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Large electrostrictive effect and strong photoluminescence in rare-earth modified lead-free $(Bi_{0.5}Na_{0.5})TiO_3$-based piezoelectric ceramics

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ABSTRACT

In this study, new lead-free luminescent electrostrictive materials have been fabricated by introducing trivalent RE^{3+} (RE = Sm, Pr and Eu) as the activator into $0.93(Bi_{0.5}Na_{0.5})TiO_3$–$0.07BaTiO_3$ (BNBT7) ceramics. A high, purely electrostrictive effect with exceptionally good temperature-independent and fatigue-free behavior was obtained in RE-modified BNBT7 ceramics. These materials are also attractive for their strong photoluminescence with bright reddish-orange emission (RE = Sm) or red emission (RE = Pr, Eu) upon blue or green light excitation. These results suggest that this kind of materials has potential application as a multifunctional device by integrating its excellent luminescence and electrostrictive properties.

Relaxor ferroelectrics are a special class of ferroelectrics that have been widely studied not only due to their behaviors and properties but also due to various applications such as electromechanical sensors and actuators [1]. One of the peculiar properties in relaxor ferroelectrics is the large electrostrictive effect [2]. In electrostriction, the sign of the field-induced deformation is independent of the polarity of the field and is proportional to the square of the applied electric field, $S = QP^2$, where Q is the electrostrictive coefficient and P is polarization [3]. Compared with the piezoelectric effect, the electrostrictive effect has several unique advantages—possessing little hysteretic loss up to high frequencies, being temperature stable, and exhibiting a fast response time. These advantages render the electrostrictors promising for precision position control [3–5]. Lead magnesium niobate is known as the best electrostrictive material with a large electrostrictive strain of 0.1% and widely used in actuator applications [6,7]. However, lead is toxic, hence making lead-free electrostrictive materials highly desirable owing to the increasing concern for environmental safety. Recently, Zhang et al. proposed a concept of using lead-free relaxor $(Bi_{0.5}Na_{0.5})TiO_3$-based ceramics as electrostrictors, which can provide high strain and minimal losses at room temperature combined with minimal temperature dependence [8,9].

Along with the intensive development of microelectronic devices toward miniaturization, light weight, and integration, researchers would like to discover some materials or devices, which can realize multiple functions. Recently, multifunctionality has renewed the interest in ferroelectrics, such as ferroelectric-photo [10], ferroelectric–elastic [11], ferroelectric–elastic–magnetic [12], ferroelectric–mechanical integration and/or coupling [13], which can lead to a remarkable progress with numerous new materials and devices for photovoltaic and spintronic applications, optical-electrical-mechanical actuator and sensor applications [10–13]. With the development of the functional material and device, new coupling effects in ferroelectrics which could realize multiple functions are quite desirable.

It is known that rare earth (RE) elements are commonly used to fabricate highly efficient luminescent materials as activator ions, or improve mechanical and electrical properties as structural modifiers [14]. In 2005, Wang et al. fabricated Pr^{3+}-doped $(1\text{-}x)BaTiO_3\text{-}xCaTiO_3$ ceramics with high electrostrictive strain, strong mechanoluminescence and electroluminescence material, which paves the way for developing new and high-performance multifunctional ferroelectrics [13]. Since then, multifunctional luminescent materials have stimulated an increasing practical interest, and considerable efforts have been made to search for potential rare-earth doped ferroelectrics, combining light emission with their intrinsic ferroelectricity, piezoelectricity, or electro-optic properties, as shown in Fig. 1 [15].

