Eu\(^{3+}\) and Ce\(^{3+}\) co-doped aluminosilicate glasses and transparent glass-ceramics containing gahnite nanocrystals

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**ABSTRACT**

Transparent zinc-aluminosilicate glass-ceramics containing cerium and europium ions were prepared by controlled thermal heating of parent glasses. Addition of CeO\(_2\) resulted in the improved transparency of the glasses in the visible spectral region. X-ray diffraction patterns of the glass-ceramics indicate the formation of the crystalline gahnite phase and there are evidences of Ce\(^{3+}\) and Eu\(^{3+}\) occupancies in this phase, as well as co-existence in the amorphous phase. Ce\(^{3+}\) emission corresponding to the allowed f-d transitions is identified, as well as an anomalous emission in the red-infrared region. The characteristic luminescence of Eu\(^{3+}\) in the red is observed. Judd-Ofelt analysis of Eu\(^{3+}\)-doped samples reveals enhanced site asymmetry around the ion and a high branching ratio for the 612 nm emission after ceramization. Due to enhanced Ce\(^{3+}\) emission and Eu\(^{3+}\) emission quenching, color tunability is possible in the red to blue spectral region, depending on the heat treatment duration.

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1. Introduction

Glasses and glass-ceramics containing rare earth ions are widely studied for their ability to host optically active trivalent lanthanide ions with various luminescent and optical applications. Besides optimized spectroscopic characteristics, other pursued features in these materials are high chemical durability and thermal stability, large rare earth solubility, etc. Particularly, transparent glass-ceramics offer the perspective of improved mechanical properties and higher absorption and emission cross sections, over a large spectral range, provided that the rare earth dopant occupies crystalline sites, while still maintaining the transparency required for applications as in solid state lasers, amplifiers, sensors, etc. [1]. Aluminosilicate glass and glass-ceramics are among the most investigated systems due to their high chemical durability and thermal stability, as well as very low thermal expansion coefficient [2,3]. Besides technological applications, aluminosilicate glass-ceramics having additional components are also commercialized in the form of cooktop panels, cookware, tile glazes, etc [3–5]. Despite the fact that silicate glasses present relatively high maximum phonon energy (~1000 cm\(^{-1}\) [6]), and low rare earth solubility [7], these glasses still occupy the top of the list in applications due to cost-effective production and wide transparency in the UV-VIS-NIR spectral range. Addition of ZnO to aluminosilicate glasses can lower the final product cost while the addition of controlled amount of TiO\(_2\) induces the desired bulk crystallization [8].

In the preparation of glass-ceramics containing rare earth ions, the main challenge lies in the control of nucleation and crystal growth mechanisms so that the transparency of the parent glass is preserved. As discussed in Rayleigh-Gans theory [1,9], the attenuation of light by the crystallites can be minimized by making sure that their average size is smaller than the wavelength of incident light. Therefore, crystals with average size 15 nm and refractive index difference between the crystalline and glassy phases of about 0.1, are suggested in order to obtain better transparency. Beall and Pinckney [10] reported that crystal sizes of about 30 nm and a refractive index difference of about 0.3 could also be suitable if the distance between crystals remains lower than six times their average size (d < 180 nm). Transparent aluminosilicate glass-
ceramics with composition SiO₂−Al₂O₃−MgO−ZnO−ZrO₂ containing β-quartz crystals of about 10 μm have also been reported [10], and most recently we reported glass and transparent glass-ceramics in the compositional system SiO₂−Al₂O₃−ZnO−TiO₂−K₂O−CeO₂ [11]. In this case, CeO₂ was used to eliminate the dark coloration introduced by Ti³⁺ ions in the glasses. Upon heating, the CeO₂ dopant is reduced to the hexagonal sesquioxide Ce₂O₃ and the residual oxygen participates in the oxidation of Ti³⁺ to Ti⁴⁺ yielding pale yellow colored glasses. Taking a further step, controlled crystallization of the glasses resulted in transparent glass-ceramics, which could be interesting host for rare earth ions.

In the light of possible optical applications, we have prepared and fully characterized the spectroscopic properties of three different series of glasses and glass ceramics, one of which doped with Eu³⁺ ions. In our investigations, we firstly tackle the effect of CeO₂ agent to increase the transparency of the parent glass, and then study the luminescence dynamics of different species in rare earth doped glass and glass-ceramics.

