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Strong photoluminescence and good electrical properties in Eu-modified $SrBi_2Nb_2O_9$ multifunctional ceramics

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ABSTRACT

Bismuth layer-structured ferroelectric (BLSFs) ceramics of $Sr_{1-x}Eu_x Bi_2Nb_2O_9$ (SBT-xEu, x=0.000, 0.002, 0.004, 0.006) were prepared by a conventional solid-state reaction method. All the samples have a bismuth oxide layered structure with a dense microstructure. The ferroelectric, piezoelectric, dielectric and optical properties of the ceramics were investigated. After Eu^{3+} doping, samples show a bright red photoluminescence upon blue light excitation of the 400–500 nm. Upon the excitation of 465 nm light, the materials have two intense emission bands peaking around 593 nm (yellow) and 616 nm (red). Meanwhile, good electrical properties with large piezoelectric constant d_{33} of 14 pC/N and large remnant polarization $2P_r$ of 11.97 μC/cm^2 are obtained at x=0.006. Moreover, this material has a high Curie temperature (T_c=429 °C) and high resistivity, which makes the material resistant to thermal depolarization up to its Curie temperature. This feature indicates that the SBN-xEu ceramics have a latent use in high temperature applications.

1. Introduction

Aurivillius bismuth-layer structure ferroelectrics (BLSFs) have received significant attention for the latent use in high-temperature sensors, non-volatile random access memory (NVRAM) and piezoelectric resonators due to their high Curie temperature, low dielectric constant, low aging rate and anisotropic electromechanical coupling factors [1,2]. BLSFs compounds have the general formula $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$, where A is a mono-, di- or tri-valent ions (or their combination) such as Sr^{2+}, Ca^{2+} *etc*, B is tetra-, penta-, or hexa-valent ions (or their combination) with appropriate size such as Ti^{4+}, Nb^{5+} *etc*, and m is number of pseudo-perovskite $(A_{m-1}B_mO_{3m+1})^{2-}$ layers which varies from 1 to 5 [3–5]. The crystal structure of BLSF can be described as perovskite-like $(A_{m-1}B_mO_{3m+1})^{2-}$ layers interleaved with bismuth oxide $(Bi_2O_2)^{2+}$ layers units along the c-axes [6,7]. While the perovskite-like layers offer large possibilities in terms of compositional flexibility, it could incorporate various cations such as Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+} for the A-site and Ti^{4+}, Nb^{5+}, W^{6+} for the B-site. The cation sites in the interleave $(Bi_2O_2)^{2+}$ layers are almost exclusively occupied by Bi^{3+} cations forming $(Bi_2O_2)^{2+}$ slabs. Some cations, include the above mentioned cations and the rare earth ions (RE^{3+}, such as Er^{3+}, Eu^{3+}, Ho^{3+}, Pr^{3+} *etc*), could improve the properties of the BLSFs. The RE^{3+} ions are always regarded as the luminous centers to design a large number of luminescent materials due to their special electronic structure [8]. Owing to the luminescent behavior of RE^{3+}, BLSFs modified by RE^{3+} show novel photoluminescence properties besides retaining the ferroelectric functions [9]. In addition, the Bi^{3+} ion can function as both an activator and a sensitizer to develop phosphors for the photoluminescence materials [10,11]. Along with the intensive development of microelectronic devices toward multiple functions, it is of interest and significance to study the potential luminescent properties of RE^{3+} doped BLSFs for multifunctional material applications.

$SrBi_2Nb_2O_9$ (SBN) ceramics have a typical layer-structured ferroelectrics (m=2). Yao et al. [12] reported that the SBN sample shows a high Curie temperature (444 °C), low dielectric loss tanδ (1.47%) and temperature-insensitive large piezoelectric coefficient. This material is believed to be a very promising candidate for high temperature applications. Additionally, it was found that the Eu^{3+} ion exhibited bright red emission at room temperature upon blue light excitation of the 400–500 nm [13]. The Eu^{3+} ion occupy the A-site (Sr^{2+}) of $SrBi_2Nb_2O_9$ ceramic [14], which may be very helpful to improve the performance of the SBN ceramics. In this work, a new lead-free luminescent BLSF was fabricated by introducing Eu ions as the activator into $SrBi_2Nb_2O_9$. The ferroelectric, piezoelectric, dielectric and photoluminescence

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properties of $Sr_{1-x}Eu_xBi_2Nb_2O_9$ ceramics were investigated.

