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# Holmium doped Lead Tungsten Tellurite glasses for green luminescent applications

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ABSTRACT

Lead Tungsten Tellurite (LTT) glasses doped with different concentrations of $Ho^{3+}$ ions have been synthesized using the melt quenching method and characterized to understand their visible emission characteristic features using optical absorption and photoluminescence spectral studies. The Judd–Ofelt (JO) parameters measured from the absorption spectral features were used to evaluate radiative properties such as transition probability ($A_R$), branching ratio ($\beta_R$) and radiative lifetimes ($\tau_R$) for the prominent fluorescent levels of $Ho^{3+}$ ions in LTT glasses. The photoluminescence spectra recorded for all the $Ho^{3+}$ doped LTT glasses at an excitation wavelength 452 nm gives three prominent emission transitions $^5F_4 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5F_4 \rightarrow {}^5I_7$, of which $^5F_4 \rightarrow {}^5I_8$ observed in visible green region (546 nm) is relatively more intense than the other two transitions. The intensity of $^5F_4 \rightarrow {}^5I_8$ emission transition in these glasses increases up to 1 mol% of $Ho^{3+}$ ions and beyond concentration quenching is observed. Branching ratios ($\beta_R$) and emission cross-sections ($\sigma_{se}$) were evaluated for the intense emission transition $^5F_4 \rightarrow {}^5I_8$ in these glasses to understand the luminescence efficiency in visible green region (546 nm). The CIE chromaticity coordinates were also evaluated in order to understand the suitability of these glasses for visible luminescence. From the measured emission cross-sections and CIE coordinates, it was found that 1 mol% of $Ho^{3+}$ ions in LTT glasses are most suitable for visible green luminescence in principle.



## 1. Introduction

Glasses doped with transition metal and rare earth ions have attracted a great deal of attention because of their applications in visible and mid-infrared regions of the electromagnetic spectrum such as lasers, optical fibers, sensors, biomedical diagnostics, infrared detectors, marine optical communications, up-conversion lasers, optical data storage, atmospheric probing and high density memory storage devices [1–5]. Recently research work on tellurium based glasses is increasing because of their promising technological applications in diversified fields [6–11]. Tellurium oxide ($TeO_2$) being a semiconductor in both crystalline and amorphous forms, with its superior physical and chemical properties, is aptly suitable for various technological devices such as ɤ-ray detectors, nonlinear optoelectronic devices and optical recording systems [12–16]. In addition to this, tellurite glasses possesses wide transmission range from 0.4 to 5 μm, high linear and non-linear refractive indices, low phonon energies (~750 $cm^{-1}$) and high rare earth ions solubility [17]. Tellurium oxide besides being a conditional glass former can form a stable glass in the presence of certain glass modifiers like tungsten trioxide ($WO_3$). Moreover these oxides show high thermal stability and mechanical strengths relative to other glass forming oxides and fluorides [16–21].

Tungsten based glasses can be prepared at relatively low temperatures (~750 °C) and also show low phonon energies (~800 $cm^{-1}$) [22,23] when compared with phosphate (~1300 $cm^{-1}$) borate (~1400 $cm^{-1}$) and silicate glasses (~1000 $cm^{-1}$) [24–26]. It is well known that the glasses with low phonon energies offer less non-radiative relaxation rates and increases the luminescent quantum efficiencies. The relatively slow crystallization rate, good transparency in a wide spectral region from visible to NIR, good mechanical strength, chemical stability and high refractive indices makes tungsten tellurium glasses the best choice as an efficient host [27–29]. It is well known that heavy metal fluoride compounds such as $PbF_2$ having very less phonon energies (~340 $cm^{-1}$) when added to a host glass can reduce phonon

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energies of the host glass drastically. Moreover fluoride compounds added to a glass can react and remove the OH content present in glass and helps in reducing the phonon energies of the host glass further. Considering the aforementioned scientific patronages offered by $PbF_2$, $WO_3$ and $TeO_2$, we prepared Lead Tungsten Telluride (LTT) glasses using these chemicals as constituent elements to study the luminescence properties of these glasses doped with different rare earth ions. The encouraging results obtained for $Pr^{3+}$ ions doped in LTT glasses for visible red lasers [27] prompted us to investigate $Ho^{3+}$ ions in LTT glasses to know about their suitability for visible green luminescence.

Among all the trivalent rare earth ions, $Ho^{3+}$ ion is one of the most attractive ion for spectroscopic studies, because of several electronic transitions it can give in the visible and IR regions [30–32], which have relatively long-lived $^5I_7$ level and large peak stimulated emission cross-sections [33,34]. It has been confirmed that mid-infrared laser emission of $Ho^{3+}$ ion is in the range of 1.2–4.9 μm [35,36]. The mid-infrared emission of $Ho^{3+}$ ion gives eye-safe potential laser emission at room temperature (RT) with a low threshold action that has smart applications in LIDAR and in atmospheric communication systems [37]. Moreover, the $^5F_4 \rightarrow {}^5I_8$ transition of $Ho^{3+}$ ion is a hypersensitive transition and hence host dependent one. Therefore glasses doped with $Ho^{3+}$ ions are the most important candidates for both visible (~547 nm) ($^5F_4 \rightarrow {}^5I_8$ ) and mid-infrared (~2 μm) ($^5I_7 \rightarrow {}^5I_8$) regions and are useful for the development of solid state lasers in visible and mid-infrared regions.

