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Structure and luminescence properties of Dy_2O_3 doped bismuth-borate glasses

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ABSTRACT

In this work heavy bismuth-borate glasses were studied as host matrices of Dy_2O_3 rare earth, for potential application as scintillator materials in high energy physics experiments and in general radiation detection systems. Glass matrices were prepared from 20BaO-xBi_2O_3-(80-x)B_2O_3 (x = 20, 30, 40 mol%) ternary systems and synthesized by the melt-quenching method at different temperatures in order to obtain high density and high transparency in the UV/Vis range. Particularly, the glass manifesting the higher transparency and with sufficiently high density was doped with Dy_2O_3 (2.5 and 5 mol%) in order to induce the luminescence characteristics. The effects of Bi_2O_3 and Dy_2O_3 on density, thermal behaviour, transmission as well as luminescence properties under UV excitation, were investigated.

The experimental results show that the synthesized glasses can be considered promising candidate materials as dense scintillators, due to the Dy^{3+} centres emission.

1. Introduction

Inorganic glasses are potential sources of affordable scintillators for particle physics. However, in calorimetric applications for high energy physics other specific properties such as high density and high transparency, over the near-ultraviolet and visible regions, need to be possessed [1,2]. In fact, larger densities result in an increased radiation absorption cross-section and, consequently, an improved signal-to-noise ratio [3–6], while high transparency avoids losses through light scattering caused by heterogeneities like grain boundaries, composition gradients and lattice imperfections. Glasses containing rare earths are promising alternatives to single crystals and ceramic and plastic scintillators due to their low-cost production and ease of manufacturing in different sizes and shapes [5]. The main disadvantage of existing oxide glass scintillators is their low density, typically below 4 g/cm^3 [7,8], that significantly limits their applications in radiation detectors. However, the introduction of heavy components such as lead as PbO or PbF_2 and Bi_2O_3 allows the density of the glasses to be easily increased to more than 6.0 g/cm^3, that is desirable for the most applications. In spite of the above mentioned advantages, lead containing glasses are considered to be toxic and incompatible with the principles of green chemistry and sustainable development [9]. Consequently, they are currently being removed from various practical applications and replaced by others glass systems such as bismuthate glasses [10] and germanate glasses [11].

The aim of this work is the development of a glassy material with high density and luminescent properties. Particularly, barium bismuth borate glasses containing dysprosium as rare earth were synthesized via the melt-quenching method. Boron oxide was selected as glass former for its extensive glass formation range, high transparency, high thermal and radiation stability [12]. The melting process was conducted in a Pt crucible instead of alumina to avoid any possible reaction with the borate melts that could potentially lead to drastic decrease of the final density by destruction of tetrahedral boron species [13,14]. The transparent glasses were characterized in terms of density, molar volume, X-Ray Diffraction (XRD), differential thermal analysis (DTA), UV-VIS spectroscopy and luminescence properties.

2. Method

Homogeneous glasses belonging to 20BaO-xBi_2O_3-(80-x)B_2O_3 system (BB series) and doped with different amounts of Dy_2O_3 (20BaO-(x-y)Bi_2O_3-yDy_2O_3-(80-x-y)B_2O_3, BBD series) were prepared by the following procedure. Firstly, appropriate amount of $BaCO_3$ (Alfa Aesar, 99.99%), Bi_2O_3 (Alfa Aesar, 99.99%), H_3BO_3 (Alfa Aesar, 99.99%) and Dy_2O_3 (Alfa Aesar, 99.99%) were mixed for 15 min in an alumina jar,

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Table 1
Ternary glass compositions (expressed in mol%), sample ID, melting temperature (T_M) and appearance.

