Research Article

Spectroscopic Studies of the Behavior of Eu$^{3+}$ on the Luminescence of Cadmium Tellurite Glasses


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The effect of europium doping on the photoluminescence of ZnO-CdO-TeO$_2$ glasses is analyzed. TeO$_2$-based glasses are of high interest as hosts for laser glasses. The Eu-doped oxide glasses were prepared by the conventional melt-quenching method. Five different concentrations of europium nitrate hexahydrate that varied from 0.3 to 1.5 mol% were used. SEM observations revealed the formation of zinc aluminates spinel and dispersed droplets of liquid-liquid phase separation in the glasses. X-Ray diffraction reveals the amorphous structure of the fabricated glasses. FT-IR and Raman spectra show the presence of TeO$_4$ and TeO$_3$/TeO$_3$ units that conform with the glass matrix. Raman spectra evidenced a band located at 1556 cm$^{-1}$ that can be related to interstitial molecular oxygen in the glass matrix. Photoluminescence of the glasses showed light emission due to the following europium transitions from its $^5$D$_2$, $^5$D$_1$, and $^5$D$_0$ levels to its $^7$F$_J$ manifolds: $^5$D$_2$ $\rightarrow$ $^7$F$_{5/2}$ (468 nm), $^5$D$_2$ $\rightarrow$ $^7$F$_{5/2}$ (490 nm), $^5$D$_2$ $\rightarrow$ $^7$F$_{5/2}$ (511 nm), $^5$D$_1$ $\rightarrow$ $^7$F$_{1/2}$ (536 nm), $^5$D$_1$ $\rightarrow$ $^7$F$_{5/2}$ (554 nm), $^5$D$_0$ $\rightarrow$ $^7$F$_{5/2}$ (579.5 nm), $^5$D$_0$ $\rightarrow$ $^7$F$_{5/2}$ (592 nm), $^5$D$_0$ $\rightarrow$ $^7$F$_{5/2}$ (613 nm), $^5$D$_0$ $\rightarrow$ $^7$F$_{5/2}$ (652 nm), and $^5$D$_0$ $\rightarrow$ $^7$F$_{5/2}$ (490 nm). The estimated decay time, $\tau$, was 0.4 ms for all the glasses.

1. Introduction

In general, glasses are good materials as host for luminescent trivalent rare earth ions; they show a wide transparency range and low propagation losses, so they can be used in different types of modern devices such as long optical displays, lasting phosphors, and solid-state lasers [1]. Tellurite glasses are interesting and useful host for luminescent trivalent lanthanide ions, showing maximum vibrational frequencies smaller than those of many other oxide glasses [2, 3]. This characteristic favors and increases the luminescence quantum efficiency from excited states of optically active ions.

On the other hand, they are chemically stable and highly homogeneous, with low phonon frequency and high linear refractive index. TeO$_2$-based glasses are promising materials for their use in nonlinear susceptibility [4, 5] and for the development of fiber and integrated optic amplifiers. In addition, these glasses are potential hosts for infrared emitting rare earth elements and can be used as lasers covering all the telecommunication bands [1, 6]. Luminescence properties and potential applications of Eu$^{3+}$ have been reported in many types of host materials, for example, silicate, borates, phosphates, vanadates, molybdates, and tungstanates [7–13]. One of the more attractive applications of Eu$^{3+}$ is regarding
the phenomenon of persistent spectral hole burning [14, 15]. The present investigation is part of a wide research about the study of the ZnO-CdO-TeO2 system doped with rare earth ions. One study has been published earlier in which the structural characterization and optical (PL) and thermal analysis of the matrix containing Eu3+ ion was reported [16]. This research shows the influence of varying the Eu3+ ions content on the photoluminescence properties of a single composition of a ZnO-CdO-TeO2 glass. It is worth to mention that the Eu3+ ions have an effect in the short length ordering of the glass structure.

