Novel Er^{3+} doped tellurite glass-ceramics

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ABSTRACT

Er^{3+} doped tellurite-based glasses were prepared using standard melting process and their physical, optical, thermal, optical and luminescence properties were measured and compared. We found that the addition of Na_2O in the TeO_2-ZnO system leads to higher emission at 1.5µm as compared to the addition of TeO_2, Bi_2O_3, BaO, Nb_2O_5. We found that Bi_2O_3 should be used in order to increase the intensity of the upconversion under 976 nm excitation. The glasses were heat treated in order to grow crystals in these glasses. Surface crystallization occurred upon heat treatment with the precipitation of multiple crystals, the composition of which depends on the glass composition. The heat treatment was found to have no impact on the intensity of the emission at 1.5 µm. However, it increases the intensity of the red upconversion, especially for Bi_2O_3 containing glass.

Keywords: tellurite glass, glass-ceramic, Er^{3+}, luminescence, upconversion

1. INTRODUCTION

Materials doped with Er^{3+} are of great interest due to the Er^{3+} intra-4f transitions, especially the one from $^4I_{13/2}$ to $^4I_{15/2}$ which corresponds to 1530 nm wavelength [1]. Er^{3+} ions can also be used to convert NIR radiation to shorter wavelengths due to the absorption of two or more photons, known as upconversion process [2l]. Therefore, Er^{3+} doped glasses can be useful materials for applications such as telecommunications, solar panels, spectroscopy, bio-imaging, just to cite a few [3].

Although silicate glasses remain the most commonly used glass hosts for rare-earth ions, efforts have been focused for the past few decades on Er^{3+} doped tellurite glasses as these glasses can be engineered with low melting point, good thermal stability and high transparency from visible to mid-IR, as compared to other glasses such as silicate glasses [4]. The tellurite glasses also possess large refractive indices. These properties can be modified by changing the glass composition. The addition of modifiers and/or intermediates in the glass network can have an impact on the structure of the glass host and also on the local environment around the Er^{3+} affecting then the luminescence properties of the glass [5]. The sites of Er^{3+} can be also modified by inducing crystal growth in the glass host. The crystals are typically obtained from a glass by heat treatment at a specific temperature above the glass transition temperature. If the crystalline phase of the desired nature and structure precipitates around the rare-earth ions, the spectroscopic properties of the glass-ceramic can be enhanced compared to their glassy counterpart [6]. The key factor during the preparation of a transparent glass–ceramic is the control of the growth of crystals with the desired composition, their size and segregation within the glassy volume. The crystals should also precipitate in the volume of the glass.

In this context, we report the study on the effect of the changes in the glass composition on the physical, thermal, luminescence properties of erbium-doped tellurite glasses. We also discuss the impact of the heat treatment on the luminescence properties of Er^{3+} ions.

2. EXPERIMENTAL

Tellurite glasses were prepared with the composition of $69.3TeO_2$-$9.9M_yO_x$-$19.8ZnO$-$1Er_2O_3$ (in mol %) where M_yO_x = Na_2O (labeled as Na glass), Bi_2O_3 (labeled as Bi glass), BaO (labeled as Ba glass), Nb_2O_5 (labeled as Nb glass) and TiO_2 (labeled as Ti glass). TeO_2, Bi_2O_3, BaO, Nb_2O_5, TiO_2, ZnO, Na_2CO_3 and Er_2O_3 (from Sigma Aldrich*)* were used as the raw materials. The 10 g batches were melted at 850°C for 10 minutes in Pt crucibles. After quenching, the glasses were annealed for 6h at 40°C below their respective T_g to release the stress from the quenching.

The thermal properties of the glasses were measured using Netzsch JUPITER F1 instrument. The glass transition temperature T_g was taken at the inflection point of the endotherm. The crystallization temperature T_p was taken at the maximum peak of the exotherm, and T_x at the onset of the crystallization peak. The heating rate was 10°C/min. The temperatures are given with an accuracy of ±3°C.

A UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu) was used to acquire the absorption spectra of the polished glasses. The absorption cross-section σ_{abs} (λ) was calculated using Equation 1:

$$\sigma_{Abs}(\lambda) = \frac{2.303}{NL}\log\left(\frac{I_0}{I}\right) \quad (1)$$

where, $\log(I_0/I)$ is the absorbance, L is the thickness of the sample (cm) and N is the rare-earth ion concentration (ions/cm^3). The Er^{3+} ions concentration was calculated from the measured density of the glasses. The accuracy of absorption cross-section measurement was ± 10%.

