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Structural and optical properties of rare-earths doped barium bismuth borate glasses

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ABSTRACT

Recently, great importance has been devoted to different glass systems doped with rare-earth ions because of their peculiar properties, in particular in the field of high-energy physics for particle energy measurement. The purpose of the present study was to investigate the optical and physical properties of Dy^{3+}, Er^{3+}, Nd^{3+} doped glasses belonging to the $20BaO\text{-}20Bi_2O_3\text{-}60B_2O_3$ system in which several rare-earths oxide concentrations were added to encounter the requirements for particle energy measurement. High density, low refractive index, high emission intensity (or high scintillation yield) are required for this purpose. Moreover, molar volume, glass transition and melting temperatures, X-ray diffraction and Raman spectra were measured and discussed in order to characterize the glass state. All the properties measured have shown a non-linear trend moving from 1 mol% to 10 mol% of rare-earths content. At the same time comparison between the trend derived by samples with same stoichiometry but containing different rare earths highlight different behaviors. In particular the highest density has been reached with the glass where Dy_2O_3 is at 2,5 mol%.

1. Introduction

The more recent discoveries in particle physic have been reached during development of innovative materials. Glasses suitable for hadronic calorimeter can be absolutely part of this group of materials because, thanks to its optical property, they can substitute very high priced single crystal detectors, opening to further possibilities in this research field. Historically, visual scintillation was employed through materials such as $CaWO_4$ [1,2] and ZnS [3] during the Rutherford's experiment. Taking in account the new generation of high energy physics (HEP) experiments the development of suitable scintillators such as bismuth germanate (BGO) [4], cesium iodide (CsI) [5–8], barium fluoride (BaF_2) [9,10], cerium fluoride (CeF_3) [11,12] and lead tungstate, $PbWO_4$, (PWO) [13,14] played a key role. Nowadays, modern detectors require very tight specifications that need multi-disciplinary efforts to develop suitable scintillators at an industrial scale. The improvements about scintillating material in HEP could be one of the key point to develop faster and more efficient devices for other application such as industrial and medical imaging devices. Three key points are fundamental to select luminescent material suitable for HEP [15,16]: density, scintillation properties, cost and environmental sustainability. The density of such material has to be higher than > 5 g/cm^3 to favor high compactness of the calorimeter which is essential to reduce the detector volume and high density results in an increased X-ray absorption cross-section and the signal-to-noise ratio [17–18]. A compact material will reduce the lateral spread of the shower in a high-magnetic field. Moreover, the stopping power of the materials, on the particles to be detected, is related to the compactness of the crystal lattice, keeping the atomic number (Z) of the component not too large, in order to reduce the lateral shower size. In fact, usually the Moliere Radius (R_m) is taken into account in the design of materials for calorimeters, because a small R_m means lower contamination of the energy measurement by other particles, which help for position reconstruction. R_m is defined experimentally by the equation $R_m \approx X_0 (Z + 1.2) / 37.74$ where X_0 is the radiation length. In high density material $\times_0$ is usually small and also Z must be not too large, to obtain a small R_m.

About the scintillation properties and radiation hardness, in order to

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obtain strong data from the particle detector, the emission light yield and the energy resolution must be as much high as possible. The emission light yield is also dependent by the geometry of the calorimeter and generally a light emission in the UV–VIS area will reduce the problems of light collection, for this reason the optical transmittance of the material in the UV–VIS region should be very high. The energy resolution of the calorimeter is affected by any source of non-uniformity of the material. For this reason, intrinsic scintillators materials should be preferred as it is easier to control the light yield uniformity in long geometry, and a controlled distribution of the doping scintillating compound could help to correct non-uniformity in the light collection in a pointing geometry. The light collection in a pointing geometry will introduce non-uniformity due to the focusing effect, which depends on the refractive index of the material. Fluoride crystals and glasses, with refractive index around 1.5, will limit this effect to a much smaller value (and therefore make it much easier to correct) than for the BGO (refractive index 2.15) or PWO (refractive index 2.3) [13,14].

Although hadronic calorimeters cover a market niche, their costs and environmental sustainability become fundamental due to the large volume (several cubic meters) used for such detectors. The main costs associate to the detector development derives from the raw materials and its manipulation to obtain the suitable final material, as well as from the cost of disposal or recycle. For example, notwithstanding the high efficiency of lutetium crystal for HEP, its application was discarded due to the high cost of the raw material. On the contrary, based on economic perspective, cerium and lead represent a valid choice due to their easy availability on the market at low prices. Moreover, considering the costs of the energy, crystals that can be grown with cheap methods and low-cost crucibles are favorable than the others. In order to limit also the processability costs crystals or glasses with low melting point but good mechanical properties, such as some lead compound (PbF_2 and $PbWO_4$), was used [13,14]. Recently environmental sustainability studies have been taken in account into the materials criteria selection for HEP and lead-free samples will be favored.

