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Photoluminescence study of Sm^{3+} doped Zinc Lead Tungsten Tellurite glasses for reddish-orange photonic device applications

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ABSTRACT

Zinc lead tungsten tellurite glasses with varying concentration of samarium ions were synthesised by melt quench method and studied their absorption, excitation, emission and decay spectral features to understand their utility in visible photonic devices. The bonding parameter evaluated from the absorption spectra reveals the nature of bonding between Sm^{3+} ions and its surrounding ligands as ionic. Judd-Ofelt intensity parameters estimated from absorption spectral features are used to evaluate radiative parameters for the fluorescent levels of Sm^{3+} ions in these glasses. The bandwidths ($\Delta\lambda_p$), emission cross-sections (σ_{se}) , and branching ratios (β_R) were evaluated from the emission spectra. The experimental lifetimes measured are correlated with radiative lifetimes and were used to determine the quantum efficiency (η) of the titled glasses. Relatively higher values of σ_{se}, β_R , η and CIE coordinates obtained for 1 mol% of Sm^{3+} ions in the as prepared glass reveals its suitability for visible photonic devices.

1. Introduction

Over the past few decades, photonic glasses doped with various rare earth (RE) ions have drawn much attention owing to their photo conducting properties and high emission efficiencies. RE doped glasses act as an active medium for various technologically important fields such as solid state lasers, fibers, optical amplifiers and optical detectors due to radiative transitions from the 4f shell energy levels, which are insensitive to the effect of surroundings because of the shielding effect of outer 5s, 5p electrons. Also 4f-4f transitions corresponding to emission lines ranging from ultraviolet to infrared region play an important role in the design and development of optical devices [1–7]. Glasses are considered to be the suitable hosts as they are capable of exhibiting interesting features like broad inhomogeneous bandwidths, tuning the wavelength and large doping capability. In addition to these novel features, simple manufacturing process, low production cost as well as good thermal stability make RE doped glasses superior to phosphors [8]. To predict new luminescent materials for their utilization in the fields of science and technology, we need to have thorough knowledge on the optical absorption as well as photoluminescence properties of RE doped variety glasses [9–12].

The absorption and emission characteristics of RE ions depend on the host matrix composition in which they are incorporated. It is well known that for efficient luminescent material, the host matrix must possess low phonon energy. A system with low phonon energy can enhance significantly radiative emission rates and give high quantum efficiency [13]. In recent years, among the oxide glasses, tellurium dioxide (TeO_2) based materials are of immense interest as they possess wide band gap, large third order optical susceptibilities and distorted structure with asymmetric covalent Te–O bonds [14,15]. In addition to the above mentioned remarkable properties, tellurium based glasses exhibit large RE ion solubility, good mechanical and chemical stability, corrosion resistance, wide transmission window (0.4–5 mm), high linear and non-linear refractive indices, high density, moisture resistant over long periods, low phonon energy (600-800 cm^{-1}) and relatively high stimulated emission cross-sections [16–18]. Due to these interesting features tellurium based glasses are suitable for potential applications in IR domes, memories, modulators and laser windows [19]. Addition of tungsten trioxide (WO_3) to TeO_2 helps to form a stable glass as TeO_2 is unable to form stable glass alone. The presence of tungsten ions in tellurite glasses influence the luminescent properties of RE ions considerably owing to their different valence states (W^{6+},W^{5+},W^{4+}). It is well known that the electronegativity of Te ions and W^{6+} ions are approximately equal hence tetrahedral structural unit WO_4 along with TeO_4 and TeO_3 structural units in the glass network results in the linkage of the form Te-O-W whereas W^{5+} ions act as modifier and are responsible for structural disorders in the tellurite network.

