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Optical Properties of Erbium doped Molybdenum Tellurite Glasses

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Abstract

The glasses with the composition of $x\text{Er}_2\text{O}_3\text{-}5\text{AgCl-}15\text{MoO}_3\text{-(}80\text{-}x\text{) TeO}_2$ ($x = 0, 0.5$ and 1 mol%, named as SMT0, SMT1 and SMT2, respectively) were synthesized using conventional melt quenching method and their optical properties were investigated through UV-Visible spectrophotometer. Density and molar volume values of the glass samples were estimated, their values were found in the range from 5.52 to 5.64 g/cm^3 and 27.737 to 28.689 cm^3 , respectively. The UV absorption spectra were recorded at room temperature in the wavelength range $200\text{-}1100\text{nm}$. From the absorption edge data, it is found that both the direct and indirect type transitions may take place. The direct and indirect band gap values are ranging from 1.92 to 2.29 eV and 1.24 to 1.77 eV, respectively. Also, the Urbach energy (E_{tail}) values were determined and their values are ranging from 0.33 to 0.54 eV. These obtained E_{tail} values are well matched with amorphous semiconductors (0.046 to 0.66 eV).

Keywords: Density; Molar volume; Optical band gap; Urbach energy; Tellurite glasses.

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1. Introduction

Studying optical properties of tellurite based glass is very significant due to their valuable characteristic features such as high refractive index, low phonon energies, stability at room temperature, non-hygroscopic properties, easy fabrication and low melting temperature, which makes potential applications in various fields like laser and nonlinear optical materials, photonic and communication applications[1-3].

TeO₂ is a conditional glass former that needs modifier ion to form vitreous state easily[4]. Transition metal oxides (V₂O₅, Fe₂O₃, MoO₃, etc.) containing glasses are of technological importance due to their increasing applications in different fields[5-7]. Especially addition of MoO₃ into the glassy matrix has vast applications in developing passive alphanumeric displays, memory devices, optical smart windows, gas sensors and micro batteries, because MoO₃ in orthorhombic phase has a unique 2-dimensional layered structure[8,9]. Furthermore, glasses containing semiconductor microcrystals AgCl, AgNO₃, AgBr, exhibits surface plasmon resonance (SPR) effect. The SPR being the collective oscillations of free electrons in the conduction band of the metal surface play a dramatic role in the enhanced optical properties[10].

In last few decades many glass science researchers have been attracted towards rare earth doped glassy materials because RE³⁺ ions are laser active ions that provide emission in a wide range of wavelength according to the chosen rare earth element, making, thus, these glasses highly perspective for utilization in the photonics applications[11-14]. Among the other rare earths, Er³⁺ ions doped glasses are widely used in telecommunications, optical amplifiers and waveguide lasers[3,15].

The measurement of optical absorption in the ultraviolet (UV) and visible region gives an idea of the optical energy band gap in both crystalline and amorphous materials. Also, it gives crucial information about the band structure. The absorption edge at low energy follows the Urbach law, which gives the degree of defect in the glass network.

This work is intended to study the optical properties of erbium doped silver molybdenum tellurite glasses such as optical absorption, Urbach energy, direct and indirect band gap. In addition, density and molar volume values have also been calculated and discussed with respect to Er_2O_3 concentration.

2. Experimental

The glasses with the composition of $x\text{Er}_2\text{O}_3\text{-}5\text{AgCl-}15\text{MoO}_3\text{-(}80\text{-}x\text{)TeO}_2$ ($x = 0, 0.5$ and 1 mol%, respectively) were synthesized using conventional melt quenching method. The appropriate weights of Analar grade chemicals (AgCl , MoO_3 , TeO_2 and Er_2O_3) were taken in mortar, grounded well by using pestle for 15 min and heated at 900°C for 2 hrs. After the completion of heat treatment, the molten liquid was cast onto a brass mould and quickly pressed with another one. The result is in the form of glass and these glass samples were used for further studies.

The glass structure was characterized by D-8 X-ray diffractometer (Bruker AXS-Model) using 1.5406 \AA from Cu K_α radiations in the scanning rate $2^\circ/\text{min}$.

The densities of the glass samples were measured at room temperature by using Archimedes method, with toluene as immersion liquid of stable density ($\rho = 0.866 \text{ g/cm}^3$). The molar volume values of the glass samples were calculated by using the relation $V_m = M/\rho$, where M is the molar mass and ρ is the density of the glass samples.

The optical absorption spectra were recorded at room temperature in the wavelength range from 200 to 1100nm by using a Perkin-Elmer lambda-30 UV-Visible spectrophotometer. The optical absorption coefficient $\alpha(\lambda)$ was calculated from the absorbance A , and the thickness of the sample d , by using the following relation,

$$\alpha(\lambda) = 2.303 \frac{A}{d} \quad (1)$$

3. Results and discussion

X-ray diffraction (XRD) pattern of the glass system are shown in Figure 1. It has been observed that a strong diffused band occurred in the pattern due to the scattering of X-rays in the non-crystalline network and the obtained broad humps in the pattern confirms the amorphous nature of the glass system.

