvantages to be used in the radiation dosimeter since they are highly

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hygroscopic and exhibit a weak glow peak at relatively low temperatures. Alkali borate glasses are considered as good candidates for dosimeter applications since they are relatively moisture resistant when compared with the pure borate glasses (Balaji Rao et al., 2004; Venkat Reddy et al., 2005). Addition of CaF_2 into the glass matrix lowers the viscosity and decreases the liquid's temperature to a substantial extent, further enhances the formation of the color center under the effect of ionizing radiation. F^- ions in CaF_2 act as co-activators and facilitate the substitution of activators into the lattice (Singh et al., 2007; Venkateswara Rao et al., 2002; Laxmi Kanth et al., 2004). The aim of the present work is to study the effect of gamma-ray irradiation on the optical absorption spectra of MgF_2 doped lithiumtetraborate glasses after being exposed to different radiation doses. Absorption in near ultraviolet/visible is used to calculate the optical band gap and band tail width.

2. Experimental

Glass system of composition [xMgF$_2$–10Al$_2$O$_3$-(40-x) TeO$_2$-50Li$_2$B$_4$O$_7$] with x = 0, 15, 20 and 40 mol%, was prepared by melt quenching method. The batches in powder form were mixed and thoroughly in an agate mortar, and melted in porcelain crucibles in an electric furnace at a temperature range of 800–950 °C for about 1 h. A porcelain crucibles containing the batch was shacked thoroughly to achieve high homogeneity. The crucibles were covered by a porcelain lid to minimize volatilization effects. The resultant melt was then casted in a brass mould, and subsequently annealed at 350 °C for 2 h. Then the furnace was switched off to cooled slowly to room temperature.

The density was measured at room temperature using the Archimedes method with xylen as the immersing liquid. Optical absorption spectra were obtained by UV–VIS spectrophotometer (Shimadzu, Japan), in wavelength range 200–1100 nm. Optical absorption spectra were measured before and after γ-irradiation.

A ^{60}Co gamma cell (2000 Ci) was used as a gamma-ray source with a dose rate 1.5 Gy/s (150 rad/s) at room temperature. Glass samples were placed in the gamma cell in a manner that allows each sample to be exposed to the same irradiation dose every time. Samples were irradiated for radiation doses; 5, 20, 40 and 70 kGy.

3. Result and discussion

Valuable information can be obtained by measuring glass density which allow information's about compactness, geometrical modification of the glass network and the changes in interstitial hole dimensions (Simon et al., 2003).

The dependence of glass density (ρ (g/cm^3)) and molar volume (V_M (cm^3)) are shown in Fig. 1 and the values are listed in Table 1.

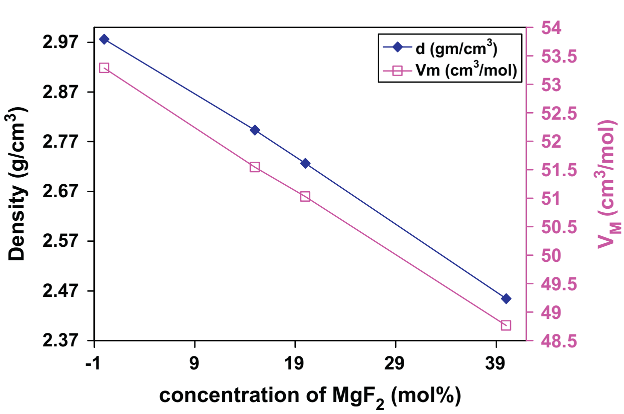

Fig. 1. Dependence of density and molar volume on MgF_2 content.

Table 1
Concentration of MgF_2, measured density and calculated molar volume for non-irradiated glass system.

Concentration of MgF_2 (mol%)	ρ (g/cm^3)	V_M (cm^3)
0	2.98	53.3
15	2.79	51.5
20	2.73	51
40	2.46	48.7

Both density and molar volume exhibit a monotonic decrease with the x increasing, which can be accounted for by the replacement of heavy Te cation by higher Mg ions. In such case one can conclude that addition of MgF_2 leads to the increase of the free volume i.e. more open structure. This behavior can be lead to the increase of non-bridging oxygen.

Optical absorption spectra measured at room temperature of different samples before and after irradiation are shown in Fig. 2. The color of the glass system before irradiation was transparent white yellow and after irradiation changes from white yellow to brown. Such color changes are most likely be due to the trapping of the electrons in the already existing defects. This may be the cause of generation of located levels that can absorb light, and the color centers may be formed (Singh et al., 2007).

No sharp absorption edges are observed, confirming the non-crystalline nature of glass samples. Inspection of obtained spectra reveals that all edges exhibit a red shift with the radiation dose. Such red shift can be attributed to the increasing of free F^- ions and number of non-bridging oxygen atoms after breaking the bonds between boron and oxygen atoms (Sharma et al., 2006a; Laxmi Kanth et al., 2005). An optical absorption band is also observed at 360 nm for dose at 70 KGy. This is most likely due to the formation of color centers at high irradiation (70 KGy), and indicating creation of defects in the glass sample by gamma irradiation (Rai et al., 2010). They suggested that the absorption in the range 360–480 nm was attributed to the absorption of O^- centers in gamma irradiated Ce: LuYAP crystal. The shift in the absorption edge to lower energies may be related to formation of non-bridging oxygen atoms (NBOs), when the glasses exposed to γ-irradiation. This may be connected with high concentration of BO_4 tetrahedral, where the binding forces between the structural units get weaker in the order [BO_3–BO_3] > [BO_3–BO_4] > [BO_4–BO_4] (Singh et al., 2010). In contrast, B_2O_3, which forms a network structure related to the silicates, gets it strength from its covalent bonds. The increased numbers of electrons due to the surrounding oxygen ions have the effect of decreasing the energy necessary for the transition across the mobility gap, thus causing a red-shift of the cut-off wavelength (Sharma et al., 2006b).

The absorption coefficient $\alpha(\omega)$ was determined at different photon energies ($\hbar\omega$), near the absorption edge for glass samples. The linear dependence of $(\alpha\hbar\omega)^{1/2}$ against photon energy ($h\omega$) reveals that indirect transition is t he dominated optical absorption mechanism according to the formula (Davis and Mott, 1970).

$$\alpha\hbar\omega(\omega) = B(\hbar\omega - E_{opt})^2$$

This is expected behavior, since in non-crystalline systems; indirect transition is the possible one, due to the lake of translation symmetry. The linear dependence of $(\alpha\hbar\omega)^{1/2}$ on photon energy ($\hbar\omega$) at different gamma doses for glass system shown in Fig. 3. The values of the optical energy gap E_g, are obtained by extrapolation of the linear region of the plots to $(\alpha\hbar\omega)^{1/2}$ = 0 and these values for non-irradiated and irradiated glass samples are listed in Table 2. It is clearly evident that, the value of E_g decreases with increasing of gamma doses and increasing of MgF_2 content.

The absorption coefficient $\ln(\alpha)$ of the optical absorption near the band edge shows an exponential dependence on photon energy