A study of Cerium Oxide incorporation in Te-Zn-Na-La oxide glasses

Maiara Mitiko Taniguchi\textsuperscript{a}, Edenilson da Silva\textsuperscript{a}, Marco Aurélio Toledo da Silva\textsuperscript{b}, Leandro Herculano\textsuperscript{c}, Marcos Paulo Belançon\textsuperscript{a}

\textsuperscript{a}Pós-graduação em processos químicos e bioquímicos, Universidade Tecnológica Federal do Paraná, Via do Conhecimento Km 1, 85503-390 Pato Branco - Brazil
\textsuperscript{b}Laboratory of Photonics and Nanostructured Materials (DFMNano), Postgraduate course in Materials Science and Engineering of Federal Technological University of Paraná (UTFPR), CEP 86036-370, Londrina, Paraná, Brazil.
\textsuperscript{c}Departamento de Física, Universidade Tecnológica Federal do Paraná, Medianeira, PR, Brazil

Abstract

The effects of Cerium incorporation in a Zinc-Tellurite glass containing Sodium and Lanthanum (TZNL) has been investigated. Samples were produced under air atmosphere and thermal, structural and spectroscopic data was acquired. The doped samples exhibited a reddish luminescence under 405 nm excitation, though its origin is attributed to Te\textsuperscript{4+} ions. Under 450 nm pumping we observed a broadband from 600-750 nm in all samples, including the matrix. X-ray diffractograms (XRD) and Fourier transform infrared spectroscopy (FT-IR) analysis confirmed that Cerium is inducing structural changes in the glass and even though Ce\textsuperscript{3+} were not detected directly, its presence is not discarded because the excitation of the Te\textsuperscript{4+} band observed in the TZNL glass is different from the reported in the literature in such way that Ce\textsuperscript{3+} may playing some role. An additional excitation/emission study is needed in order to clarify the question.

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Email address: marcosbelancon@utfpr.edu.br (Marcos Paulo Belançon\textsuperscript{a})
1. Introduction

The need to upscale the electricity production from solar and a few other emerging technologies are pushing the glass science to innovate further[1]. Taking just the example of photovoltaic (PV) industry, about 150GWp[2] of capacity were installed last year, corresponding to about 500 millions panels which are covered by float glass. PV’s are already pushing glass industry[3] to increase production, and emerging technologies[4] in this field and others are demanding enhanced glass materials.

Rare-earth’s (RE) have a straight relation with glasses at the industry level. By mass Cerium oxide is the most consumed RE and for optical applications it is widely used as UV blocking agent in PV’s cover[5]. Considering a thickness of 3 mm for this cover one can estimate that PV’s industry consumed more than 5 million tons of float glass last year, and even though Cerium is a RE its price is quite low once it is the most abundant RE, making up to 50% of the total RE ore in the most important deposits[6].

On the other hand tellurite glasses are interesting hosts due its unique structure, high refractive index and low melting temperature[7]. Tellurites can be fiberized[8], sputtered[9] and other techniques as laser ablation of the glass have been developed[10]. The incorporation of Cerium in this family of glasses has oftenly the purpose to introduce $\text{Ce}^{3+}$ ions to quench a transition in $\text{Er}^{3+}$ [11, 12, 13] which enhances the gain in optical amplifiers operating at 1.53$\mu$m. In the context we have presented above we decided to investigate structural and spectroscopic properties in the UV-Vis range of Cerium doped glasses of the system 73.3$\text{TeO}_2$, 19.6$\text{ZnO}$, 4.9$\text{Na}_2\text{CO}_3$ and 2.2$\text{La}_2\text{O}_3$ (TZNL) in %mol.

2. Materials and methods

Samples were prepared by weighting high purity raw materials as purchased from Sigma Aldrich and named as xCe, where x is the molar concentration of Cerium oxide in the TZN sample. The dopant was added to the composition without changing the stoichiometric relation between the components of the TZN matrix. Next the raw materials were melted at 800°C and poured into stainless steel mold pre-heated to 300°C, just below the glass transition temperature.