2. Experimental

In previous work [11], we prepared glass and glass ceramics with wt% compositions:

Gn1: 50.6SiO₂ + 23.0Al₂O₃ + 18.4ZnO + 5TiO₂ + 3K₂O, and

Gn2: 50.6SiO₂ + 23.0Al₂O₃ + 18.4ZnO + 5TiO₂ + 3K₂O + 0.5 wt% CeO₂ in excess

The parent glasses were prepared by the conventional melt-quenching technique and the derived glass-ceramics were obtained by controlled thermal processing of the glasses to induce crystal nucleation and growth. Having previously verified that Ce⁴⁺ could eliminate the brown color of Gn1 glass, for this work we prepared a glass co-doped with Ce³⁺ and Eu³⁺ (Gn3: [50.6SiO₂ + 23.0Al₂O₃ + 18.4ZnO + 5TiO₂ + 3K₂O] + 0.5CeO₂ wt % + 0.5 wt% Eu₂O₃, both in excess), aiming to investigate the luminescence properties of the rare-earth ions in the glass and glass-ceramic.

The high purity precursors SiO₂ (99%, Vitrovita, Brazil), Al₂O₃ (99%, Almatis, USA), ZnO (99.7%, J. T. Baker, USA), TiO₂ (99.5%, Riedel De Haen, Germany), anhydrous K₂CO₃ (99%, Nuclear, Brazil), CeO₂ (99.0%, Vetec, Brazil) and Eu₂O₃ (99.98%, Aldrich, USA) were homogeneously mixed and melted in a Pt crucible at 1620 °C for 4 h. The glass melts were quenched at room temperature, onto a pre-heated cast iron mold, and subsequently annealed at 600 °C for 12 h to relieve internal stresses. Differential scanning calorimetry (DSC) studies of the powdered and bulk samples were performed in order to determine the characteristic glass transition temperature (Tg), crystallization on-set and peak temperature (Tp), using a calorimeter model STA 449 F3 of NETZSCH-Gerätetechnik GmbH, Selb, Germany. In order to obtain glass-ceramics, the glass samples were subjected to thermal processing at 670 °C for 3 h to induce nucleation and at 880 °C for various periods of time (2, 25, 50 and 100 h) to promote the growth of the crystalline phase. Samples are named following the duration (in hours) of the final heat-treatment at 880 °C, for example, G2-2_2, G2-2_5, etc.

To identify the crystallite phases developed in the resulting glass-ceramics, X-ray diffraction (XRD) data were recorded in a Rigaku Ultima IV X-ray diffractometer (Tokyo, Japan), equipped with a 40 kV power supply and 20 mA output of CuKα radiation (1.5406 Å). Scanning was carried out in the 2θ range 10 to 80°, with a step of 0.02° [20]. Transmission electron micrographs were captured using a Tecnai G2 (FEI Company, Hillsboro, OR) TEM machine, operating at 200 kV.

The UV–Vis spectra of the samples were measured using a Perkin-Elmer Lambda 25 spectrophotometer with 1 nm resolution. The photoluminescence spectra were recorded using a Horiba Jobin Yvon spectrofluorimeter model Fluorolog FL-1057, equipped with CW and pulsed Xe lamps. The visible signals were collected by a single photo-counting detector (PDP-850) at 60° with respect to the excitation beam. The excitation spectra were corrected by the lamp profile and detector’s response. Excited state lifetime values of Eu³⁺ 5D₀ level were obtained from the fit of emission decay curves at 612 nm (excited at 393 nm), using the decay-by-delay phosphorimetric analysis in the same fluorimeter. In the case of Ce³⁺ ions, the lifetime values were obtained by single exponentially fitting the emission decay curves at 360 nm measured using the TCSPC mode, with excitation at 289 nm by a Delta Diode.

3. Results and discussion

The optimization of the nucleation and crystallization procedures, by adjustment of temperature and heat treatment time is of chief importance to obtain glass-ceramics with controlled volume fraction of crystalline phases and crystal sizes. In order to nucleate the crystal centers and to allow consequent growth, it is necessary to know the glass characteristics temperatures, Tg, Tp, and crystallization behavior of the parent glass. The crystallization behavior of Gn1 and Gn2 glasses, were previously discussed [11]. The DSC (10 K/min) glass transition temperature of Gn1 and Gn2 glass samples are 710 and 680 °C, respectively while the crystallization onset temperatures (Tp) are at about 833 and 813 °C, and the crystallization peaks (Tg) are around 868 and 850 °C, respectively. We argue that the decrease in the characteristic temperatures from Gn1 to Gn2 should be related to the incorporation of Ce³⁺ or to the reduction of Ce⁴⁺ to Ce³⁺ ions in the Gn2 glass, which can interfere with the glass structure and facilitate devitrification. By comparing the DSC curves of Gn1 bulk and powder samples, it was observed [11] that bulk crystallization occurs.