The upconversion and 1.5 μm emission spectra were measured using a JobinYvon iHR320 spectrometer fitted with a Hamamatsu P4631-02 detector. Glasses were excited at room temperature using a single mode fiber pigtailed laser diode (CM96UF76P-10R, Oclaro) emitting the light at 976 nm. To be able to compare the intensity of the emission, the measurements were performed on glasses crushed into powder.

The Panalytical EMPYREAN multipurpose X-Ray Diffractometer with a nickel filtered copper K-Alpha radiation was used to measure the XRD pattern of the glasses. The samples were crushed into fine powder and spread over a "zero-background holder" Si-plate. The spectra were obtained using the Bragg-Brentano geometry and by rotating the sample holder around the Phi-axis at a constant speed of 16 revolutions per minute.

3. RESULTS AND DISCUSSION

Glasses were prepared by adding Na_2O (Na glass), TiO_2 (Ti glass), Nb_2O_5 (Nb glass), BaO (Ba glass) and Bi_2O_3 (Bi glass) in order to check if the spectroscopic properties of the glass can be enhanced by changing the glass composition. The thermal and the physical properties of the glasses are summarized in the Table 1.

Table 1: Physical and thermal properties of the investigated glasses

Sample code	Density ±0.02 (g/cm^3)	T_g ±3 (°C)	T_x ±3 (°C)	T_p ±3 (°C)	ΔT (T_x-T_g) ±6 (°C)
Na	5.09	308	354	420	46
Ti	5.37	373	512	540	135
Nb	5.34	398	547	571	150
Ba	5.53	348	384	410	26
Bi	6.14	342	377	417	35

The glasses exhibit different densities, having a general trend: the heavier is additive element the larger is the density. The thermal properties of the glasses are presented in Table 1 as the determination of T_g, T_x, and T_p is essential to know the nucleation and growth rate of crystals. The measurement of the thermal properties allows one to calculate ΔT, an empirical parameter often used to determine if a glass has a good resistance towards crystallization as evidenced by its ΔT greater than 90 °C. According to the table 1, the Nb and the Ti samples are the most stable against crystallization due to their ΔT higher than 100°C.

The absorption spectra of the glasses in visible, around 980 and 1530 nm ranges are shown in Figure 1a, b and c, respectively.

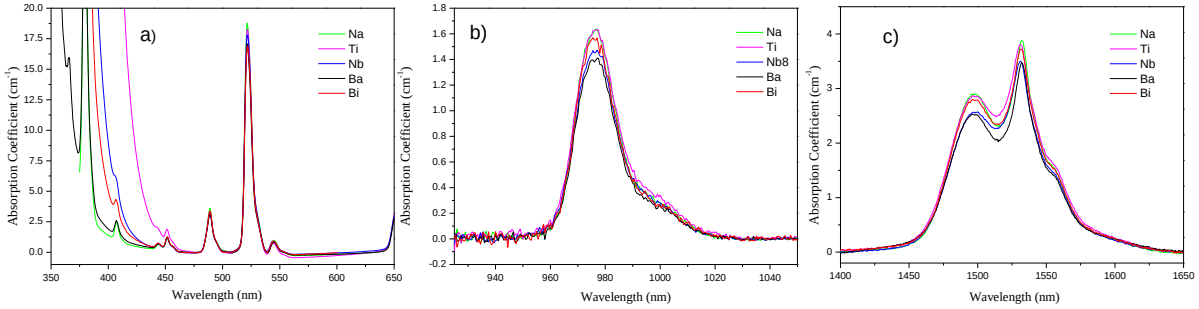

Figure 1. Absorption spectra of the glasses (a), and absorption bands centered at 980 nm (b) and centered at 1530 nm (c).

The spectra of the glasses exhibit absorption bands which are related to the 4f-4f transitions of the Er^{3+}ions. Changes of the UV-edge in Ti, Nb and Bi-glasses can be explained by the absorption due to presence of Ti^{3+}, Nb^{5+} and Bi^{3+} ions respectively. As shown in Figure 1b and c, the glasses exhibit similar shape of absorption bands indicating that the Er^{3+} ions have similar site in the glasses. Therefore, Te and Zn are suspected to be the main cationic neighbors of Er^{3+}. The absorption coefficients and cross-sections are presented in Table 2.

Table 2: Absorption coefficient (α) and cross-section(σ_{abs}) of the investigated glasses.