Density and molar volume values are tabulated in the Table 1 and their values were found to be in the range from 5.52 to 5.64 g/cm³ and 27.737 to 28.689 cm³, respectively. The density measurement is very crucial tool to examine the structure of the glass network. It can be seen that from Table 1, the density values decreases with increase in mol% of Er₂O₃. The variation of molar volume values are expected exactly opposite to that of density variation is depicted in Figure 2. The decrease in density of the glasses is may be due to the heavier Er₂O₃ molecular mass compared to the other element in the glass system.

The typical optical absorption spectra of the glass system as shown in Figure 3. An expression of absorption coefficient a as a function of photon energy $h\nu$ for direct and indirect inter-band electronic transition can be written as,

$$ah\nu = B(h\nu - E_{opt})^n \quad (2)$$

where B is a constant and $h\nu$ is the photon energy, E_{opt} is the optical energy band gap and n is a number which characterizes the transition process. The exponent, n takes the values: 1/2 and 2 for direct and indirect allowed transitions, respectively. The optical absorption coefficient values are well fitted to both direct and indirect band gaps and their values can be determined from the expression (2) by extrapolating the absorption coefficient to zero absorption in the $(ah\nu)^2$ and $(ah\nu)^{1/2}$ vs $h\nu$ plot at $(ah\nu)^2=0$ and $(ah\nu)^{1/2}=0$, as shown in Figures 4 and 5. The values of direct and indirect band gaps vary from

1.92 to 2.29 eV and 1.24 to 1.77 eV, respectively, they are tabulated in Table 1. Variation of direct and indirect band gap as a function of Er_2O_3 mol% is shown in Figure 6. It is observed that, there is an anomalous variation in both direct and indirect band gap values. The Urbach energy values are presented in Table 1, which corresponds to the width of the band tail, caused by the localized states. The absorption at lower photon energy usually follows Urbach rule, the width of the band tail (E_{tail}) can be estimated by using the relation,

$$\alpha(\nu) = B \exp\left(\frac{h\nu}{E_{tail}}\right) \quad (3)$$

Urbach energy (E_{tail}) values are ranging from 0.33 to 0.54 eV. The obtained E_{tail} values are well matched with amorphous semiconductors (0.046 to 0.66 eV). The observed increase of the optical band gap is attributed to the substitution of TeO_2 by Er_2O_3 . The addition of small amount of rare-earth ion is capable of disturbing the order and consequently increases the optical band gap energy[16] as shown in Table 1.

Table 1: Density (ρ), molar volume (V_m), optical band gap for direct (E_{gd}) and indirect (E_{gi}) transitions and Urbach energy (E_{tail}) of Er_2O_3 -AgCl-MoO₃-TeO₂ glasses.

Glass code	Density (ρ) (g/cm^3)	Molar volume (V_m) (cm^3)	Direct band gap (E_{gd}) (eV)	Indirect band gap (E_{gi}) (eV)	Urbach energy (E_{tail}) (eV)
SMT0	5.64	27.737	1.92	1.24	0.41
SMT1	5.56	28.309	2.25	1.72	0.42
SMT2	5.52	28.689	2.29	1.77	0.44

