Optical Materials 78 (2018) 457–464

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Spectroscopic study of Pr^{3+} ions doped Zinc Lead Tungsten Tellurite glasses for visible photonic device applications

Ritu Sharma [a], A.S. Rao [a,*], Nisha Deopa [a], M. Venkateswarlu [b], M. Jayasimhadri [a], D. Haranath [c], G. Vijaya Prakash [d]

[a] Department of Applied Physics, Delhi Technological University, Bawana Road, New Delhi, 110 042, India
[b] Department of Physics, K L University, Vaddeswaram, 522 502, Guntur (Dt), Andhra Pradesh, India
[c] CSIR-National Physical Laboratory, Dr.K.S. Krishnan Marg, Pusa Road, New Delhi, 110 012, India
[d] Nanophotonic Lab, Department of Physics, IIT-Delhi, Hauz Khas, New Delhi, 110 016, India

ARTICLE INFO

Article history:
Received 21 November 2017
Received in revised form
24 February 2018
Accepted 25 February 2018

Keywords:
Glasses
Luminescence
Optical materials
Oxides
Optical properties

ABSTRACT

Zinc Lead Tungsten Tellurite (ZnPbWTe) glasses doped with different Pr^{3+} ion concentrations having the composition 5ZnO + 15PbO + $20WO_3$ + (60-x)TeO_2 + xPr_6O_{11} (where $x = 0.5$, 1, 1.5, 2.0 and 2.5 mol%) were prepared by using sudden quenching technique and characterized to understand their visible emission characteristic features using spectroscopic techniques such as absorption, excitation and emission. The Judd-Ofelt (J-O) theory has been applied to the absorption spectral features with an aim to evaluate various radiative properties for the prominent fluorescent levels of Pr^{3+}ions in the as-prepared glasses. The emission spectra recorded for the as-prepared glasses under 468 nm excitation show three prominent emission transitions $^3P_0 \rightarrow {}^3H_6$, $^3P_0 \rightarrow {}^3F_2$ and $^3P_1 \rightarrow {}^3F_4$, of which $^3P_0 \rightarrow {}^3F_2$ observed in visible red region (648 nm), is relatively more intense. The intensity of $^3P_0 \rightarrow {}^3F_2$ emission transition in the titled glasses increases up to 1mol% of Pr^{3+} ions and beyond concentration quenching is observed. Branching ratios (β_R) and emission cross-sections (σ_{se}) were estimated for $^3P_0 \rightarrow {}^3F_2$ transition to understand the luminescence efficiency in visible red region (648 nm). The CIE chromaticity coordinates were also evaluated in order to understand the suitability of these glasses for visible red luminescence devices. From the emission cross-sections, quantum efficiency and CIE coordinates, it was concluded that 1mol% of Pr^{3+} ions in ZnPbWTe glasses are quite suitable for preparing visible reddish orange luminescent devices.

1. Introduction

Recently, Rare Earth (RE) doped crystalline and non-crystalline materials are playing a vital role in the field of science and technology because of their applications in diversified fields [1–4]. Quite recently, studies on non-crystalline materials (glasses) doped with RE ions have attracted great deal of attention by researchers because of their potential applications in designing lasers, fiber communication, color display devices, sensors and hole burning memories, etc. [5,6]. Further, RE doped glassy matrices are considered as luminescence material due to their higher emission efficiencies corresponding to 4f-4f and 4f-5d electronic transitions [7]. The sharp fluorescence pattern observed from 4f-4f electronic transitions in UV to NIR regions owing to shielding effect of 5s, 5p orbital on 4f orbitals. Furthermore, intensity, effective bandwidths of emission transitions and thereby quantum efficiency depends much on the structure of the host matrix. Therefore selecting a good host matrix with relatively higher luminescence efficiency is very much essential for the design and development of a good photonic device [8].

It is reported in literature that, heavy metal oxide glasses are quite suitable for the development of non-linear optical devices, electro-optic modulators, electro-optic switches, solid state laser materials and IR technologies because of their high density, refractive index and low phonon energy [9–12]. In general, the host glass with relatively low phonon energies can give high quantum efficiency and therefore useful for the designing of a good photonic device [13]. Tellurite glasses are one such kind of materials having lowest phonon energy [~800 cm^{-1}] and high refractive index [14,15]. Further, tellurite glasses have recently gained wide

* Corresponding author.
E-mail address: drsrallam@gmail.com (A.S. Rao).

https://doi.org/10.1016/j.optmat.2018.02.054
0925-3467/

attention due to their physical and chemical properties. They also exhibit excellent chemical stability, good mechanical strength, slow crystallization rate, high homogeneity and good transparency in the spectral region from visible to NIR region [16,17].

Addition of WO_3 to tellurite glasses has potential applications in the field of IR technologies, nonlinear optics and fiber optics because of their high linear refractive index. Presence of ZnO in the host glass is having unique characteristics owing to its dual nature as glass former (ZnO_4) as well as network modifier [18,19]. Also ZnO containing glasses are thermally stable, sublime and appreciably covalent in character [20]. Addition of PbO to a ternary glassy network (TeO_2-WO_3-ZnO) can reduce the rate of crystallization by acting as a network modifier and enhances the radiative emissive property of the host glass. Among the two network modifier oxides, i.e., ZnO and PbO, it is expected that ZnO can shorten the time taken for solidification of glasses during the quenching process [21,22]. Pondering on the aforementioned scientific patronages offered by various chemical constituents, for the present work we prepared a germane optical glassy system namely Zinc Lead Tungsten Tellurite (ZnPbWTe) glass doped with Pr^{3+} ions. The prime aim of the present work is to find out a visible photonic device with relatively good quantum efficiency. Among the RE ions, Praseodymium is one of the interesting ion because of its significant importance in visible luminescent devices under blue excitation. Pr^{3+} is a significant optical activator with its several meta stable states ($^3P_0$, $^1D_2$, $^1G_4$) that can offer stimulated emissions in blue, green, orange, red and infrared regions [23,24]. Further, Pr^{3+}doped glasses are very good candidates to develop 1.3 μm optical amplifier for telecommunication applications [25,26]. It is also reported that Pr^{3+} doped glasses possess lasing action from $^1D_2 \rightarrow {}^3H_4$ transition around 600 nm [27]. Because of the aforementioned various scientific applications, the glasses doped with Pr^{3+} ions having low phonon energies are quit suitable for the design and development of solid state lasers and optical fiber amplifiers in visible region.

