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The temperature-dependent piezoelectric and electromechanical properties of cobalt-modified sodium bismuth titanate

Chun-Ming Wang[a,b,*], Liang Zhao[a], Yun Liu[b], Ray L. Withers[b,**], Shujun Zhang[c], Qian Wang[a]

[a]School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China
[b]Research School of Chemistry, The Australian National University, Australian Capital Territory, Canberra 0200, Australia
[c]Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

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Abstract

Lightly cobalt-modified, Aurivillius-type, sodium bismuth titanate ($Na_{0.5}Bi_{4.5}Ti_4O_{15}$, NBT) ceramics were synthesized by substituting a small amount of cobalt ions onto the Ti^{4+} sites using conventional solid-state reaction. X-ray photoelectron spectroscopy (XPS) analysis coupled with bond valence sum calculations show that the dopant cobalt ions substitute for Ti^{4+} ions in the form of Co^{3+}. The resultant cobalt-modified NBT ceramics (NBT-Co) exhibit better piezoelectric and electromechanical properties by comparison with pure NBT. With only 0.3 wt% Co^{3+} substitution, the piezoelectric properties of the NBT-Co ceramics are optimal, exhibiting a high piezoelectric coefficient ($d_{33} \sim 33$ pC/N), a low dielectric loss tan δ ($\sim 0.1\%$ at 1 kHz), a high thickness planar coupling coefficient ($k_t \sim 34\%$) as well as a high Curie temperature ($T_c \sim 663$ °C). Such NBT-Co ceramics exhibit nearly temperature-independent piezoelectric and electromechanical properties up to 400 °C, suggesting that these cobalt-modified NBT ceramics are promising materials for high temperature piezoelectric applications.

Keywords: Bismuth layer-structured ferroelectrics; Aurivillius type; Sodium bismuth titanate; Piezoelectric ceramics

1. Introduction

The $Bi_2O_2 \cdot A_{n\text{-}1}B_nO_{3n+1}$ family of bismuth layer-structured ferroelectrics (BLSFs) have received significant attention for their potential use in non-volatile ferroelectric random-access memory [1–3] and high-temperature piezoelectric devices [4–6], owing to their electrically fatigue-free properties and relatively high Curie temperature T_c, respectively. However, due to the fact that the spontaneous polarization of BLSFs is largely restricted to the *a–b* plane in plate-like grains perpendicular to the *c* axis, it is difficult to obtain high piezoelectric activity in ordinary sintered BLSF ceramics with randomly oriented grain structure. This low piezoelectric activity limits the practical applications of BLSF ceramics as high temperature piezoelectric materials, so considerable efforts have been devoted to improve the piezoelectric properties of BLSFs [7–15].

Taking into consideration the anisotropic character of the microstructures and properties of BLSF ceramics, texturing technologies have been widely employed in an attempt to improve their piezoelectric properties [11–13]. In general, the electrical conductivity within the *a–b* plane, where the high piezoelectric activity appears, is higher than that in the orthogonal *c* direction [14]. This makes the poling process difficult, and also limits high temperature applications as the conductivity increases with increasing temperature [15]. Furthermore, it is desirable to obtain high piezoelectric activity using a simple conventional sintering approach. An alternative approach to improve the piezoelectric activity of BLSF ceramics is to introduce dopant cations. Cobalt is known to be an effective dopant cation to enhance the piezoelectric activity of perovskite-structured as well as BLSF materials [16–18].

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[*] Corresponding author at: School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China.

[**] Corresponding author.

E-mail addresses: wangcm@sdu.edu.cn (C.-M. Wang), Ray.Withers@anu.edu.au (R.L. Withers).

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The ferroelectric and piezoelectric properties of the $n=2$ BLSF $ABi_2(Nb,Ta)_2O_9$ (A=Ca, Sr, Ba or Pb) and the $n=3$ BLSF $Bi_4Ti_3O_{12}$ and their derivatives have been investigated extensively [19–27]. The $n=4$ BLSFs such as $ABi_4Ti_4O_{15}$ (A= Ca, Sr, Ba or Pb) have also been extensively investigated [28–35]. By contrast, the electrical and piezoelectric characteristics of the $n=4$ BLSFs $M_{0.5}Bi_{4.5}Ti_4O_{15}$ (M=Na or K) have not been sufficiently studied, although several reports on these materials have appeared [36–40]. Hence we prepared cobalt-modified $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (abbreviated as NBT) piezoelectric ceramics via a conventional solid state reaction recently, and the resultant cobalt-modified NBT exhibited good room temperature piezoelectric properties [41]. For high temperature applications, however, piezoelectric materials should have a largely temperature-independent electromechanical resonant frequency, strong anisotropic electromechanical properties as well as good piezoelectric properties in the desired high temperature range. Thus, in this work, we systematically investigate the dielectric, piezoelectric and electromechanical properties of cobalt-modified NBT ceramics at elevated temperature.

