OPTICAL ABSORPTION SPECTRUM AND JUDD-OFELT ANALYSIS STUDY OF Eu\(^{3+}\) DOPED ZINC OXYCHLORIDE TELLURITE GLASSES.

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ABSTRACT

A series of glass samples in the TeO\(_2\) - ZnO - ZnCl\(_2\) - Li\(_2\)O - Eu\(_2\)O\(_3\) glass system has been successfully made by the melt quenching technique. The density, the refractive index, the optical absorption, the Judd-Ofelt parameters and the spontaneous transition probabilities have been determined. Judd-Ofelt analysis was performed for the glass system to evaluate the spontaneous emission probability as well as the quality factor (\(Q\)), branching ratio (\(\beta\)) and radiative lifetime (\(\tau_{\text{rad}}\)). The variation of Judd-Ofelt parameters (\(\Omega_2\), \(\Omega_4\) and \(\Omega_6\)) were analyzed as a function of ZnCl\(_2\) concentration. It was found that the \(\Omega_2\), \(\Omega_4\), \(\Omega_6\), \(Q\) and \(\tau_{\text{rad}}\) increase with ZnCl\(_2\) concentration.

INTRODUCTION

Among many potential host materials for rare earth ions, zinc tellurite glasses show important advantages such as low-phonon energy environment to minimize nonradiative losses as well as possessing good chemical durability and optical properties [1]. The tellurite glasses are known to have a relatively high refractive index (1.8 < \(n\) < 2.3), a low melting temperature and represent something of a compromise between the requirement for both a low phonons energy as well as good mechanical characteristics [2]. Zinc tellurite glasses represent one of the best potential host materials for several rare earth dopants for laser applications [1]. The rare earth absorption and fluorescence spectra are quite sensitive to the local environment of the ion. Eu\(^{3+}\) is especially well suited as a probe ion as the \(^{5}F_{0}\) \(\rightarrow\) \(^{5}D_{2}\) absorption and \(^{5}D_{0}\) \(\rightarrow\) \(^{7}F_{2}\) emission in the Eu\(^{3+}\) are hypersensitive transitions and their intensities are very sensitive to the local environment [3]. The purpose of this paper is to investigate the spectroscopic properties as a function of ZnCl\(_2\) concentration by using Judd-Ofelt parameter theory. Intensity parameters, radiative lifetime and branching ratio were determined from absorption spectra.

EXPERIMENT DETAILS

A series of glass samples, \((79 - z)\)TeO\(_2\) - 10ZnO - zZnCl\(_2\) - 10Li\(_2\)O - 1Eu\(_2\)O\(_3\) where \(z = 0, 10, 20, 25, 30\) mol\% were prepared by melting mixtures of high-purity TeO\(_2\), ZnO, ZnCl\(_2\), Li\(_2\)O and Eu\(_2\)O\(_3\) in a platinum crucible. The mixture was heated in an electrical furnace at a temperature 850\(^\circ\)C for 30 minutes. To ensure proper mixing and homogeneity, the molten liquid was shaken frequently and vigorously. After being checked, the melt was cast by pouring into a preheat stainless steel split mould to
quench to form a glass. The glass was immediately transferred to an annealing furnace at 260°C, 10°C above \( T_g \). It was kept for 3 hours to relieve any residual stress, which could cause embrittlement. At the end of this annealing process, the glass left to slowly cool down to room temperature.

The amorphous nature of these samples has been confirmed by X-ray diffraction technique using Bruker axs D5005 X-ray Diffractometer. For optical measurement, the annealed glass plates were polished well on both side to dimension 20 mm x 20 mm x 2 mm. The optical absorption spectra of the glass were recorded using Jenway 6505 UV-vis Spectrophotometer.

**RESULTS AND DISCUSSION**

The absorption spectrum of Eu\(^{3+}\) for glass sample SZC3 with composition 59TeO\(_2\) - 10ZnO - 20ZnCl\(_2\) - 10Li\(_2\)O - 1Eu\(_2\)O\(_3\) recorded in the 350 – 600 nm at room temperature are shown in Figure 1. The ultraviolet (UV) cut-off is evident on the left in Figure 1 and several absorption lines are also observed. The absorption peak around 362, 375, 381, 393 and 464 cm\(^{-1}\) correspond to the transitions from ground state of \( ^7\Gamma_0 \) to the excited state of \( ^5\Delta_4, ^5\Gamma_4, ^5\Gamma_2, ^5\L_6 \) and \( ^5\Delta_2 \) respectively. Using an absorption spectra, Judd-Ofelt (J-O) analysis was performed to determine the J-O parameters \( \Omega_2, \Omega_4 \) and \( \Omega_6 \). The assignment of these absorption bands and the values of the measured (\( P_{mea} \)) and calculated (\( P_{cal} \)) oscillator strength obtained from J-O theory is tabulated in Table 1. The \( P_{mea} \) of the transitions was obtained by using an equation

\[
P_{mea} = \frac{mc^2}{\pi \epsilon^2 N} \int E(\lambda) d\lambda.
\]

