Piezoelectric Er^{3+}-doped $(Ba_{1-x}Ca_x)(Sn_{0.06}Ti_{0.94})O_3$ ceramic: Photoluminescence sensitive to morphotropic phase boundary

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ABSTRACT

The 0.5 mol% Er^{3+}-doped piezoelectric $(Ba_{1-x}Ca_x)(Sn_{0.06}Ti_{0.94})O_3$ lead-free ceramics were prepared via a conventional solid-state sintering process. The confirmed morphotropic phase boundary of this material locates at $x = 0.03$ through measuring x dependence on dielectric and ferro-/piezoelectric performances. It was found that photoluminescence of Er^{3+}-doped $(Ba_{1-x}Ca_x)(Sn_{0.06}Ti_{0.94})O_3$ ceramics is sensitive to the structural phase transition. With the increase of x from 0.01 to 0.06, the photoluminescence peak intensity at 550 nm first increases and then decreases, giving to the optimal value at $x = 0.03$. The typical characteristic, photoluminescence sensitive to morphotropic phase boundary, can be used to develop a non-contact and sensitive way to indicate phase transition region of rare-earth doped lead-free piezoelectric ceramics.

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1. Introduction

Lead-based piezoelectric materials, such as Pb(Zr,Ti)O₃, have been widely used in sensors, actuators and other electronic devices [1,2]. However, the main constituent of these lead-based materials is lead, which is a very toxic substance. For the need of environmental protection and human health, some lead-free piezoelectric materials, such as $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) (piezoelectric coefficient d_{33} ~91 pC/N), $K_{0.5}Na_{0.5}NbO_3$ (KNN) (d_{33} ~108 pC/N), have been extensively studied [3—6], but their piezo-/dielectric performances are inferior to that of the lead-based piezoelectric materials, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$—$PbTiO_3$ (d_{33} ~ 1280 pC/N) [7]. Recently, the lead-free $(Ba_{1-x}Ca_x)(Sn_{0.06}Ti_{0.94})O_3$ (BCST) ceramics have aroused significant interest because of the high d_{33} of ~440 pC/N at an optimal composition of $x = 0.03$ near the morphotropic phase boundary (MPB) [8].

Generally, a small amount (<0.5%) of rare earth doping in piezoelectric ceramics can effectively enhance the ferro-/piezoelectric performances and does not obviously change the phase structure [9,10]. Wei et al. reported that the d_{33} of KNN-based ceramics increased from ~82 pC/N to ~108 pC/N by doping Pr^{3+} ions [4]. In addition, the rare earth ions doped perovskite oxide ceramics can also possess the excellent photoluminescence (PL) performance [11].

It is well known that the high piezoelectric performance can be obtained only while the composition locates at MPB region [12—14]. For the quinary BCST system, its accurate phase diagram has not been confirmed now. The slight compositional variety near the MPB may cause a heavy decrease of d_{33}. In general, the MPB is mainly indicated through measuring the dependence of composition on the dielectric and piezoelectric coefficients [13]. During the measurements, the electrodes and physical contact are necessary and some pollution will be introduced into the materials inevitably [15]. Thus, developing a non-contact, quick-response and compositional-change-sensitive way to estimate the piezoelectric properties near the MPB area is of considerable significance. Some rare earth ions, such as Er^{3+} ion often possesses high hypersensitivity to the change of the lattice symmetry. Therefore, it is possible to design a structural-transition-sensitive PL tool to indicate MPB of rare-earth doped lead-free piezoelectric ceramics.

In this work, the 0.5 mol% Er^{3+}-doped lead-free BCST ceramics were synthesized via a conventional solid-state sintering process. It was observed that the PL of Er^{3+}-doped BCST ceramics were sensitive to the variety of Ca content. The structural-transition-sensitive PL tool to indicate MPB of rare-earth doped lead-free piezoelectric ceramics possesses the advantages of high sensitivity, non-contact and quick response.

