



Structural and optical properties of cerium oxide doped barium bismuth borate glasses

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ABSTRACT

This study focuses on the characterization of heavy metal oxide glasses containing CeO₂ as dopant with the aim to enhance its density, as many optical applications of glasses (eg: heavy particles measurement in high energy physics) are heavily dependent on the density of the glass itself. Different concentrations of CeO₂ were added to a barium bismuth borate base glass and the relative structural and optical properties were studied. The structure of the obtained material was analysed by means of density measurement, molar volume calculation, X-Ray diffraction, thermal analysis and Raman spectroscopy. The results show that CeO₂ promotes the formation of a crystalline phase and improves the density of the base glass. Optical properties were studied, such as transmittance and luminescence, and the obtained results suggest that the crystalline formation scatters light transmittance through the sample, preventing luminescent emission. Further improvements in glass formulation have been suggested in order to enhance its optical properties together with its density.

1. Introduction

The interest in CeO₂ doped materials is continuously increasing and nowadays these materials are employed in advanced applications such as solid oxide fuel cells, dielectrics, biosensors and scintillators [1]. One of the most interesting aspects of cerium concerns the two valence states, Ce³⁺ and Ce⁴⁺, that occur in the glass network as a function of the type of host material as well as on the specific synthesis condition [2]. These oxidations states are responsible of a lot of final properties shown by the glass materials and its applications span different fields of interest. The principal mechanism behind the interest in cerium doped materials is the relevant charge transfer absorption (Ce⁴⁺ + e⁻ → Ce³⁺) in the UV–VIS spectral region [3]. The charge transfer between these two cerium oxidation states has been also related to the polaron hopping phenomenon observed in borate and lead borate glasses, demonstrating that CeO₂ could promote conductivity in a glass matrix, opening to potential electrical application of these glasses [4–7]. Moreover Ce³⁺ ion exhibits intense narrow-band intra-4f luminescence in a wide range of hosts, therefore CeO₂ doped glasses are also promising materials for photonic applications, due to the typical 5d–4f

emission [8–10]. As other lanthanides, cerium is characterized by a partially filled 4f shell that is shielded by 5s² and 5p⁶ electrons and due to the wide gap between 5d–4f energy levels, any cross-relaxation mechanism is absent as well as multiphonon relaxation of excitation population, leading Ce³⁺ as one of the most efficient luminescent ions. It has been demonstrated that presence of both Ce⁴⁺ and Ce³⁺ in the same glass composition results into enhanced luminescence properties: in borosilicate glasses Ce⁴⁺ acts as a quenching centre for the Ce³⁺ emission due its relevant charge transfer absorption [3]. For this reason, Y₃Al₅O₁₂: Ce³⁺, LaCl₃: Ce³⁺, Lu₂SiO₅: Ce³⁺ and some glasses activated with Ce³⁺ ions are widely commercialized as efficient phosphors and radiation scintillators [8–12].

As scintillators, borate glasses have been reported among the most interesting hosts for luminescent centres because of their high transparency and easy manufacturing for mass production, although the low-density values (< 5 g/cm³) displayed by these glasses strongly limit the detection of high energy particles, representing the main drawback of these glasses [8, 13]. To overcome this limit, in this study we focused the attention on the structural changes induced by the CeO₂ addition in a bismuth barium borate glass matrix. It is well known that chemical

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Table 1
Formulations of the investigated glasses (mol%).

| Sample | BaO | Bi ₂ O ₃ | B ₂ O ₃ | CeO ₂ |
|--------|-----|--------------------------------|-------------------------------|------------------|
| A1 | 20 | 19 | 60 | 1 |
| A2.5 | 20 | 17.5 | 60 | 2.5 |
| A5 | 20 | 15 | 60 | 5 |
| A7.5 | 20 | 12.5 | 60 | 7.5 |
| A10 | 20 | 10 | 60 | 10 |
| U | 20 | 20 | 60 | 0 |

composition of the glass host is a key aspect of the optical response of rare earth (RE) doped material due to the structural rearrangements induced by RE interacting with the other components of the glass matrix [13].

The aim of this work is to investigate the correlations between structural changes induced by increasing amounts of CeO₂ added to the 20BaO-(20-x)Bi₂O₃-60B₂O₃-xCeO₂ glass system with the final properties of the materials especially aiming at increased density which is a fundamental requirement for applications in high energy physics.