It is expected that addition of WO_3 will reduce non-radiative losses

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and helps in enhancing the quantum efficiency of TeO_2 glasses [20,21]. Glasses containing ZnO have gained so much of importance because of its special optical, electrical and magnetic properties. In addition, ZnO is having low toxicity, non-hygroscopic nature, large excitation binding energy and intrinsic emitting property. These kinds of unparalleled properties make it a potential candidate for developing several useful devices such as solar energy converters, ultraviolet emitting lasers and gas sensors [22]. Due to the unique dual characteristic of PbO as network modifier (if Pb-O is ionic) as well as network former (if Pb-O is covalent), PbO containing glasses doped with RE ions are of significant interest for nonlinear optical effects as they possess high chemical stability, refractive indices and spontaneous emission probabilities. Moreover addition of PbO enhances the resistance against devitrification and reduces the melting temperature [23,24]. In the backdrop of various scientific patronages offered by the chemical constituents such as ZnO, PbO, WO_3 and TeO_2 for the present investigation, we prepared a germane glassy system namely Zinc Lead Tungsten Tellurite (ZnPbWTe) glass and doped it with varying concentrations of Sm^{3+} ions to study their luminescence efficiency in visible region.

Among all the RE ions, Sm^{3+} are one of the most widely studied ions for photonic application. Sm^{3+} ions with $4f^5$ configuration possess strong reddish-orange fluorescence in the visible region and hence suitable for applications such as high density optical memory storage, under sea communication, solid state laser in visible region [25,26]. Host matrices containing Sm^{3+} ions possess broad emission bands due to $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) transitions. It is well known from the literature that the fluorescence intensity of Sm^{3+} ions depends on the glass network as well as on the concentration of RE ions [27]. As the energy gap ($\sim 7250\ cm^{-1}$) existing between $^4G_{5/2}$ metastable state and $^6F_{11/2}$ lower level of Sm^{3+} ions is considerably large, the reddish orange emission which occurs at ~ 600nm need not gets affected desperately by the phonon energy of the host matrix [28,29]. Sm^{3+} doped laser materials are found to be more superior to the other RE doped materials because of the absence of lower lying excited states.

In the present study, optical absorption, luminescence and decay spectral measurements are carried out for ZnPbWTe glasses doped with different concentrations of Sm^{3+} ions. From these measurements various spectral properties such as J-O intensity parameters, radiative properties, quantum efficiency, CIE chromaticity coordinates for different florescent levels of Sm^{3+} ion are estimated in order to elucidate the suitability of the titled glasses for reddish-orange luminescent device application.

2. Experimental

In the present work, Sm^{3+} ions doped ZnPbWTe glasses with the chemical composition (60-x) TeO_2-20WO_3-15PbO-5ZnO-xSm_2O_3 (Where x = 0.5, 1, 1.5, 2, 2.5 mol%) were prepared by using melt quenching technique. These glasses are designated as glass A, B, C, D and E based on RE ion concentration from 0.5 to 2.5 mol% respectively. Glass compositions weighed as per the aforementioned formula were mixed thoroughly, grinded in an agate mortar to get homogeneous powder. Such powders placed in a silica crucible are heated at 830 °C in an electric furnace for about 55 min. The melt was stirred for homogeneous mixing of all the constituents. This melt was then poured on a preheated brass plate and then compressed quickly with another brass plate. The glass samples were annealed at 250 °C for 1 h to remove thermal strains and air bubbles. Thus clear transparent glass samples were obtained. In process of getting uniform thickness and smoothness these samples were polished with the help of emery powder. The Archimedes principle and Brewster's angle method (He-Ne laser with a wavelength 650 nm) were employed to measure density and refractive indices of the prepared samples respectively. Density and molar volume for the as prepared glasses have been presented in Table 1. From Table 1 it is observed that density of the as prepared glasses are increasing with increase in Sm^{3+} ion concentration. The absorption spectra were recorded using a JASCO model V-670 UV-vis-NIR spectrophotometer with a spectral resolution of 0.1 nm. The photoluminescence (PL) emission and excitation spectra for all these glasses were recorded at room temperature using RF-5301 PC spectrofluorometer. The decay spectral recordings were done using an Edinburg FLSP900 fluorescence spectrometer with a spectral resolution of 0.1 nm with the help of Xenon lamp as an excitation source.

