Influence of modifiers on optical properties of ZnF$_2$-TeO$_2$ glass system
doped with Eu$^{3+}$ ions

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ZnF$_2$-MO-TeO$_2$ (MO = PbO, ZnO and CdO) glasses doped with Eu$^{3+}$ ions have been prepared and samples are
characterized by X-ray diffraction and differential scanning calorimetric studies. Optical absorption, photoluminescence,
infrared spectra and thermoluminescence studies have been carried out; from the measured intensities of various absorption
bands of these glasses the Judd-Ofelt parameters $\Omega_2$, $\Omega_4$ and $\Omega_6$ have been evaluated. The Judd-Ofelt theory could
successfully be applied to characterise the absorption and luminescence spectra of these glasses. From this theory various
radiative properties like transition probability $A$, branching ratio $B_R$, the radiative life time $\tau_R$ and the emission cross-section
$\sigma_\beta^R$ for various emission levels of these glasses have been determined and reported. The analysis of these results with the aid
of IR spectra and thermoluminescence studies, it has been identified that CdO mixed tellurite glass as the most favourable
host for Eu$^{3+}$ doping and to give high luminescence efficiency.

TeO$_2$ based glasses are well-known for their high density, high refractive index and for their excellent transparency in the far infrared region and due to their potential applications as IR domes, optical filters, modulators, memories and laser windows. Further, these glasses are considered as very good materials for hosting lasing rare-earth ions since they provide a low phonon energy environment to minimize non-radiative losses. A number of recent investigations on mechanical, electrical and optical properties of these glasses mixed with different modifiers are available in literature$^{4-6}$.

Qiu et al.$^7$ and Tanaka et al.$^8$ have reported the detailed studies on electrical properties of TeO$_2$ glasses containing certain metal oxides like Sb$_2$O$_3$, MoO$_3$, and Fe$_2$O$_3$. Quite recently, we too, have reported the influence of As$_2$O$_3$, P$_2$O$_5$ and Bi$_2$O$_3$ on the stability of ZnF$_2$-TeO$_2$ glass network by studying different physical properties$^{9,10}$; these studies have indicated that the stability of ZnF$_2$-TeO$_2$ glass network is relatively high when the concentration of these oxides is about 10% in the glass matrix.

Among various rare-earth ions europium ion has got variable valency states, Eu$^{3+}$ and Eu$^{2+}$. Eu$^{3+}$ is quite stable even at high temperatures in crystalline and glassy host matrices. Eu$^{3+}$ has the 4f electronic configuration with $^7F_0$ ground state$^{11}$. 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$^{12,13}$. These two transitions ($^5D_0\rightarrow^7F_2$ and $^5D_0\rightarrow^7F_1$) are expected to occur in the red and orange regions respectively and their integrated emission intensity ratio (R/O ratio) is strongly influenced by site asymmetry and co-valency of the bonds with the ligand anions$^{14,15}$. The emission intensity of the transitions $^5D_0\rightarrow^7F_2$ and $^5D_0\rightarrow^7F_1$ depend on the Judd-Ofelt parameters $\Omega_2$ and $\Omega_4$ respectively. The intensity of the emission $^5D_0\rightarrow^7F_2$ and the value of the $\Omega_2$ parameter depend on the short range effects such as covalency and structural changes in the vicinity of the Eu$^{3+}$ ion. On the other hand, the intensity of the emission transition $^5D_0\rightarrow^7F_6$ and the value of $\Omega_6$ parameter depend mainly on long range effects related to the bulk properties of the glasses$^{15}$. Recent studies of Hirao et al.$^{16}$ in phosphate and borophosphate glasses doped with Eu$^{3+}$ ions suggest that the in-homogeneous broadening of the emission lines can be systematized in terms of factors such as the presence of non-bridged oxygens in the coordination sphere of the Eu$^{3+}$ ion and the extent of polymerisation in glass structure. The laser induced fluorescence line narrowing technique involving $^5D_0\rightarrow^7F_0$ emission has also been used to investigate the local structure and structural in-homogeneities of glasses$^{13}$.