The \( P_{cal} \) of an electric-dipole absorption transition from initial state to final state, involving J-O parameters (\( \Omega_2, \Omega_4, \Omega_6 \)) which depend on the host matrix \([4,5,6,7]\). The \( P_{cal} \) can be calculated using the equation

\[
P_{calc} = \frac{8\pi^2 mc}{3\hbar(2J+1)} \left( \frac{n^2 + 2}{9n} \right) \sum_{i=2,4,6} \Omega_i \left\| U_i \right\|^2.\]

The \( \Omega_2, \Omega_4, \Omega_6 \) were derived from \( P_{mea} \) using a least-squares fitting approach. \( \Omega_2 \) are important for investigating of local structure, bonding in the vicinity and transitions properties of rare-earth ions. Some important radiative properties can be calculated by use of the values of \( \Omega_2 \).

Theoretically computed radiative properties of Eu\(^{3+}\) in the glass system including radiative transition probabilities (\( A \)), branching ratio (\( \beta \)) and radiative lifetime (\( \tau_{rad} \)) are listed in Table 2. Judd-Ofelt analysis was performed to determine the \( \tau_{rad} \) for these samples. The spontaneous transition probability is given by

\[
A = \frac{64\pi^4}{3\hbar^3 (2J+1)} \left[ \frac{n(n^2 + 2)}{9} S_{ed} + n^3 S_{md} \right]
\]

where the electric-dipole line strengths,

\[
S_{ed} = e^2 \sum_{i=2,4,6} \Omega_i \left\| U_i \right\|^2
\]

and the magnetic-dipole line strengths, \( S_{md} = \frac{e^2 \eta^2}{4mc^2} \left\| L + 2S \right\|^2 \).
The fluorescence branching ratio of transitions is given by $\beta = \frac{A}{\sum A}$. The total radiative transition probabilities $A_{\text{total}}$ for seven emission transitions ($^7\text{F}_0, ^7\text{F}_1, ^7\text{F}_2, ^7\text{F}_3, ^7\text{F}_4, ^7\text{F}_5, ^7\text{F}_6$) are summed up to obtain the $\tau_{\text{rad}}$ from the $^5\text{D}_0$ state using equation $\tau_{\text{rad}} = \frac{1}{A_{\text{total}}}$. According to the equation, the $\tau_{\text{rad}}$ lifetimes of these levels are determined to be 0.759 ms as given in Table 2. The predicted spontaneous-radiative transition rate for $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is 991 s$^{-1}$ and fluorescence branching ratio is 75%, showing this transition can be expected to be the most intense emission in the glasses.

Figure 1: Absorption spectrum of Eu$^{3+}$ ion for glass sample 59TeO$_2$ - 10ZnO - 20ZnCl$_2$ - 10Li$_2$O - 1Eu$_2$O$_3$ at room temperature.

The absorption spectra of the (79 – z)TeO$_2$ - 10ZnO - (z)ZnCl$_2$ - 10Li$_2$O - 1Eu$_2$O$_3$ glass system with various ZnCl$_2$ content (z = 0, 10, 20, 25, 30 mol %) is shown in Figure 2. It can be seen that the transitions $^7\text{F}_0 \rightarrow ^5\text{L}_6$ and $^7\text{F}_0 \rightarrow ^5\text{D}_2$ occur in all sample, but for transition $^7\text{F}_0 \rightarrow ^5\text{D}_4$ and $^7\text{F}_0 \rightarrow ^5\text{G}_2$ can only be observed clearly for ZnCl$_2$ concentration more than 20 mol %. The increase in ZnCl$_2$ leads to a shift of the UV cut off to shorter wavelengths. In Figure 2, the absorption edge of rare-earth Eu$_2$O$_3$ doped glass occurs in the near-UV region. The optical absorption edge becomes more prominent as Eu$_2$O$_3$ is incorporated in the glass. The J-O parameters ($\Omega_2, \Omega_4, \Omega_6$) for various ZnCl$_2$ content is
shown in Table 3. These $\Omega_2, \Omega_4, \Omega_6$ parameters were derived using least-squares fitting approach between the $P_{\text{mea}}$ and the $P_{\text{cal}}$. The values for the optical spectroscopic ratio or spectroscopic quality factor $Q = \Omega_4 / \Omega_6$ introduced by Jacobs and Weber [8] is also inserted. It can be clearly seen that all J-O parameters ($\Omega_2, \Omega_4, \Omega_6$) show increase with ZnCl$_2$ concentration as shown in Figure 3. It increases from $1.270 \times 10^{-19}$ to $1.517 \times 10^{-19}$ cm$^2$, $0.244 \times 10^{-19}$ to $0.644 \times 10^{-19}$ cm$^2$ and $0.118 \times 10^{-19}$ to $0.193 \times 10^{-19}$ cm$^2$, respectively with ZnCl$_2$ concentration from 0 mol % to 30 mol %.

