Journal of Molecular Structure 1093 (2015) 166–171

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Luminescence and spectroscopic properties of ZnF_2–MO–TeO_2 glasses doped with Ho^{3+} ions

C. Laxmikanth [a], J. Anjaiah [a,b,*], P. Venkateswara Rao [c], B. Appa Rao [d], N. Veeraiah [e]

[a] Department of Physics, The University of Dodoma, Tanzania
[b] Department of Physics, Geethanjali College of Engineering & Technology, Keesara, RR Dist. 501 301, India
[c] Department of Physics, The University of the West Indies, Mona Campus, Kingston 7, Jamaica
[d] Department of Physics, Osmania University, Hyderabad 500 007, T.S., India
[e] Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur, AP 522 510, India

HIGHLIGHTS

- Relatively less disorder is present in ZTHo glass network.
- Ho^{3+} ion shows the highest covalent environment in ZTHo glass.
- Judd–Ofelt (JO) theory has been applied to investigate JO and radiative parameters.
- The highest value of β_r for the $^5S_2 \rightarrow {}^5I_8$ transition in ZTHo glass is useful for laser transition.

ARTICLE INFO

Article history:
Received 9 January 2015
Received in revised form 11 March 2015
Accepted 11 March 2015
Available online 2 April 2015

Keywords:
Optical absorption
Fluorescence
Judd-Ofelt parameters
IR
Holmium and tellurite glasses

ABSTRACT

ZnF_2–TeO_2 glasses mixed with the three different modifier oxides (MO) viz., ZnO, CdO and PbO doped with Ho_2O_3 were prepared. These glasses were characterized by X-ray diffraction, and IR spectra. Optical absorption and fluorescence spectra of these glasses have been studied. From the measured intensities of various absorption bands of these glasses the Judd–Ofelt parameters Ω_λ ($\lambda = 2, 4, 6$) have been evaluated and compared with those of other reported glass systems. From the Judd–Ofelt theory various radiative properties like transition probability A, branching ratio β_R, the radiative life time τ_R, and the emission cross-section σ_P for various emission levels of these glasses have been determined and reported.

Introduction

Tellurite glasses were considered as the best materials for optical components such as IR domes, optical filters, modulators, memories and laser windows in view of their high transparency in the far infrared region and for their high density and refractive index. Further, these glasses are considered as very good materials for hosting lasing rare-earth ions since these provide a low phonon energy environment to minimize non-radiative losses. A number of recent investigations on mechanical, electrical and optical properties of various tellurite glasses mixed with different modifiers are available in literature [1–8]. A considerable number of these studies on various physical properties have also been reported in the recent past from our laboratory on some TeO_2 based glass systems [9–13]. Addition of ZnF_2 into TeO_2 glass matrices lowers the viscosity and is expected to decrease the liquidus temperature to a substantial extent and further it acts as an effective mineralizer [14]. Among the three modifier oxides, viz., ZnO, CdO and PbO, ZnO is expected to shorten the time taken for solidification of glasses during the quenching process. Both ZnO and CdO are thermally stable, sublime and appreciably covalent in character [15]. Addition of PbO into the glass matrix produces low rates of crystallization, since PbO has the ability to form stable glasses due to of its dual role; one as glass former when Pb–O bonding is covalent and the other as modifier when bonding is ionic [16]. In view of these qualities, all the three modifier oxides are interesting oxides and make the glasses more stable against devitrification and resistant to moisture.

Among various rare earth ions, Ho^{3+} ion exhibits several electronic transitions in the visible and infrared regions. As a

* Corresponding author at: Department of Physics, The University of Dodoma, Tanzania. Tel.: +255 768224886.
E-mail address: anjaiah.juluru@gmail.com (J. Anjaiah).

http://dx.doi.org/10.1016/j.molstruc.2015.03.018
0022-2860/

consequence there are many laser transitions in its emission spectrum; this ion exhibits eye safe potential laser even at room temperature with a low threshold action [17–19] that have attractive applications in atmospheric communication systems. A quite good number of recent studies on the lasing action of Ho^{3+} ion in various glass matrices are available in literature [20,21]. Further when the glasses are mixed with different network modifying ions we may expect the structural modifications and local field variations around Ho^{3+} ion; such changes may have strong bearing on various luminescence transitions of Ho^{3+} ions.

Thus the objective of the present investigation is to characterize the optical absorption and the fluorescence spectra of Ho^{3+} ions in ZnF_2–TeO_2 glasses mixed with three different modifier oxides viz., ZnO, CdO and PbO; the study is further intended to throw some light on the relationship between the structural modifications and luminescence efficiencies with the aid of IR spectral data.

Experimental

For the present investigation the following compositions have been chosen:

ZTHo glass: $40ZnF_2$–$10ZnO$–$49TeO_2$:$1Ho_2O_3$,
CTHo glass: $40ZnF_2$–$10CdO$–$49TeO_2$:$1Ho_2O_3$,
PTHo glass: $40ZnF_2$–$10PbO$-$49TeO_2$:$1Ho_2O_3$.

