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Lead-free $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ ceramics exhibiting large strain with small hysteresis

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Abstract

This work attempted to reduce hysteresis in electric field-induced strain properties of lead-free $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ceramics by modification with a $(Ba,Ca)ZrO_3$(BCZ) solid solution. It was found that BCZ induced a phase transition from a ferroelectric state to a relaxor, resulting in a large strain at the transition region like other previous reports on Bi-based ceramics. Although previous works on Bi-based ceramics reported the normalized strain over 600 pm/V with large hysteresis over 50%, BCZ modified BNKT showed a much lower hysteresis of 25% while maintaining a large normalized strain of 549 pm/V, which is believed to open a new road to further reduce the strain hysteresis in Bi-based lead-free relaxors.

Keywords: A. Sintering; C. Piezoelectric properties; D. Perovskites; E. Actuators

1. Introduction

Recently, bismuth sodium titanate $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) based ceramics have attracted much attention since a giant electric field-induced strain (EFIS), $d^*_{33}=S_{max}/E_{max}$ of 560 pm/V, was observed in $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$–$K_{0.5}Na_{0.5}NbO_3$by Zhang et al. in 2007 [1]. Thenceforth large strains were reported in many BNT-based solid solutions with $SrTiO_3$ [2], $Ba(Al_{1/2}Sb_{1/2})O_3$(BAS) [3],or $Bi_{1/2}K_{1/2}TiO_3$ (BKT) [4–10] when there happened a ferroelectric-nonpolar phase transition, which was recently interpreted as a ferroelectric–relaxor crossover [11]. The large strain in BNT-based ceramics was attributed to the field-induced phase transition from a nonpolar relaxor to a ferroelectric phase under high electric fields, which was confirmed by *in situ* synchrotron X-ray diffraction [12], neutron diffraction [13], transmission electron microscopy [14], and direct volume change measurements [15].

However, a critical problem that hinders the practical application of BNT-based materials to actuators is the large hysteresis in the strain versus electric field (*S*–*E*) loop. Although very large strains of 0.4–0.45% can be obtained in them [4–10], such strains can be only observed under very high electric fields of 6–7 kV/mm, which are too high to be applied in electrical devices because of problems in insulation. Therefore, this study focuses on the reduction of strain hysteresis in BNKT ceramics by co-doping of $BaZrO_3$ (BZ) and $CaZrO_3$ (CZ). According to our recent works, it was found that $CaZrO_3$ (CZ) modification of BNKT [16] resulted in a large EFIS ($d^*_{33}=603$ pm/V) with a large *S*–*E* hysteresis while $BaZrO_3$ (BZ) modification [17] led to a lower EFIS ($d^*_{33}=437$ pm/V) with a smaller hysteresis.

2. Experimental

A conventional solid state reaction route was applied to prepare the powders with a series of compositions of $(1-x)Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3-x(Ba_{0.8}Ca_{0.2})ZrO_3$ ($x=0$, 0.01, 0.02, 0.03, 0.04, and 0.05; BNKT–BCZ). Powders of Bi_2O_3, K_2CO_3, $BaCO_3$, TiO_2, $CaCO_3$, ZrO_2 (99.9%, Kojundo Chemical) and Na_2CO_3 (99.9%, Ceramic Specialty Inorganics) were used as raw materials. Firstly, the powders were weighed according to the chemical formula and then ball-milled for 24 h in anhydrous ethanol with zirconia balls.

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The slurry was dried and calcined at 850 °C for 2 h. The calcined powder was added with polyvinyl alcohol as a binder and uniaxially pressed into circular disks with a diameter of 12 mm at 98 MPa. The green compacts were sintered in a covered alumina crucible at 1150 °C for 2 h in air.

The relative density of a fired specimen was determined by the Archimedes method. The crystal structure was analyzed using an X-ray diffractometer (XRD, RAD III, Rigaku, Japan), and the surface morphology was observed with a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-65OFF, Japan). Electrical measurements were carried out after screen-printing Ag paste on both sides of a disk-shaped specimen and subsequent firing at 700 °C for 30 min. The dielectric constant and loss tangent of poled specimens were measured with an impedance analyzer (HP4194A). The polarization–electric field (*P*–*E*) and EFIS hysteresis loops were measured in silicon oil using a modified Sawyer–Tower circuit and a linear variable differential transducer, respectively.

3. Result and discussion

Fig. 1 compares the fractured surface micrographs between undoped BNKT and 5 mol% BCZ-added BNKT ceramics. Undoped BNKT revealed, as seen in Fig. 1(a), a dense microstructure with grain sizes in the range of 0.5–3 μm. When 5 mol% BCZ was added into BNKT, the average grain size was increased, as shown in Fig. 1(b). The increased sinterability by ABO_3 modifiers in BNT-based ceramics has also been reported in other literatures [16,17].