Further, when these glasses are mixed with different network modifying ions, we may expect the
structural modifications and local field variations around Eu\(^{3+}\) ion; such changes may have strong bearing on various luminescence transitions of Eu\(^{3+}\) ions, in ZnF\(_2\)-MO-TeO\(_2\) glasses (where MO stands for PbO, ZnO and CdO). Among various tellurite glass systems, the alkali free lead tellurite glasses are observed to be relatively moisture resistant, possess low rate of crystallisation. In contrast to the conventional alkali or alkaline earth oxide modifiers, PbO has the ability to form stable glasses due to its dual role, one as modifier (if Pb-O is ionic) and other as glass former (if Pb-O is covalent)\(^{17}\). Similarly, the zinc oxide has the ability to get into tellurite network forming ZnO tetrahedra which link adjacent TeO\(_4\) chains together through bridging oxygens\(^{18}\). Thus the objective of present investigation is a detailed study on different optical properties (viz., optical absorption, fluorescence, thermoluminescence and IR spectra) of ZnF\(_2\)-PbO-TeO\(_2\), ZnF\(_2\)-ZnO-TeO\(_2\) and ZnF\(_2\)-CdO-TeO\(_2\) glasses doped with europium ions and to identify the most favourable host for Eu\(^{3+}\) ions for high luminescence efficiency.

For the present investigation the following compositions have been chosen: Glass A: 40ZnF\(_2\)-10ZnO-49TeO\(_2\): 1Eu\(_2\)O\(_3\); Glass B: 40ZnF\(_2\)-10CdO-49TeO\(_2\): 1Eu\(_2\)O\(_3\) and Glass C: 40ZnF\(_2\)-10PbO-49TeO\(_2\): 1Eu\(_2\)O\(_3\). ZnF\(_2\) is introduced in the glass network since it acts as modifier, fluorine ions break the local symmetry while Zn\(^{2+}\) ions occupy interstitial positions or may form Zn-O-Te linkages because of their close ionic radii.

**Experimental Procedure**

Appropriate amounts of Analar grade reagents of TeO\(_2\) (99.99% pure, Aldrich), PbO, ZnO, CdO, ZnF\(_2\) and Eu\(_2\)O\(_3\) were thoroughly mixed in an agate mortar and melted in a platinum crucible between 600-650°C in a PID temperature controlled furnace for about 30 min 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 are found to be less than 0.5%. The amorphous state of the glasses was checked by X-ray diffraction spectra.

The density \(d\) of the glasses was determined to an accuracy of 0.001 by standard principle of Archimedes’ using \(o\)-xylene (99.99% pure) as the buoyant liquid. The glass transition temperatures \(T_g\) and crystallization temperature \(T_c\) of these glasses were determined by differential scanning calorimetry traces, recorded using universal V23C TA differential scanning calorimeter with a programmed heating rate of 20°C per minute in the temperature range 30-550°C to an accuracy of ± 1°C.

The samples were then ground and optically polished. The final dimensions of the samples used for the present measurements were about 1 cm\(\times\)1 cm\(\times\)0.2 cm. The optical absorption spectrum of the glasses was recorded at room temperature in the wave-length range 350-800 nm using Shimadzu-UV-VIS-NIR Spectrophotometer Model 3100. Infrared transmission spectra for these glasses were recorded using a Perkin-Elmer Spectrometer in the wave number range 400-4000 cm\(^{-1}\) by KBr pellet method. By using xenon arc lamp, the intense line \(\lambda_{\text{exc}} = 393.8\) nm was indentified as the excited wavelength and the same was used to record the photoluminescence spectrum of all glasses. The photoluminescence spectrum of the glasses was recorded on Hitachi-F 3010 Fluorescence Spectrophotometer in the wave-length range 550-750 nm up to a resolution of 0.1 nm.