Sample code	**NEr^{3+} ±5% (10^{20}·ions/cm^3)**	**α at 980 nm (cm^{-1})**	**σ_{abs} at 980 nm ±10% (10^{-21}·cm^2)**	**α at 1530 nm (cm^{-1})**	**σ_{abs} at 1530 nm ±10% (10^{-21}·cm^2)**
Na	4.48	1.62	3.62	3.88	8.66
Ti	4.66	1.63	3.50	3.81	8.16
Nb	4.09	1.48	3.62	3.49	8.52
Ba	4.57	1.41	3.09	3.47	8.76
Bi	4.19	1.55	3.70	3.72	8.88

Within the accuracy of the measurement, the glasses exhibit similar absorption cross-section at 980 and 1530 nm. Figure 2a and c present the emission spectra of the glasses in IR and in visible, respectively.

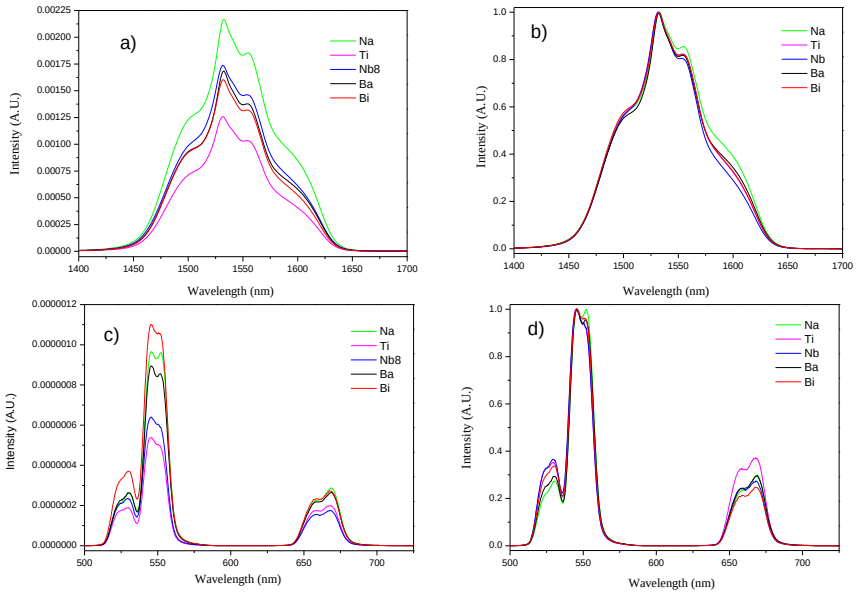

Figure 2: Emission spectra at 1.5 µm (a) and upconversion spectra (c) and normalized emission spectra at 1.5 µm (b) and normalized upconversion spectra (d) of the investigated glasses (λ_{exc}=976 nm).

The emission spectra of the glasses exhibit the typical emission band corresponding to the transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions located in amorphous site [7]. The glasses exhibit similar emission shape, indicating that Er^{3+} site in not strongly impacted by the composition (Figure 2b). However, a difference in intensity of the emission is noticeable. The Na and Ti glasses exhibit the highest and the lowest intensity of emission, respectively. As reported in [8], the addition of Na_2O in the tellurite glass is suspected to lead to the disruption of the tellurite network while the addition of TiO_2 is expected to reinforce the network due to the replacement of Te–O–Te inter-chain linkages by stronger Te–O–Ti bridges [9]. Therefore, these changes in the glass network might lead to different OH content and/or different Er-Er distance in the glasses and so to different intensity of the emission at centered at 1.5 µm. The upconversion spectra of the glasses are presented in Figures 2c and d. The spectra show two bands at 545 and 660 nm after excitation at 976 nm. These bands are due to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}, respectively. As shown in Figure 2d, the green upconversion is stronger than the red upconversion for all the glasses: the Bi glass having the highest green emission and the Ti glass the lowest. One can notice that the shape of the visible emissions is similar in all glasses confirming that the Er^{3+} sites are similar in all the glasses.

The glasses were heat treated at their T_g +20 for 17 h to form the nuclei and then at their T_p for 1 and 6 hours to grow the nuclei into crystals. The heat treatments were performed in air. The Na, Ti, Ba and Bi became opaque and look like glass-ceramics after 6 h at T_p. However, the heat-treated Nb glass became metallic after heat treatment and was excluded from the further investigation. All glasses were found to crystallize starting from the surface. The XRD patterns were measured in order to identify the crystals precipitating in the glasses. They are shown in Figure 3.

