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Optical Properties of quaternary TeO_2–ZnO–Nb_2O_5–Gd_2O_3 glasses

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Abstract

Quaternary tellurite glass systems in the form $75TeO_2$–15ZnO–$(10-x)Nb_2O_{5-x}Gd_2O_3$, where (x=0.0, 0.5,1.0,1.5,2.0 and 2.5 mol%) have been prepared by the melt quenching technique. Optical absorption studies are carried out on the glass systemin the wavelength range of 380–500 nm. The cut-off wavelength λc, optical band gap E_{opt}, Urbach energy ΔE and refractive index n values were calculated from optical absorption data. Also, different physical parameters such as, molar refraction RM, metallization criterion M, electronic polarizability of the oxide ion α_o^{2-} (calculated from E_{opt}), and optical basicity Λ have been determined. The FTIR absorption spectra for all glasses in the range of wave numbers 350–4000 cm^{-1} has been recorded and designated.

Keywords: Glasses; Tellurite; Rare Earth oxides; UV spectra; FTIR absorption spectra

1. Introduction

In materials engineering design prediction and understanding over the physical properties are essential to develop new class of functionalized materials. Recently, growing attention has been paid to tellurite-based glasses due to the promising materials for photonics and optoelectronics due to its unique physical properties [1–14]. Heavy metal oxide (ZnO) have been used as potentially promising component materials for tellurite-based fibers [1]. Design and optimization of tellurite hybrid micro structured optical fiber TeO_2–Li_2O–WO_3–MoO_3–$Nb_2O_5$with high nonlinearity and low flattened chromatic dispersion for optical parametric amplification had been achieved [3]. Rare work has been focused on gadolinium oxide in glass [14]. Hence, the glass tellurite–zinc–niobium–gadolinium TZNG need to synthesize and physically characterize in order to provide scientific data for future industrial applications.

The objectives of this project are to study the optical properties of TZNG glass,estimation of the average electronic polarizability, energy gap, and the optical basicity of the glass systems. Also, to study the effect of replacement by Nb_2O_5 by Gd_2O_3 on optical properties of tellurite glasses and to bring new information and parameters of these glasses.

2. Experimental work

The tellurium-based glasses form $75TeO_2$–15ZnO–(10–x) $Nb_2O_{5-x}Gd_2O_3$, where (x=0.0,0.5,1.0,1.5,2.0 and 2.5 mol%) have been prepared by the melt quenching technique of tellurium(II) oxide (TeO_2, 99.99% purity, Loba), niobium(V) oxide (Nb_20_5, 99.99% purity, Aldrich), zinc oxide (ZnO, 99.999% purity, Aldrich) and gadolinium (III) oxide (Gd_2O_3,99.9% purity, Aldrich) as explained before [15]. The prepared cubic samples were polished by a lapping machine with 600 grade and soft fine AlO_3 powder. Opposite faces were finished optically flat and parallel with a high mirror-like surface. The compositions of the glass samples employed in the present study are given in Table 1.

The optical absorption spectra in the visible and near ultraviolet region were recorded at room temperature. These curves were traced for highly polished thin glass samples using a Perkin-Elmer 402 double beam spectrophotometer in the

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Table 1
Density, molar volume, oxygen packing density, experimental UV cut off, energy gap, energy tail, calculated and refractive index of the quaternary TeO_2–ZnO–Nb_2O_5–Gd_2O_3 glassy samples.

Glass composition	P (g/cm$^{3)}$ [15]	V_M (cm^3) [15]	OPD (g atom/L)	λ_c (nm)	E_{opt} indirect (eV)	ΔE (eV)	n
TZNG1 ($75TeO_2$–15ZnO–$10Nb_2O_5$)	5.168	30.665	70.112	392	2.925	0.115	2.418
TZNG2 ($75TeO_2$–15ZnO–$9.5Nb_2O_5$–$0.5Gd_2O_3$)	5.254	30.256	70.729	390	2.93	0.1254	2.416
TZNG3 ($75TeO_2$–15ZnO–$9Nb_2O_5$–$1Gd_2O_3$)	5.349	29.811	71.450	389	2.94	0.1256	2.413
TZNG4 ($75TeO_2$–15ZnO–8.5Nb2O5–$1.5Gd_2O_3$)	5.51	29.027	73.035	388	2.95	0.1261	2.411
TZNG5 ($75TeO_2$–15ZnO–$8Nb_2O_5$–$2Gd_2O_3$)	5.582	28.738	73.421	387	2.953	0.1265	2.410
TZNG6 ($75TeO_2$–15ZnO–$7.5Nb_2O_5$–$2.5Gd_2O_3$)	5.788	27.800	75.539	384	2.968	0.128	2.406

wavelength range of 3800–500 nm. The FTIR transmission spectra for all observed glasses in the range of wave numbers 350–4000 cm^{-1} has been recorded.