For recording thermoluminescence emission, glasses were irradiated with X-rays for 30 min with Norelco X-ray unit operated at 35 kV, 10 mA; thermoluminescence output of these glasses was recorded with a rate of heating of 1°C/s, on a computerised Nucleonix-TL set-up (Nucleonix Pvt Ltd., Hyderabad).

**Results**

Our visual examination, absence of peaks in X-ray diffraction spectra, existence of glass transition temperature \(T_g\) and crystallization temperature \(T_c\) in differential scanning calorimetry study curves indicate that the glasses prepared were of high quality glasses. From the measured values of the density \(d\) and calculated average molecular weight \(M\), various physical parameters such as europium ion concentration \(N_e\), mean europium ion separation \(R_i\) that are useful for understanding physical properties of three series of the glasses are evaluated and presented in Table 1.

Fig. 1 shows the differential scanning calorimetric (DSC) traces of the glasses under investigation. The curves of these glasses exhibit an endothermic effect due to glass transition temperature \(T_g\), and an exothermic peak (\(T_c\)) due to the crystal growth; the presence of single glass transition temperature indicates the homogeneity of the glasses under
investigation. The difference between the two temperatures $T_c$ and $T_g$ show a maximum value for glass B (Table 2).

The optical absorption spectrum of Eu$^{3+}$ doped ZnF$_2$-MO-TeO$_2$ (where MO = ZnO, CdO and PbO) glasses has revealed the following sharp absorption bands (Fig. 2): $^7F_0 \rightarrow ^5L_6$, $^5D_3$, $^5D_2$, and $^7F_1 \rightarrow ^5D_1$.

The photoluminescence spectrum with the excitation wavelength 393.8 nm recorded at room temperature of Eu$^{3+}$ doped glasses (Fig. 3) has exhibited the following emission transitions:

$^5D_0 \rightarrow ^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$.

Fig. 4a presents the thermoluminescence glow curves of three series of the glasses X-ray irradiated at room temperature. The comparison of TL light output of Eu$^{3+}$ doped glasses with that of pure samples shows a considerable increase in the TL emission due to Eu$^{3+}$ doping for all the three glasses. However, the amplification ratio is observed to be much higher for glass B (Fig. 4b).

Trap depth parameters associated with these glow peaks are computed using Chen’s formulae:

$$E_t = 1.52 \left( KT_M^2 / \tau \right) - 1.58 \left( 2KT_M \right), \quad \ldots \ (1)$$

$$E_s = 0.976 \left( \left( KT_M^2 / \delta \right) \right), \quad \ldots \ (2)$$

for the first order kinetics.

### Table 1 — Various physical properties of Eu$^{3+}$-doped ZnF$_2$-MO-TeO$_2$ glasses

<table>
<thead>
<tr>
<th>Property</th>
<th>Glass A (ZnO)</th>
<th>Glass B (CdO)</th>
<th>Glass C (PbO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index, $n_d$</td>
<td>1.568</td>
<td>1.565</td>
<td>1.570</td>
</tr>
<tr>
<td>measured at $\lambda = 589.3$ nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, d (g cm$^{-3}$)</td>
<td>5.409</td>
<td>5.316</td>
<td>5.839</td>
</tr>
<tr>
<td>Average molecular weight, $\bar{M}$</td>
<td>124.44</td>
<td>128.59</td>
<td>134.73</td>
</tr>
<tr>
<td>Eu$^{3+}$ ion concentration, $N_e$ ($10^{21}$/c.c.)</td>
<td>9.29</td>
<td>8.96</td>
<td>10.1</td>
</tr>
<tr>
<td>Interionic distance of Eu$^{3+}$, in (Å)</td>
<td>1.357</td>
<td>1.589</td>
<td>1.85</td>
</tr>
<tr>
<td>Polaron radius, in (Å)</td>
<td>0.547</td>
<td>0.640</td>
<td>0.745</td>
</tr>
<tr>
<td>Field strength, $F$ (10$^{16}$/cm$^2$)</td>
<td>6.68</td>
<td>4.87</td>
<td>3.59</td>
</tr>
</tbody>
</table>