2. Materials and Methods

The glasses formulations investigated in this work are listed in Table 1. The previously studied U glass is the reference sample to which CeO₂ has been added as dopant in partial substitution of Bi₂O₃ [14, 15]. Samples name and composition are reported in Table 1.

All glasses were obtained from reagent grade compounds (Sigma-Aldrich) using a conventional melt-quenching technique. The following raw materials were employed: BaO (99.99%), Bi₂O₃ (99.99%), B₂O₃ (99.97%), CeO₂ (99.9%). After mixing for 15 min in an alumina jar, all batches were melted in a platinum crucible reaching temperatures of 1000 °C to 1250 °C, depending on the glass composition, for 180 min using a heating cycle of 10 °C/min. To achieve homogeneous mixing of all the constituents the crucible was shaken once after the first 90 min. Platinum was used in place of alumina for the crucible in order to avoid contamination with the borate melts, as this could potentially lead to drastic decrease of the final density due to the braking of the tetrahedral boron species. Subsequently, each melt was poured using a plate quenching technique in order to obtain thin samples (thickness = 1 mm) taking as reference the typical value of thickness employed in the manufacturing of scintillating materials for high energy physics to enhance optical transmission. Each melt was annealed 10 °C below its glass transition temperature (T_g) for 2 h to relieve thermal stress and to reduce the number of the defects in order to improve the transmittance of the final glass material. The annealing process was conducted inserting each glass specimen between two steel plates, pre-heated at 400 °C, into the furnace at the annealing temperature. From experimental observation, the pre-heating temperature of the steel plates at 400 °C is suitable for all the samples investigated in this study. Finally, each surface of each glass specimens was polished starting from a 400 mesh SiC abrasive paper up to 2500 mesh and polished with colloidal silica suspension (silica particle size = 3 μm), in order to avoid undesired scattering of light due to irregular surface roughness.

Density was measured through helium pycnometer (Quanta Chrome - Micropycnometer) using at least 1 cm³ of glass for each measure. The density value for each specimen and its standard deviation were obtained as the average of 15 repeated measures performed on the same specimen. Using the density value derived from the experimental characterization, the molar volume (V_m) was calculated for each glass by using formula [16]:

$$\text{Molar Volume (V}_m\text{)} = \frac{\sum_i^n x_i m_i}{\rho} \quad \left[\frac{\text{cm}^3}{\text{mol}} \right]$$

where x is the molar fraction and m is the weight of each component (i) of the glass formulation and ρ is the measured density. The same error

calculated for the average value of density was associated to the molar volume.

The thermal behaviour of each glass was measured using DSC analysis (Netzsch, DSC 404) performed in air at the heating rate of 10 °C/min on sample ground to an average particle size lower than 30 μm. The DSC measurements were carried out on ca. 30 mg of sample in a platinum crucible. The glass transition temperature (T_g) was calculated as the intersection between the tangent on to the initial straight line before baseline shifting and the tangent to the slope line. The error on such a measurement equals the sensitivity of the instrument (10 °C).

Raman scattering spectra of the glasses were measured at room temperature with a laser Raman spectroscopy (JASCO Co., NRS-3100) with solid state laser (520 nm wavelength). All the Raman spectra were normalized to allow the spectra comparison and were post-processed by a non-parametric background subtraction in order to correct intensity. Finally, intensity was normalized to the integrated area of the full spectrum.

Moreover, structural properties were investigated through X-Ray Diffraction (XRD, Bruker) by packing the finely ground samples into an aluminium sample holder at room temperature and scanning from 2θ = 10° to 75° with a step size of 0.01°2θ.

Optical transmittance spectra, in the range 400–700 nm with a resolution of 0.05 nm, were obtained using a UV-VIS spectrometer Ocean Optics, USB4000-XR1 / DH-2000-BAL using 1 mm thickness of glass. A JASCO FP6500 Spectrofluorometer, equipped with Xe lamp and photomultiplier tube as detector, was used to measure the photoluminescence spectra. The measured wavelength range was 220–750 nm with a resolution of 1 nm, the error on the measured intensity can be considered as 1%. All experimental characterizations were performed at room temperature, with the exception of thermal analysis. Furthermore, only the UV-VIS range has been considered for optical transmittance and photoluminescence this being the range of interest for the specific purpose of this study.