Appropriate amounts (all in wt.%) of analar grade reagents of TeO_2 (99.99% pure, Aldrich), PbO, ZnO, CdO, ZnF_2 and Ho_2O_3 were thoroughly mixed in an agate mortar and melted in a platinum crucible between 630 and 680 °C in a PID temperature controlled furnace for about ½ h until a bubble free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at 200 °C. The weight losses were found to be less than 0.5%. The amorphous state of the glasses was checked by X-ray diffraction studies.

The densities ρ of the glasses were determined to an accuracy of 0.001 g/cm^3 by standard principle of Archimedes' using O-xylene (99.99% pure) as the buoyant liquid. The samples were then ground and optically polished. The final dimensions of the samples used for the present measurements were about 1 cm × 1 cm × 0.2 cm. The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 370–2100 nm using Shimadzu-UV–VIS-NIR Spectrophotometer Model 3100. By using xenon arc lamp, the intense line $\lambda_{exc.}$ = 450 nm was identified and the same was used to record the photo-luminescence spectrum of all the glasses. The photo-luminescence spectra of the glasses were recorded on Hitachi – F 3010 Fluorescence Spectrophotometer in the wavelength range 460–700 nm up to a resolution of 0.1 nm. Infrared transmission spectra for these glasses were recorded using a Perkin Elmer Spectrometer in the wavenumber range 400–4000 cm^{-1} by KBr pellet method.

Table 1
Various physical properties of ZnF_2–MO–TeO_2:Ho_2O_3 glasses.

Property	ZTHo	CTHo	PTHo
Refractive index, n_d	1.569	1.571	1.570
Density, ρ (g/cm^3)	5.591	5.618	5.646
Average molecular weight, $\overline{M}$	121.4	128.5	122
Holmium ion concentration, N_i (10^{19}/cm^3)	20.4	20.5	8.8
Inter-ionic distance of holmium ions, R_i (Å)	16.98	16.96	22.46

3. Results

Our visual examination, absence of peaks in X-ray diffraction pattern indicates that the glasses prepared were of high quality glasses. From the measured values of the density ρ and calculated average molecular weight $\overline{M}$, various physical parameters such as holmium ion concentration N_i, mean holmium ion separation R_i that are useful for understanding optical properties of these glasses, are evaluated and presented in Table 1.

Fig. 1 shows the optical absorption spectra of ZnF_2–MO–TeO_2 glass containing Ho_2O_3, recorded at room temperature in the wavelength region 400–2100 nm. The spectra exhibited eight clearly resolved absorption bands all from the ground state $^5I_8$

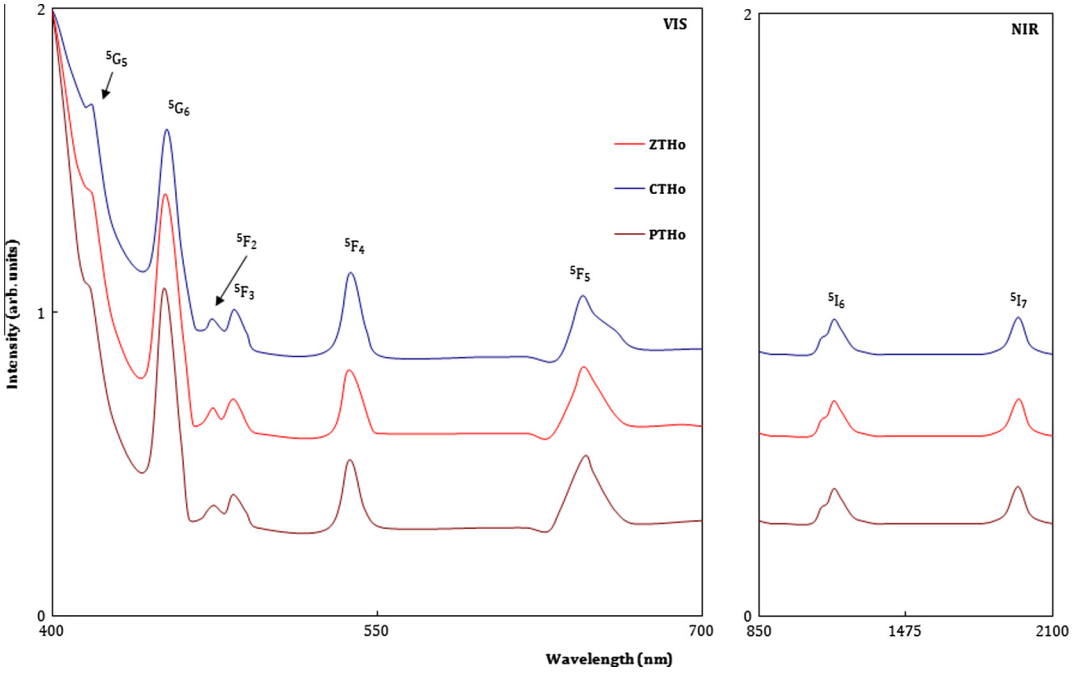

Fig. 1. Optical absorption spectrum of Ho^{3+} doped ZnF_2–MO–TeO_2 glass (ground state $^5I_8$).