In this work, a new lead-free luminescent electrostrictive material with the electrostrictive–photoluminescence coupling effect was fabricated by introducing RE (RE = Sm, Pr and Eu) ions as the activator into $0.93(Bi_{0.5}Na_{0.5})TiO_3$–$0.07BaTiO_3$ (BNBT7). The BNBT7 − xRE (x = 0–0.01) ceramics were prepared by the conventional sintering technique. The crystal structures of the sintered ceramics were determined by X-ray powder diffraction analysis (XRD) (D8 Advance, Bruker Inc., Germany). The photoluminescence (PL) spectra at RT were tested using a spectrofluorometer (FLS920, Edinburgh Instruments, UK). The electric-field-induced polarization (P–E) and strain (S–E) measurements were carried out using an aix-ACCT TF2000FE-HV ferroelectric test unit (aix-ACCT Inc., Germany) connected with a miniature plane mirror

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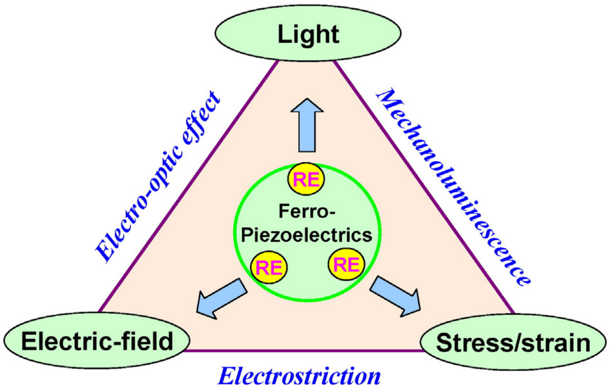

Fig. 1. Schematic illustration of multiple functions of RE-doped ferro−/piezoelectrics.

interferometer and the accessory laser interferometer vibrometer (SP-S 120/500; SIOS Mebtechnik GmbH, Ilmenau, Germany).

Fig. 2 shows the *P*–*E* hysteresis loops, *S*–*E* curves and *S*–P^2 curves of (a) BNBT7 and (b) BNBT7–0.006RE (RE = Sm) ceramics. Pure BNBT7 ceramic displays a typical ferroelectric behavior with butterfly shaped strain hysteresis loops. A large strain of 0.28% is obtained in BNBT7 samples. However, one drawback for the use as material for devices is the huge intrinsic losses induced by the large hysteresis. Due to the large hysteresis, the *S*–P^2 curve of the BNBT7 ceramic is obviously deviated from liner relation, meanwhile, a low electrostrictive coefficient Q_{33} of 0.016 m^4/C^2 is observed. As a small amount of RE (RE = Sm, 0.6 mol%) was introduced into BNBT7, the hysteresis behavior is significantly decreased, and very slim *P*–*E* and *S*–*E* profiles with the high strain level of 0.13% comparable with lead-containing electrostrictors [16,17] are obtained (Results of Pr, Eu-modified ceramics are presented in Fig. 1S of supplementary information). The profile of *S* versus P^2 can be fitted well to a straight line, indicating purely electrostrictive behavior. The destabilization of the ferroelectric order and emergence of purely electrostrictive behavior induced by RE modification can be linked to the phase transition behavior, as discussed in Fig. 2 S (see supplementary information).

Fig. 2(c) summarizes the electrostrictive coefficient Q_{33} of BNBT7 − *x*RE (RE = Pr, Sm and Eu) system. All the RE addition, Sm, Pr and Eu effectively improved the electrostrictive properties of the ceramics. Large Q_{33} in the range of 0.021–0.028 m^4/C^2 are achieved in the modified samples. Fig. 2(d) shows that BNBT7 − *x*RE ($x = 0.006$, RE = Sm) exhibits a higher Q_{33} (0.028 m^4/C^2) than other BNT-based electrostrictors [8,9,18–21], mostly with $Q_{33} < 0.025$ m^4/C^2 and even exceeds Pb-based electrostrictors [16,17,22,23]. Moreover, it is interesting to find that the Q_{33} is almost unchanged with both electric-field cycling and temperature (Fig. 3S of supplementary information). The general variation of the Q_{33} up to 10^6 cycles is within 1.2%, 1.7% and 1.8% of original value, at RT, 80 °C and 160 °C, respectively. These results indicate the materials have excellent potential for those demanding high cycle applications such as microelectromechanical systems actuators.