The X-ray diffraction patterns of the Gn2 parent glass and its derived glass-ceramics are given in Ref. [11]. It is observed that there is an increase in crystallization up to 25 h of heat treatment, but no further development for longer heat treatment times. Still, the broad humps in the XRD patterns in 20 range of 10–40° evidence the existing glassy phase even after 100 h of ceramation. The XRD scattering peaks of Gn2-x, and Gn3-x (x = 2, 25, 50 and 100 h) samples confirm the formation of crystalline cubic ZnAl₂O₄ spinel phase (PDF file no. 71-968), known as gahnite, with no trace of any other phase. The average crystal size of gahnite gradually increases from 4.1 to 5.8, 6.6 and 6.8 nm, for 2, 25, 50 and 100 h of heat-treatments, as previously reported [11]. Representative TEM micrographs of samples Gn1-x heat treated for 2 and 100 h at 880 °C after nucleation at 670 °C for 3 h, are given in Fig. 1.

As previously discussed, the addition of CeO₂ to the Gn1 glass samples results in more transparent yellowish glasses (Gn2) due to the oxidation of Ti³⁺ to Ti⁴⁺ induced by the reduction of Ce⁴⁺ ions to Ce³⁺. Fig. 2 shows the optical transmission spectra of the Gn1, Gn2 and Gn3 glasses and glass-ceramics, in the 250–1100 nm spectral region. For the Gn3_100 sample, which were nucleated at 670 °C for 3 h and then heat treated at 880 °C for 100 h, the absorption bands of Eu⁵⁺ ions are not observable due to the low dopant concentration and large host absorption in the UV–Vis range. The inset of Fig. 2 shows the photographs of the samples. As it can be seen by the photographs and spectra, the Gn3 glass is more transparent than Gn1 and Gn2 glasses and glass-ceramics. However, ceramation further decreases the transparency of both Gn2 and Gn3 series. The fundamental absorption edge of the Gn1 glass at about 3.70 eV shifts to 3.64 eV and 3.60 eV after incorporation of
CeO$_2$ and further ceramization up to 100 h, respectively.

Fig. 3(a) illustrates the luminescence spectra of the Gn1 and Gn2 glasses and Gn2 glass-ceramics, excited at 314 nm. The spectrum of Gn1 glass consists of a broadband at around 550 nm which is attributed to the emission from Ti$^{3+}$ ions [11]. The emission spectra of the Gn2 glass and the derived glass-ceramics shows a major broadband component at 350 nm while Ti$^{3+}$ band is present in much lower intensity, confirming the oxidation mechanism proposed in Ref. [11]. The broadband around 350 nm is attributed to the characteristic radiative d-f transitions of Ce$^{3+}$. It is interesting to notice that in going from Gn2 glass to Gn2 glass ceramics a progressive red shift is observed, indicating a change in site symmetry around the dopant, because the 5d excited state of Ce$^{3+}$ is highly localized and strongly influenced by the crystal field imposed by the first coordination sphere ligands. A similar red spectral shift has also been reported in YAG:Ce nanoparticles containing acetate hydrate due to the increase in Gd$^{3+}$ concentration and crystal size [12]. In our case, it is likely that the red shift for the Gn2 glass
ceramics is associated to the incorporation of Ce$^{3+}$ in the garnet crystalline phase. As a control experiment, for posterior comparison with Eu$^{3+}$-doped samples, we have also measured luminescence with excitation at 393 nm as it is seen in Fig. 3(b). The resulting spectra consist of a band in the range 400–600 nm and a more structured band around 700 nm, which is not observed for the glassy Gn2 sample. In fact, by normalizing the spectra to this latter band, one can see that the intensity of the higher energy band progressively decreases with increasing heat treatment time. This observation gives strong evidence of Ce$^{3+}$ ions in two different environments (glassy and crystalline). It is worth mentioning that for both excitations at 314 and 393 nm, the spectral features were confirmed by measurements using a long pass filter at 500 nm.