### Table 2 — Data on DSC studies of Eu$^{3+}$-doped ZnF$_2$-MO-TeO$_2$ glasses (temperatures are given in absolute scale)

<table>
<thead>
<tr>
<th>Glass</th>
<th>$T_g$</th>
<th>$T_c$</th>
<th>$(T_c - T_g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>350.2</td>
<td>510.0</td>
<td>159.8</td>
</tr>
<tr>
<td>B</td>
<td>351.3</td>
<td>530.0</td>
<td>178.7</td>
</tr>
<tr>
<td>C</td>
<td>331.2</td>
<td>470.0</td>
<td>138.8</td>
</tr>
</tbody>
</table>

In the above equation $K$ is Boltzmann constant, $\tau = T_M - T_1$, $\delta = T_2 - T_M$, $\mu_\delta = \delta / (T_2 - T_1)$ where $T_M$ is the glow peak temperature and $T_1$ (rising end) and $T_2$ (falling end) are the temperature at the half widths of the glow peaks. Summary of the data on thermoluminescence peaks and corresponding trap depth parameters of the present glasses is furnished in Table 3.

It may be noted here that prior to TL measurements we have recorded the optical absorption spectrum of all
Fig. 3—Fluorescence spectra of Eu³⁺ doped ZnF₂-MO-TeO₂ glasses (λ_ex=393.8 nm) All transitions are from the upper state $^5D_0$

Fig. 4a—Thermoluminescence emission of pure (solid line) and Eu³⁺ doped (dotted line) glasses

Fig. 4b—Amplification ratio of TL light output for Eu³⁺ doped ZnF₂-MO-TeO₂ glasses

Table 3—Data on various trap depth parameters of Eu³⁺-doped ZnF₂-MO-TeO₂ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>$T_M$ (K)</th>
<th>$\tau$ (K)</th>
<th>$\delta$ (K)</th>
<th>$\mu_e$</th>
<th>$E_1$ (eV)</th>
<th>$E_2$ (eV)</th>
<th>Area (arb.units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>396.2</td>
<td>40.2</td>
<td>41.8</td>
<td>0.5097</td>
<td>0.3980</td>
<td>0.3115</td>
<td>615</td>
</tr>
<tr>
<td>B</td>
<td>391</td>
<td>44.3</td>
<td>51.9</td>
<td>0.5395</td>
<td>0.3408</td>
<td>0.2443</td>
<td>789</td>
</tr>
<tr>
<td>C</td>
<td>443.3</td>
<td>36.3</td>
<td>29.7</td>
<td>0.45</td>
<td>0.5803</td>
<td>0.5489</td>
<td>659</td>
</tr>
</tbody>
</table>

the glasses before and after X-ray irradiation. After the X-ray irradiation no additional absorption bands are observed other than those obtained in non-irradiated glasses; the positions of the existing bands remain unchanged but the relative intensities of the bands are only slightly affected.

Fig. 5 shows infrared transmission spectra of ZnF₂-MO-TeO₂:Eu₂O₃ glasses. The spectrum of crystalline TeO₂ has exhibited two fundamental IR absorption bands at 772 cm⁻¹ [(ν₁ (A₁) − equatorial band)] and at 650 cm⁻¹ [(ν₂ (A₂) − axial band)] of TeO₂; however, in the spectra of all the three glasses the equatorial band is observed to be missing and only the band due to ν₁₇₁₀ symmetry is observed. In addition, a band presumably due to MOₙFₘ (ref. 20) complexes is detected (in the range 1085-1100 cm⁻¹, band 3) in the spectra of all the three glasses. Further, the IR spectra of glasses containing PbO and ZnO exhibited absorption bands (band 1) at 458 cm⁻¹ (assigned to PbO₄ structural vibrations²¹) and at 455 cm⁻¹ (due to ZnO₄ structural vibrations¹⁸). When the glasses are doped with Eu₂O₃ the intensity of the axial band is found to be decreased and its meta-centre is observed to shift towards slightly lower wavenumber;
no considerable change in position and intensity of the other band is observed in the case of ZnO and PbO modifier glasses. However, the intensity and shifting of this band in case of CdO glasses (glass B) is found to be insignificant, indicating high stability the glass network containing CdO as modifier than that of the glass containing ZnO as modifier. The summary of the data on positions of various bands observed in the IR spectra of ZnF₂-MO-TeO₂:Eu²⁺ is presented in Table 4.