X-ray diffraction (XRD) were obtained from the glass powder using a Rigaku Miniflex 600 diffractometer with CuKa radiation of wavelength 1.5418
Å with 30 kV and 15mA current. The scan range was set to $2\theta$ from 5° to 80° with a step size of 0.02°. The differential scanning calorimetry (DSC) data was acquired with a TA Instruments DSC Q20 using Air atmosphere, with flow rate of 50 mL/min and heating rate of 10°C/min. A platinum crucible was used and the samples were heated until 520°C. Infrared transmittance spectra were obtained using Fourier transform infrared (FT-IR) spectroscopy in attenuated total reflectance (ATR) mode in a Perkin Elmer Frontier. The spectra were collected in the range 4000-400 cm$^{-1}$ with a resolution of 2 cm$^{-1}$ and averaged 32 scans. UV-VIS absorbance were measured in a PerkinElmer Lambda 45 spectrometer. Visible and near infrared photoluminescence (PL) spectra were obtained with a LaserLine SP-2A portable spectrometer under diode laser excitation.

3. Results

In figure 1 we show the DSC curves in the range 100-520° and the temperatures of glass transition ($T_g$), onset crystallization ($T_x$) and crystallization peak ($T_c$) obtained are summarized in table 1.

| Sample | $T_g$ | $T_x$ | $T_c$ |
|--------|-------|-------|-------|
| Matrix | 309.1 | 451.9 | 506.2 |
| 0.10Ce | 313.8 | 417.0 | 444.2 |
| 0.50Ce | 315.8 | 433.8 | 461.7 |

Table 1: $T_g$, $T_x$ and $T_c$ obtained from the curves shown in figure 1.

As one can see, the $T_g$ has increased with increasing Cerium concentration, and even though the $T_x$ obtained is lower in the doped samples compared to the TZNL matrix, we believe they are not related to the same crystal phase.

In figure 2 we can see the x-ray diffractograms for three samples. We have annealed one piece of the sample 0.10Ce for 11 hours at 470°C and the diffractogram (not shown here) is similar to those obtained by Sobczyk et al[14] in a similar glass, including for the crystallized sample. As they have explained, ZnTeO$_3$ and La$_2$Te$_4$O$_{11}$ crystals are formed above 450°C, and the concentration ratio between them is sensitive to the temperature. This could explain why $T_x$ is lower in our doped samples because Cerium may be changing this balance or introducing a new crystal phase.
Figure 1: DSC curves evidencing the crystallization peak around 450°C in doped samples.

We have fitted the diffractograms by four lorentzians obtaining a chi² of about 0.0012 in all cases, which resulted in fitted curves as the shown in cian in the figure 2. The most intense band is centered at 28.7°, which is known to be sensitive to the Zinc content in Zinc-Tellurite[15] glasses. The only difference found here for this peak among the samples is in its area, which corresponds to 38.2% of the total area for the matrix, 35.0% for 0.1Ce and 33.3% for 0.5Ce.

The FTIR spectra are shown in figure 3, where the absorption band in the range 500-900cm⁻¹ have been deconvoluted fitting the spectra by four gaussians. A quite small band around 450-470cm⁻¹ is attributed to the Te-O-Te symmetric stretching mode[16], and in the range 500-900cm⁻¹ a broadband is detected as it is expected from a Zinc-Tellurite glass[17]. TeO₄ by-piramidal, TeO₃ and TeO₃⁺₁ trigonal structures are responsible for the bands at 610-
680 cm\(^{-1}\) and 750 cm\(^{-1}\), respectively. The modifier Zn\(^{2+}\) creates additional TeO\(_{3+1}\) polyhedra which are responsible for the band at 779–790 cm\(^{-1}\)[18, 19]. Lousteau et al[20] have observed the \(^{2}F_{7/2}\) absorption band of Ce\(^{3+}\) around 2200 cm\(^{-1}\) in a tellurite fiber quite similar to our glass. This band was not detected in our samples, indicating that we may have a prevalence of Ce\(^{4+}\) over Ce\(^{3+}\) oxidation states.