3. Results

Fig. 1 reports the XRD patterns of all the investigated glasses and it is possible to observe that most of the samples show the presence of a crystalline phase identified as Barium Cerium Oxide, BaCeO₃ (BCO). In fact, narrower and more defined peaks moving from A2.5 to A10 can be detected in the spectra corresponding to crystalline BaCeO₃. At the same time in all the investigated samples two glassy bands can be detected, at approximately 15°2 Theta and 25–30°2 Theta, typical of a borate glass structure where triangular BO₃ and tetragonal BO₄ units coexist [17]. A strong decrease in intensity of the latter glassy band can be observed in A5, A7.5 and A10 spectra.

Raman spectra analysis (Fig. 2) shows a narrow peak in the spectra at 460 cm⁻¹. The width of the Raman bands in a glassy material can be used as indicator of structural disorder: the higher the disorder, the wider the bands and vice versa [18]. This peak can therefore be associated with the presence of crystalline BaCeO₃. The main glassy broad bands detected are located in the range of 200–600 cm⁻¹ and they can be associated with bridged anion modes due to Bi-O-Bi vibrations. Therefore, the increasing of crystalline peak and the corresponding decreasing of the glassy bands in the range from 200 to 600 cm⁻¹ can be justified with an increased amount of CeO₂.

The density trend is reported in Fig. 3: circular markers are used to indicate the samples showing crystalline phases that cannot be compared directly to the glass samples, indicated with triangular markers in the same figures. For each property the average values are related to the amount of dopant with an estimated standard deviation of 1%. The average density values experimentally obtained falls in the range of 5.5–6.5 g/cm³ and nonlinear trend as a function of the increasing content of dopant can be observed. About molar volume the average values are in the range 17–23.5 cm³/mol. The highest density, that is one the main results expected from this research, is reached for A1.

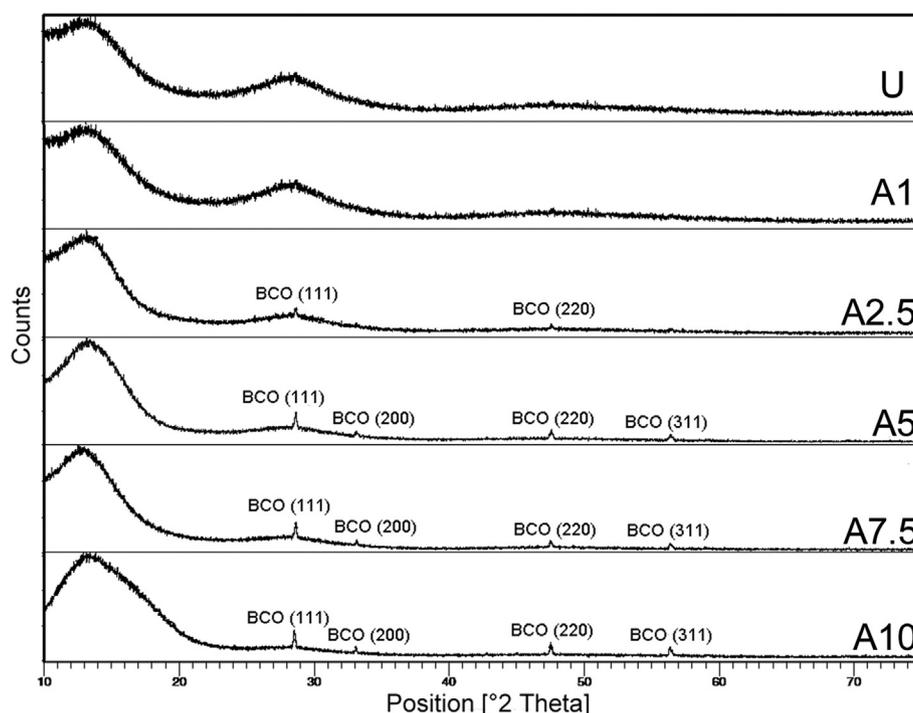


Fig. 1. XRD patterns of the investigated glasses. The identified crystalline phase is Barium Cerium Oxide (ICCD:01-075-0431) labelled as BCO.

