Journal of the European Ceramic Society xxx (2017) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Impacts of acceptor doping on the piezoelectric properties and domain structure in NBT-based lead-free ceramics

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ARTICLE INFO

Article history:
Received 26 January 2017
Received in revised form 12 April 2017
Accepted 18 April 2017
Available online xxx

Keywords:
Acceptor doping
Domain structure
NBT-based
Dynamic behavior
Lead-free piezoelectrics

ABSTRACT

The domain structure and piezoelectric properties of Mn-doped $0.79(Na_{0.5}Bi_{0.5})TiO_3$-$0.14(K_{0.5}Na_{0.5})TiO_3$-$0.07BaTiO_3$ (BNBK79) ceramics were studied. The relationship between macroscopic properties and microstructure was established. The pure and Mn doped BNBK79 ceramics show different dynamic behavior in strain behavior and polarization hysteresis, due to the different domain structure and domain switching behavior. The BNBK79 ceramics show dominating irregular watermarks domain configuration before poling, changes to simple parallel stripes after poling, while BNBK79-Mn ceramics show more complicated domain configurations, where regular domain stripes containing Herringbones assembled with watermarks are dominated before poling, and the Herringbones remain after poling. The pinning effect induced by $Mn''_{Ti} - V^{\cdot\cdot}_{O}$ defect dipoles accounts for the complicated domain structure and hinders the domain switching, resulting in "hard" properties (low dielectric loss of 0.6% and high mechanical quality factor Q_m of 1100), makes BNBK79-Mn ceramics promising for high-power piezoelectric applications.

1. Introduction

Ferroelectric is important functional material used for diverse applications, such as ferroelectric nonvolatile memory, piezoelectric transducers, actuators, sensors, thermal imaging, to name a few. Ferroelectric materials are characterized by their spontaneous polarization being switched by external electric field, where the polarizations with same orientations form ferroelectric domains. Ferroelectric domains are the key to understand the property in ferroelectric materials, due to the fact that the domain reorientation and domain wall motion are closely associated with the piezoelectric and dielectric properties [1–6]. Thus, it is desirable to tailor the domain structure as well as domain rotations for tuning the electrical properties of a ferroelectric material.

The domain structure of a ferroelectric material depends on numerous factors, including crystal phases, poling conditions, internal stress/strain and defects [2,7–11], etc. Doping strategy can be used to modulate the domain structure and domain wall motion. Lower valence additives, such as $Mn^{2+,3+}$, $Fe^{2+,3+}$, Co^{3+}, Ni^{3+}, and Cr^{3+}, are generally chosen as acceptor dopants and incorporated into the higher valence B-site in ABO_3 perovskites [12–16]. For charge balance, acceptor doping will introduce oxygen vacancies, being trapped at the high-energy areas, such as domain walls, and forming defect dipoles with the acceptor cations. These defect dipoles align parallel to the polarization direction, leading to an internal bias field, which will reduce the domain wall mobility, i.e. improve the stability of domain configuration, and account for the enhanced mechanical quality factor Q_m and decreased dielectric loss.

$(Na, Bi)TiO_3$ (NBT) based lead free ceramics have been actively studied for replacing lead-based ferroelectric materials. NBT ceramic has a ABO_3 perovskite structure with rhombohedral $R3c$ space group at room temperature [17], the depolarization temperature T_d and the maximum dielectric temperature T_m are around 185 and 340 °C, respectively [18]. The remnant polarization P_r of NBT is 38 μC/cm^2, however, the high coercive field E_c (~73 kV/cm) [19], together with the decreased resistivity induced by Bi volatilization during the high temperature sintering, leads to a hard poling procedure and low piezoelectric coefficient d_{33} ~100 pC/N [20]. Analogous to PZTs, the piezoelectric properties of NBT could be

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http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.047
0955-2219/

enhanced by forming morphotropic phase boundary (MPB) with other ferroelectric end members [21,22], such as $PbTiO_3$, $BaTiO_3$, (Bi, K)TiO_3 and (Bi, Li)TiO_3, to name a few [23–29]. However, previous investigations have shown that d_{33} and T_d in the same system can be enhanced only at the expense of each other [30]. Nevertheless, a ternary $0.79(Na_{0.5}Bi_{0.5})TiO_3$-$0.14(K_{0.5}Na_{0.5})TiO_3$-$0.07BaTiO_3$ (BNBK79) solid solution with tetragonal phase was reported to possess medium values of T_d and d_{33}, being on the order of 238 °C and 135 pC/N, respectively [31]. In addition, through Mn-doping, the Q_m is enhanced to 1100, with decreased dielectric loss of 0.6%, showing "hardening" effect, promising for high-power piezoelectric applications. However, the impact of the acceptor doping to the domain structure, and the relationship between macroscopic properties and domain structure, are still unclarified.

In this research, the domain structure of BNBK79 and BNBK79-Mn ceramics before and after poling were observed, the domain switching characteristics based on the strain behavior and polarization hysteresis were studied. The impacts of acceptor doping on the domain structure, domain switch and electrical properties were discussed.

2. Experimental section

The piezoelectric BNBK79 and BNBK79-Mn ceramics were prepared by conditional solid-state reaction method. The raw materials K_2CO_3 (99.0% Alfa Aesar), Na_2CO_3 (99.5%, Alfa Aesar), Bi_2O_3 (99.99%, MCP), $BaCO_3$ (99.9% Alfa Aesar), TiO_2 (99.99%, Ishihara) and MnO_2 (99.9%, Alfa Aesar) were weighed according to the nominal compositions. The powder was calcined at 850–880 °C for 2 h and pressed into pallet disks with 12.5 mm in diameter and 1.5 mm in thickness, then isostatically pressed at 200 MPa, followed by sintering in air at 1050–1150 °C for 2 h.

