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The Polarizability and Optical Characteristics of Zinc Phosphate Glasses Doped Terbium Embedded with Copper Oxide Nanoparticles

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Abstract. Tuning the concentration of nanoparticles (NPs) to accommodate wider application demanded a better understanding of the physicals and structural properties of the glass. A series of zinc phosphate glasses with the composition of $(57-x) \text{P}_2\text{O}_5 - 40\text{ZnO} - 3\text{Tb}_2\text{O}_3 - x\text{CuO}$, ($0 \leq x \leq 2$ mol %) has been prepared by melt quenching technique and their physical and optical characterization have been studied. The X-Ray Diffraction technique and UV-Vis Spectroscopy have been used to characterize the glass sample. The XRD confirms the amorphous nature of the prepared glasses. The physical properties of glasses with different CuO NPs such as density, molar volume, refractive index and electronic polarizability are determined. It is found that both density and molar volume decreases with increasing CuO NPs concentration. The optical band gap (4.54 eV-2.96 eV) and the Urbach energy (0.19 eV-0.54 eV) are showing a decreasing trend with the increasing amount of CuO NPs. This is due to the formation of non-bridging oxygen, (NBO) in the glass network. The glass exhibits high refractive index ~ 2.40 and polarizability $\sim 1.12 \times 10^{-23} \text{ cm}^3$ and is useful for solid-state laser and optoelectronic devices.

Introduction

Phosphate as glass host possess a lot of advantages such as high thermal expansion coefficient which easily for fiber preparation process [1]. phosphate has some drawbacks such as low chemical durability [2]. Many efforts have been dedicated to improve the chemical durability of the phosphate glasses, for example adding zinc oxide causes the depolymerization of phosphate P-O-P linkage network and transform into P-O-Zn network linkage [3]. In this way, the aqueous attack to the phosphate glass system can be prevented [4]. The lanthanide ions such Tb^{3+} ion receive much attention due to their application in laser development. Phosphate glasses doped Tb^{3+} is capable as promising material for green solid state laser. [5]. This is attributed to the $4f-4f$ transition that gives the green and red emission [6]. Besides that, it is reported that glass contain zinc aluminum phosphate glasses doped Tb^{3+} exhibits high refractive index and high chemical durability. [7]. Hence, this glass has high possibility for optoelectronic application. Rare earth doped glass contain metal NPs gives a significant and tremendous effect on the optical properties of the glass [8]. CuO NPs may be identified to enhance the electrical point towards the maximizing the quantum efficiency of the glass [9]. In this view it is very important to examine the influence of CuO NPs in Tb^{3+} doped phosphate glass. Thus, it is the aim of this paper to determine the physical and optical behavior of Tb^{3+} doped zinc phosphate glasses. The effect of CuO NPs on the density, molar volume, ionic packing density polarizability, optical energy band gap, Urbach energy and phonon cut off wavelength are analyzed and discussed in details.

Experimental

Zinc phosphate glasses doped terbium embedded with CuO NP glasses in the composition $(59-x) P_2O_5 - 30ZnO - 3Tb_2O_3 - xCuO$ with x within the range of 0.0 mol% to 2.0 mol% are prepared by conventional melt quenching technique. The glass samples are prepared using analytical grade powdered chemical reagent of high purity (Sigma Aldrich, 99.99%) such as Phosphorus pentoxide (P_2O_5), Zinc oxide (ZnO), Terbium oxide (Tb_2O_3) and Copper oxide (CuO). The constituent proportions of the glass composition as shown in Table 1 are weighed using high precision balance (Electronic Balance Precise XT 220A) and mixed thoroughly. Glass constituents about 15 g are mixed together in alumina crucible and melted in a furnace at 1150°C for 1 hour 30 minutes. Then, the glass melt is poured onto a steel plate and annealed at 300°C for 4 hours to ensure the release of the thermal and mechanical stress completely.

Table 1: The chemical composition of the prepared glass sample.

Sample	Chemical composition (mol%)			
	P_2O_5	ZnO	Tb_2O_3	CuO
PZTbCu0.0	56.5	40	3.0	0
PZTbCu0.5	56.0	40	3.0	0.5
PZTbCu1.0	55.5	40	3.0	1.0
PZTbCu1.5	55.0	40	3.0	1.5
PZTbCu2.0	54.5	40	3.0	2.0

The density of the glass sample is measured by applying the Archimedes Principle. The amorphous nature of the prepared glasses is analyzed using X-Ray diffraction measurement (XRD). The XRD spectra are recorded using X-Ray Diffractometer (Model: Siemens Diffractometer D5000) in the 2θ range of 10°- 90° ($K\alpha=1.54 \text{ \AA}$) at 40 kV and 100 mA, at room temperature. The UV-Vis NIR absorption measurements in the range 200nm-2500nm are carried out using Shimadzu spectrophotometer (Model: PC UV-Vis NIR) with resolution $\pm 1\text{nm}$. The glass density was determined by using the equation

$$\rho = \frac{W_a}{W_a - W_L} (\rho_x) \quad (1)$$

where ρ_x is the density of immersion liquid. W_a is the weight of the glass in air and W_L is the weight of the sample when immersed in immersion liquid. The molar volume V_m is calculated by using the obtained density and weight of one mole of the sample by using the equation

$$V_m = \sum_i i \frac{x_i M_i}{\rho} \quad (2)$$

where x_i and M_i refers to the molar fraction and molecular weight of the i^{th} of the component respectively.