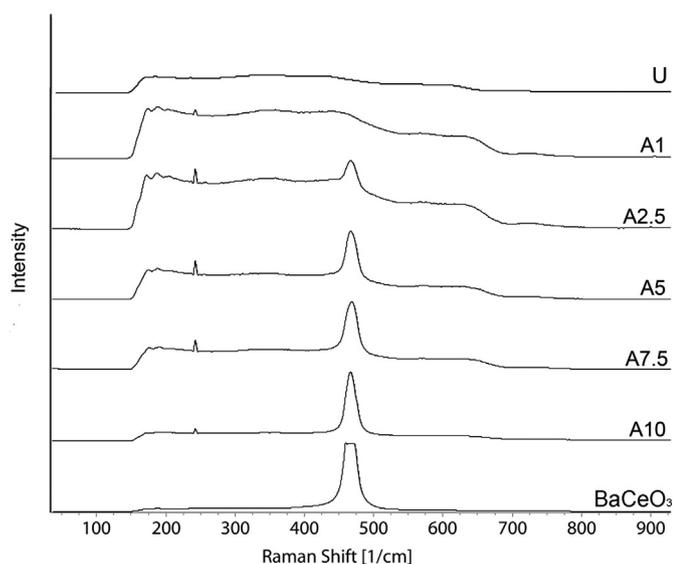


Fig. 2. Raman spectra of the investigated glasses.

The DSC spectra (in Fig. 4 the spectra of U, A1 and A10 are illustrated as an example) of all glasses show crystallisation peaks that come less small and broad with increasing dopant amount. This suggests a restrained tendency to crystallize for the sample without dopant, as already reported in other studies on bismuth borate glasses, that increases according to the dopant amount [19]. The numerical results of the thermal analysis have been detailed in Table 2 where the increase of T_g , T_c and T_m depending on the dopant concentration is reported.

The optical transmittance in the UV–VIS region, recorded at room temperature (Fig. 5) shows a strong lack of transmission when the dopant amount is increased above 5 mol% and this can be also seen in the pictures of the specimens reported in the same figure. It is worth noting that A1, A2.5 and A5 show a band edge at about 400 nm that is related to the Ce^{3+} content [20, 21]. Although the thickness of each sample has been kept as small as possible to avoid the inherent

absorbance due to long optical path length, the overall transmittance is very poor and falls below 15%.

Some preliminary luminescent properties, codified in terms of emission intensity at a specific excitation wavelength (406 nm), were performed on these glasses [22, 23]. The excitation spectrum shown in Fig. 6 reports a small excitation peak at 258 nm associated to the d-f emissions $^5D_1 \rightarrow ^2F_{5/2}$ or $^5D_4 \rightarrow ^2F_{7/2}$ [21]. The same peak can't be associated to the Bi^{+3} that could be recorded in the UV region, as demonstrated in previous work on the same glass system [14, 15]. Unfortunately, Fig. 7 clearly shows the absence of the specific emission peak. However, it is worth pointing out that the highest signal intensity is reached for the sample A5 which could be used as starting composition for the design and optimization of glasses for specific luminescence behaviour.

4. Discussion

From the results obtained from XRD and Raman analyses, it is clear that crystallisation occurs at CeO_2 concentrations higher than 1 mol% and that the amount of this crystalline phase increases with the increase of the CeO_2 content into the glass formulation. This result is consistent with the strong attitude of CeO_2 to arrange crystalline phases in the glass structure [24]. This crystalline phase has been identified as Barium Cerium Oxide through the XRD and Raman analyses. All the Raman spectra recorded (Fig. 2) do not contain the typical band at 806 cm^{-1} generally associated to the boroxol rings which result therefore to be absent in these samples [25]. The broad band identified in the range of $200\text{--}600\text{ cm}^{-1}$ is typical of a transverse optical mode, arising from the delocalized B–O stretch involving the boroxol rings network contribution [26–29]. In fact, it has been previously discussed that CeO_2 addition in glasses leads to the general increase of the oxygen availability in the network leading to a structure change from a trigonal BO_3 based environment into a tetrahedral BO_4 based one [30]. This trend is also confirmed by the decrease of the glassy band in the XRD spectra around $25\text{--}30^\circ 2\text{ Theta}$. About physical properties such as density and molar volume a strong distinction must be made between the samples that show BCO as a crystalline phase and the others. Taking in