Considering glasses materials one of the main challenging point is about density that have to be higher than 5 g/cm^3 in hadronic calorimeter detectors to detect the particles. Unfortunately, the typical density of glass, such as silicate glass, is around 2–3 g/cm^3. Moreover, the scintillating properties of these materials must be enhanced through the use of dopants homogeneously distributed avoiding presence of aggregates, impurities or crystalline phases. For this reason, also the structural properties must be properly considered. Starting from high density and enhanced scintillating properties that are required for hadronic calorimeter respectively, heavy metals and rare earths (RE) have been mixed in order to obtain glasses. Specifically, Dy_2O_3, Nd_2O_3 and Er_2O_3 have been chosen as dopants according to the wide literatures in which these oxides have been commonly used in optical application [19–31]. Therefore, the purpose of the present study was to investigate how different rare earths such as Dy^{3+}, Er^{3+}, Nd^{3+} affect the glass density properties of a barium bismuth borate base glass encountering one of the main requirement for the investigated application. Furthermore the luminescent properties were evaluated as a function of rare-earths oxide concentrations. Beyond the very specific behavior of the rare earths considered, also the influence of the base glass must be taken in account to avoid potential undesired effects such as quenching. Compositional (three different dopants) and concentration effect of RE were systematically investigated starting from a basic glass: $20BaO\text{-}20Bi_2O_3\text{-}60B_2O_3$. In particular density, refractive index (RI), optical transmittance and emission intensity have been investigated and discussed considering the requirements needed for HEP and their possible employment. Moreover, molar volume, glass transition and melting temperatures, X-ray diffraction, and Raman spectra have been measured and discussed in order to correlate the glass state with the final optical properties.

Table 1
List of the investigated glass compositions (mol%).

Series with Dy_2O_3 as rare earth (A)				
Sample	BaO	Bi_2O_3	B_2O_3	Dy_2O_3
A1	20	19	60	1
A2	20	17.5	60	2.5
A5	20	15	60	5
A7	20	12.5	60	7.5
A10	20	10	60	10

Series with Er_2O_3 as rare earth (B)				
Sample	BaO	Bi_2O_3	B_2O_3	Er_2O_3
B1	20	19	60	1
B2	20	17.5	60	2.5
B5	20	15	60	5
B7	20	12.5	60	7.5
B10	20	10	60	10

Series with Nd_2O_3 as rare earth (C)				
Sample	BaO	Bi_2O_3	B_2O_3	Nd_2O_3
C1	20	19	60	1
C2	20	17.5	60	2.5
C5	20	15	60	5
C7	20	12.5	60	7.5
C10	20	10	60	10

Glass without rare earths (U)				
Sample	BaO	Bi_2O_3	B_2O_3	RE
U	20	20	60	0

2. Materials and methods

2.1. Glasses formulation

In this work several glasses have been melted starting from reagent grade compounds from Sigma-Aldrich. In particular the following raw materials have been employed: BaO (Sigma-Aldrich, 99.99%), Bi_2O_3 (Sigma-Aldrich, 99.99%), B_2O_3 (Sigma-Aldrich, 99.97%), Dy_2O_3 (Sigma-Aldrich, 99.9%), Nd_2O_3 (Sigma-Aldrich, 99.9%), Er_2O_3 (Sigma-Aldrich, 99.9%). The starting point from which the glasses formulation have been chosen must be found in bibliographic research [32–37] and consist of the following glasses formulation $20BaO\text{-}(20\text{-}x)\ Bi_2O_3\text{-}60B_2O_3\text{-}xRE_2O_3$. In Table 1 the list of all the glasses melted and characterized.

Glass samples have been prepared by conventional melt-quenching technique. The components have been mixed together for 15 min in an alumina jar, put in a platinum crucible and melted from room to the melting temperature (1000 °C to 1250 °C depending on the composition) for 90 min, with a heating cycle of 10 °C per minute. The crucible has been shaken once after the first 90 min of the melting for the homogeneous mixing of all the constituents. 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 Subsequently, the melt was poured through plate quenching technique and the obtained 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 this study, the melting temperature has been evaluated experimentally, observing the behavior of each glass at high temperature to keep the melted glass as much homogeneous as possible. In fact, as also already reported in literature, glasses containing bismuth oxide form~~s~~ metallic bismuth when the melting