X-ray diffraction patterns of the BCZ-modified BNKT system are shown in Fig. 2. All samples showed a single phase perovskite structure without any traces of secondary phase. In undoped BNKT ($x=0$), there coexisted tetragonal and rhombohedral phases because peak splits at both 40° and 46°were simultaneously observed, corresponding to the (111)/($\bar{1}$11) of rhombohedral and (002)/(200) of tetragonal symmetry, respectively. This result is consistent with a previous work on $(1-y)$BNT$-y$BKT ceramics where a morphotropic phase boundary was found when $y=0.16$–0.20 [18,19] Such a transition was also reported by previous studies on BNKT ceramics doped with Zr [4], Nb [6], and Ta [8].

The effect of BCZ modification on the field-induced polarization (*P*–*E*) and strain (*S*–*E*) hysteresis loops of BNKT ceramics is displayed in Fig. 3. In case of undoped BNKT ($x=0$), typical ferroelectric *P*–*E* and *S*–*E* loops were observed that were characterized by definite squareness in the *P*–*E* loop as well as a butterfly-shaped *S*–*E* curve. As the BCZ content in the BNKT–BCZ solid solution increases, both the remanent polarization (P_r) and coercive field (E_c) gradually decreased, resulting in a *P*–*E* loop close to those of nonpolar materials as can be seen in many other reports on BNT-based materials [4–10].

When BCZ content reached higher than 0.03, this study also showed a vanishing of negative strain that was denoted as the difference between zero field strain and the lowest strain at E_c. At $x=0.02$, the largest strain of 0.3% was observed similar to other previous reports on BNT-based materials [4–10].

Fig. 4 compared unipolar field-induced strain (*S*–*E*) hysteresis loops of BNKT ceramics modified with CZ, BZ, and BCZ. From the *S*–*E* loop, the hysteresis was determined by calculating $\Delta S/S_{max}$, which had been proposed by Kumar et al. [20]. The normalized strain S_{max}/E_{max} and hysteresis were found to be 603 pm/V and 49% for 3 mol% CZ-modified BNKT while those values for 2 mol% BZ-modified BNKT were 437 pm/V and 33%, respectively. However, 2 mol%

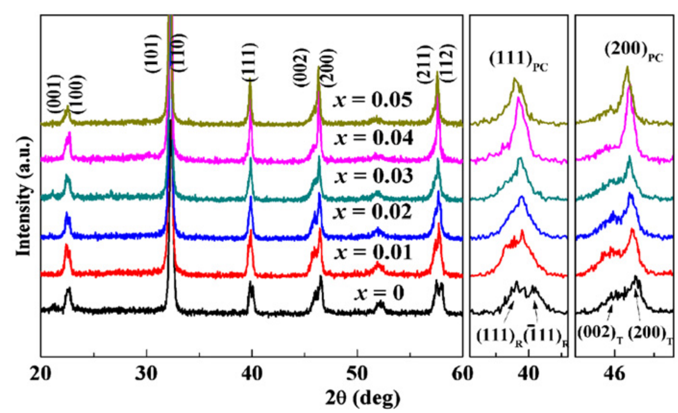

Fig. 2. X-ray diffraction patterns of BCZ-modified BNKT ceramics as a function of BCZ content (x).

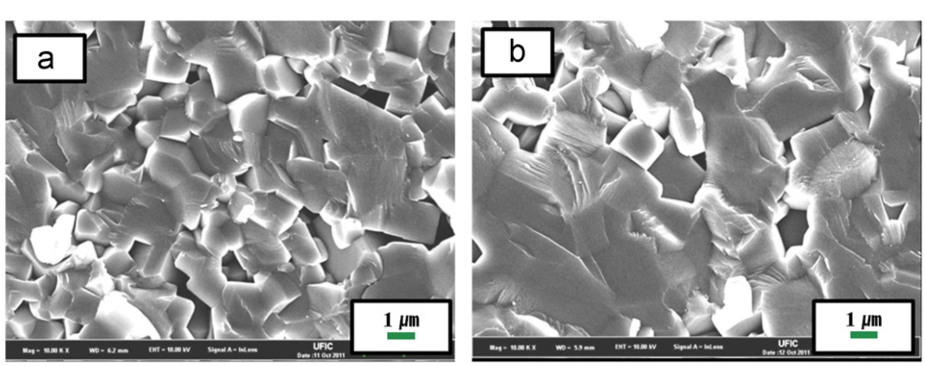

Fig. 1. Fractured surface micrographs of (a) undoped BNKT and (b) BCZ-modified BNKT ceramics sintered at 1150 °C for 2 h.