2. Materials and Methods

The glasses were fabricated using zinc oxide (ZnO, Fluka Analytical), cadmium oxide (CdO, 99.5%), tellurium dioxide (TeO2 ≥ 99%), and europium nitrate hexahydrate (Eu(NO3)2 ⋅ 6H2O, 99.99%) from Sigma Aldrich. In Table 1 the nominal composition of the mixtures is presented. The powders were weighted in an OHAUS analytical weighing scale, model GAI10 with a precision of 0.0001 g. A series of five glasses doped with Eu3+ ions were obtained varying the concentration of the europium ions. The content of metallic oxides of the glass matrix was fixed and only the concentration of europium nitrate hexahydrate was varied from 0.3 to 1.5% mol (Table 1). The glasses were manufactured by the melt-quenching method in high alumina crucibles at 100°C in a Thermolyne 48000 furnace with a dwell time of 30 minutes. After quenching, the glasses were annealed at 350°C for 30 minutes.

2.1. Structural Characterization. X-ray diffraction (XRD) analysis was performed in a Philips 3040 using the Cu Kα line. The glassy material was crushed and milled under 30 μm for XRD measurements. Scanning electron microscopic (SEM) was carried out in a Philips XL 30ESEM. The samples were prepared as follows: fresh fractured glass pieces were chemically etched (2 vol% hydrofluoric acid for 10 s) to obtain clean surfaces and then were silver coated for SEM/EDS analysis. The elemental composition distribution of the present phases in the glass was determined by spot analysis by Energy Dispersive X-ray Spectrometry (EDS).

Infrared (IR) spectra of the glasses were obtained using a Perkin-Elmer 1600 series FT-IR spectrometer in the range of 4000–400 cm⁻¹ at intervals of 4 cm⁻¹. Micro-Raman spectroscopy analysis was performed on all samples using a micro-Raman X’plora equipment BX4iTF OLYMPUS V5.

<table>
<thead>
<tr>
<th>Element</th>
<th>V1 (% at.)</th>
<th>V2 (% at.)</th>
<th>V3 (% at.)</th>
<th>V4 (% at.)</th>
<th>V5 (% at.)</th>
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<tr>
<td>O</td>
<td>48.75</td>
<td>45.19</td>
<td>45.19</td>
<td>44.82</td>
<td>53.30</td>
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<tr>
<td>Al</td>
<td>1.03</td>
<td>0.87</td>
<td>0.69</td>
<td>0.74</td>
<td>0.63</td>
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<td>Si</td>
<td>0.58</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cd</td>
<td>16.83</td>
<td>17.97</td>
<td>18.05</td>
<td>17.96</td>
<td>15.42</td>
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<td>Te</td>
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<td>27.13</td>
<td>27.04</td>
<td>26.66</td>
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<tr>
<td>Eu</td>
<td>0.36</td>
<td>0.42</td>
<td>0.37</td>
<td>0.44</td>
<td>0.55</td>
</tr>
<tr>
<td>Zn</td>
<td>7.67</td>
<td>8.23</td>
<td>8.47</td>
<td>8.79</td>
<td>7.17</td>
</tr>
</tbody>
</table>

HORIBA Jobin-Yvon, using a He-Ne laser with a wavelength of 632.8 nm.

2.2. Luminescence and Decay Times. The photoluminescence spectra were recorded by means of a Horiba Jobin-Yvon Fluorolog 3 spectrofluorometer working with a 450 W ozone-free Xe lamp. Decay time curves were monitored using an Opolette HE 355 LD + UVDM system tuning at 392 nm. The resulting emission and transient fluorescence signal was analyzed with a Jobin-Yvon Triax 550 monochromator and detected with a Horiba-Jobin Yvon i-Spectrum Two intensified charge coupled device.

3. Results and Discussion

3.1. SEM. SEM observation of glass surfaces (micrographs of selected glasses are shown in Figure 1) have confirmed the presence of zinc aluminate spinel (ZnAl2O4) and disperse droplets of liquid-liquid phase separation in the glasses. For V1 glass (Figure 1(a)), the presence of small crystals was detected, and EDS analysis demonstrated that it is composed of Al, Zn, and O in concentrations similar to those of zinc aluminate spinel. Thus, corrosion between the molten mixture and the crucible walls occurred during fusion. In general, incorporation of aluminum from crucible corrosion appears in all glasses as it can be seen in Table 2. The concentration of aluminum has a tendency to decrease as the proportion of europium increases. In Figure 1, micrographs of V2 and V5 glasses (Figures 1(b) and 1(d)) exhibit two distinguishable zones in the surface. The first consists of dispersed droplets and the second one is a homogeneous and amorphous phase that is related to the glassy nature of the sample. At this respect, V3 glass surface (Figure 1(b)) is the most homogeneous and amorphous since no other phase was detected. In Table 2, it is possible to observe that CdO and TeO2 concentration decrease with the increment in europium concentration. These results indicate that volatilization of the oxides took place during fabrication.