David and Moss defined plot of absorption coefficient ($\alpha (h\nu)$) versus photon energy to calculate the energy band gap using the relation:

$$\alpha (h\nu) = \frac{A (h\nu - E_{opt})^n}{h\nu} \quad (3)$$

where A is the absorbance, $h\nu$ is the photon energy and E_{opt} is optical band gap and n is the value depends on type of transition. There are two types of transition $n=1/2$ for indirect transition while $n=2$ for direct transition. Both of the transitions are due to the interaction of electromagnetic wave with an electron which causes the electron in the valence band to jump the conduction band. The exponential of the band tail defined in optical absorption edges used to measure the Energy band gap (ΔE) of amorphous semiconductor. The plot of absorption coefficient versus photon energy can be written as

$$\alpha(\nu) = B \exp\left(\frac{h\nu}{\Delta E}\right) \quad (4)$$

where B is a constant. The Urbach energy ΔE measured by plotting $\ln\alpha$ versus photon energy. The measured ΔE signify the width of the band tail of the localized state in the energy band gap. The refractive index (n) is important to determine the electronic polarizability and local field effects of the materials. The refractive index can be calculated by the equation

$$\frac{n^2+1}{n^2-1} = 1 - \sqrt{\frac{E_{opt}}{20}} \quad (5)$$

The Lorentz Lorents equation are used to calculate the molar refractivity R_m and electronic polarizability α_m as follows (6) and (7)

$$R_m = \frac{n^2-1}{n^2+1}(V_m) \quad (6)$$

$$\alpha_m = \left(\frac{3}{4\pi N_a}\right) R_m \quad (7)$$

Results and Discussion

Fig.1 shows typical XRD pattern of glass sample shows a broad halo hump at 10° to 40° . Presence of broad halo hump at low angle and absent of existence of crystalline peak indicates that the glass sample are amorphous in nature. The absent peak of CuO NPs is due to the small concentration of CuO NPs compared to the concentration of host and modifier. The measured density and molar volume are tabulated in Table 2. The density and molar volume behaves an inverse relationship. The density of the glasses decrease from 3.43 gcm^{-3} to 3.07 gcm^{-3} while the molar volume increases from 361.94 g/mol to 401.13 g/mol with the increment of CuO NPs. The decrease in density is attributed to the introduction of CuO NPs that has lower molecular mass (79.55 g/mol) compared to larger molecular mass of P_2O_5 (125.95 g/mol). Besides that another reason is due to the creation of (NBO) which essentially alters the glass structure. The changes in density modified the geometrical construction in the glass network. [10]. The decrease in the molar volume due to the smaller ionic radius of Cu^{2+} ion (0.074 \AA) compared to the P^{5+} (0.29 \AA) [11,12]. The increase in refractive index from 2.08 to 2.40 with the increase of CuO NPs related to the decrease in energy band gap and relates with compactness of the glass. The Cu atoms will fits at the interstitial site by compressing the original structure state of P-O bond make the glass more compact. This causes the lattice strain to increase so that the light pass through the sample will slow [13]. The electronic polarizability are in the range (0.89 \AA^3 - 1.21 \AA^3). This is due to (NBO) that bind less and more polarize than bridging oxygen (BO) [14].

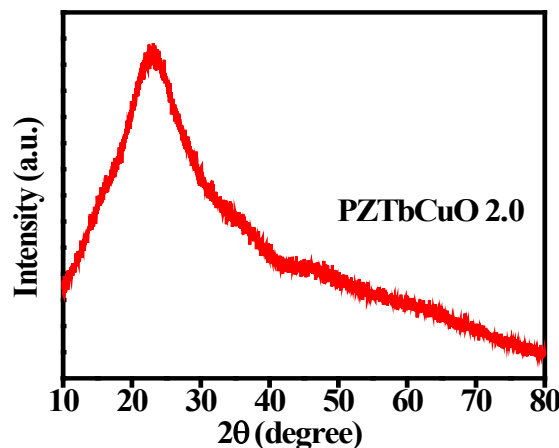


Figure 1: A typical XRD pattern of glass sample PZTbCuO2.0.

Table 2: Physical properties of zinc phosphate glasses doped with Tb^{3+} embedded with CuO NPs.