The values in the parenthesis of Table 4 represent the positions of IR absorption bands of europium free glasses.

Discussion

ZnF₂-MO-TeO₂ glasses containing Eu₂O₃ have a complex composition and are an admixture of network formers and modifiers. TeO₂ belongs to intermediate class of glass forming oxides; it is an incipient glass network former and as such does not readily form glass because the octahedral Te-O polyhedron is highly rigid (when compared with other glass forming oxides like GeO₂ etc.) to get required distortion of Te-O bonds, necessary for forming a stable network. Earlier neutron scattering experiments and Raman spectral studies on TeO₂ glasses containing different modifiers have revealed that the basic building block of TeO₂ glass structure is a trigonal bipyramid commonly called TeO₄E, where one of the three equatorial directions is occupied by the 5s² electronic pair (E) of the tellurium atom with two equatorial bonds of lengths 1.91 Å and two axial bonds of lengths 2.08 Å. The environment of these Te atoms is completed by two other longer interactions of lengths 2.9 Å and the three-dimensional close packing is constituted from vertices sharing TeO₄ groups (Te₄O₁₆–Te) reinforced by weaker Te-O interactions of lengths 2.9 Å, this structure leads to long chains of tetrahedrons where the long chain molecules are entwined and the introduction the Eu³⁺ ions causes cross-linking of the glass structure. If we consider the network modifiers (CdO, ZnO and PbO) to be incorporated between the long chain molecules in the vicinity of Eu³⁺ ion, then the symmetry and or covalency of the glass at the Eu³⁺ ions should be different for different modifiers.

It is well-known that there is a shielding of the 4f electrons of the rare-earth ions and this shielding allows these ions to serve as active in solid laser hosts. These ions exhibit sharp absorption and luminescence transitions as surrounding ligand atoms weakly perturbs them. The spectral intensities for the observed bands of these glasses, which are often expressed in terms of oscillator strength of forced electronic dipole transitions, have been analysed with the help of Judd-Ofelt theory, using:

\[ f = \frac{8\pi^2 mc}{3h(2J+1)} \frac{(n_d^2 + 2)^2}{9n_d} \sum_{\lambda=2}^{6} \Omega_{\lambda} \left( \psi_j \parallel U^\lambda \parallel \psi_j \right) \]  

\[ f_{exp} = 2.302 \left( \frac{mc^2}{N_A \pi e^2} \right) \int \varepsilon(v) dv, \]  

where (2J+1) is the multiplicity of the lower states, \( m \) is the mass of the electron and \( v \) is the peak absorption in cm⁻¹. Experimental values of oscillator strengths were evaluated from the expression:

\( f_{exp} = 2.302 \left( \frac{mc^2}{N_A \pi e^2} \right) \int \varepsilon(v) dv, \)
Table 5—The absorption band energies, the oscillator strength $f_{exp}$, $f_{theor}$ for the observed transitions, Judd-Ofelt intensity parameters, spectroscopic quality factor, bonding parameter and rms deviation of Eu$^{3+}$-doped ZnF$_2$-MO-TeO$_2$ glasses.