2. Experimental procedure

$Sr_{1-x}Eu_xBi_2Nb_2O_9$ (SBT-*x*Eu, $x=0.000$, 0.002, 0.004, 0.006) ceramics were prepared by a conventional solid-state reaction method. The high purity oxides and carbonates powders, $SrCO_3$ (99%, Sinopharm Chemical Reagent), Bi_2O_3 (98%, Sinopharm Chemical Reagent), Nb_2O_5 (99.5%, Sinopharm Chemical Reagent) and Eu_2O_3 (99.99%, Sinopharm Chemical Reagent) were used as the raw materials, which had been treated carefully by a drying process. Then, all raw materials were weighted at stoichiometric proportion and wet milled in polyethylene bottles with ZrO_2 balls for 15 h with 180 rounds per minute in alcohol. After drying, the mixed powders were calcined at 850 °C for 2 h. The calcined powders were milled again for 15 h with 180 rounds per minute. Next, the obtained dry powders were mixed with an appropriate amount of PVA (8 wt%) binder and then were pressed into 12 mm and 15 mm diameter, 0.3 mm and 1 mm thickness discs under a uniaxial pressure of 200 MPa. The 12 mm diameter and 0.3 mm thickness discs were used for the ferroelectric, piezoelectric and photoluminescence properties measurement, and the 15 mm diameter and 1 mm thickness discs was selected for the dielectric properties measurement. After burning off PVA at 550 °C, the samples were sintered in an alumina crucible at 1120 °C for 3 h in air. Finally, the sintered pellets were polished and covered with silver paste on both sides, then fired at 850 °C for 20 min.

The crystalline structure of the crushed samples was analyzed by X-ray diffraction (XRD) methods (D8 Advanced, Bruker. Inc., Germany). The microstructure evolution was observed using a scanning electron microscope (SEM, JSM-6380LV, Tokyo, Japan). The ferroelectric hysteresis loops were measured through standardized ferroelectric test system (TF2000, Germany). The piezoelectric coefficient d_{33} was measured with a Piezo-d_{33} meter (Sznocera Piezotronics INC, China). The temperature dependence of dielectric properties for the samples was performed using a Broadband Dielectric Spectrometer (Novocontrol Germany) at temperatures ranging from room temperature to 700 °C with a heating rate of 3 °C/min. The photoluminescence (PL) spectra at RT were measured using aspectrofluorometer (FLS920, Edinburgh Instruments, UK).

3. Results and discussion

Fig. 1 shows the XRD patterns of the SBN-*x*Eu ceramics in the 2θ range of 20–70°. As shown, all the samples have been crystallized into a bismuth oxide layer-type structure without any traceable secondary phases. This implies that Eu^{3+} have diffused into the crystal lattice of SBN and formed a stable solid solution with SBN. It also observed that the main diffraction peaks of all the samples in position and intensity change unobvious. This can be attributed to the similarity in ionic radii and electrical valence of Sr^{2+} (1.44 Å, CN=12) and Eu^{3+} (1.23 Å, CN=12). In addition, the strongest diffraction peak is the (115) orientation, which corresponds well with the (112m+1) highest diffraction peak in BLSFs. This indicates that all ceramics have the bismuth layer-structured compounds with the layer number $m=2$.

