



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

Silvia Barbi^{a,*}, Consuelo Mugoni^b, Monia Montorsi^c, Mario Affatigato^d, Corrado Gatto^e, Cristina Siligardi^b

^a Interdepartmental centre for applied research and services in advanced mechanics and motoring, Modena 41125, Italy

^b Department of Engineering “E. Ferrari”, University of Modena and Reggio Emilia, Modena 41125, Italy

^c Department of Science and Methods for Engineering, University of Modena and Reggio Emilia, Reggio Emilia 42122, Italy

^d Physics Department, Coe College, Cedar Rapids, IA 52402, United States

^e Italian National Institute for Nuclear Physics, Naples 80126, Italy



ARTICLE INFO

Keywords:

Cerium oxide
Borate
Structure
Density

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

* Corresponding author.

E-mail address: silvia.barbi@unimore.it (S. Barbi).

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]:

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

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 $2\theta = 10^\circ$ to 75° with a step size of $0.01^\circ 2\theta$.

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 $15^\circ 2\theta$ and $25\text{--}30^\circ 2\theta$, 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 $200\text{--}600 \text{ cm}^{-1}$ 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 $5.5\text{--}6.5 \text{ g/cm}^3$ 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 $17\text{--}23.5 \text{ cm}^3/\text{mol}$. The highest density, that is one the main results expected from this research, is reached for A1.

Download English Version:

<https://daneshyari.com/en/article/7899543>

Download Persian Version:

<https://daneshyari.com/article/7899543>

[Daneshyari.com](https://daneshyari.com)