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# Influence of tungsten on the emission features of $Nd^{3+}$, $Sm^{3+}$ and $Eu^{3+}$ ions in $ZnF_2$–$WO_3$–$TeO_2$ glasses

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ABSTRACT

The glasses of the composition $(45-x)ZnF_2$–$xWO_3$–$49TeO_2$:$1.0Nd_2O_3/Sm_2O_3/Eu_2O_3$ with $x$ varying from 5 to 20 mol% were synthesized. Optical absorption, fluorescence spectra (in the spectral range 400–2300 nm) and also fluorescence decay were studied at ambient temperature. The Judd–Ofelt theory analysis was applied to characterize the absorption and luminescence spectra of $Ln^{3+}$ ions in these glasses. Following the luminescence spectra, various radiative properties like transition probability $A$, branching ratio $\beta$ and the radiative life time $\tau$ for ${}^4F_{3/2} \to {}^4I_{11/2}$, ${}^4G_{5/2} \to {}^6H_{7/2}$, ${}^5D_0 \to {}^7F_2$ emission levels respectively for $Nd^{3+}$, $Sm^{3+}$ and $Eu^{3+}$ doped glasses of these glasses have been evaluated. The variations observed in these parameters were discussed following of varying co-ordinations (tetrahedral and octahedral positions) and the valence states of tungsten ions in the glass network. A significant enhancement in the intensities of ${}^4F_{3/2} \to {}^4I_{11/2}$ ($Nd^{3+}$), ${}^4G_{5/2} \to {}^6H_{7/2}$ ($Sm^{3+}$) and ${}^5D_0 \to {}^7F_2$ ($Eu^{3+}$) emission lines has been observed with increase of $WO_3$ content; this is attributed to the increase in the concentration $W^{5+}$ ions in the glass network that acts as modifiers. The quantitative analysis of these results (with the aid of the data on ESR, IR and Raman spectral studies) has indicated that the glasses mixed with around 15 mol% of $WO_3$ have the optimum concentration for yielding the highest quantum efficiency with low phonon losses for the above-mentioned principal transitions.

## 1. Introduction

Tellurium oxide based glasses are well known due to their high density, high transparency in the mid infrared region (~5.0–11.0 μm), high linear and non-linear refractive index, good stability against moisture [1–5]. In view of such qualities, these glasses find potential applications as IR domes, optical fibers, modulators, non-linear optical devices and infrared laser windows. These are also considered as good glasses for hosting rare earth ions since they provide a low phonon energy (~750 nm, lower than geramanate, phosphate and silicate glasses) environment that minimizes non-radiative losses [6–8]. The presence of tungsten ions in these glasses, further, makes them suitable for optoelectronic devices since they exhibit photochromism and electrochromism properties. Tungsten ions are expected to have profound influence on luminescence characteristics of rare earth ions in tellurite glasses, for the simple reason that these ions exist in different valence states viz., $W^{6+}$, $W^{5+}$ and also in $W^{4+}$ as per the following thermo reversible disproportionate reaction:

$$W^{5+} + W^{6+} \leftrightarrow W^{4+} + W^{6+}$$

regardless of the oxidation state of the tungsten ion in the starting glass batch [10–13,9].

Among these, $W^{6+}$ ions participate in the glass network with different structural units like $WO_4$ ($T_d$) and $WO_6$ ($O_h$). The $WO_4$ units form the linkages of the type Te–O–W with $TeO_4$ and $TeO_3$ structural units in the glass network since the electronegativities (2.1 for Te ion and 2.0 for $W^{6+}$ ion) are very close to each other. On the other hand $W^{5+}$ ($5d^1$) ions forming the complexes of $W^{5+}O_3^-$, act as modifiers and induce structural disorder in the tellurite network by transforming $TeO_4$ to $TeO_{3+1}$ structural units in the glass network. Hence, the varying concentration of $WO_3$ in the glass network results varying environment of luminescent ions present in the tellurite glass network. As a consequence, interesting changes in the luminescent characteristics of lasing ions is expected.

The addition of $ZnF_2$ to tellurite glass matrix is anticipated to contribute to the chemical inertness of the glasses since there is a possibility for the formation of covalent bonding between tellurite and zinc ions through non-bridging oxygens (Te–O–Zn) [14,15].