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Energy (cm$^{-1}$)</th>
<th>$f_{exp}$ ($\times$ 10$^6$)</th>
<th>$f_{theor}$ ($\times$ 10$^6$)</th>
<th>Judd-Ofelt parameters, $\Omega_{4i}$ ($\times$ 10$^{20}$ cm$^2$)</th>
<th>rms deviation (\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3L_6$</td>
<td>25375</td>
<td>61.4</td>
<td>61.4</td>
<td>$\Omega_2$ = 287</td>
<td>(\sigma) = 1.2271</td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3D_4$</td>
<td>24040</td>
<td>32.45</td>
<td>32.44</td>
<td>$\Omega_4$ = 485</td>
<td></td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3D_2$</td>
<td>21499</td>
<td>8.4</td>
<td>5.83</td>
<td>$\Omega_6$ = 101.9</td>
<td></td>
</tr>
<tr>
<td>$^7F_1 \rightarrow ^3D_1$</td>
<td>18676</td>
<td>19.24</td>
<td>11.99</td>
<td>$\Omega_{4i}/\Omega_6$ = 4.75</td>
<td></td>
</tr>
<tr>
<td>Glass B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3L_6$</td>
<td>25375</td>
<td>27.22</td>
<td>27.16</td>
<td>$\Omega_2$ = 256</td>
<td>(\sigma) = 0.1162</td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3D_4$</td>
<td>24040</td>
<td>26.17</td>
<td>25.96</td>
<td>$\Omega_4$ = 502</td>
<td></td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3D_2$</td>
<td>21499</td>
<td>6.88</td>
<td>6.78</td>
<td>$\Omega_6$ = 107</td>
<td></td>
</tr>
<tr>
<td>$^7F_1 \rightarrow ^3D_1$</td>
<td>18676</td>
<td>18.88</td>
<td>19.44</td>
<td>$\Omega_{4i}/\Omega_6$ = 4.69</td>
<td></td>
</tr>
<tr>
<td>Glass C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3L_6$</td>
<td>25375</td>
<td>30.02</td>
<td>29.94</td>
<td>$\Omega_2$ = 608</td>
<td>(\sigma) = 4.4887</td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3D_4$</td>
<td>24040</td>
<td>14.05</td>
<td>13.94</td>
<td>$\Omega_4$ = 112</td>
<td></td>
</tr>
<tr>
<td>$^7F_0 \rightarrow ^3D_2$</td>
<td>21499</td>
<td>25.53</td>
<td>16.05</td>
<td>$\Omega_6$ = 49.6</td>
<td></td>
</tr>
<tr>
<td>$^7F_1 \rightarrow ^3D_1$</td>
<td>18676</td>
<td>19.09</td>
<td>45.33</td>
<td>$\Omega_{4i}/\Omega_6$ = 2.258</td>
<td></td>
</tr>
</tbody>
</table>

The values of $\Omega_4$ shows the following order for the glasses: for glass A, $\Omega_4 > \Omega_2 > \Omega_6$; for glass B $\Omega_4 > \Omega_2 > \Omega_6$ and for glass C $\Omega_2 > \Omega_4 > \Omega_6$. The comparison of J-O parameters show the highest value of $\Omega_2$ for glass C (Table 5).

The bonding parameter ($\delta$), defined as:

$$\delta = [(1 - \bar{\beta})/\bar{\beta}] \times 100,$$

has also been computed for all the three glasses. In Eq (5), $\bar{\beta} = \sum \beta / N$ and $\beta$ (the nephelauxetic ratio) = $\nu_c / \nu_a$. $\nu_c$ and $\nu_a$ are the energies in cm$^{-1}$ of the corresponding transitions in the complex and aquo-ion respectively, and $N$ refers to the number of levels used to compute $\bar{\beta}$ values. The computation shows the highest $\delta$ value for glass A (Table 5).