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2. Experimental

0.5mol% Er^{3+}-doped $(Ba_{1-x}Ca_x)(Sn_{0.06}Ti_{0.94})O_3$ ceramics (BCST-Er) were prepared via a solid-state reaction technique. Raw materials of $CaCO_3$ (99.5%), $BaCO_3$ (99.5%), SnO_2 (99.5%), TiO_2 (98.7%), and Er_2O_3 (99.5%) were mixed with the addition of alcohol, then dried, and calcined at 1150 °C for 4 h. Thereafter, calcined powders were mixed with 5 wt% polyvinyl alcohol (PVA) solution and then pressed into disk-shaped pellets (10 mm in diameter). After burning out PVA at 600 °C, the samples were finally sintered at 1430 °C for 2 h in air. All the resultant pellets were polished to about 0.8 mm in thickness and coated with silver electrodes on both sides to make electrical contact for the electric properties measurements. Then the ceramics were poled under a DC electric field of 4 kV/mm at room temperature in silicone oil for 30 min.

The crystalline structure of the powder samples was characterized by an X-ray diffraction (XRD) apparatus (PW3040/60, Philip, Netherlands) with Cu Kα radiation. The up-conversion (UC) PL emissions were recorded by using a FLS920 spectrofluorometer (Edinburgh, UK) under the excitation of a 980 nm laser. Polarization-electric filed (*P-E*) hysteresis loops were measured by a ferroelectric analyzer (RTI-Multiferroic-4 kV, Radiant, USA) at 10 Hz. The piezoelectric coefficient d_{33} was measured by a quasi-static d_{33} m (ZJ-3, Institute of Acoustics, Chinese Academy of Science, China). A LCR impedance analyzer (HP 4294A, USA) was employed to measure the relative dielectric constant ε_{33} at 1 kHz and to determine the electromechanical coupling factor k_p by the resonance method.

3. Results and discussion

Fig. 1 shows the XRD patterns of the BCST-Er ceramics with different Ca content. The samples of $x = 0.01$ and $x = 0.02$ exhibit an orthorhombic phase with a single peak of (200) at 2θ near 45° [16]. The single peak of (200) in the sample of $x = 0.03$ splits into two mixed diffraction peaks, which suggests a orthorhombic/tetragonal coexistence phase. Therefore, the orthorhombic/tetragonal MPB locates at $x = 0.03$. The BCST-Er samples of $x = 0.04$, 0.05 and 0.06 with an obvious split of the (002)/(200) peaks possess pure tetragonal phase [17].

It should notes that the impurities in raw materials are mainly nonorganic metal-oxides (MgO, CaO, Al_2O_3, Fe_2O_3, etc.) [18]. It has been reported that the impurities of slight (<1−2%) nonorganic metal-oxides in raw materials don't obviously affect the ferro-/

piezoelectric performances of titanate-based piezoelectric ceramics [19]. The PL of rare earth-doped ceramic materials are mainly sensitive to the lattice symmetry around rare earth ions [5]. From Fig. 1, by compared with the standard XRD card, the lattice symmetry of our materials is not influenced by these impurities materials of slight (<1−2%) nonorganic metal-oxides. In theory, the slight (<1−2%) impurities materials will not obviously affect the PL performance. In practice, due to the color's influence of red Fe_2O_3 on PL, the slight impurities material of Fe_2O_3 in our materials may slightly decrease the relative strength of PL peak [20], which will not affect our main conclusion of PL variety indicating morphotropic phase boundary of Er^{3+}-doped $(Ba_{1-x}Ca_x)(Sn_{0.06}Ti_{0.94})O_3$ ceramics, in view of the experimental samples being prepared on basis of the same raw materials.