2. Experimental procedure

Conventional solid state reaction was used to prepare Co-doped sodium bismuth titanate ($Na_{0.5}Bi_{4.5}Ti_4O_{15}$) piezoelectric ceramics. Analytical grade Na_2CO_3 (99.8%), Bi_2O_3 (99.8%), TiO_2 (99.9%) and CoO (99.9%) were used as starting materials. The compositions investigated in the present work were NBT and NBT+0.3 wt% CoO (abbreviated as NBT-Co3). The weighed chemicals were wet milled in polyethylene bottles with ZrO_2 balls for 12 h in ethanol. The milled powders were dried and calcined at 800 °C for 3 h. After calcinations, the mixture was milled again under the same conditions. The milled powders were dried, ground and granulated with a polyvinyl alcohol (PVA) binder. The granulated powder was then pressed into pellets (15 mm in diameter by 2.0 mm in thickness) at a pressure of 150 MPa. In order to prevent evaporation of Na and Bi ions and to retain the desired stoichiometry, the green pellets were put into sealed Al_2O_3 crucibles and embedded in powder having exactly the same chemical composition. Finally, pure NBT and NBT-Co3 ceramics were sintered at 1120 and 1080 °C, respectively, because cobalt modification lowers the sintering temperature and increases the density of the NBT ceramics.

The density of the sintered samples was determined by the Archimedes method. The X-ray diffraction (XRD) patterns were obtained by an X-ray diffractometer (D8 Advance, Bruker AXS GMBH) using Cu$K_{\alpha 1}$ ($\lambda=1.5406$ Å) radiation. Microstructural characterization of the sintered ceramics was conducted by scanning electron microscopy (SEM, Hitachi S-4800). The X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCA-LAB MKII apparatus. Samples for the electrical measurements were first polished and then silver electrodes screen-printed on both surfaces followed by firing at 550 °C for 20 min. These electroded samples were then poled in silicone oil under a DC electric field of 130 kV/cm at 200 °C. The piezoelectric coefficient, d_{33}, was measured using a quasi-static d_{33} meter (Institute of Acoustics, Academia Sinica, ZJ-2). A modified Sawyer-Tower circuit and a linear variable differential transducer driven by a lock-in amplifier (Stanford Research System, model SR830) were used to determine the polarization hysteresis loops of the polarization versus electric field (P–E), which were measured at a temperature of 200 °C with a frequency of 1 Hz. The temperature-dependent dielectric spectra measurements were performed with a 4294A impedance analyzer (Agilent Technologies). The resonant and anti-resonant frequencies were obtained from the 4294A impedance analyzer. The mechanical quality factor (Q_m), the electromechanical coupling factors (k_p, k_t) and the frequency constants (N_p, N_t) were calculated according to Onoe's equations [42].

3. Results and discussion

Fig. 1 shows an SEM image of the as-synthesized NBT-Co3 ceramics. The plate-like grains of the NBT-Co3 ceramics are highly anisotropic with the in-plane grain size much longer than the thickness along the c direction. The highly anisotropic grains are attributed to a high grain growth rate in the direction perpendicular to the c axis of the four-layer BLSF crystal. The X-ray diffraction patterns of the NBT and NBT-Co3 piezoelectric ceramics are shown in Fig. 2 and confirm the presence of a single phase, $n=4$, BLSF structure. The diffraction peak with the highest intensity is the (119) peak, in good agreement with the intensity of the $(1\,1\,\underline{2n+1})$ peaks observed in BLSFs [43]. The peaks of the NBT-Co3 ceramics are slightly shifted towards the lower angle side by comparison with the pure NBT ceramics, requiring a slight expansion of the lattice on Co incorporation.

The density of the NBT is 7.268 g cm^{-3}, while the density of the NBT-Co3 is 7.398 g cm^{-3}, indicating that the introduction of Co increases the densities. Related to the theoretical density of NBT, ~7.619 g cm^{-3}, the relative densities of both the NBT and NBT-Co3 ceramics are determined, greater than 95%. The X-ray photoelectron spectroscopy is presented in

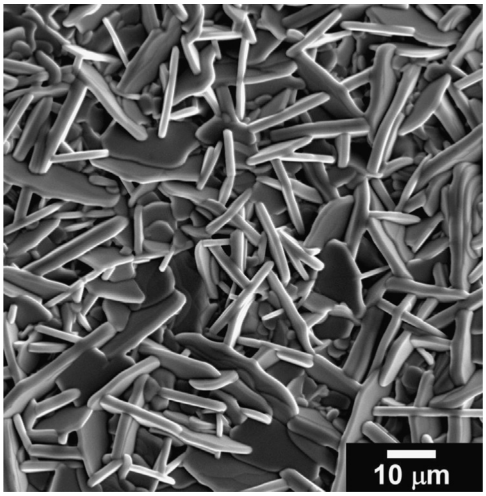

Fig. 1. Morphology of the NBT-Co3 ceramics.