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Concentration dependent luminescence properties of Sm^{3+}-ions in tellurite–tungsten–zirconium glasses

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ABSTRACT

Tellutite glasses doped with Sm^{3+} ions with composition of $TeO_2 + WO_3 + ZrO_2 + Sm_2O_3$ (TWZSm) have been prepared by conventional melt-quenching technique and investigated their vibrational, optical and luminescence properties through Raman, absorption, emission and decay analysis. The amorphous nature of the sample was confirmed by X-ray diffraction and SEM analysis. The Judd–Ofelt (JO) theory has been performed to investigate the intensity parameters (Ω_λ, $\lambda = 2$, 4 and 6) which inturn used to predict luminescence properties. The chromaticity coordinates as well as pump wavelength dependent luminescence have been investigated. The decay curves are perfectly single exponential at lower concentration and gradually changes to non-exponential nature for higher concentrations (>0.1 mol%). The non-exponential decay curves are well fitted to the Inokuti–Hirayama (IH) model for $S = 6$ which indicates that the energy transfer between the donor and acceptor is of dipole–dipole type. The experimental lifetimes (τ_{exp}) are found to be shortened with increase of Sm^{3+} ions due to the concentration quenching. Among the prepared glasses, 1.0 mol% Sm_2O_3 ions doped glass exhibits higher value of characteristic emission parameters and quantum efficiency for the $^4G_{5/2}$ level suggests that it could be useful for optical devices, particularly visible laser applications.

1. Introduction

Optical spectroscopy is an important tool to study the nature of glasses for the past many years. Investigation of the absorption and luminescence properties of rare earth (RE) doped luminescent materials have found diverse applications in the fields of lasers, telecommunications, optical fiber cables, solar concentrators, optical detectors and the production of wide variety of optical components (as windows, prisms, beam splitters, etc.,). In order to identify new optical devices for specific applications with enhanced performance, active work is being carried out by selecting appropriate new hosts doped with RE-ions.

Tellurite based glass has been selected for present investigation due to their special class of properties as reasonably wide transmission region (0.35–5.0 μm), good glass stability and corrosion resistance, relatively low phonon energy among other oxide glasses, high liner and nonlinear refractive indices. The basic structure of the tellurite glasses is a TeO_4 trigonal bipyramid (tbp) with a lone pair of electrons in one of its equatorial sites. Under normal conditions, tellurium oxide does not have the ability to form a glass structure easily without modifier (alkali oxide, alkaline-earth oxide, transition-metal oxide, or another glass former) [1,2]. Researchers have different opinions as to why it is so difficult to form a glass of pure TeO_2. Neov et al. [1,2] hypothesized that TeO_2 could not form a glass by itself because the Te–O bond is hardly covalent to permit the requisite amount of distortion for a glass structure. Another prevalent view is that the repulsive forces due to the lone pair of electrons resist the free movement of the trigonal bipyramid (tbp) in space during the cooling of the melt and hence the formation of glass [3,4]. However, binary tellurite glass has the effect of lone pair of electrons, which is limited by the introduction of new structural units that are compatible with TeO_4 (tbp) and thus the glass formation becomes easier. The glasses containing the transition ions are being used in the present days to probe the glass structure since their outer d-electron orbital functions have a broad radial distribution and due to their high sensitive response to the changes in the surrounding actions. Among various transition ions, tungsten and zirconium oxides are opted, which acts as good network formers. Recently the optical and acoustic properties of tellurite glasses in the TeO_2–WO_3–ZrO_2 system have been investigated by Yousef et al. [5].

Glasses doped with RE-ions are still attractive as a possible active media for solid state lasers operating in the visible (VIS), near-infrared (NIR) and infrared (IR) spectral region. The Sm^{3+}

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ion is one of the most interesting RE-ions for analyzing the luminescence properties due to its use in high density optical storage, under sea communication, color displays and visible solid state lasers [6]. Moreover, it has $4f^5$ electronic configuration which exhibits orange-red fluorescence in the visible region with strong fluorescence intensity, large emission cross-section and high quantum efficiency [7]. Further, the Sm^{3+} ion is well suited to analyze the energy transfer processes, since its emitting $^4G_{5/2}$ level has comparatively high quantum efficiency and shows different quenching channels [8]. The luminescence intensity of Sm^{3+} ion depends on the concentration of RE ions as well as surrounding environment.

The present work reports the physical, structural, optical and luminescence properties of Sm^{3+} ions in tungsten–zirconium–tellurite glasses. On the basis of the absorption spectrum, Judd–Ofelt [9,10] analysis has been applied to investigate phenomenological intensity parameters, Ω_2, Ω_4 and Ω_6. The other related optical parameters such as oscillator strength, transition probability, branching ratio and radiative lifetime have also been calculated. The decay characteristic for $^4G_{5/2}$ level of Sm^{3+}-ions has also been analyzed. The CIE chromaticity coordinates for all the concentrations are calculated from emission spectra, which falls in the reddish-orange region. The phenomena of concentration quenching and their related mechanisms have been explained by using energy level diagram.