Table 1: Values of the $P_{\text{mea}}$ and $P_{\text{cal}}$ for the chosen absorption of Eu$^{3+}$ for 59TeO$_2$ - 10ZnO - 20ZnCl$_2$ - 10Li$_2$O - 1Eu$_2$O$_3$ glass.

| Wave length $\lambda$(nm) | Energy (cm$^{-1}$) | Assignments | Area $|E(y)|dy$ | Reduced matrix elements | Oscillator strengths, $P$ |
|--------------------------|-------------------|--------------|---------------|-------------------------|--------------------------|
|                          |                   |              | $|U_2|^2$ | $|U_4|^2$ | $|U_6|^2$ | $P_{\text{mea}}$ (x10$^{-7}$) | $P_{\text{calc}}$ (x10$^{-7}$) |
| 362                      | 27624             | $^7F_0\rightarrow^5D_4$ | 9.6077 | 0.0000 | 0.0011 | 0.0000 | 2.1514 | 3.2019 |
| 375                      | 26635             | $^7F_0\rightarrow^5D_4$ | 15.7938 | 0.0000 | 0.0007 | 0.0000 | 3.5367 | 1.9539 |
| 381                      | 26211             | $^7F_0\rightarrow^5G_2$ | 36.8522 | 0.0006 | 0.0000 | 0.0000 | 8.2523 | 4.5207 |
| 393                      | 25445             | $^7F_0\rightarrow^5L_6$ | 40.8690 | 0.0000 | 0.0000 | 0.0155 | 9.1500 | 9.1493 |
| 464                      | 21551             | $^7F_0\rightarrow^5D_2$ | 11.5157 | 0.0008 | 0.0000 | 0.0000 | 2.5787 | 4.8136 |

Deviation parameter, $\delta_{\text{rms}} = 3.3562 \times 10^{-7}$

Judd-Ofelt parameters (cm$^2$): $\Omega_2 = 1.248 \times 10^{-19}$, $\Omega_4 = 0.454 \times 10^{-19}$, $\Omega_6 = 0.101 \times 10^{-19}$

Table 2: Predicted spontaneous-radiative transition rate ($A$), fluorescence branching ratio ($\beta$) and lifetime ($\tau_{\text{rad}}$) of Eu$^{3+}$ in 59TeO$_2$ - 10ZnO - 20ZnCl$_2$ - 10Li$_2$O - 1Eu$_2$O$_3$ glass.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy (cm$^{-1}$)</th>
<th>Reduced matrix elements</th>
<th>$A_{\text{ed}}$ (s$^{-1}$)</th>
<th>$A_{\text{md}}$ (s$^{-1}$)</th>
<th>$\beta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5D_0\rightarrow^7F_6$</td>
<td>12437</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^5D_0\rightarrow^7F_5$</td>
<td>13495</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^5D_0\rightarrow^7F_4$</td>
<td>14534</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>177.46</td>
</tr>
<tr>
<td>$^5D_0\rightarrow^7F_3$</td>
<td>15479</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^5D_0\rightarrow^7F_2$</td>
<td>16339</td>
<td>0.0032</td>
<td>0</td>
<td>0</td>
<td>799.52</td>
</tr>
<tr>
<td>$^5D_0\rightarrow^7F_1$</td>
<td>16977</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^5D_0\rightarrow^7F_0$</td>
<td>17361</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$A_{\text{total}}$ (s$^{-1}$) = 1317.2 , $\tau_{\text{rad}}$ (ms) = 0.759

The trend for the $\Omega$ parameters in the glass system is such that $\Omega_2 > \Omega_4 > \Omega_6$. It is well known that the parameter $\Omega_2$, exhibits the dependence on the covalency between rare earth ions and ligands anions, since $\Omega_2$ reflect the asymmetry of the local environment at the Eu$^{3+}$ ion site. The higher the value of $\Omega_2$ the less centrosymmetrical the ion site is.
and the less ionic its chemical bond with the ligands [9]. The slight increase of $\Omega^2$ with an increasing of ZnCl$_2$ concentration in the glass system could indicate the increase of covalent character because of the different site occupancy of the ions on average [10].