Fig. 2 shows the FE-SEM images of the nature surface for the pure and Eu^{3+}-modified SBN ceramics sintered at 1120 °C for 3 h. It can be seen that the ceramics have a dense structure and plate-like grains, which is the typical morphology feature of BLSF ceramics. Due to the grain is structurally high anisotropic, the grain growth is preferentially in the *a-b* plane perpendicular to the *c*-axis of the BLSFs crystal, the length*l*of the plate-like grain is much bigger than the thickness *t*. Moreover, the grain size initially increases with the increasing Eu^{3+} contents, and then decreases with the further increase of Eu^{3+} contents. This implies that the appropriate content of Eu^{3+} is beneficial to the grain growth of the ceramics. Kan et al. [15] and Hou et al. [16] both reported that grain growth during sintering is closely associated with ion migration. In the present work, the reduced grain growth rate can be linked with an increase in the activating energy for ion migration and reduction in the surface or grain boundary energy [16,17]. In addition, all ceramics have a high relative density ($\rho_{rd} > 90\%$, shown in Table 1), suggesting all samples have been well sintered.

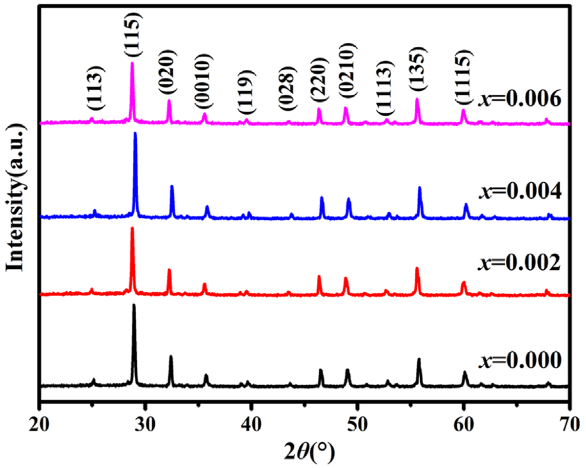

Fig. 1. The XRD patterns of the SBN-*x*Eu ($x=0.000$–0.006) ceramics in the 2θ range of 20–70°.

Fig. 3 shows the temperature dependence of the dielectric constant (ε_r) and dielectric loss ($\tan\delta$) for the SBN-*x*Eu ceramics at 1 MHz. The values of Curie temperature and room temperature $\varepsilon_r/\tan\delta$ of the SBN-*x*Eu ceramics are summarized in Table 1, the Curie temperatures (T_c), which corresponding to the ferroelectric-paraelectric phase transition, changes slightly when the contents of the Eu^{3+} is in the range of 0.000–0.004. When the Eu^{3+} content reaches 0.006, the Curie temperatures (T_c) drop sharply. Shimakawa et al. [18,19] suggested that the Curie temperatures (T_c) depend strongly on the crystal structure distortion. The decrease of T_c at high Eu^{3+} content may be related to the lattice distortion [18–20], the electronic configuration [21], the decrease of electronegativity (Sr^{2+}:0.95, Eu^{3+}:1.20) [22] and the Bi^{3+} amounts [20,22,23]. The dielectric loss tangent ($\tan\delta$) of all samples are lower than 2% without significant conductivity appearing even at temperature as high as 400 °C, which suggest that the ceramics are suitable for high temperature applications. Moreover, it can be clearly seen that the loss tangent of the modified ceramics are lower than that of pure SBN, confirming the significantly improved insulation. For samples of SBT-0.002Eu, the $\tan\delta$ is found to be only 0.96%.

Fig. 4 shows the temperature dependence of the DC resistivity of the SBN-*x*Eu ceramics measured in the temperature range of 500–700 °C, and the activation energy E_a values versus the content of Eu^{3+} are listed in this graph. It is found that the resistivity increased with the increase of Eu^{3+}content, but all the samples are higher than $10^4\ \Omega$ cm at 700 °C. In Aurivillius compounds, the structure built up by $(A_{m-1}B_mO_{3m+1})^{2-}$ layers and $(Bi_2O_2)^{2+}$ layers along *c*-axis [24]. The resistivity in the *c*-axis is higher than that in the *a-b* plane owing to the $(Bi_2O_2)^{2+}$ layers act as the insulating layer in the structure of Aurivillius compounds [25,26]. High resistivity is important for their use in high temperature piezoelectric devices, which is benefit to achieve high electric field poling at high temperature and get higher piezoelectric properties [27,28]. The activation energy (E_a) was calculated according to the