Fig. 2 shows the piezoelectric coefficient (d_{33}) and planar mode electromechanical coupling coefficient (k_p) of the BCST-Er ceramics as a function of x. With the increase of x, both the d_{33} and k_p increase firstly and then decrease, giving to the maximum value of d_{33} ~467 pC/N and k_p ~41% at $x = 0.03$. The inset of Fig. 2 shows the relative dielectric constants (ε_{33}) of BCST-Er ceramic with different Ca content (x). The BCST-Er ceramic sample of $x = 0.03$ possess the highest ε_{33} of ~4533. On basis of the piezo-/dielectric measurement results in Fig. 2, the MPB region of BCST-Er material locates at $x = 0.03$, which agrees well with the report in literature [8].

The *P-E* hysteresis loop of BCST-Er ceramics under an electric field of ~4 kV/mm is shown in Fig. 3. The inset of Fig. 3 describes the ferroelectric remnant polarization strength (P_r) of BCST-Er ceramics with different Ca content (x). With the increase of x, P_r increases firstly and then decreases with an extreme value at $x = 0.03$, which corresponds to the MPB region [8].

Fig. 4 shows the PL emission spectrum of BCST-Er ceramics under a light irradiation excitation with a wavelength of 980 nm at room temperature. The excitation spectrum of Er^{3+} doped materials monitored at 550 nm exhibits the most intense peak at 980 nm [21], which indicates that the laser diode operating at 980 nm is the most efficient pump source. The PL emission consists of two strong green emissions located at approximately 525 nm and 550 nm ($^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions), and a relatively weak red emission band at 670 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition), which agrees well with the literature [22−24]. Generally, the electronic transitions between the partially filled 4*f* levels are sensitive to the PL, these transitions become allowed if the local symmetry around Er^{3+} is reduced [15]. Thus the electronic transitions induced by the compositional transition of the BCST-Er ceramics may be
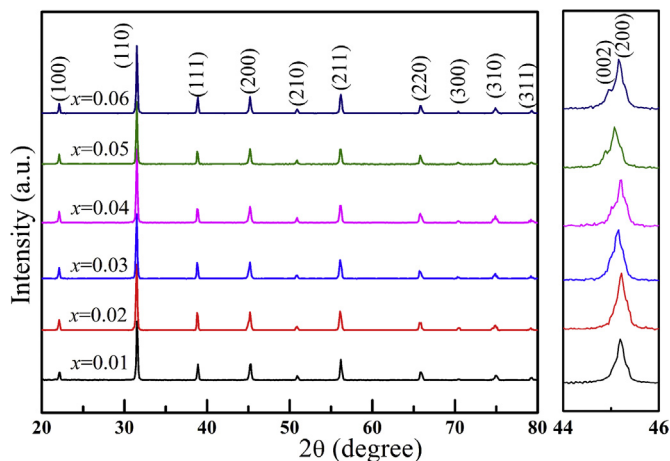

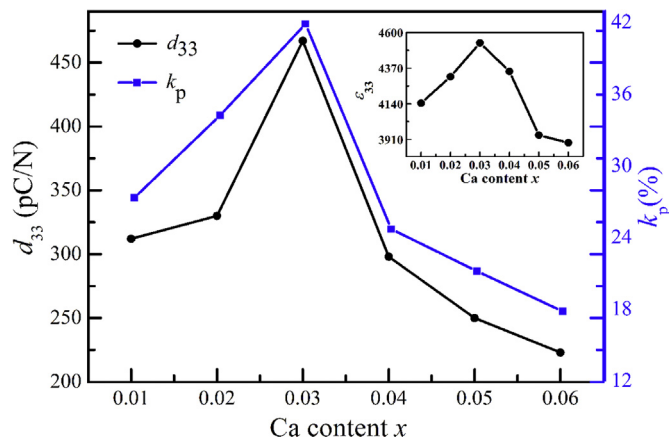**Fig. 1.** XRD patterns of the BCST-Er ceramics with different *x*.

Fig. 2. *x* dependence on the d_{33} and k_p of BCST-Er ceramics (The inset shows the relative dielectric constants (ε_{33}) of BCST-Er ceramics with different Ca content (x)).