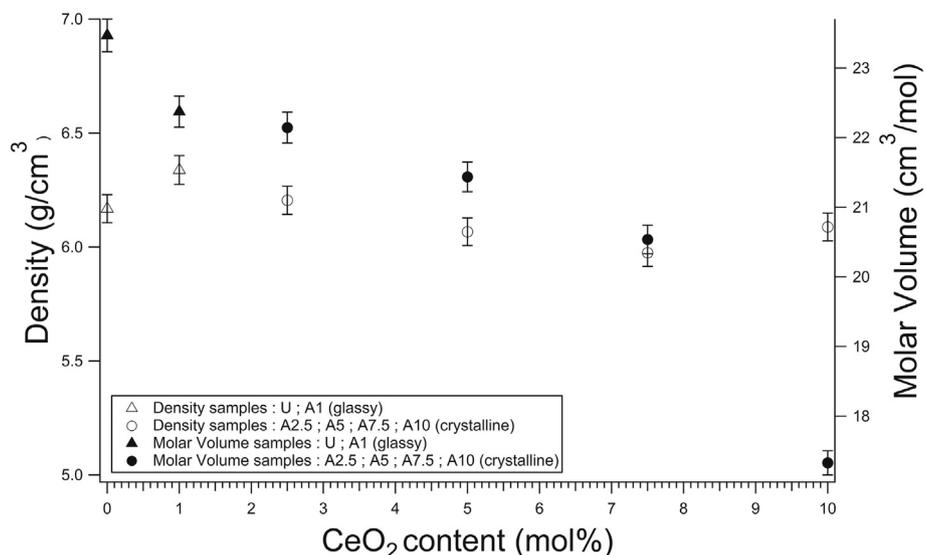


Fig. 3. Density and Molar Volume vs mol% of CeO₂.

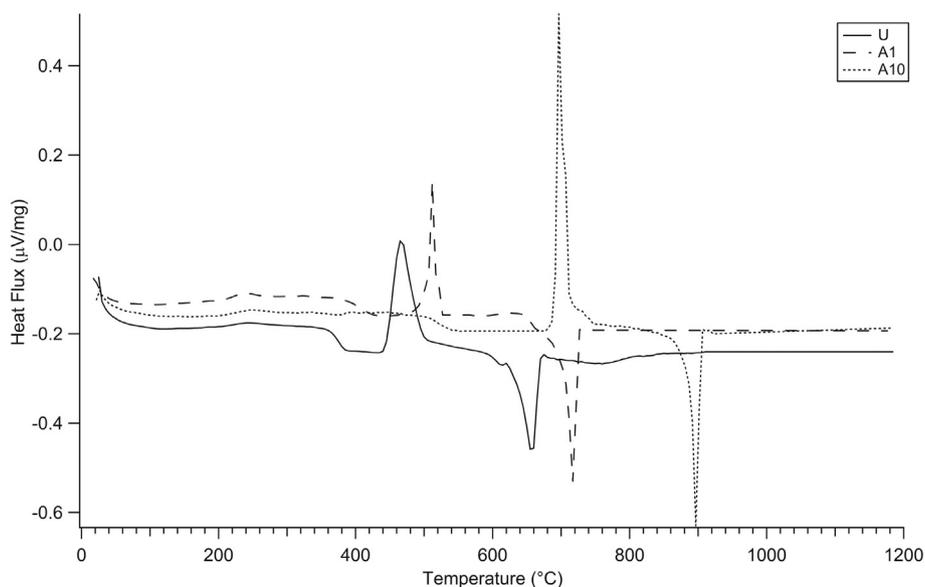


Fig. 4. DSC curves of samples U, A1 and A10. Instrument sensitivity equal to 10 °C.

Table 2
T_g T_c and T_m of all the investigated samples (associated uncertain ± 10 °C).

| Sample | T _g (°C) | T _c (°C) | T _m (°C) |
|--------|---------------------|---------------------|---------------------|
| U | 380 | 470 | 660 |
| A1 | 400 | 520 | 710 |
| A2.5 | 420 | 550 | 750 |
| A5 | 460 | 570 | 810 |
| A7.5 | 500 | 640 | 890 |
| A10 | 525 | 700 | 900 |

account the results shown in Fig. 3 an increase in density can be observed for the glassy samples if the dopant is increased, whereas the opposite for the semi-crystalline samples. Previous studies on CeO₂ doped barium borate glasses have shown an increased density with increasing concentration of cerium in substitution of barium oxide [31]. This effect, for totally glassy samples, has been attributed to the shift of the boron group from BO₃ to BO₄ and to the presence of Ce⁴⁺ groups in the interstitial position of glass network which promotes an increase of the compactness of the structure [34]. This explanation is coherent with