3. Result and discussion

3.1. Absorption spectral analysis

In order to understand the radiative properties of RE ions doped materials, it is important to record and analyse their absorption spectra. The sharp absorption lines arising from 4f-4f electronic transitions can be electric dipole, magnetic dipole or electric quadruple in character. The absorption spectra of different concentrations of Sm^{3+} doped ZnPbWTe glasses in UV–vis and NIR region were recorded. Fig. 1& Fig. 2 (b) show the absorption spectrum of 1 mol% of Sm^{3+} doped ZnPbWTe glass (glass B) in the wavelength range 900–1650 nm (NIR region) and 350–800 nm (UV–vis region) respectively. Fig. 2 (a) shows the photograph of all the as prepared glasses. From Fig. 2 (b) it is clear that in UV- vis region only two absorption bands were observed at 402 and 460 nm corresponding to the transitions $^6H_{5/2} \rightarrow {}^6P_{3/2} + {}^4F_{7/2}$ and $^4I_{13/2}$ respectively. Strong absorption of the host glass may be responsible for the disappearance of some of the absorption bands in the UV–vis region. Since the intensities of the observed bands in the UV–vis region are reasonably small, they were not considered for calculating the oscillator strength of the titled glasses. The absorption spectra for the remaining glasses are same as that of glass B with slight changes in their intensities for various bands and hence they were not shown here. The variation in intensity of the absorption spectral features can be obtained either by changing the concentration of RE ions or glass composition [30]. Seven bands are observed for all the glasses in the NIR region which arises from $^6H_{5/2}$ ground state. The absorption peaks observed for the as prepared glasses are at 942, 1080, 1229, 1373, 1478, 1526, 1588 nm correspond to the transitions $^6H_{5/2} \rightarrow {}^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$ and $^6F_{1/2}$ respectively. The bands are assigned as per the data given by Carnall et al. [31].

The experimental oscillator strength (f_{exp}) is a measure of the energies of an absorption transition originating from the ground state of RE ions in a host matrix. The f_{exp} parameter is evaluated from the expression given in the literature by taking area under the absorption curve [32]. Overlapping of transition $^6H_{5/2} \rightarrow {}^6F_{3/2}$ and $^6H_{5/2} \rightarrow {}^6H_{15/2}$ may be responsible for lowering of f_{exp} values corresponding to transition $^6H_{5/2} \rightarrow {}^6F_{1/2}$. By applying the J-O theory [33,34] the calculated oscillator strength (f_{cal}) of an electric dipole transition which depends on three J-O intensity parameters (Ω_2, Ω_4, Ω_6) have been evaluated from the least square fit method. The estimated values of f_{exp} and f_{cal} are tabulated in Table 1. From the tabulated values it is observed that the rms deviation values obtained between f_{cal} and f_{exp} are small which suggests the good fit between the two values and also confirms the validity of the J-O theory. The J-O intensity parameters (Ω_2, Ω_4, Ω_6) are represented in Table 2 along with the reported values [5,35–41].

It is observed that Ω_2, Ω_4, Ω_6 parameters are following same trend ($\Omega_6 > \Omega_4 > \Omega_2$) for the glasses under investigation and are highest for glass B. The J-O intensity parameters are of immense interest in order to determine covalency between RE and oxygen ion as well as the symmetry around RE ions in the given host. These parameters also play significant role in providing the information about the efficiency and performance of the luminescent material. Covalency dependent parameter Ω_2 is connected to the structural changes as well as symmetry of ligand field around the Sm^{3+} ion site. On the other hand the bulk properties such as rigidity of the medium in which RE ions are present and the viscosity depend on the magnitudes of intensity parameters Ω_4 and Ω_6. From Table 2 it is clear that the titled glasses exhibit low value