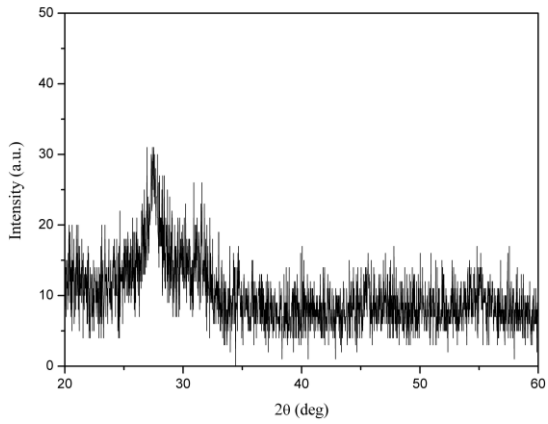


Fig1: Typical XRD pattern of Er₂O₃-AgCl-MoO₃-TeO₂ glass

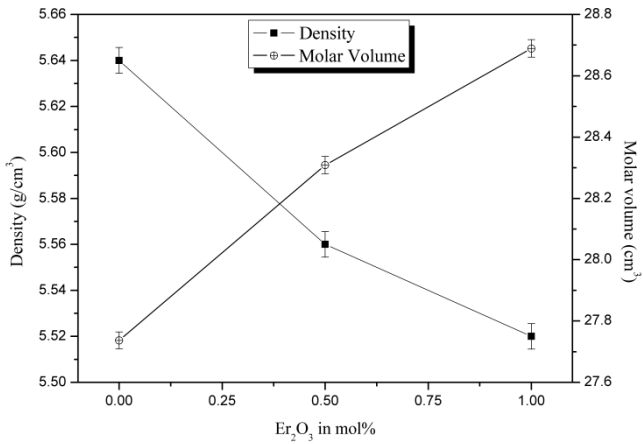


Fig 2: Variation of density and molar volume with respect to Er₂O₃ mol%

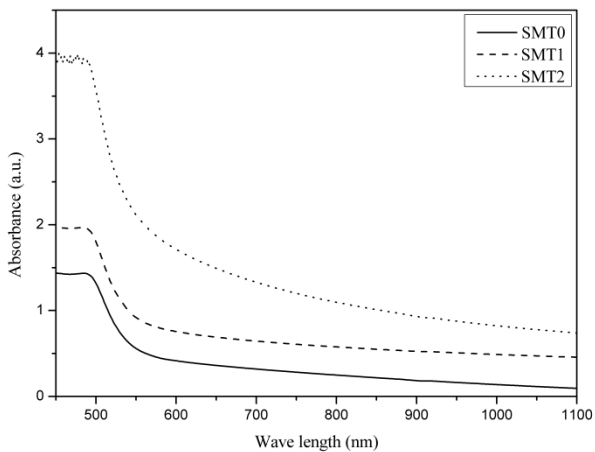


Fig3: Optical absorption spectra of SMT glass series

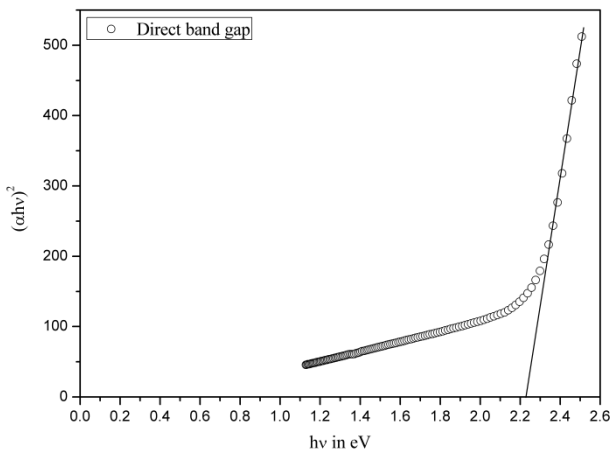


Fig 4: Typical plot of $(\alpha h\nu)^2$ versus $h\nu$

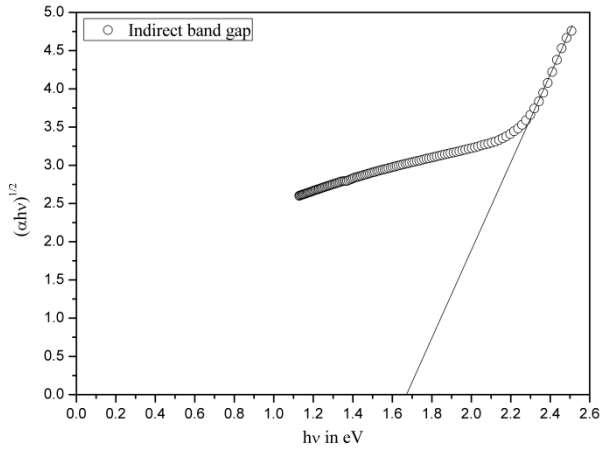


Fig 5: Typical plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$

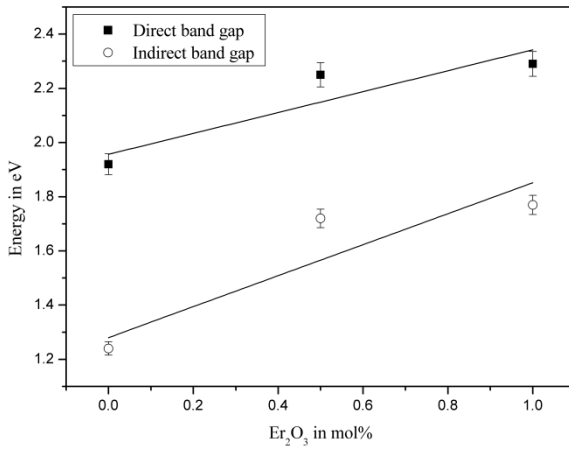


Fig 6: Variation of direct and indirect band gap as a function of Er_2O_3 mol%

4. Conclusions

The glasses of different compositions of Silver chloride, molybdenumtellurite glasses doped with trivalent erbium ions have been successfully prepared by conventional melt quenching method. The physical and optical parameters such as density, molar volume, direct, indirect optical band gaps and Urbach energies of the glasses were determined. These values are well matched with the other erbium glasses as reported in the earlier workers. The addition of small amount of rare-earth ion is capable of disturbing the disorder and consequently increases the optical band gap energy.

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