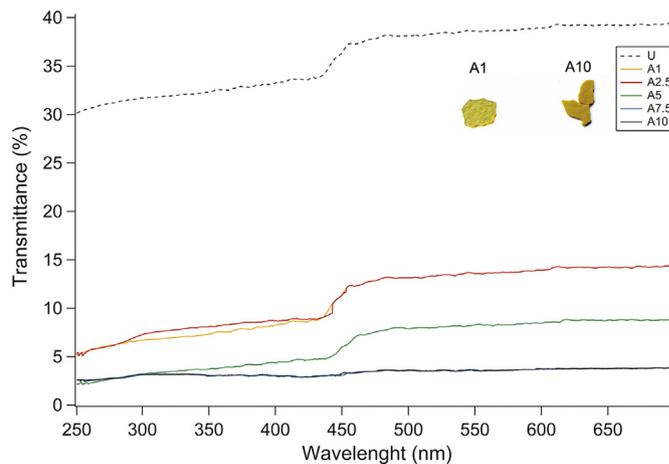


Fig. 5. Optical transmittance of the investigated glasses in the UV-VIS region.

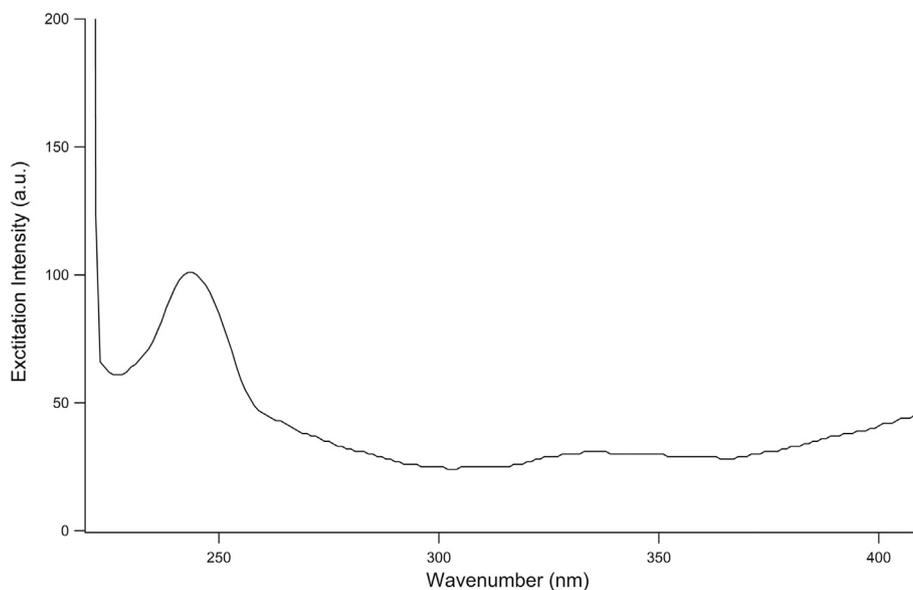


Fig. 6. Excitation spectrum of the investigated glasses ($\lambda = 406$ nm).

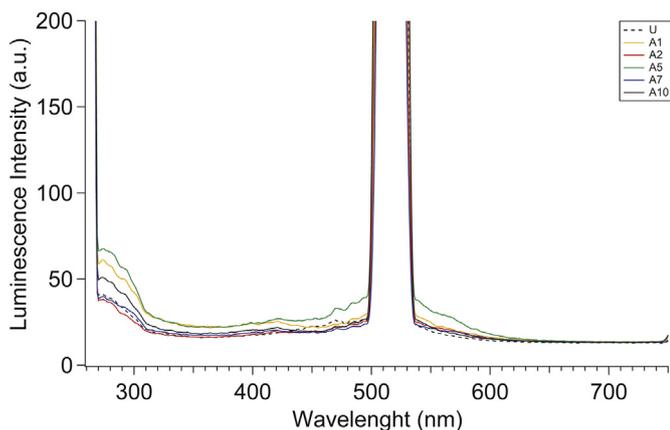


Fig. 7. Luminescence spectra of the investigated glasses (λ_{ex} : 258 nm).