3.2. XRD. In Figure 2 diffraction patterns of the glasses are presented. All samples have shown an amorphous structure evidenced by a broad band localized in the range of 2θ from 20° to 40°, indicating the presence of structural ordering or several small crystallizations [16]. It is interesting to notice...
Figure 1: Micrographs of glasses surface: (a) V1, (b) V2, (c) V3, and (d) V5.

Figure 2: Diffraction patterns of all fabricated glasses. It can be seen that all the samples are amorphous.

that the band has a well-defined maximum at $2\theta = 29.7^\circ$ [17]. This particular characteristic of the band can be related to an intermediate range order of the glass structure.

3.3. FT-IR. The infrared spectra of the glasses in the range of 1100 to 370 cm$^{-1}$ are displayed in Figure 3. The spectra of all glasses are similar to that of crystalline $\alpha$-TeO$_2$ [18], which conformed with TeO$_4$ groups in trigonal bipyramid (tbp) units. As modifier ions concentration increases in the glass matrix, TeO$_{3+1}$ groups and TeO$_3$ trigonal pyramids (tp) are progressively formed, causing a substantial change in the glass structure. That is, the incorporation of modifier ions (Cd$^{2+}$, Zn$^{2+}$, and Eu$^{3+}$) generates nonbonding oxygen (NBO) breaking the continuity of the glass matrix [19, 20].

Figure 3: Infrared spectra of the obtained glasses, a broad absorption band at 676 cm$^{-1}$ can be identified and it corresponds to the asymmetric stretching vibrations of Te-O bonds in TeO$_3$ groups.
In tellurite glasses, the absorption bands in the range of 700 to 600 cm\(^{-1}\) are related to the stretching vibration of Te-O bonds in TeO\(_4\) and TeO\(_3\) groups. For TeO\(_4\) groups, absorption occurs about 650–600 cm\(^{-1}\) and for TeO\(_3\) groups around 700–650 cm\(^{-1}\) [7, 21, 22]. In the glasses under study, a broad absorption band appears in the range of 870–520 cm\(^{-1}\) with a minimum at 676 cm\(^{-1}\) and it was assigned to asymmetric stretching vibrations of Te-O bonds of TeO\(_4\) groups. Moreover, a less intense absorption band appears in the range of 500 to 400 cm\(^{-1}\), which shifts to lower frequencies of 452 to 435 cm\(^{-1}\) that can be attributed to stretching vibrations of Cd-O bonds [24]. At low wavenumber values, there are small absorption peaks for V3, V4, and V5 located at 420–410 cm\(^{-1}\) corresponding to ZnO units [24]. It seems that the increment in Eu\(^{3+}\) ions content possibly promotes the formation of the ZnO\(_4\) units in the glass matrix.

3.4. Raman. In general, Raman spectra of all glasses present a similar behavior among them, as it can be seen in Figure 4. The absorption bands at 114, 345, 663, and 751 cm\(^{-1}\) are typical of TeO\(_4\)-based glasses such as TeO\(_2\)-La\(_2\)O\(_3\)-TiO\(_2\) [25], TeO\(_2\)-ZnO-Na\(_2\)CO\(_3\)-Er\(_2\)O\(_3\) [26], WO\(_3\)-TeO\(_2\) [27], PbO-WO\(_3\)-TeO\(_2\) [28], TeO\(_2\)-TiO\(_2\)-Nd\(_2\)O\(_3\)-WO\(_3\) [29], TeO\(_2\)-ZnO-Na\(_2\)O [30], Ag\(_2\)OTeO\(_2\) [31], and ZnO-CdO-TeO\(_2\) [32]. The first two bands at low Raman frequencies, 114 and 345 cm\(^{-1}\), are assigned to the Boson peak [20, 26] and oscillations of Te-O bonds in TeO\(_4\) tetrahedra characteristic of α-TeO\(_2\) [33–37], respectively.