The phase of the as-sintered ceramics was studied by X-ray diffraction with Cu Kα radiation (PANalytical Xpert Pro MPD, Almelo, Netherlands). All the poling in this work was carried out at a dc field of 40 kV/cm for 10 min at room temperature. The d_{33} was measured by Berlincourt d_{33} meter. The planar electromechanical coupling factor k_p and the dielectric properties were measured by the impedance phase-gain analyzer (HP4294A, Agilent, USA). The polarization hysteresis was determined at different frequencies and electric fields using a modified Sawyer–Tower circuit driven by a high-voltage power supply (Trek Model 610, TREK, USA). The electric field-induced strain was measured by a linear variable differential transducer driven by a lock-in amplifier (Model SR830, Stanford Research Systems, USA). The high-field piezoelectric coefficient d_{33}^* was calculated from the unipolar S–E (strain versus electric field) curves. For domain observation, the un-poled and poled samples were first polished and then annealed at 100 °C for 12 h to remove the stress on the polish surface, and finally chemically etched at room temperature in a mixed aqueous solution of HCl/HF acids. The exposed domain patterns were observed by scanning electron microscopes ("Nova NanoSEM 630, FEI, USA" for BNBK79 ceramics; "S-4800, Hitachi, Japan" for BNBK79-Mn ceramics).

3. Results and discussion

3.1. Structure and dielectric properties

Fig. 1 shows the XRD patterns of BNBK79 and BNBK79-Mn ceramics over the 2θ range of 20°–60°. A perovskite structure with no trace of impurity was achieved for the two compositions. Generally, the tetragonal symmetry of perovskite phase can be characterized by the splitting of the [002] and [200] peaks, with the intensity ratio $I_{[002]}/I_{[200]}$ being on the order of 1/2. Apparently,

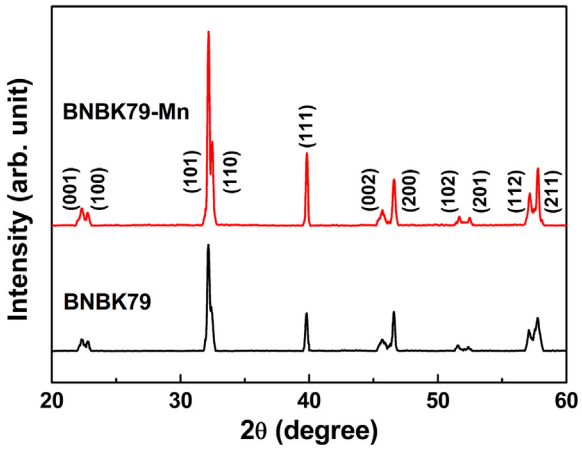

Fig. 1. XRD patterns of BNBK79 and BNBK79-Mn ceramics.

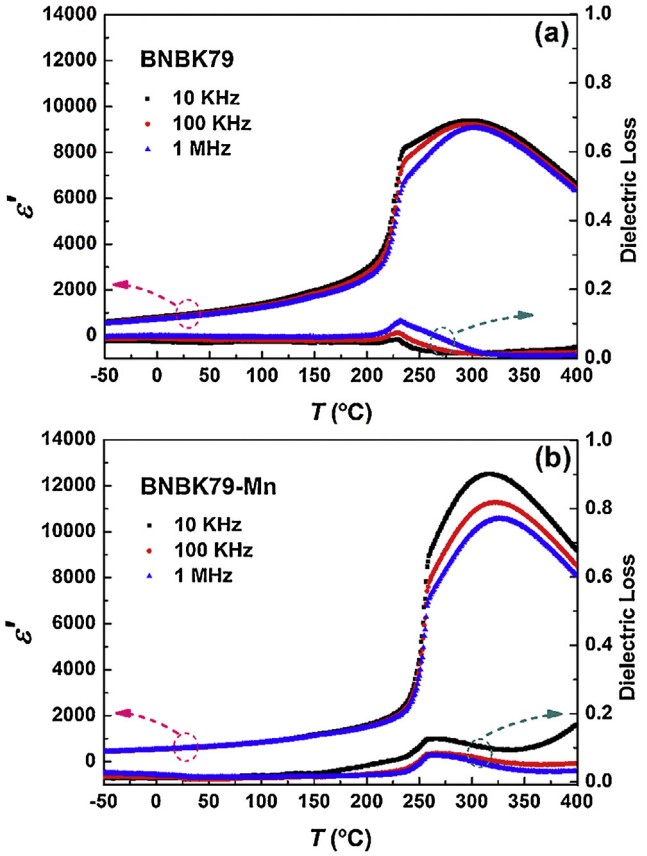

Fig. 2. Dielectric properties of BNBK79 (a) and BNBK79-Mn (b) ceramics, respectively.

both BNBK79 and BNBK79-Mn ceramics are of tetragonal phase. In addition, the intensities of the diffraction peaks for BNBK79-Mn ceramics are stronger than those in pure counterparts, demonstrating better crystallization behavior and lower grain boundary density, which is also confirmed by the higher relative density and larger grain size in BNBK79-Mn ceramics (as given in Table 1).

Fig. 2 shows the dielectric constant ε' and dielectric loss for poled BNBK79 and BNBK79-Mn ceramics as function of temperature and frequency. For both ceramics, two anomalies were observed in the $\varepsilon' \sim T$ curves, corresponding to the depolarization temperature T_d and maximum dielectric constant temperature T_m, respectively. It is worth to note that both the T_d and T_m in BNBK79-Mn ceramics

Please cite this article in press as: Y. Qin, et al., Impacts of acceptor doping on the piezoelectric properties and domain structure in NBT-based lead-free ceramics, *J Eur Ceram Soc* (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.047