2. Experimental methods

The tungsten–zirconium–tellurite glasses with molar composition: $70TeO_2 + (25 - x)\ WO_3 + 5ZrO_2 + xSm_2O_3$, where x = 0.05, 0.1, 0.5, 1.0, 2.0 and 3.0 mol%, referred as TWZSm005, TWZSm01, TWZSm05, TWZSm10, TWZSm20 and TWZSm30, respectively, were prepared by melt-quenching technique. Batch composition of 30 g of homogeneous mixture was melted at 900 °C for 1 h in an electric furnace using a platinum crucible. The melt was cast on to a preheated brass mold and pressed with another brass plate to get a flat disk of 2 mm thickness and then annealed at 330 °C for 12 h to remove thermal strains. The obtained glasses were polished for their physical and spectroscopic measurement. The refractive indices were measured by Brewster's angle method using diode laser (λ = 650 nm) and Si detector. The densities were measured by the Archimedes' principle using double distilled water as an immersion liquid. The X-ray diffraction (XRD) spectra were recorded with JEOL 8030 X-ray diffractometer using Cu Kα radiation. The Raman spectrum of the undoped TWZ glass was recorded using Jobin Yvon Lab Raman spectrometer. The absorption spectrum was measured with a Perkin Elmer Lambda-950 spectrophotometer. The excitation, luminescence and decay measurements were carried out with a Jobin YVON Fluorolog-3 spectrofluorimeter with xenon lamp as a light source in continues as well as pulsed mode. SEM and EDS maps were collected using Caral Zeiss EVO-MA15 scanning electron microscope. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Density and molar volume measurements

By applying Archimedes's principle, the weight of the samples was measured in air and in double distilled water using a microbalance. Then, the density 'ρ' was determined using the relation [11],

$$\rho = \frac{w_a}{w_a - w_x}\rho_x \tag{1}$$

where 'w_a' is the weight of the sample in air, 'w_x' is the weight of the sample in water and 'ρ_x' is the density of water (ρ_x = 1 g/cm^3). The corresponding molar volume (V_m) was calculated using the relation [11],

$$V_m = \frac{M_T}{\rho} \tag{2}$$

where 'M_T' is the total molecular weight of the multi-component glass system given by

$$M_T = x_{TeO_2}Z_{TeO_2} + x_{WO_3}Z_{WO_3} + x_{ZrO_2}Z_{ZrO_2} + x_{Sm_2O_3}Z_{Sm_2O_3} \tag{3}$$

where x_{TeO_2}, x_{WO_3}, x_{ZrO_2} and $x_{Sm_2O_3}$ are the molar fractions of the constituent oxides and Z_{TeO_2}, Z_{WO_3}, Z_{ZrO_2} and $Z_{Sm_2O_3}$ are the molecular weights of the constituent oxides, respectively. The necessary conditions are $(R_m/V_m) > 1$ and $(R_m/V_m) < 1$ for metals and nonmetals, respectively, where 'R_m' is molar refractivity [11]. The decisive factor of metallization (M) is determined using the formula [12]

$$M = 1 - (R_m/V_m) \tag{4}$$

The evaluated physical properties of TWZSm glasses are represented in Table 1. The density increases with increase of the Sm^{3+} ion concentration. The molar volume increased from 29.521 to 29.931 cm^3 with increase of Sm^{3+}-ion concentration. The values of linear refractive index of the glasses (TWZSm) are found to be in the range of 2.062–2.215 at 650 nm, which is found to be higher than those found in TeO_2–ZnO (2.02–2.10 at 643.8 nm) [13], TeO_2–$LiNbO_3$ (2.06–2.11 at 632.8 nm) [14], K_2O–Nb_2O_5–TeO_2 (1.97–2.13 at 632.8 nm) [15] and Na_2O–Nb_2O_5–TeO_2 (2.06–2.08 at 632.8 nm) [16]. The metallization factors for the prepared glasses are in the range from 0.479 to 0.466, which is an evidence for nonmetallic nature of the present TWZSm glass system.

3.2. X-ray diffraction, SEM and EDS analysis

XRD is an unique technique for amorphous materials as only long range periodic order or disorder can be examined. The XRD measurement was performed for all the samples and was similar to the TWZSm10 glass shown in Fig. 1. The results reveal the absence of sharp peaks that characterizes amorphous nature of the present glass. Fig. 2 depicts the SEM (inset 1 μm and 30 μm) and EDS micro graphs of the glass with different magnification. It is very clear that no nucleation part or crystal growth were observed in the SEM images even at highest magnification of 1 μm, which confirms the non-defective microstructure of the glasses and the absence of cracks and unmelted portions. The EDS analysis of the TWZSm10 glass shows that the composition of major phase which exhibits the presence of O, W, Te, Sm and Zr elements. Further, the EDS spectrum reveals that the samples are free from contamination. Without any impurities which shows as glassy surface with no clusters.

3.3. Raman analysis

The Raman spectrum of TWZ undoped glass is shown in Fig. 3 which explores the information about the vibrational mode frequencies of the glass. The Raman spectrum exhibits the following bands at 348, 457, 669 and 928 cm^{-1} corresponding to various TeO_3 and TeO_4 structural units. The low frequency peak around 348 cm^{-1} is assigned to the symmetric bending vibrations of the TeO_4 group (usually observed in the range of 345–348 cm^{-1} spectral range) [17]. The peak around 457 cm^{-1} (≈460 cm^{-1}) corresponds to the stretching vibrations of the bands of Te–O–W [2,18,19] due to the substitution of TeO_4 tetrahedra by WO_4 tetrahedra. The Raman band near 669 cm^{-1} is ascribed by the glass network fragments consisting of WO_6 octahedra bonded together by oxygen vertices, most likely with the W–O bond stretching in W–O–W linkages [20]. The Raman band near 928 cm^{-1} is ascribed to the complete-symmetry vibrations of WO_4 tetrahedra by