Besides the excellent electrostrictive properties, the RE-modified samples also exhibit strong photoluminescence. Fig. 3(a1)–(a3) shows the photoluminescence excitation (PLE) spectra and photoluminescent (PL) emission of BNBT7 − *x*RE ($x = 0.006$, RE = Sm, Pr and Eu) ceramics. The energy level schemes of Sm^{3+}, Pr^{3+} and Eu^{3+}, ions, are shown in Fig. 3(b1), (b2) and (b3), respectively. For Sm-modified samples, the remarkably strong and sharp excitation peaks in the wavelength range of 390–510 nm are observed, which are owing to the typical *f*–*f* transitions from the $^6H_{5/2}$ ground state to the $^4G_{7/2}$, $^4P_{5/2}$, $^6P_{5/2}$, and $^4I_{11/2}$ excited states of Sm^{3+} [15]. Under the blue light excitation of the 400 nm to 500 nm, a strong reddish-orange emission is noted. These emission peaks are mainly attributed to the characteristic *f*–*f* transition emissions of Sm^{3+} at 565 nm (green emission, $^4G_{5/2} \rightarrow {}^6H_{5/2}$), 600 nm (red emission, $^4G_{5/2} \rightarrow 6H_{7/2}$), and 646 nm (red emission, $^4G_{5/2} \rightarrow 6H_{9/2}$) [15]. Pr-doped ceramics exhibit strong red emitting properties with a single peak centered at 611 nm upon blue light excitation (440–505 nm). The excitation spectrum consists three strong absorption peaks, located at 449 nm, 471 nm, and 487 nm, which are mainly attributed to the typical

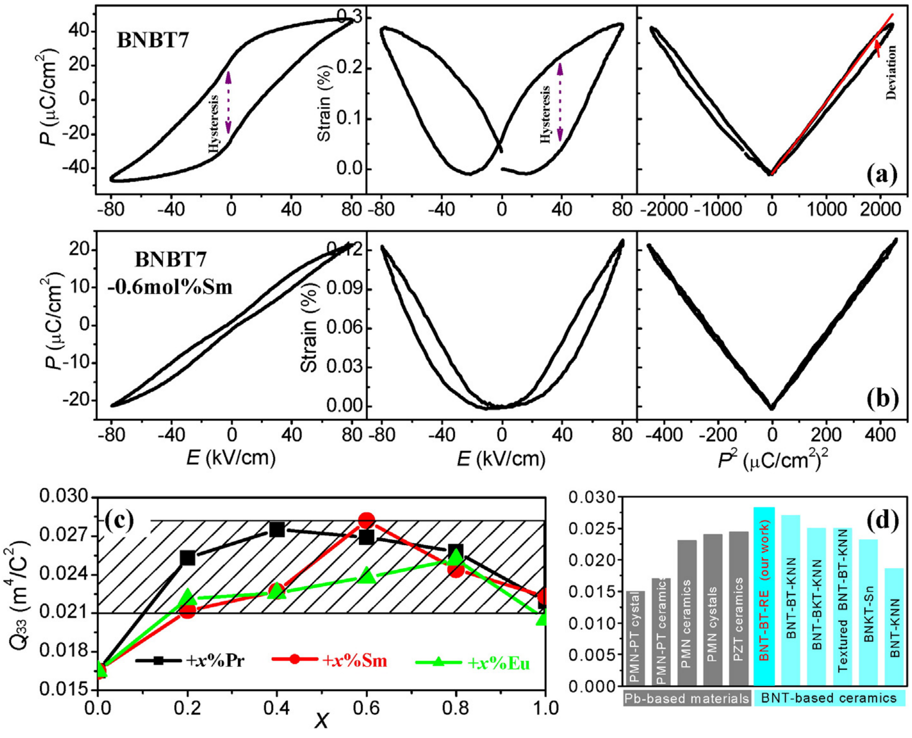

Fig. 2. *P*–*E*, *S*–*E* hysteresis loops and *S*–P^2 curves for (a) BNBT7 and (b) BNBT7–0.006Sm ceramics. (c) Variation of electrostrictive coefficient Q_{33} as a function *x*, for BNBT6–*x*RE (RE = Sm, Pr, Eu) samples. (d) Room-temperature electrostrictive coefficient Q_{33} of Pb-based electrostrictors [16,17,22,23] and lead-free BNT-based electrostrictors (BNBT7 − *x*Sm in this work and other BNT-based ceramics [8,9,18–21]).