In general, the parameter $\Omega_2$ is related to the covalency and/or structural changes in the vicinity of the Eu$^{3+}$ ion (short-range effect) and $\Omega_4$ is related to the long-range effects. The larger modifier ion (Cd$^{2+}$ ionic radius, 1.03 Å) give rise to a large average distance between the TeO$_4$ chains which results in the average Eu-O distance to increase, therefore producing a weaker field around the Eu$^{3+}$ ion leading to a low value of $\Omega_2$ when compared with that of glass A (Zn$^{2+}$ ionic radius, 0.74 Å). Further support for this argument can also be cited from the value of the bonding parameter $\delta$: the value of $\delta$ for these glasses follows the order glass B < glass A indicating the high covalent environment for Eu$^{3+}$ ions in glass A. However, in the case of glass C the decrease cannot be accounted for in terms of the ionic radii (Pb$^{2+}$ ionic radius, 1.2 Å) but rather that the Pb$^{2+}$ ion is more strongly bounded to the oxygen which reduces the covalency of the Eu-O bond.

Using J-O parameters $\Omega_{4i}$, the radiative properties of fluorescent transitions from $^3D_0$ level for the present glasses are determined. The spontaneous emission probability $A$, for electric dipole transition is calculated using the expression:

$$A = \frac{64 \pi^2 e^4 n_s^2 (n_p^2 + 2)^2}{3h (2J' + 1)} \sum_{\lambda=2}^6 \Omega_{4i} \|U^\lambda\|^2,$$

where $n_s$ and $n_p$ are the energies in cm$^{-1}$ of the corresponding transitions in the complex and aquo-ion respectively, and $N$ refers to the number of levels used to compute $\bar{\beta}$ values. The computation shows the highest $\delta$ value for glass A (Table 5).
where \((2J'+1)\) is the multiplicity of the upper state and \(v\) is the wavenumber of the fluorescence peak. 
Then the total emission probability \(A_T\) involving all the intermediate terms is calculated using:

\[
A_T(\psi_f) = \sum_{\psi_r} A(\psi_r, \psi_f)
\]  

(7)

The radiative lifetime \(\tau_R\) of a state is calculated using the relationship:

\[
\tau_R = \frac{1}{A_T(\psi_f)}
\]  

(8)

The fluorescent branching ratio is obtained from the equation:

\[
\beta_r(\psi_f, \psi_r) = \frac{A(\psi_f, \psi_r)}{A_T(\psi_f)}
\]  

(9)

Finally, the stimulated emission cross-sections of the measured fluorescent levels are evaluated using:

\[
\sigma_E = \frac{A(\psi_f, \psi_r) \lambda^4}{8 \pi c n^2 \Delta \lambda},
\]

(10)

where, \(\lambda\) is the peak position of the emission line and \(\Delta \lambda\) is the effective bandwidth of the emission transitions.

The values of the transitions probability \(A(\psi_f, \psi_r)\), the total transition probability \(A_T(\psi_f)\) and the fluorescence branching ratio \(\beta_r\) evaluated using the Eqs (7)-(9) for the transitions originated from \(^5D_0\) level are presented in Table 6.

The radiative properties of Eu\(^{3+}\) ions (or any of Ln\(^{3+}\) ions) depend on the number of factors such as network former and modifier of the glass. The value of \(\beta_r\) (i.e. the branching ratio) of the luminescence transitions characterizes the lasing power of the potential laser transitions. The \(\beta_r\) values obtained for the luminescent transitions originated from \(^5D_0\) level for all the three glasses have been furnished in Table 4. It is well-established that an emission level with \(\beta_r\) value greater than 50% becomes a potential laser emission\(^{11}\). Referring to the data on emission transitions, the transition \(^5D_0\rightarrow^7F_2\) has the highest value of \(\beta_r\) for all the three glasses; this transition may therefore be considered as a possible laser transition. However, the comparison of \(\beta_r\) values of this transition for the three glasses show the largest value for glass B (CdO) indicating these glasses to exhibit better lasing action among the three glasses (Table 6). The predicted lifetime \(\tau_R\) of \(^5D_0\) level for glass B is observed to be the larger than that of glass A indicating, the higher is the ionic radius of modifier ion, the higher is the radiative lifetime and the lesser presence of higher vibrational frequencies\(^{32}\) leading to high non-radiative losses in glass A than in glass B. Thus, from the radiative lifetimes it is also evident