The fitting procedure has show similar results for the matrix and the 0.10Ce sample. However, for the sample 0.50Ce the peaks are different. For example, the band near \(\sim 800\) cm\(^{-1}\) in the matrix is attributed to TeO\(_{3+1}\) polyhedra[18, 19], and the prevalence of the band at \(\sim 750\) cm\(^{-1}\) in the sample 0.50Ce, which is attributed to TeO\(_{3}\)/TeO\(_{3+1}\) trigonal suggests that increasing Cerium oxide concentration we are converting TeO\(_{3+1}\) polyhedra into TeO\(_{3+1}\) trigonal units.

Optical absorbance spectra are shown in figure 4, where we can see some
band around 450 nm in our matrix similar to the observed by Costa et al.[21] in the binary lithium-tellurite glass, which is attributed to Te$^{4+}$ ions. The cut-off wavelengths were estimated as indicated in the figure and by adding Cerium its position has moved from 445 nm in the matrix to 529 nm and 571 nm in 0.10Ce and 0.50Ce samples, respectively. This redshift is attributed to the conversion of TeO$_3$ units into TeO$_4$ units[22, 16].

In figure 5 we show the luminescence spectra for three samples under 405 nm laser excitation, and in the inset a picture from the sample 0.10Ce demonstrating the green/yellow emission we have detected which is attributed to Te$^{4+}$ ions[21]. In this experiment we were not able to detect any luminescence from the matrix. It is important to mention that for the sample 0.50Ce the lower intensity can be related to re-absorption during our measurement once the cut-off wavelength for this sample is at 571 nm.
Exciting the sample at $\sim 450$nm under naked eye we could not observe any emission. However our measurements indicated the presence of a band as it is shown in figure 6.

TZN denotes for an additional sample prepared without Lanthanum, which confirmed that this raw material had some Praseodymium impurities. On the other hand the broadband around 650 nm is also attributed to Te$^{4+}$. By comparing the figures 5 and 6 to the excitation-emission contour plot demonstrated by Costa et al[21] one can conclude that TZNL samples exhibit similar Te$^{4+}$ emission under 450 nm excitation, with the band centered at 650 nm. But under 405 nm excitation the Lithium-Tellurite binary system keeps about the same emission spectrum and in TZNL the center has moved to higher energies, around 570 nm.
Figure 5: Ce$^{3+}$ doped TZNl luminescence spectra under 405 nm excitation. The inset shows a picture of one of the samples.

Unfortunately we were not able to detect luminescence under 405 nm excitation from our matrix to figure out what of this two centers would be observed. To address this question additional experiments to collect excitation spectra of the samples should be performed, aiming to identify if Ce$^{3+}$ is playing a role in the energy diagram of the Te$^{4+}$ emissions we have presented in this work.

4. Conclusion

TZNL samples doped with Cerium oxide were prepared under air atmosphere. The experiments carried out confirmed the predominance of the amorphous phase in all samples, however it also indicated structural changes induced by the dopant. Such modification favored the crystallization of the sample at lower temperature than in the undoped sample and in a slightly increase of $T_g$. X-ray diffraction has show a consistence with the position
of the main lorentzian (28.7°) in the diffractograms for all samples, which is related to the Zinc content of the glass, but the decrease in its area with increasing Cerium concentration suggests some structural change induced by the dopant. An interesting luminescence center was observed and its origin attributed to Te$^{4+}$. Finally, even though Ce$^{3+}$ could not be detected by our FTIR measurements we do not discard the possibility that this ion is playing some role in the excitation/emissions mechanisms in TZNL doped samples. In order to clarify this question an emission/excitation study is needed, and we hope to accomplish that in a future work.

Figure 6: TZNL matrix and 0.10Ce luminescence spectra under 450 nm excitation and using a 500 nm longpass filter. The blue curve named TZN is from an additional sample prepared without Lanthanum oxide.
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