Figure 4 shows the dependence of the $Q$ as a function of ZnCl$_2$ concentration. The $Q$ increase from 2.062 to 4.491 for 20 mol % ZnCl$_2$ then decrease to 3.341 for 30 mol % ZnCl$_2$. It indicates that the higher the value of $Q$, the better is the optical glass and the stronger the laser $^5D_0 \rightarrow ^7F_2$ transitions. On the other hand, the efficiency of $^5D_0 \rightarrow ^7F_1$ transition becomes reduced [11,12].

![Absorption spectrum of Eu$^{3+}$ in the (79 – z)TeO$_2$ - 10ZnO - zZnCl$_2$ -10Li$_2$O - 1Eu$_2$O$_3$ glass system, where z = 0, 10, 20, 25 and 30.](image)

The $\tau_{rad}$ increases substantially with the introduction of zinc chloride into the tellurite matrix as shown in Figure 4. The $\tau_{rad}$ increased from about 0.617 ms in sample SZCl to 0.759 ms in sample SZC3 where 20 mol% ZnCl$_2$ was introduced into the tellurite matrix. The $\tau_{rad}$ is also desired to be as long as possible in order to permit a greater pulsed power. For higher ZnCl$_2$ content, the $\tau_{rad}$ decreases from 0.759 to 0.665 ms for 30 mol % ZnCl$_2$. This change clearly shows a maximum at about 20 mol % ZnCl$_2$, at a maximum $\tau_{rad}$. This is evident that halide ZnCl$_2$ does modify the local electrostatic field

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symmetry of the rare earth ion Eu$^{3+}$ and can produce a substantial increase of the intrinsic radiative lifetime. The chloride ion Cl$^{-}$ may be replaced an oxygen ion somewhere in coordination sphere and disturbing the local electron density so the electrostatic environment of rare earth ion was altered.

Table 3: Calculated Judd-Ofelt parameters and spectroscopic ratio $Q$ for Eu$^{3+}$ in the (79 – z)TeO$_2$ - 10ZnO - (z)ZnCl$_2$ - 10Li$_2$O - 1Eu$_2$O$_3$ glass system.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mol% ZnCl$_2$</th>
<th>$\delta_{rms}$ (10$^{-7}$)</th>
<th>Judd-Ofelt Parameters (10$^{-6}$) cm$^2$</th>
<th>$Q = \frac{\Omega_4}{\Omega_6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZC1</td>
<td>0</td>
<td>4.427</td>
<td>$\Omega_2$ 1.270</td>
<td>$\Omega_4$ 0.244</td>
</tr>
<tr>
<td>SZC2</td>
<td>10</td>
<td>4.572</td>
<td>$\Omega_2$ 1.317</td>
<td>$\Omega_4$ 0.367</td>
</tr>
<tr>
<td>SZC3</td>
<td>20</td>
<td>3.356</td>
<td>$\Omega_2$ 1.248</td>
<td>$\Omega_4$ 0.454</td>
</tr>
<tr>
<td>SZC4</td>
<td>25</td>
<td>3.692</td>
<td>$\Omega_2$ 1.413</td>
<td>$\Omega_4$ 0.527</td>
</tr>
<tr>
<td>SZC5</td>
<td>30</td>
<td>3.451</td>
<td>$\Omega_2$ 1.517</td>
<td>$\Omega_4$ 0.644</td>
</tr>
</tbody>
</table>

Figure 3: Variations of intensity parameters ($\Omega_2$, $\Omega_4$, $\Omega_6$) with ZnCl$_2$ concentration of (79 – z)TeO$_2$ - 10ZnO - (z)ZnCl$_2$ - 10Li$_2$O - 1Eu$_2$O$_3$ glass system.
The OH content of these glass also decreased with zinc chloride as shown from the FTIR spectra, suggesting that this compound may react with the OH group, probably giving zinc oxide and HCl [13]. This dehydration effect may explain the fact that the fluorescence intensities and lifetimes appear to reach a maximum for 20 mol% ZnCl2 after which it may lead to an increase in ion-ion interactions, clustering and nonradiative decay from 7F6 to ground 7F0 along with multiphonon relaxation, which is responsible for the subsequent decrease of the lifetimes.

**CONCLUSIONS**

The $\Omega$ intensity parameters, the radiative transition rates, the branching ratio and the fluorescence lifetimes were successfully calculated based upon the experimental absorption spectrum and the Judd-Ofelt theory. It was found that $\Omega$, $Q$, $A$, $\beta$ and $\tau_{rad}$ increased with increasing of ZnCl2 content. The progressive replacement of TeO2 by ZnCl2 improved the optical quality of the glasses and the halide ZnCl2 does modify the local electrostatic field symmetry of the rare earth ion, Eu3+. The optical properties of Eu3+ ions doped in halide tellurite glass suggest that it is a good laser material at 612 nm ($^{3}D_{0} \rightarrow ^{3}F_{2}$ transition).
REFERENCES