The excitation spectra measured by monitoring the luminescence in the range 350–400 nm, and at 700 nm were investigated. The results obtained by monitoring the UV-blue band were practically identical, so representative curves ($\lambda_{\text{em}}$ = 350 nm) are shown in Fig. 3(c), along with spectra monitored at 700 nm for the glassy Gn2 and representative glass ceramic Gn2_50. In both cases, there is a characteristic excitation band at 314 nm, which corresponds to the f–d transitions of Ce$^{3+}$ ions. However, the excitation spectra for the 700 nm emission of glass ceramics differs from that of Gn2 glass. It presents two additional bands centered at around 400 and 540 nm, which, in agreement with the emission spectra, might be associated to Ce$^{3+}$ ions in the garnet phase. In addition, for both, Gn2 and Gn2_50 an excitation band below 280 nm is perceived when the emission is monitored at 500 nm. Further investigation of the origin of these bands were done by measuring emission spectra at 400 nm and at 540 nm. As expected, the spectra in Fig. 3(b) were reproduced for $\lambda_{\text{exc}}$ = 400 nm but, interestingly, no emission at all was observed for $\lambda_{\text{exc}}$ = 550 nm, and so far we have no explanation for this observation.

The luminescence and excitation spectra of Gn3 samples are presented in Fig. 4. The characteristic emission lines of Eu$^{3+}$ ions excited at 393 nm are observed at 577, 590, 612, 652, 700 and 524 nm, $f_1$–$d_1$ (331 nm), $f_2$–$d_2$ (577 nm) and $f_3$–$d_3$ (585 nm). For wavelengths below 350 nm a broad band is perceived, which is likely to be due to the host matrix absorption. The Eu$^{3+}$ luminescence decay curves monitored at 612 nm with excitation at 393 nm are presented in Fig. 5(a). The decays were fitted to single exponential functions to yield average lifetime values as presented in Table 1. As it can be seen, the lifetime of Eu$^{3+}$-doped Gn3 glass sample is the highest (1.77 ms) and it progressively decreases to a maximum of ~20% of this value as the heat treatment time increases to 100 h. The change in lifetime indicates a change in the Eu$^{3+}$ environment upon crystallization, even though no significant spectral change has been observed. The possibility of Eu$^{3+}$ to Ce$^{3+}$ energy transfer is not discarded, but it must be further investigated in order to be confirmed.

The luminescence decay curves were also measured at 360 nm, where Ce$^{3+}$ emits, and Ce$^{3+}$ ions doped glass and glass-ceramics for the emission centered at about 612 nm is also shown in Fig. 4. Both spectra show identical profile of the Eu$^{3+}$ excited state bands, displaying spectral lines that correspond to the transitions $^7F_0$–$^2D_4$ (360 nm), $^7F_0$–$^2L_2$ (380 nm), $^7F_0$–$^7L_5$ (393 nm), $^7F_{0,1}$–$^3D_3$ (413 nm), $^7F_0$–$^2D_2$ (463 nm), $^7F_0$–$^7D_1$ (524 nm), $^1F_1$–$^1D_1$ (531 nm), $^1F_2$–$^1D_0$ (577 nm) and $^1F_2$–$^1D_0$ (585 nm). For wavelengths below 350 nm a broad band is perceived, which is likely to be due to the host matrix absorption. The Eu$^{3+}$ luminescence decay curves monitored at 612 nm with excitation at 393 nm are presented in Fig. 5(a). The decays were fitted to single exponential functions to yield average lifetime values as presented in Table 1. As it can be seen, the lifetime of Eu$^{3+}$-doped Gn3 glass sample is the highest (1.77 ms) and it progressively decreases to a maximum of ~20% of this value as the heat treatment time increases to 100 h. The change in lifetime indicates a change in the Eu$^{3+}$ environment upon crystallization, even though no significant spectral change has been observed. The possibility of Eu$^{3+}$ to Ce$^{3+}$ energy transfer is not discarded, but it must be further investigated in order to be confirmed.

For both Gn3 and Gn3_50 samples. It is worth noting that the intensity ratio of Eu$^{3+}$ emission bands at 612 and 590 nm ($I_{612}/I_{590}$) is often used as a parameter to evaluate the symmetry of the Eu$^{3+}$ sites [13,14]. As measured, $I_{612}/I_{590}$ increases from 6.25 to 7.44 by increasing the heat-treatment time of Gm3 glass ceramics up to 100 h. Therefore, we can conclude that the asymmetry around the Eu$^{3+}$ ions sites increases by increasing the crystallinity of the sample. Finally, we have used the Judd-Ofelt approach to analyze the radiative properties of the samples before and after ceramicization. Rather than using the absorption spectra (with only a few limited number of transitions.