The study on absorption and emission characteristics of $Nd^{3+}$ ($4f^3$) ion has been subject of extensive investigation in a number of

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crystalline and glass materials because of its prospective applications in NIR laser technology [16–20]. The transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$ (around 430 nm) in the absorption spectra is a characteristic of coordination of this ion. Generally this band is desirable in the construction of compact and efficient laser source pumped by diode laser. The impact of changing environment in the glass network due to the variation in the concentration of the tungsten ions is expected to very high on this transition.

Samarium containing glasses are known to have an unusual elastic behaviour due to valance instability [21]. This ion exists in trivalent and divalent states but between these two states, $Sm^{3+}$ ($4f^5$) is found to be more stable. Samarium exhibits promising characteristics for spectral hole burning studies [22,23]. The decay of exited states in $Sm^{3+}$ involves different mechanisms depending on the matrix. Earlier studies on optical absorption, fluorescence and lifetime measurements of $Sm^{3+}$ ions in oxyfluoroborate and oxide glasses have indicated the quenching of the fluorescence of $^4G_{5/2}$ level [24,25]; this is attributed to quadrupole–quadrupole interaction among the samarium ions. Similarly, a number of earlier studies on spectroscopic properties of $Sm^{3+}$ ions in different glass matrices have revealed that the fluorescence yield of this rare earth ion is strongly dependent on its environment inside the glass network [26–31].

Europium ion, another interesting rare earth ion, has got variable valency states, $Eu^{3+}$ and $Eu^{2+}$. $Eu^{3+}$ ($4f^6$ ion) is quite stable even at high temperatures in crystalline and glassy host matrices. The transitions, $^7F_0 \rightarrow {}^5D_2$ in the absorption spectrum and $^5D_0 \rightarrow {}^7F_2$ in the emission spectrum of $Eu^{3+}$ are reported to be hypersensitive; the integrated emission intensity ratio of $^5D_0 \rightarrow {}^7F_2$ (red) and $^5D_0 \rightarrow {}^7F_1$ (orange) transitions (R/O ratio) is strongly influenced by site asymmetry and covalency of the bonds with the ligand anion [32,33]. The effect of surrounding ions on the luminescence of europium in glass has been reported in several works [34–36] which clearly indicated that the relative intensities of the $Eu^{3+}$ emission peaks depend strongly on the variations in the glass network at the vicinity of this ion. $Eu^{3+}$ ion has the additional feature of interest; phonon side band studies can give information about the electron–phonon coupling strength with the host lattice and also throw light whether, non-radiative or radiative decay is favoured.

The thorough literature survey on $TeO_2$ glasses as laser host materials, indicates that though some considerable number of studies on $WO_3$–$TeO_2$ glasses are available [37,38], still there is a lot of scope to investigate the influence of the tungsten ions on the emission characteristics of rare earth ions. The objective of the present investigation is to study the fluorescence features of three different rare earth ions viz., $Nd^{3+}$, $Eu^{3+}$ and $Sm^{3+}$ ions in the visible and infrared regions in $ZnF_2$–$WO_3$–$TeO_2$ glass system with the gradual increase of $WO_3$ content in the glass network at the expense of $ZnF_2$. The results of ESR, IR and Raman spectral studies have also been used to have a comprehensive pre-knowledge over the structural changes in the glass network due to the variations in the concentrations of $WO_3$ at the vicinity of rare earth ions which influence the luminescence efficiency.

## 2. Experimental

Within the glass forming region (Fig. 1) of $ZnF_2$–$WO_3$–$TeO_2$ glass system, a particular composition $(50-x)ZnF_2$–$xWO_3$–$49TeO_2$:$1Ln_2O_3$ (with $x$ ranging from 5 to 20) is chosen for the present study. The details of the composition are:

$LnW_5$: $45ZnF_2$–$5WO_3$–$49TeO_2$: $1Ln_2O_3$

$LnW_{10}$: $40ZnF_2$–$10WO_3$–$49TeO_2$: $1Ln_2O_3$

$LnW_{15}$: $35ZnF_2$–$15WO_3$–$49TeO_2$: $1Ln_2O_3$

$LnW_{20}$: $30ZnF_2$–$20WO_3$–$49TeO_2$: $1Ln_2O_3$

where Ln = Nd, Sm and Eu.