In the present work, LTT glasses doped with $Ho^{3+}$ ions at different concentrations were prepared to study the absorption and photoluminescence spectral properties to understand the suitability of these materials for visible luminescence. From the absorption and emission spectral measurements, different radiative properties such as transition probability, radiative lifetimes, branching ratios and emission cross-sections were estimated for the observed emission transitions of $Ho^{3+}$ ions. The CIE color coordinates are also evaluated from the measured emission spectra to understand the utility of these glasses for green light emission.

## 2. Experimental

### 2.1. Synthesis of LTT glasses

LTT glasses doped with different concentrations of $Ho^{3+}$ ions with chemical composition of $15PbF_2$–$25WO_3$–$(60-x)TeO_2$–$xHo_2O_3$ ($x$=0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%) were prepared by using the melt quenching method. The samples are referred according to the doping concentration of $Ho_2O_3$ as LTTHo01, LTTHo05, LTTHo10, LTTHo15, LTTHo20 and LTTHo25 glasses. 10 g batches of homogeneous mixture of starting chemicals were taken in a silica crucible and melted in an electric furnace at a temperature of 735 °C for 45 min. The melt was then air quenched by pouring on to a pre-heated brass mold and pressed quickly with another brass mold. The glasses thus obtained were annealed at 400 °C for about 3 h to remove thermal strains. In order to measure the optical spectra, the glasses were polished (0.2 cm thickness) for optical quality.

### 2.2. Physical and optical measurements

The densities of $Ho^{3+}$ ions doped LTT glasses were measured by using Archimedes's principle with water as an immersion liquid. The refractive indices of the prepared glasses were measured using Brewster's angle method with He–Ne laser operating at 632 nm. Using refractive indices and densities, some other physical properties were also measured using suitable formulae [5,38] and are given in Table 1. In the present study the physical properties are changing from glass to glass with increase in the concentration of $Ho^{3+}$ ions, indicating the change in environment around the doped $Ho^{3+}$ ions. The optical absorption spectra were measured for all the glass samples from 400 to 2200 nm at room temperature with a specified resolution of 0.1 nm using a Jasco V-670 UV–vis–NIR spectrometer. Schimadzu RF-5301 PC Spectrofluorophotometer was used to record the photoluminescence excitation and emission spectra for all these glasses at room temperature.

## 3. Results and discussion

### 3.1. Physical properties

The physical properties of glassy materials play a vital role in prediction of optical properties. Density and refractive index of glass samples play an important role in evaluating the other physical properties such as average molecular weight, mean atomic volume, etc. All such physical properties evaluated for the present LTT glasses are given in Table 1. Fig 1(a) shows the variation of density and refractive indices of the titled glasses with $Ho^{3+}$ concentration. From Fig 1(a) it can be observed that the density and refractive indices of titled glasses moderately increase with the increase of $Ho^{3+}$ ion concentration. Increase in density of the LTT glasses indicates increase in compactness of the glass by increasing the number of bridging oxygen. This leads to increase in the rigidity of the prepared glasses. Fig 1(b) shows the variation of inter atomic distance and average molecular weight with $Ho^{3+}$ ion concentration in titled glasses. From Fig 1(b) it can be observed that the average molecular weight increases whereas inter atomic distance decreases with the

**Table 1**
Various physical properties of $Ho^{3+}$ ions in LTT glasses.

| Physical property | LTTHo01 | LTTHo05 | LTTHo10 | LTTHo15 | LTTHo20 | LTTHo25 |
|---|---|---|---|---|---|---|
| Refractive index ($n_d$) | 2.400 | 2.404 | 2.407 | 2.415 | 2.435 | 2.437 |
| Density, $d$ (g/cm$^3$) | 6.608 | 6.618 | 6.631 | 6.643 | 6.656 | 6.668 |
| Average molecular weight, $\bar{M}$ (g) | 190.7 | 191.5 | 192.6 | 193.7 | 194.8 | 195.9 |
| $Ho^{3+}$ ion concentration, $N$ ($10^{22}$ ions/cm$^3$) | 0.208 | 1.040 | 2.072 | 3.096 | 4.113 | 5.123 |
| Mean atomic volume (g/cm$^3$/atom) | 8.875 | 8.880 | 8.886 | 8.893 | 8.898 | 8.905 |
| Optical dielectric constant ($p\ \partial t/\partial p$) | 4.733 | 4.783 | 4.793 | 4.835 | 4.932 | 4.938 |
| Dielectric constant ($\epsilon$) | 5.733 | 5.783 | 5.793 | 5.835 | 5.932 | 5.938 |
| Reflection losses ($R$%) | 0.169 | 0.170 | 0.170 | 0.171 | 0.174 | 0.174 |
| Molar refraction ($R_m$) (cm$^{-3}$) | 17.70 | 17.79 | 17.87 | 18.00 | 18.20 | 18.28 |
| Polaron radius ($r_p$) (Å) | 5.013 | 2.935 | 2.332 | 2.040 | 1.856 | 1.725 |
| Inter-atomic distance ($r_i$) (Å) | 7.838 | 4.588 | 3.646 | 3.189 | 2.901 | 2.697 |
| Molecular electronic polarizability, $\alpha$ ($10^{-23}$ cm$^3$) | 7.023 | 1.411 | 0.708 | 0.475 | 0.361 | 0.290 |
| Field strength, $F$ ($10^{15}$ cm$^{-2}$) | 1.193 | 3.483 | 5.513 | 7.205 | 8.707 | 10.07 |
| Optical basicity ($\Lambda_{th}$ ) | 0.464 | 0.467 | 0.470 | 0.474 | 0.478 | 0.482 |