The calculated, average, refractive index of the samples is 1.81 for both Gn3 and Gn3_100 samples. It is worth noting that the refractive index of the glass–ceramic is, in fact, the average refractive index of the residual glass and the obtained crystal. However, for the transparent glass-ceramics, the refractive index difference between glassy and crystalline phases should be as small as 0.1–0.3 [13,14]. The radiative emission probabilities, branching ratio and Judd–Ofelt intensity parameters for the two representative samples are given in Tables 2 and 3. The branching ratio of the 612 nm emission is slightly higher in the case of Gn3_100 (~69%) than in Gn3 (~64%). Furthermore, as compared to other glasses, the $I_{612}/I_{590}$ values in our studied glass and glass-ceramics is comparable to or higher than previously reported values for germanate [16,17].
boro-tellurite (60% [16]), ZBLA (10% [17]), pentaphosphate (61% [18]), zirconium fluoride (24.2% [18]) and tungsten-phosphate (69% [15]) glasses. As a general rule, the emission bands with branching ratios higher than 50% are known to be suitable for laser action [19]. The increase in the values of $\Omega_2$ and $\Omega_6$, when going from $\text{Gn}_3$ to $\text{Gn}_3_{100}$ indicates the increase in site asymmetry at the vicinity of the $\text{Eu}^{3+}$ ions and increased rigidity of the sample, respectively [13,14]. The values of $\Omega_6$ are less commonly reported in the literature but our result is comparable to other glasses and the value of $\Omega_2$ for $\text{Gn}_3_{100}$ is higher than that for several compositions as seen in Table 3.

### Table 1
Lifetime values of $\text{Eu}^{3+}$: and $\text{Ce}^{3+}$ ions doped into alumina-silicate glasses and glass-ceramics of the $\text{Gn}_2$ and $\text{Gn}_3$ series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_{\text{Eu}^{3+}}$ (ms)</th>
<th>$\lambda_{\text{exc}}$ = 393 nm</th>
<th>$\lambda_{\text{em}}$ = 612 nm</th>
<th>$\tau_{\text{Ce}^{3+}}$ (ns)</th>
<th>$\lambda_{\text{exc}}$ = 289 nm</th>
<th>$\lambda_{\text{em}}$ = 360 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Gn}_2$</td>
<td>–</td>
<td>3.12</td>
<td></td>
<td>1.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Gn}<em>2</em>{2h}$</td>
<td>–</td>
<td>1.62</td>
<td></td>
<td>1.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Gn}<em>2</em>{25h}$</td>
<td>–</td>
<td>1.61</td>
<td></td>
<td>1.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Gn}_3$</td>
<td>1.77</td>
<td>6.77</td>
<td></td>
<td>5.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Gn}<em>3</em>{2h}$</td>
<td>1.57</td>
<td>4.48</td>
<td></td>
<td>4.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Gn}<em>3</em>{25h}$</td>
<td>1.44</td>
<td>3.64</td>
<td></td>
<td>3.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Gn}<em>3</em>{100h}$</td>
<td>1.44</td>
<td>3.60</td>
<td></td>
<td>3.60</td>
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### Table 2
Calculated radiative parameters of two representative $\text{Eu}^{3+}$ doped samples.

<table>
<thead>
<tr>
<th>Transitions $^7 \text{D}_0 \rightarrow$</th>
<th>Wavelength (nm)</th>
<th>$\text{Gn}_3$</th>
<th>$\text{Gn}<em>3</em>{100}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^7 \text{F}_0$</td>
<td>577</td>
<td>38.47</td>
<td>6.81</td>
</tr>
<tr>
<td>$^7 \text{F}_1$</td>
<td>590</td>
<td>71.96</td>
<td>12.74</td>
</tr>
<tr>
<td>$^7 \text{F}_2$</td>
<td>612</td>
<td>359.6</td>
<td>63.65</td>
</tr>
<tr>
<td>$^7 \text{F}_3$</td>
<td>652</td>
<td>21.18</td>
<td>3.75</td>
</tr>
<tr>
<td>$^7 \text{F}_4$</td>
<td>700</td>
<td>21.18</td>
<td>3.75</td>
</tr>
<tr>
<td>$^7 \text{F}_5$</td>
<td>744</td>
<td>3.33</td>
<td>0.59</td>
</tr>
<tr>
<td>$^7 \text{F}_6$</td>
<td>800</td>
<td>0.37</td>
<td>0.06</td>
</tr>
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</table>