3. Results and discussion

Theprepared quaternary $75TeO_2$–15ZnO–(10–x)$Nb_2O_{5-x}Gd_2O_3$ are yellow and transparent. Table 1 collected values of density, molar volume and oxygen packing density of the quaternary TeO_2–ZnO–Nb_2O_5–Gd_2O_3 glassy samples. The results showed that the density increased from5.168 to 5.788g/cm^3 due to increase of Gd_2O_3 from 0.0 mol% to 2.5 mol%. The increase in the density is attributed to the average molecular weight of the glass, which is higher than that of TeO_2 [16]. The values of the molar volume decreased from 30.67 cm^3 to 27.80 cm^3 due toincrease of Gd_2O_3 from 0.0 to 2.5 mol% as reported in Table 1. This change in molar volume was due to the change in the structure caused by the change on interatomic spacing. Also, Table 1 collected the oxygen packing density OPD has been increased from 70.11 to 75.54 (g atom/L).

The optical absorption spectra of the prepared glasses $75TeO_2$–15ZnO–$(10-x)Nb_2O_{5-x}Gd_2O_3$, where (x=0.0, 0.5,1.0,1.5,2.0, 2.5 mol%) are shown in Fig. 1 in the ranges from 380–500 nm at room temperature. It is found that optical absorption edge is not sharply defined in the present glasses, which clearly indicates their glassy nature. The cut off wavelength $\lambda_c$was in the ranges from 384 to 390 nm. The optical band gap E_{opt} values of the glasses can be calculated using the relation (proposed by Davis and Mott) between the absorption coefficient α (ν) and photon energy (ħν) of the incident radiation, and is given below by Eq. 1 [17,18],

$$\alpha(\nu) = \frac{A(\hbar\nu - E_{opt})^n}{(\hbar\nu)} \quad (1)$$

Where E_{opt} is the optical band gap energy, A is a constant and theexponent n takes different values depending on the mechanism of inter band transitions [17]. For amorphous materials, indirect transitions are valid according to Tauc's relation [19]. The power part n=1/2, 3/2,2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden optical transitions, respectively. The values of indirect optical band gap energy E_{opt} can be obtained from Eq.1 by extrapolating the absorption coefficient to zero absorption in the $(\alpha\hbar\nu)^{1/2}$vs. (ħν) plot (Tauc's plot), as shown in Fig. 2. The values of the E_{opt} for the glass samples are collected in Table 1. The E_{opt} values increased from 2.925 to 2.968 eV for indirect transition due to increase of Gd_2O_3 from 0.0 to 2.5 mol%. The present value optical energy gap confirms the recent data E_{opt}=3.0 eV for the glass 15 g $\{70TeO_2-25WO_3–5La_2O_3\}-0.06$ g Gd_2O_3[14]. The increase in the optical band gap with Gd_2O_3 as explained before [20].

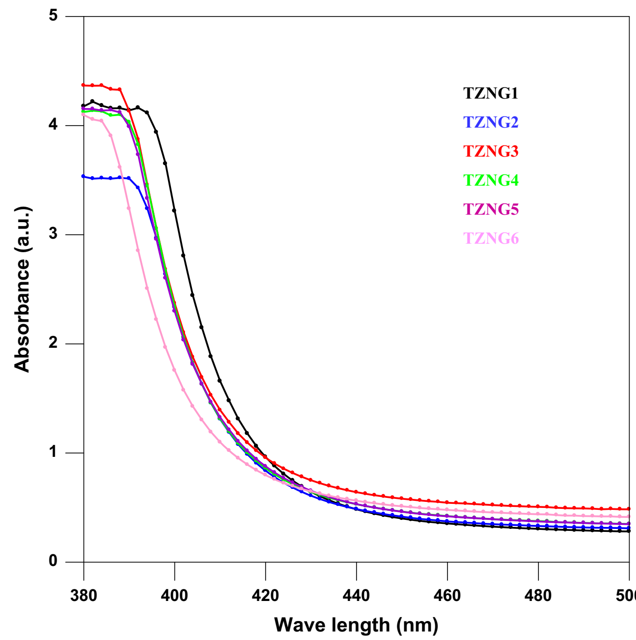

Fig. 1. UV absorption spectra of $75TeO_2$–15ZnO–$(10-x)Nb_2O_{5-x}Gd_2O_3$, (x=0.0, 0.5,1.0,1.5,2.0, 2.5 mol%) glass samples.

At lower values of the absorption coefficient ($\alpha < 10^4$ cm^{-1}), the extent of the exponential tail of the absorption edge characterized by the Urbach energy [21] is given by Eq. 2,

$$\alpha(\nu) = \alpha_o \exp\left[\frac{(\hbar\nu)}{\Delta E}\right] \quad (2)$$

where α_o is constant and ΔE is the width of the band tails of electron states in the forbidden band gap and which is also known as the Urbach energy. The graph of ln(α) vs. photon energy (ħν) for the present glass system (Urbach plot) is shown in Fig. 3. The values of Urbach energy (ΔE) were calculated from the reciprocal of the slope of the linear region (in the lower photon energy) of the curves and are listed in Table 1. The ΔE values increased from 0.115 to 0.128 eV due to increase of Gd_2O_3 from 0.0 to 2.5 mol%. The increase in the energy tail for the present quaternary tellurite glasses suggested that the degree