Composition	Sample ID	T_M (°C)	Appearance
$20BaO\text{-}20Bi_2O_3\text{-}60B_2O_3$	BB-20	950	Pale yellow
$20BaO\text{-}20Bi_2O_3\text{-}60B_2O_3$		1050	Pale yellow
$20BaO\text{-}20Bi_2O_3\text{-}60B_2O_3$		1100	Light yellow
$20BaO\text{-}20Bi_2O_3\text{-}60B_2O_3$		1200	Dark
$20BaO\text{-}30Bi_2O_3\text{-}50B_2O_3$	BB-30	950	Light yellow
$20BaO\text{-}30Bi_2O_3\text{-}50B_2O_3$		1050	Amber
$20BaO\text{-}30Bi_2O_3\text{-}50B_2O_3$		1100	Amber
$20BaO\text{-}30Bi_2O_3\text{-}50B_2O_3$		1200	Dark
$20BaO\text{-}40Bi_2O_3\text{-}40B_2O_3$	BB-40	950	Amber
$20BaO\text{-}40Bi_2O_3\text{-}40B_2O_3$		1050	Amber
$20BaO\text{-}40Bi_2O_3\text{-}40B_2O_3$		1100	Amber
$20BaO\text{-}40Bi_2O_3\text{-}40B_2O_3$		1200	Dark

Table 2
Compositions of glasses containing Dy_2O_3 (expressed in mol%), holding times tested at the melting temperature of 1050 °C and sample ID.

Composition	Holding time (h)	Sample ID
$20BaO\text{-}17.5Bi_2O_3\text{-}60B_2O_3\text{-}2.5Dy_2O_3$	1	1BBD-17.5
$20BaO\text{-}17.5Bi_2O_3\text{-}60B_2O_3\text{-}2.5Dy_2O_3$	3	3BBD-17.5
$20BaO\text{-}17.5Bi_2O_3\text{-}60B_2O_3\text{-}2.5Dy_2O_3$	6	6BBD-17.5
$20BaO\text{-}15Bi_2O_3\text{-}60B_2O_3\text{-}5Dy_2O_3$	1	1BBD-15
$20BaO\text{-}15Bi_2O_3\text{-}60B_2O_3\text{-}5Dy_2O_3$	3	3BBD-15
$20BaO\text{-}15Bi_2O_3\text{-}60B_2O_3\text{-}5Dy_2O_3$	6	6BBD-15

according to the target glass composition (Tables 1 and 2), and synthesized by the melt-quenching method. Melting of the glasses was performed in an electrical furnace (Lenton, mod. EHF 17/17) under air atmosphere. Subsequently, the melt was poured onto a graphite mould and the obtained bulk samples were annealed at 10 °C below their glass transition temperature (T_g) in order to relieve the thermal stress and to reduce the number of the defects thus, improving the transmittance of the final glassy materials.

In detail, the glasses belonging to BB series were synthesized at different melting temperatures 950, 1050, 1100 and 1200 °C for 1 h as illustrated in Table 1, with a heating cycle of 10 °C per minutes from room to the melting temperatures. Different melting temperatures were tested in order to monitor the aesthetic properties of glasses in terms of colour and transparency, considering their well-known dependence on the oxidation-reduction equilibrium of bismuth. Subsequently, the glass with the higher transparency and a sufficiently high density (BB20) was selected as the host matrix for scintillating Dy_2O_3. Different amounts of Dy_2O_3 (2.5 and 5 mol%) were added to the batch compositions, replacing Bi_2O_3 (Table 2) and the raw materials were melted at 1050 °C employing three different holding times (1, 3 and 6 h). In this way, the effect of melting duration on glasses transparency and homogeneity was monitored, according with recent scientific literature [15].

The densities of the glass specimens were measured by the Archimedes method on five different samples for each glass composition. The molar volume (V_M) and the oxygen packing density (O) of each glass were evaluated from the density (ρ) and the molecular weight (M) according to the following Eqs. (1) and (2) respectively:

$$V_M = (\Sigma_i\ n_i M_i)/\rho \quad (1)$$

$$O = (\rho/M) \times n, \quad (2)$$

where n_i is the molar fraction of the oxide component, i, M_i its molecular weight, and d is the glass density and n is the number of oxygen atoms per formula unit.