<table>
<thead>
<tr>
<th>Emission transition</th>
<th>Transition probability (A(\psi_f, \psi_r))</th>
<th>Branching ratio (\beta_r) %</th>
<th>Emission Cross-section (\sigma_E \times 10^{30})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^5D_0 \rightarrow ^7F_2)</td>
<td>7794</td>
<td>24.54%</td>
<td>3.42</td>
</tr>
<tr>
<td>(^5D_0 \rightarrow ^7F_1)</td>
<td>21204</td>
<td>66.78%</td>
<td>5.83</td>
</tr>
<tr>
<td>(A_{r} (s^{-1}))</td>
<td>31749</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiative lifetime (\tau_R (\mu s)) = 31.49; R (red) to O (orange) ratio = 1.1725</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^5D_0 \rightarrow ^7F_2)</td>
<td>7019</td>
<td>22.43%</td>
<td>2.96</td>
</tr>
<tr>
<td>(^5D_0 \rightarrow ^7F_1)</td>
<td>21442</td>
<td>68.52%</td>
<td>6.77</td>
</tr>
<tr>
<td>(A_{r} (s^{-1}))</td>
<td>31290</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiative lifetime (\tau_R (\mu s)) = 31.95; R (red) to O (orange) ratio = 1.1497</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^5D_0 \rightarrow ^7F_2)</td>
<td>18449</td>
<td>39.35%</td>
<td>7.74</td>
</tr>
<tr>
<td>(^5D_0 \rightarrow ^7F_1)</td>
<td>27736</td>
<td>59.16%</td>
<td>8.95</td>
</tr>
<tr>
<td>(A_{r} (s^{-1}))</td>
<td>46879</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiative lifetime (\tau_R (\mu s)) = 21.33 ; R (red) to O (orange) ratio = 1.1511</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
that the interaction of Eu$^{3+}$ ion with the glass network is much lower in glass B.

In Eu$^{3+}$ doped sample, the ratio of intensities of $^3D_0\rightarrow^3F_2$ emission in the near red region and $^3D_0\rightarrow^3F_1$ (orange emission) is a sensitive function of covalency and site symmetry. High values of this ratio indicates Eu$^{3+}$ ion is bound to more covalent atoms$^{33,34}$. Recollecting the data for this ratio for the present glasses is observed to be the highest for glass A (ZnO glass) when compared with that of other two glasses. From this it can be concluded that Eu$^{3+}$ ion has more ionic environment in the glass B when compared to its presence in the glass A.

The action of X-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electron may traverse in the glass network depending upon their energy and the composition of the glass and are finally be trapped, thus forming colour centres (or alternatively they may form excitons with energy states in the forbidden gap). The trapping sites may be the metal cations that constitute the glass structure, ions of admixtures of the main composition and the structural defects due to impurities in the glass. Thus this process leads to the formation of (i) tellurium electron centres, (ii) non-bridging oxygen hole centres and (iii) tellurium oxygen hole centres. Thermoluminescence is a consequence of radiative recombination between the electrons (released by heating from electron centre) and an anti-bonding molecular orbital of the nearest of the oxygen hole centres. Out of the three Judd-Ofelt parameters, the values of $\Omega_4$ and $\Omega_6$ depend strongly on the vibrational frequencies of Eu$^{3+}$ ions linked to the ligand atoms. The comparison of these parameters obtained for these glasses show an higher value for glass B. This indicates the vibrational transitions are less intense for this glass which may be more favourable for the formation of high concentration of colour centres at deeper trap depth in these glasses.

Finally, the analysis on the results of optical absorption, photoluminescence, thermoluminescence and infrared spectra of ZnF$_2$–MO–TeO$_2$ glasses doped with Eu$_2$O$_3$ indicates; among the three glasses, ZnF$_2$–CdO–TeO$_2$–Eu$^{3+}$ glass can be considered as the better candidate for practical applications.

References