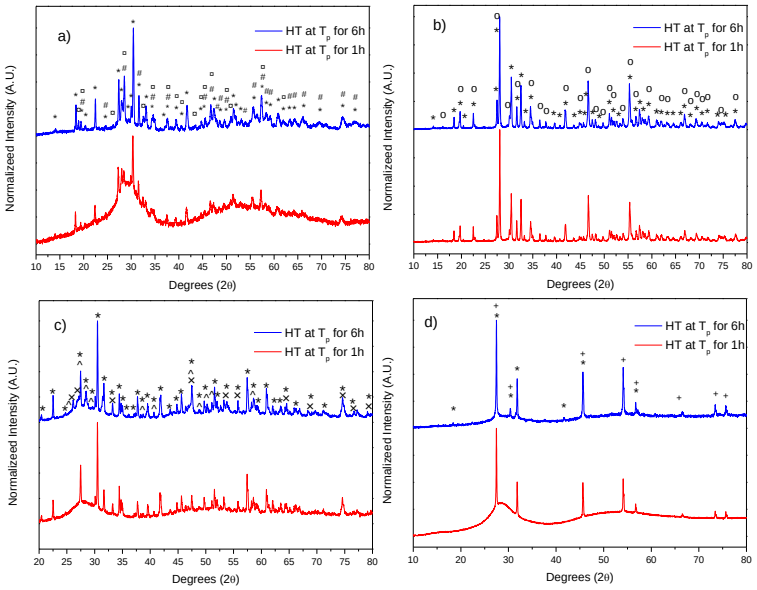

Figure 3. XRD pattern of the Na (a), Ti (b), Ba (c) and Bi (d) glasses heat treated at T_p for 1 h and 6 h.

All XRD pattern exhibit sharp peaks confirming that all the glasses crystallized during the heat treatment. They are all composed of the common phase $Zn_2Te_3O_8$ (*). This is also the main crystalline phase observed after crystallization of Na and Ba-glasses. The other peaks in the Na sample correspond to $ZnTeO_3$ (#), and $NaTe_3$ (¤). The peaks in Ba glass can be related to BaO (×) and $BaTe_2O_5$ (^). Ti sample also contains significant amount of $Zn_2Te_3O_8$ phase, however the most intense peaks in the pattern correspond to $TiTeO_3$ crystals (o). In the case of Bi glass, the main crystalline phase precipitating after the heat treatment is Bi_2O_3 (+), whereas $Zn_2Te_3O_8$ contribution can be seen only after 6h of the heat-treatment, in agreement with [10]. One should point out that Ti sample seems completely crystallized as the fingerprint of the glass has totally disappeared compared to the other glasses, especially Na glass.

The heat treatment was found to have no significant impact on the intensity of the emission centered at 1.5 µm within the accuracy of the measurement as presented in Figure 4.

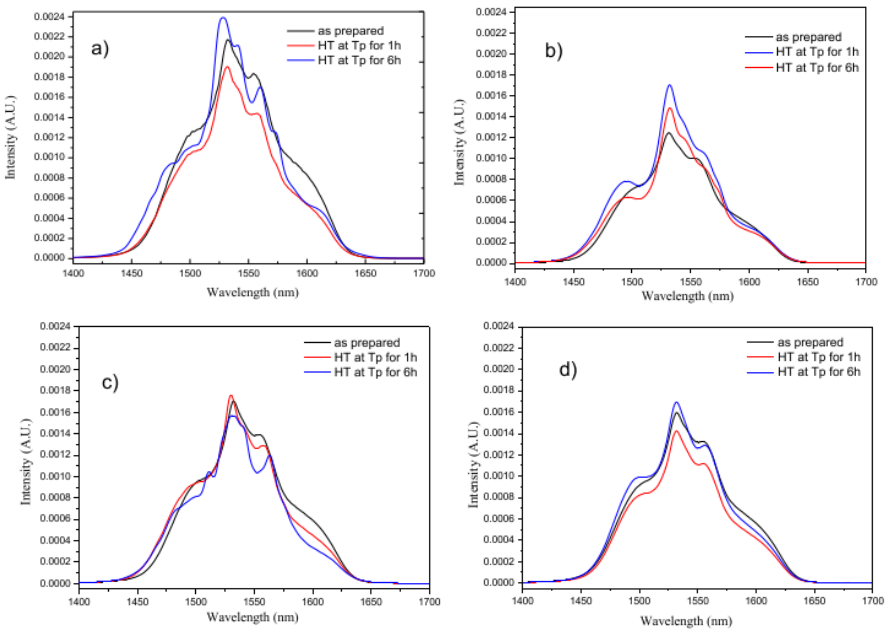

Figure 4. Emission spectra centered at 1.5 µm of the Na (a), Ti (b), Ba (c) and Bi (d) glasses after heat treatment (λ_{exc}=976 nm).