Physical Properties	PZTbCu 0	PZTbCu0.5	PZTbCu1.0	PZTbCu1.5	PZTbCu2.0
Density ρ (g/cm ³)	3.43	3.33	3.25	3.14	3.07
Molar Volume (cm ³ mol ⁻¹)	36.19	37.27	38.09	39.33	40.11
Molar refractivity R_m	22.60	25.34	26.49	27.61	28.29
Electronic polarizability α $\times 10^{24}$ cm ³	0.89	1.00	1.06	1.09	1.12
Energy band gap (eV)	4.45	3.42	3.11	3.00	2.96
Urbach energy (eV)	0.19	0.34	0.52	0.54	0.58
Refractive Index n	2.08	2.29	2.36	2.39	2.40

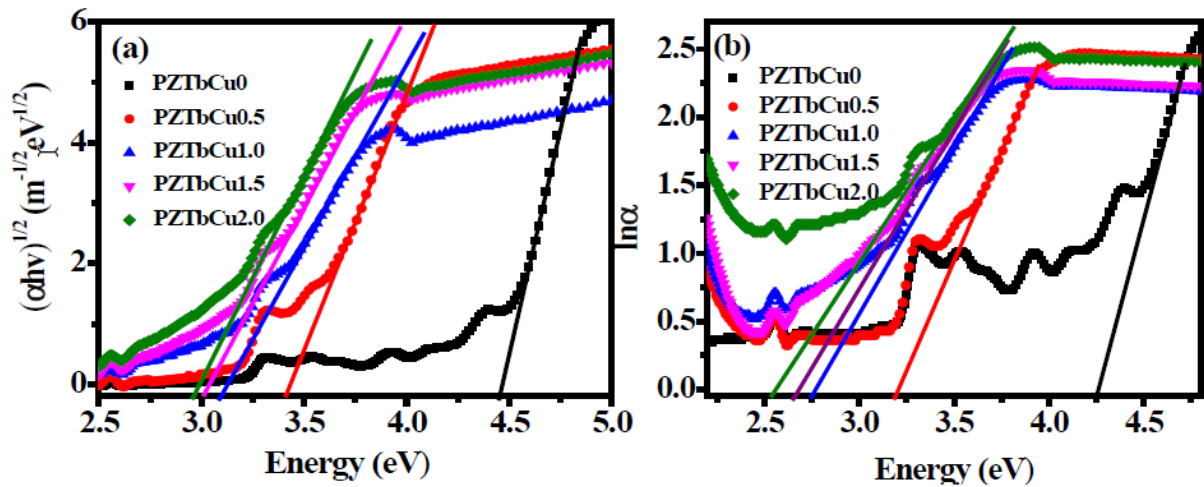


Figure 2: The plot of the (a) optical energy band gap indirect transitions (b) Urbach energy.

The increase in refractive index from 2.08 to 2.40 with the increase of CuO NPs related to the decrease in energy band gap and relates with compactness of the glass. Furthermore increase in refractive index also due to alteration in the glass network. Incorporation of CuO NPs modified the structure of phosphate and oxygen which alter the glass network by introduce more formation of (NBO) at the expense of (BO) [13]. The electronic polarizability is in the range $(0.89-1.21) \times 10^{-23}$ cm³. Notably the (NBO) form ionic bonds possess larger electronic polarizability over the covalent bond in BO's. This is due to (NBO) bind less tightly with an excited electron and more polarize than BO [14]. The increase in molar refraction (22.60--28.29) cm³/mol relative to materials polarizability [8]. The optical energy band gaps of the prepared glass are calculated by using the absorption edges via Tauc plot. Fig.2 (a) shows the Tauc plot of zinc phosphate glasses doped Tb^{3+} embedded with CuO NPs. It is observed that energy band gap inversely proportional with increasing amount of CuO NPs. This is possibly attributed to the transformation of (BO) into (NBO) in the doped CuO NPs glass structure as discuss by Nehal et al. [15]. Besides that, another reason is due to more developed negative charged presents in (NBO), thus assists in easy way of excitation of electron in higher wavelength [16]. Hence reduce the optical energy band gap. The disorder and absent of long range order in amorphous materials possess the phonon accompanying with the tail density states into the forbidden energy band gap. The Urbach energy was defined by linear plot of energy $\ln\alpha$ against photon energy shown in Fig. 2(b). It is observed that that the Urbach energy increases with increasing CuO NPs concentration. Besides, it is known that materials which possess larger values of Urbach energy has high probability to convert the weak bond into the defects [17]. The systematically increase of Urbach energy is due to the higher generation of bonding defects and (NBO) due to the breaking of covalent bonds when large metal atoms such as Cu^{2+} occupied the network [18,19]. Besides that glass with higher Urbach energy tend to possess a higher disorder and more glassy in nature [18].

Conclusion

A series of zinc phosphate glasses doped with Tb^{3+} at various concentrations of CuO NPs are prepared via melt quenching technique. The CuO NPs dependent variation physical and optical properties have been discussed. The prepared samples are verified to be amorphous in nature. The energy band gaps are in the range 4.45 eV- 2.96 eV respectively. The Urbach energy decreases with the increasing concentration of CuO NPs. Overall, the glasses might be useful for the production of a solid state laser.

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