The mineralogical analysis was performed by X-ray diffraction (XRD) in order to understand the nature of the studied samples. XRD patterns were collected using a powder diffractometer (Philips PW3710) with a Ni-filtered Cu Kα radiation in the 10–80° 2θ range, step size 0.02° and 3 s time step. The thermal properties of the glassy materials were determined with a Netzsch, STA 409 differential thermal analyser (DTA) on sample ground to an average particle size of less than 30 μm. The DTA measurements were carried out on ca. 30 mg of sample in a Pt crucible. Bulk samples of 1 × 1 × 1 cm^3 were prepared and polished with SiC abrasive papers and 0.03 μm alumina paste in order to decrease the surface roughness, that is desired for the optical and luminescence properties. UV–visible absorption spectra were acquired in the wavelength range of 200–1100 nm by using Ocean Optics HR4000CG-UV-NIR spectrophotometer equipped with ocean optics DH-2000-BAL (Balanced Deuterium Tungsten Halogen Light Source) lamp. The absorption coefficient, α (ω) was calculated as a function of wavelength considering the following equation:

$$\ln T = -\alpha\ t \quad (3)$$

where t is the sample thickness.

The band gap was determined from the UV–Vis spectra by considering the relationship reported below:

$$(\alpha h\upsilon)^n = h\upsilon - E_{opt} \quad (4)$$

where α is an energy independent constant, E_{opt} is optical band gap energy and the exponent $n = 1/2$ denote the allowed direct transition.

The theoretical optical basicity (Λ_{th}) was, also, calculated on the basis of the following equation proposed by Duffy and Ingram [16].

$$\Lambda_{th} = X_1\Lambda_1 + X_2\Lambda_2 + \ldots X_n\Lambda_n \quad (5)$$

where X_1, X_2,…, and X_n are equivalent fractions based on the amount of oxygen in each oxide contributing to the overall material stoichiometry and Λ_1, Λ_2, …, and Λ_n are the basicities assigned to the individual oxides.

The luminescence properties under UV excitation were studied with a UV–Vis spectrophotometer. The emitted scintillating light has been detected by a photodetector (either a PMT or an SiPM) and recorded with a custom Data Acquisition (DAQ) systems (PADE) developed by Fermilab Electronics support group. The resolution of fluorescence excitation and emission measurements is 0.2 nm.

3. Results

The obtained glasses were transparent and completely free of bubbles, except those melted at 1200 °C. In the BB series the colour changed with the composition and the melting temperature (Table 1). In particular, it varied from pale yellow to amber by increasing the amount of Bi_2O_3 or the temperature from 950 to 1100 °C, becoming dark at 1200 °C independently by the starting composition. The synthesis of BB series conducted at 1050 °C allowed obtaining at the same time transparent, homogeneous and high density samples thus, in the present paper the following discussion is focused on these glasses. Among these, the BB-20 glass (containing 20 mol% of Bi_2O_3) was selected as the best glass matrix to accommodate Dy_2O_3 (BBD series) for their higher transparency and homogeneity with respect to the other glasses as well as high density. The substitution of Bi_2O_3 by 2.5 and 5 mol% of Dy_2O_3 in the BBD series does not produce any significant change in the glass colour.

3.1. X-ray powder diffraction (XRD)

The X-Ray powder diffraction confirmed the vitreous nature of all the samples obtained at 1050 °C. In Fig. 1 the spectrum of BB-20 is illustrated as an example. The bands detected at approximately 25–30°2theta and 45–50°2theta, are typical of a borate glass structure where BO_3 and BO_4 units coexist [17].

3.2. Density (ρ), molar volume (V_M) and packing oxygen (O)

Density of glass is generally explained in terms of competition