Furthermore, the bands located at 663 and 751 cm\(^{-1}\) are related to stretching vibrations of TeO\(_{ax}\) in TeO\(_4\) and TeO\(_3\)/TeO\(_{3}\) groups, respectively [7, 8, 22]. Particularly, the absorption band at 663 cm\(^{-1}\) corresponds to vibrations in tBP of TeO\(_4\) groups that constitute the continuous network [32]. Jha et al. [30] reported that this band is related to a strong crystallization band of α-TeO\(_2\) localized around 670 cm\(^{-1}\). The band at 751 cm\(^{-1}\) is generated by [TeO\(_3\)]\(^{−}\) and [TeO\(_4\)]\(^{−}\) units [38]. These structural changes in the glass matrix are induced by the introduction of ZnO and CdO that produce the breakdown of Te-O-Te bonds [32, 35]. These results are in agreement with FT-IR analysis where TeO\(_4\) and TeO\(_3\)/TeO\(_{3}\) groups were also identified. It can be appreciated that trigonal pyramids are the predominant structure in this glass matrix and this is caused by a rather high NBO concentration. However, the shape of the peak, which is clearly intense and defined, can indicate a tendency to form an ordered network of intermediate range order. Furthermore, there is an absorption band at 1556 cm\(^{-1}\) that increases its intensity as the Eu\(^{3+}\) ions concentration rises, and it corresponds to the Q rotational-vibrational band of O\(_2\) in air [39]. Interstitial molecular oxygen generation was detected and quantified by Raman spectroscopy for SiO\(_2\) glasses [40]. It was found that O\(_2\) molecules have an effect on the defect processes of silica. In addition, generation of molecular oxygen confined in voids inside bulk GeO\(_2\) glass after laser irradiation has also been identified by Raman spectroscopy [41]. In the tellurite glasses, the molecular oxygen is most likely produced during glass fabrication. The change in oxidation state of Te from TeO\(_2\) to TeO\(_3\) produces structural voids around it, incrementing the interstitial space in the glass matrix [14]. We consider that, in our glasses, the TeO\(_2\) or TeO\(_3\) units sharing two O atoms form a OTe(OO)TeO bridge [40, 42]. Then, the breakdown of this bridge can be the origin of the O\(_2\) molecules trapped in the structural voids in the glass.

3.5. Luminescence. Excitation spectra of the ZnO-CdO-TeO\(_2\)-Eu\(^{3+}\) glasses monitored at 613 nm are shown in Figure 5. It can be seen that there are several bands originated from
variation of the decay time related to the different Eu\(^{3+}\) ions concentration in the glasses. The estimated decay time, \(\tau\), was 0.4 ms for all the glasses. This value is comparable in magnitude with decay times reported for other tellurite glasses in the range of 0.25 to 0.9 ms [18, 25, 43, 44]. In Eu\(^{3+}\) doped zinc-tellurite glasses, a higher probability of radiation transition occurs, for all emission levels of Eu\(^{3+}\) ions. Then, the lifetime is shorter and this is a consequence of the high refractive index of the glass [18].

4. Conclusions

For all europium ions content, yellow and visible transparent homogeneous glasses were obtained. Aluminum impurities in the glasses were detected by SEM/EDS analysis, determining that the high alumina crucible reacted with the melt during fusion. FT-IR and Raman spectroscopies analysis showed that TeO\(_3\)/TeO\(_5\) groups are the predominant structural units in the glass matrix. This is explained in terms of the high concentration of ZnO and CdO, which introduce nonbonding oxygen breaking down the TeO\(_4\) network. In Raman spectra, we see an unusual band that is characteristic of molecular oxygen, which probably forms during fabrication. In this respect, we suggest that TeO\(_3\) or TeO\(_5\) units form OTe(OO)TeO bridges sharing two oxygen atoms. This can be interpreted in terms of the fact that Eu\(^{3+}\) ions are probably promoting the oxygen bridge breakdown and then the formation of O\(_2\) molecules. Therefore, the produced molecular oxygen occupies the interstitial space in the glass matrix. Photoluminescence and lifetime analysis revealed that the variation in Eu\(^{3+}\) concentration does not influence significantly these properties. However, it does play
an important role in the structural change and formation of interstitial O\(_2\) molecules.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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**References**


