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Photoluminescence investigations on Dy^{3+} ions doped Zinc Lead Tungsten Tellurite glasses for optoelectronic devices

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ABSTRACT

Dy^{3+} doped Zinc Lead Tungsten Tellurite (ZnPbWTe) glasses have been synthesized by conventional melt quench method and their luminescence behavior was analyzed using optical absorption, excitation, photoluminescence (PL) and PL decay spectral studies. The Judd-Ofelt (J-O) intensity parameters evaluated from the absorption spectra are used to determine various radiative parameters such as transition probability (A_R), branching ratio (β_R) and radiative lifetimes (τ_R) for the prominent emission transitions of Dy^{3+} ions in ZnPbWTe glasses. Under 384 nm excitation, PL spectra recorded for the titled glasses, exhibit two intense peaks; one in yellow at 575 nm and the other one in blue at 483 nm region. Among these two, yellow band (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) is relatively more intense than the blue one (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$). The intensity of PL spectra increases up to 1 mol% of Dy^{3+} ions in ZnPbWTe glasses and beyond concentration quenching is observed. Branching ratios (β_R) and emission cross-sections (σ_{se}) were estimated for ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition to understand the potential utility of these glasses for laser action in visible region. The CIE chromaticity coordinates, color correlated temperature (CCT), color purity and Y/B ratios were also estimated to understand the suitability of these glasses for w-LEDs. The luminescence quantum efficiency evaluated for the titled glasses showing highest value for 1 mol% of Dy^{3+} ions present in the as prepared glasses. From the measured emission cross-sections, quantum efficiency and CIE coordinates, it was observed that 1 mol% of Dy^{3+} ions in ZnPbWTe glasses are aptly suitable for optoelectronic devices such as lasers and w-LEDs.

1. Introduction

Recently, Rare Earth (RE) doped glassy and crystalline materials have attracted a great deal of attention because of their applications in diversified fields such as modern lighting technology, display, telecommunications, photovoltaics, optical fibers, solid state lasers and mid-infrared lasers etc. [1–5]. Generally, RE doped glasses are superior to crystalline materials due to their homogeneous light emitting capacity, simple manufacturing procedures, low production cost and better thermal stability. Currently, researchers working in the field of optoelectronic devices are paying more attention in developing visible optical devices suitable for white light emitting diode (w-LED) [6]. Further, w-LEDs have received much attention owing to their excellent properties such as environment friendliness, energy saving, small volume, long life span and high reliability. In order to improve benefits related to environment and reducing consumption of global energy as well as fossil fuels, w-LEDs are suitable replacement for incandescent and fluorescent lamps [7–9].

Tellurite based heavy metal oxide glasses are very interesting to study as they are having special characteristic features such as low phonon energies, high refractive index, high dielectric constant, low melting temperature and good RE ion solubility [10]. It is well known that the materials containing tungsten oxide (WO_3) possess electrochromic as well as photo-chromic properties and are useful in smart windows, display devices and sensors [11,12]. Further, WO_3 suppresses non-radiative losses and enhances quantum efficiency [13]. To obtain more efficient laser system, heavy metal compound such as lead oxide is added to the conventional glasses as its presence can improve the effective fluorescence [14]. The lead oxide (PbO) is having ability to form stable glasses over a wide range of concentrations due to its large mass, low field strength, high polarizability and thereby acting as glass former/modifier. Further remarkable characteristic of PbO as glass modifier in PbO_6 structural unit and glass former in PbO_4 structural unit, make glasses moisture resistant [15]. Furthermore, lead oxide based glasses possess high refractive indices, wide infrared transmittance, good thermal and chemical stabilities and high spontaneous emission probabilities [16–18]. Among the glass components, ZnO based materials have received significant consideration due to its low

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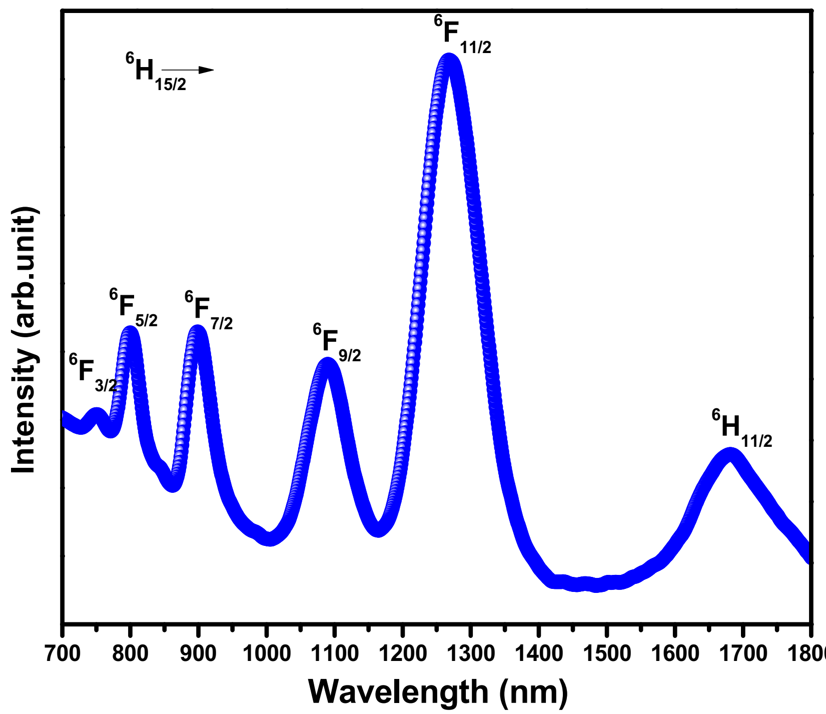