However, one can notice that the shape of the emission especially for the Na and Ba glasses changed after heat treatment: sharp peaks can be seen in the emission band of the heat treated glasses indicating changes in the Er^{3+} sites during the heat treatment. It is possible to think that Er^{3+} ions enter in some of the crystals precipitating in the Na and Ba glasses. Some changes of the emission bands can be seen from the Bi and Ti glasses but the emission bands are still broad indicating that most of the Er^{3+} ions might remain in amorphous site.

The upconversion spectra of the glasses after pumping at 976 nm can be found in Figure 5.

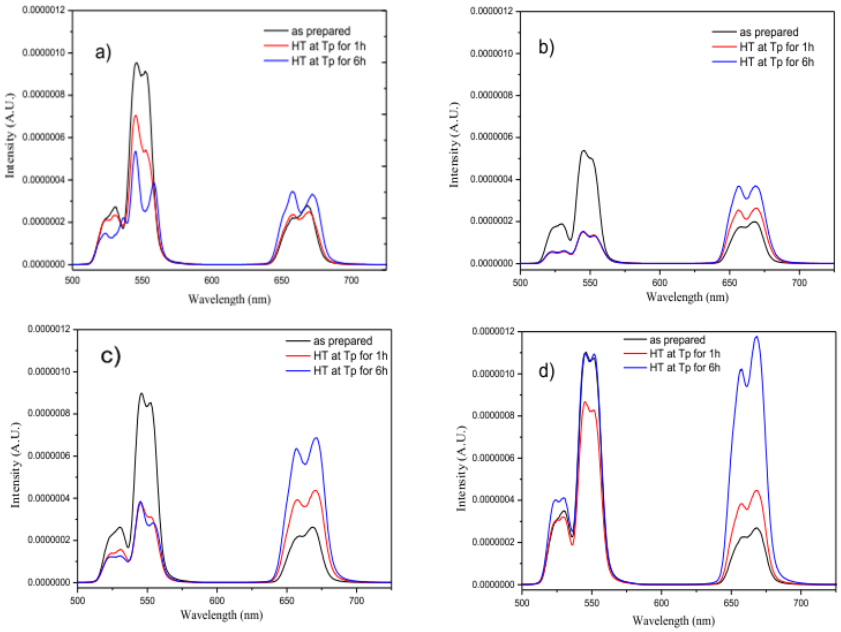

Figure 5. Upconversion spectra of the Na (a), Ti (b), Ba (c) and Bi (d) glasses after heat treatment (λ_{exc}=976 nm).

For all the glasses, the intensity of the green upconversion decreases while the intensity of the red upconversion increases after heat treatment. One should remind that the green emission band at 550nm is associated to a hypersensitive transition [11]. Therefore, changes in this emission tend to confirm that the site of the Er^{3+} ions is modified after heat treatment. It is clearly shown that the Bi glass-ceramic is a promising composition for red upconverter applications.

4. CONCLUSION

Glasses within the glass system 69.3 TeO_2- 9.9 M_xO_y- 19.8 ZnO- 1.0 Er_2O_3 (in mol %) where M_xO_y = Na_2O, Bi_2O_3, BaO, Nb_2O_5 and TiO_2 were prepared and characterized. From their emission at 1.5 μm, Er^{3+} ions are suspected to be surrounded by Te and Zn atoms in all the glasses. The Na glass was found to exhibit the highest emission centered at 1.5 μm and the Ti glass the lowest emission. The glasses were heat-treated at T_g+ 20°C for 17 h and then at T_p for 1 h and 6 h to produce glass-ceramics. All glasses exhibit surface crystallization with the precipitation of multiple crystals. $Zn_2Te_3O_8$ is the common phase found in all glasses, but the additives change significantly the devitrification behavior of the glass. Although the heat treatment has no impact on the intensity of the emission at 1.5 μm, it decreases the intensity of the green upconversion whereas it increases the intensity of the red upconversion, especially for the Bi glass. We clearly show that the Bi_2O_3 containing glass is a promising composition for red upconverter applications.

5. ACKNOWLEDGEMENT

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