Table 3
Judd-Olfel intensity parameters of $\text{Eu}^{3+}$ ions in the two representative glass $\text{Gn}_3$ and glass-ceramic $\text{Gn}_3_{100}$ samples, in comparison to the literature.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$U_2$ (10$^{-20}$ cm$^2$)</th>
<th>$U_4$ (10$^{-20}$ cm$^2$)</th>
<th>$U_6$ (10$^{-20}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Gn}_3$</td>
<td>6.19</td>
<td>2.51</td>
<td>0.23</td>
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<tr>
<td>$\text{Gn}<em>3</em>{100}$</td>
<td>8.36</td>
<td>3.06</td>
<td>0.44</td>
</tr>
<tr>
<td>Fluorosilicate glass</td>
<td>7.44</td>
<td>0.72</td>
<td>0.02</td>
</tr>
<tr>
<td>Borophosphate glass</td>
<td>2.98</td>
<td>0.42</td>
<td>0.02</td>
</tr>
<tr>
<td>Telluro-fluoroborate glass</td>
<td>6.92</td>
<td>3.43</td>
<td>0.02</td>
</tr>
<tr>
<td>Tellurite ceramics</td>
<td>2.95</td>
<td>0.39</td>
<td>0.02</td>
</tr>
<tr>
<td>Lead-zinc phosphate glass</td>
<td>6.52</td>
<td>2.29</td>
<td>0.98</td>
</tr>
<tr>
<td>Sodium phosphate glass</td>
<td>4.12</td>
<td>4.69</td>
<td>1.83</td>
</tr>
<tr>
<td>Pentaphosphate crystal</td>
<td>3.66</td>
<td>1.43</td>
<td>3.07</td>
</tr>
</tbody>
</table>

The chromaticity diagram (CIE 1931) is a useful tool to define the color purity of luminescent materials through two calculated dimensions $(x, y)$ [25]. The spectra of the $\text{Eu}^{3+}$-$\text{Ce}^{3+}$ co-doped $\text{Gn}_3$ glass and $\text{Gn}_3_{100}$ glass-ceramic, presented in Fig. 4, were employed to calculate the chromaticity coordinates. The values are given in Table S1 (Suppl. Materials). Fig. 6 presents the CIE-1931 chromaticity diagram. As seen, under 393 nm excitation, the glassy sample $\text{Gn}_3$ presents red color, which progressively evolves into the blue region by increase of the heat-treatment time and consequent induction of the crystalline phase in $\text{Gn}_3_{x}$ ($x = 0, 2, 25, 50$ and $100$ h) glass ceramics. Thus, the blue emission associated to $\text{Ce}^{3+}$ ions significantly contributes to the emission of the glass ceramics, and the emission can be tuned in the blue-red spectral range by selection of the heat-treatment duration. This tunability offers the perspective of combining colors in samples co-doped with green emitting $\text{Th}^{3+}$ ions to generate white light.

4. Conclusions

Zinc-aluminosilicate glasses were prepared by the conventional melt quenching technique and subjected to controlled thermal processing to successfully obtain transparent glass ceramics containing nanosized gahnite phase. The addition of $\text{CeO}_2$ to the parent glass, results in the improved transparency of the glasses in the visible region through reduction of $\text{Ce}^{4+}$ to $\text{Ce}^{3+}$ concomitantly with $\text{Ti}^{3+}$ to $\text{Ti}^{4+}$ oxidation. Upon ceramization, the samples have their transparency decreased in both, the singly $\text{CeO}_2$-doped
samples and CeO2/Eu2O3 co-doped samples. Emission of Ce3+ ions corresponding to allowed f-d transition is identified for different chemical environments (glassy and crystalline). An anomalous, additional emission is observed in the red-infrared region. The luminescence of Eu3+ ions gradually quenches by increasing the heat-treatment times probably due to some interaction with Ce3+ ions—energy transfer has not been discarded. This hypothesis is corroborated by decreased Eu3+ donor level lifetime values while larger values are measured for Ce3+ acceptor level, upon ceramization. The Judd-Ofelt analysis of Eu3+-doped samples reveals enhanced site asymmetry around the Eu3+ ions and a high branching ratio for the emission at 612 nm, after ceramization. Due to enhanced Ce3+ emission and Eu3+ quenching, color tunability is possible in the red to blue region, depending on heat treatment duration.

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