Fig. 1. Absorption spectrum of 1 mol% Dy^{3+} ions (glass B) in ZnPbWTe glass.

cost, direct wide band gap, intrinsic emitting property, large excitation binding energy, nontoxic and hygroscopic nature [19]. ZnO in the host glass exhibits dual nature as glass former as well as network modifier. Further, ZnO containing glasses are having significant importance due to its thermally stable and sublime nature. The aforementioned various scientific patronages possessed by the chemical constituents such as ZnO, PbO, WO_3 and TeO_2 prompted us to prepare a glassy system namely Zinc Lead Tungsten Tellurite (ZnPbWTe) glasses doped with different RE ions to study the effect of glass composition on the luminescence behavior of the doped RE ions.

Among the RE doped glasses, Dy^{3+} activated luminescent materials have attracted much attention and revolutionized the modern lighting and display fields, as it is capable of emitting ample wavelengths based on their 4f-4f transitions [20]. It is well known that the visible luminescence of trivalent dysprosium (Dy^{3+}) possess mainly two bands in the visible region corresponding to the transition $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue) and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow). It is important to optimize the local environment to obtain white light from Dy^{3+} doped glasses at suitable yellow to blue (Y/B) intensity ratio [21]. By changing the content of Dy^{3+} and/or composition of the host material white light emission at a modulated yellow to blue (Y/B) intensity ratio is possible [22]. The lasing action of Dy^{3+} ions in visible region also finds several applications in diversified fields of science and technology such as commercial display sensors and fiber optic amplification [23]. In the present work ZnPbWTe glasses are prepared by varying Dy^{3+} ion concentration and investigated thoroughly using the absorption, emission and lifetime measurements to select the efficient host material for solid state laser and w-LED applications.

2. Experimental

2.1. Synthesis

Dy^{3+} doped ZnPbWTe glasses were prepared by conventional melt quenching technique with the following composition.

$(60 - x)TeO_2 + 20WO_3 + 15PbO + 5ZnO + xDy_2O_3$ (where x = 0.5 mol% for glass A, x = 1.0 mol% for glass B, x = 1.5 mol% for glass C, x = 2.0 mol% for glass D and x = 2.5 mol% for glass E). Analar grade chemicals such as TeO_2, WO_3, PbO, ZnO and Dy_2O_3 were taken as the starting materials. The raw materials were thoroughly mixed in an agate mortar until a smooth and homogeneous mixture was obtained. The mixture thus obtained is poured into a silica crucible and heated at 830 °C in an electric furnace for about 55 min to obtain bubble free homogeneous melt. Such melts were then quenched suddenly on a preheated brass mould and pressed quickly by another brass mould. The prepared glass samples were subsequently annealed at 250°C for 1 h to remove thermal strains/cracks and then polished to do spectral measurement.

2.2. Characterization

Density and refractive index are the two important parameters to study the structural modification of glass network. For all the glasses under investigation densities were measured by employing the Archimedes method using water as an immersion liquid. The refractive indices were measured by Brewster's angle method using He-Ne laser (650 nm line) as the source. Optical absorption spectra have been recorded for all the ZnPbWTe glasses in NIR region using Perkin Elmer UV–vis-NIR spectrometer Lambda 950 (USA). The excitation and emission spectra for all the glasses were recorded using RF-5301PC Spectrofluorophotometer at room temperature. Fluorescence decay spectral recordings were carried out using Edinburgh FLSP900 fluorescence spectrometer having 0.1 nm spectral resolution. All the figures are plotted with the help of origin 9.2 software.

3. Result and discussion

3.1. Absorption spectral measurements (hypersensitive transition and J-O intensity parameters)

Fig. 1 shows the absorption spectrum of glass B recorded at room temperature in the wavelength range 700–1800 nm. The absorption spectra for all the as prepared glasses are alike in absorption features with slight variation in intensity. Hence absorption spectra of the