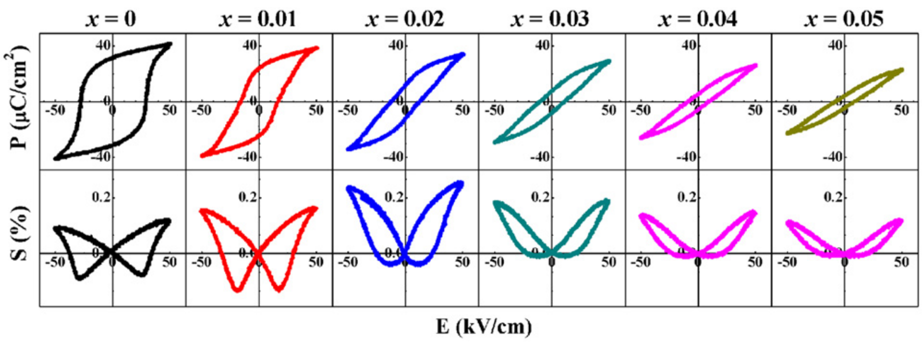

Fig. 3. .Effect of BCZ modification on the *P–E* and *S–E* hysteresis loops of BNKT ceramics.

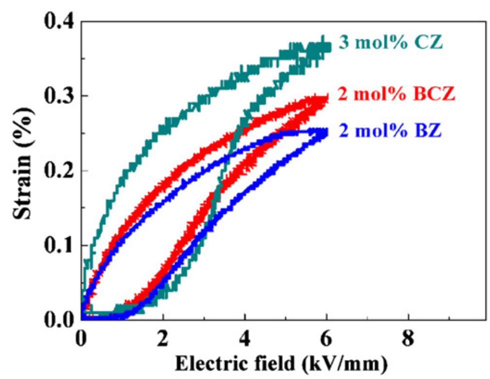

Fig. 4. .Unipolar *S–E* loops of BZ-, CZ-, and BCZ-modified BNKT ceramics as a function of modifier content.

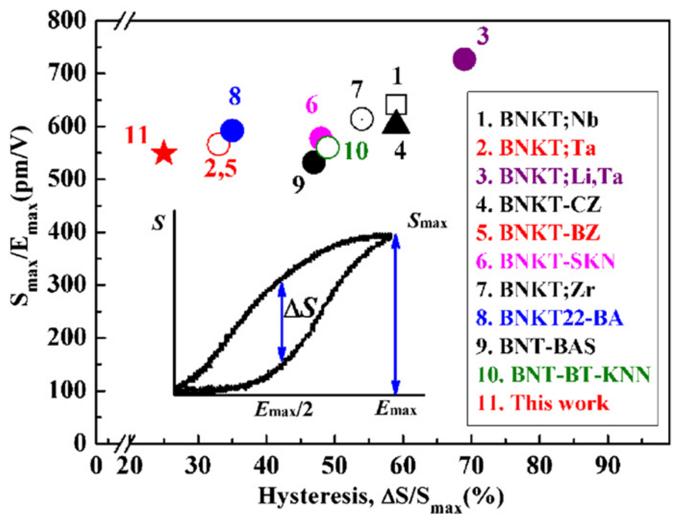

Fig. 5. The normalized strain S_{max}/E_{max} versus hysteresis S_{max}/E_{max} for various BNT-based lead-free ceramics; BNT–BT–KNN [1], BNT–BAS [3], BNKT22–BA [5], BNKT–LiTa [9], BNKT–CZ [16], BNKT–BZ [17], BNKT–SKN [21], Zr [4], Nb [6], and Ta [8] modified BNKT ceramics.

BCZ-modified BNKT showed $S_{max}/E_{max}=549$ pm/V and $\Delta S/S_{max}=25\%$. This result clearly demonstrates that the hysteresis in BNT-based ceramics can be significantly reduced by co-doping two modifiers at the same time.

The most meaningful finding in this work was illustrated in Fig. 5, which compares the room temperature normalized strain versus hysteresis in the unipolar *S-E* loop for various BNT-based ceramics. The largest S_{max}/E_{max} of 727 pm/V was reported on Li- and Ta-doped BNKT [9] while its hysteresis reached 70%. It is seen that the hysteresis can be decreased by lowering the S_{max}/E_{max}. However, this work seems remarkable in terms of the large normalized strain with relatively low hysteresis of 25%. Considering the fact that Pb-based piezoelectric or electrostrictive ceramics reveal a much lower hysteresis (less than 10%), further studies are requested to more reduce the hysteresis of BNT-based ceramics.

4. Conclusion

Effect of BCZ modification on the microstructure, crystal structure, ferroelectric, and EFIS properties of lead-free $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ ceramics has been investigated. It was found that BCZ induced a ferroelectric-to-relaxor transition which was accompanied by a large enhancement in EFIS like other previous reports on modified BNKT ceramics. However, BCZ-modified BNKT showed a much lower *S–E* hysteresis of 25% while maintaining a large normalized strain of 549 pm/V, which is believed to open a new road to further reduce the strain hysteresis in Bi-based lead-free relaxors because their large *S–E* hysteresis has been one of the critical issues in practical applications.

Acknowledgments

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