In the present work, preparation and characterization of ZnPbWTe glasses were done by varying Pr^{3+}ions concentration using melt quenching technique to study their physical, optical and luminescent properties with an aim to identify a better glass for visible photonic applications.

2. Experimental

2.1. Glass preparation

ZnPbWTe glasses doped with different concentrations of Pr^{3+} ions were prepared by conventional melt quenching technique with the following composition 5ZnO + 15PbO + $20WO_3$+ (60-x) TeO_2+ xPr_6O_{11}(where $x = 0.5$, 1, 1.5, 2.0 and 2.5 mol%). For our convenience these glasses are designated as glass A-E depending on the '*x*' value from 0.5 to 2.5 mol% respectively. All the chemicals used to prepare ZnPbWTe glasses were of analar grade with 99.9% purity. The chemical constituents taken as per the aforementioned stoichiometric ratio were thoroughly mixed in an agate mortar for about 3 h to get homogeneous mixing and then melted using a silica crucible at 830 °C in a programmable electrical furnace (Indfur made) for about 55 min. The resultant melts were stirred 4–6 times before quenching to get homogeneous mixture. Such melts were then poured on a preheated brass plate and pressed quickly with another pre heated brass plate. The prepared samples were annealed in another furnace for about 1 h at 250°C to remove thermal strains that were produced due to sudden quenching. The glasses thus obtained were highly polished to achieve a uniform thickness of 0.159 cm.

2.2. Physical and optical measurements

Archimedes's principle is used to measure densities of the as prepared glasses with distilled water as an immersion liquid. The refractive indices of all the as-prepared glasses were measured by using Brewster's angle method with He-Ne laser operating at 632 nm. The XRD spectrum was monitored by using high resolution X-ray diffractometer Bruker; Model D8 advance which operates at 40 KV and 40 mA. Perkin-Elmer's Frontier spectrometer was used to record FT-IR spectrum of the un-doped ZnPbWTe glass. The optical absorption spectra were recorded for all the prepared glass samples from 400 to 2400 nm at room temperature with a spectral resolution of 0.1 nm using a Jasco V-670 UV–vis–NIR spectrometer. Schimadzu RF-5301PC spectrophotometer is used to record Photoluminescence (PL) spectra. The PL decay spectral measurements were taken from Edinburg FLSP900 fluorescence spectrometer having 0.1 nm spectral resolution.

3. Results and discussion

3.1. XRD spectral analysis

Fig. 1 shows the XRD spectrum of an un-doped ZnPbWTe glass. Absence of sharp peaks and instead a broad hump observed in the XRD spectrum, clearly confirms the amorphous nature of the as prepared ZnPbWTe glass.

3.2. FT-IR spectral analysis

Fig. 2 shows the FT-IR spectrum of an un-doped ZnPbWTe glass in the range 500–4000 cm^{-1}. The shoulder observed at 664 cm^{-1} is due to the stretching vibrations of Te-O bonds in TeO_4 trigonal bi pyramid unit [28]. It is well known that addition of glass modifiers into tellurite glass results in the opening of glass network which leads to the formation of non-bridging oxygen by allowing TeO_{3+1} and TeO_3 structural units. The band observed at 944 cm^{-1} is due to the stretching vibrations of W-O$^-$ and W-O bond in WO_4 or WO_6 unit as well as ϑ_1 vibrations of WO_4 group [29]. The shoulders observed in the region 1600-3000 cm^{-1} are attributed to the presence of hydrogen bonding. The characteristic band observed at 3437 cm^{-1} is due to the fundamental vibrations of OH group [30]. In order to obtain high quantum efficiency for the glassy material, the

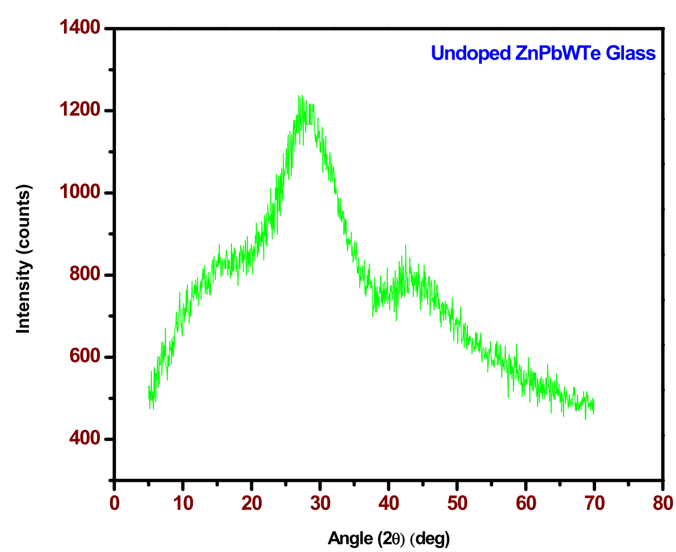

Fig. 1. XRD spectrum of an un-doped ZnPbWTe glass.