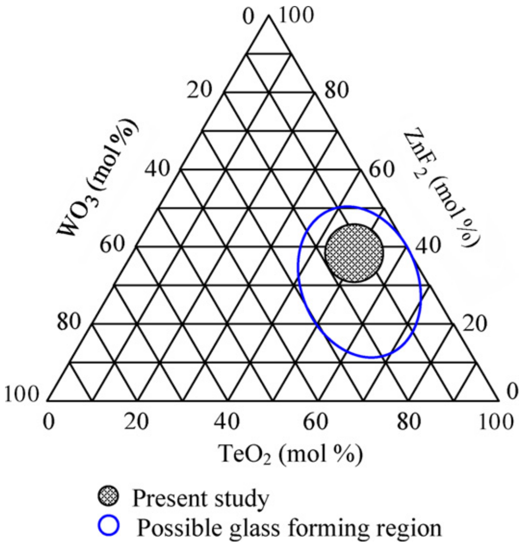

**Fig. 1.** Approximate glass forming region of $ZnF_2$–$WO_3$–$TeO_2$ glass system.

Appropriate amounts (all in mol%) of reagent grades of $ZnF_2$, $WO_3$, $TeO_2$, $Nd_2O_3$, $Sm_2O_3$ and $Eu_2O_3$ (METALL, China, 4N pure) powders were thoroughly mixed in an agate mortar and melted in a thick-walled platinum crucible in the temperature range 650–700 °C in an automatic temperature controlled furnace for about 1 h until a bubble free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed from 250 °C with a cooling rate of 1 °C/min. The samples used for optical absorption, luminescence spectra studies were prepared by suitable grinding and optical polishing to the dimensions of 1 cm × 1 cm × 0.2 cm.

The amorphous state of the glasses was checked by X-ray diffraction using Xpert PRO'panalytical X-ray diffractometer with $CuK_\alpha$ radiation. Scanning electron microscopy studies were also carried out on these samples to observe the crystallinity if any using HITACHI S-3400N Scanning Electron Microscope. The energy dispersive spectroscopy measurements were conducted on a Thermoinstruments Model Noran system 6 attached to scanning electron microscope. Thermal analysis of these samples was carried out (by TA instruments Model Q20 V24.2 Build 107) with the heating rate of 10 °C/min in the temperature range 30–800 °C. The density of the glasses was determined to an accuracy of (±0.0001) by the standard principle of Archimedes' using o-xylene (4N pure) as the buoyant liquid. The mass of the samples was measured to an accuracy of 0.1 mg using Ohaus digital balance Model AR2140 for evaluating the density. The refractive index $n_d$ of the glasses was measured (at $\lambda = 589.3$ nm) using Abbe refractometer with monobromo naphthalene as the contact layer between the glass and the refractometer prism. Infrared transmission spectra were recorded on a JASCO-FT/IR-5300 spectrophotometer to a resolution of 0.1 $cm^{-1}$ in the spectral range 400–2000 $cm^{-1}$ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa. The Raman spectra were recorded on an NIR excitation line (1064 nm) using a Bio-Rad spectrometer FTS 175C equipped with an FT Raman supplementary accessory working in a back-scattering geometry system.

The optical absorption spectra of the glasses were recorded at room temperature in the spectral wavelength range covering 400–2300 nm to a spectral resolution of 0.1 nm using JASCO Model V-670 UV–vis–NIR spectrophotometer. The luminescent spectra of the samples were recorded at room temperature on a Photon Technology International (PTI) Spectrofluorometer. This instrument contains autocalibrated quadrascopic monochrometer for wavelength selection and quadracentric sample compartment. The light source is high intensity continuous xenon lamp with high sensitivity TE-cooled InGaAs detector with lock-in amplifier and chopper for noise suppression and an additional emission mono with a 600 groove grating blazed at 1.2 μm. The system provides unmatched NIR luminescence recording capability from 500 to 2.2 μm. The other details of luminescence recording were reported in our earlier papers [39,40]. The fluorescence decay curves were recorded using Jobinyvon spectrofluorolog-3 with pulsed xenon lamp of 450 W. The electron spin resonance (ESR) spectra of the coarsely powdered samples were recorded at room temperature on JEOL JES-TES100 X-band EPR spectrometer; the magnetic field was kept at 5 mT/min and modulated at 100 kHz.

## 3. Results

From the measured values of density d and calculated average molecular weight $\overline{M}$, various physical parameters such as rare earth ion concentration $N_i$ and mean Ln ion separation $r_i$ of these glasses