the data obtained from Raman characterization for glass containing the lowest amount of CeO_2 (1 mol%). Fig. 3 clearly indicates that density decreases linearly with increasing amounts of CeO_2 in those samples showing crystalline phase. This trend is also confirmed considering that the CeO_2 density is equal to 7.22 g/cm^3 and therefore greater than the density of the glass matrix (6.25 g/cm^3) [32]; on the contrary the density of the identified crystalline phase (BaCeO_3) is 6.36 g/cm^3 and therefore lower than CeO_2 density [33]. At the same time the molar volume decreases when the CeO_2 content is increased and this can be associated to a structural rearrangement promoting a more packed structure that is coherent with the crystalline phases detection from XRD analysis. Molar weight must be taken into account when measuring glass density, and in this case the decreasing the molar volume cannot be related to the increase of the density due to the CeO_2 addition, and this because CeO_2 has been added in substitution of Bi_2O_3 that has a significantly higher molar weight with respect of CeO_2 (465.96 g/mol vs 172.11 g/mol). The DSC curves (of the thermal analysis) confirm an enhanced tendency to crystallisation when the dopant is increased, and the numerical results, listed in Table 2, confirm an almost linear increase of T_g , T_c and T_m when increasing of the dopant concentration. This result is consistent with the more packed structure promoted CeO_2 and is aligned with what we have previously discussed for density and molar volume trends. Moreover, it must be considered that the melting temperature of cerium oxide is considerably higher than the one of

bismuth oxide and therefore the melting temperature of the formulation is affected in the same way. The structural modifications induced by ceria addition have also been studied analysing the optical properties of the final glasses. The transmittance of light in glass for high optical application must be enhanced in order to achieve particle detection, signal optimization and therefore in order to maximize the efficiency of the detector. With this in mind samples A1 and A2.5 show in general the best results and should be considered as the best candidates. Moreover, also the measurement of the refractive index of each specimen (data not reported) suggests that a lack of transmittance is also due to an increasing phenomenon of light scattering due the difference of refractive index estimated equal at least 0.06 between doped and undoped glass samples. Furthermore, a cut off wavelength can be observed depending on glass composition and falling at about 400 nm, attributed to the characteristic peak of Ce^{3+} which generates a yellowish appearance [21]. From a luminescent spectrum it is possible to evaluate the intensity of an emission phenomenon at a particular wavelength, considering the presence of one or more peaks of emission. The obtained results point out the absence of any peak of luminescent emission. Although an excitation phenomenon is activated, we must consider the possibility that this particular glass matrix acts as a shield for luminescent emission, absorbing it, in this way all the emission investigated in this study are non-radiative in the UV–VIS region [15]. But it can be noted that for samples A1 and A5 the intensity of the shoulders near the excitation peaks, are greater than the others despite the weak transmittance. It can be concluded that for CeO_2 doped glass the crystallinity degree plays a key role in the optical property and nevertheless the weak transmittance of sample A1, the one without crystalline phase, can be taken in account as best candidate considering the overall results, and in particular in terms of density reaching an average value of 6.4 g/cm^3 .

5. Conclusions

This paper illustrates a systematic investigation of CeO_2 addition to a $20\text{BaO}-(20-x)\text{Bi}_2\text{O}_3-60\text{B}_2\text{O}_3-x\text{CeO}_2$ glass system. Structural, thermal and optical properties were measured, and the obtained results were discussed. One of the first interesting findings is that the density of this kind of glasses can be enhanced with small quantity of CeO_2 as dopant. This trend cannot be associated to the CeO_2 addition because it enters in substitution of heavier oxide (Bi_2O_3). As a matter of fact, the results in terms of density and molar volume illustrated above clearly support

the presence of structural rearrangements promoting a more compact network in glasses as a function of CeO₂ increasing content. This is confirmed also by Raman spectroscopy and thermal analysis. Above 1 mol% of dopant crystalline BaCeO₃ is detected into the glass as confirmed by XRD measurements. The presence of this crystalline phases further promotes a highly interconnected network which leads to a more packed structure (confirmed also by the V_m trend). The overall results suggest that the best candidate for future studies about glasses for high energy physics containing cerium is the glass with 1 mol% CeO₂ content reaching the highest density measured in this work and associated with the best perspective in terms of optical properties, even if further improvements must be done in order to promote glass transmittance and emission in the UV-VIS.

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