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Enhanced piezoelectric properties of Nb and Mn co-doped $CaBi_4Ti_4O_{15}$ high temperature piezoceramics

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ABSTRACT

The properties of $CaBi_4Ti_4O_{15}$ (CBT), $CaBi_4Ti_{3.95}Nb_{0.05}O_{15}$ (CBTN) and $CaBi_4Ti_{3.95}Nb_{0.05}O_{15}$ + 0.2 wt% MnO_2 (CBTN–Mn) ferroelectric ceramics with bismuth layer structure were studied. Significant enhancement of piezoelectric coefficient was obtained for CBTN–Mn ceramics (d_{33} = 23 pC/N), being nearly three times that of CBT counterpart (d_{33} = 8 pC/N). Together with its high Curie temperature (T_c = 790 °C), low dielectric loss ($\tan\delta$ = 0.2%), high resistivity ($\rho = 4.2 \times 10^6\ \Omega$ cm at 500 °C) and good thermal stability up to 700 °C, the CBTN–Mn ceramic is a potential material for high temperature piezoelectric applications.

1. Introduction

In last few decades, ferroelectric ceramics with bismuth layer structure have been actively studied for non-volatile random-access memory and high temperature piezoelectric applications, owing to their fatigue-free characteristics and high Curie temperature T_c, respectively [1–3]. The general formula of bismuth layer-structured ferroelectrics (BLSF) is $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, which can be described as regular stacking of $(A_{m-1}B_mO_{3m+1})^{2-}$ pseudo-perovskite blocks, separated by fluorite-like $(Bi_2O_2)^{2+}$ layers along the *c* axis [4,5]. The $(Bi_2O_2)^{2+}$ act as insulating paraelectric layers, limiting the spontaneous polarization of BLSF materials in the *a*–*b* plane, i.e., the pseudo-perovskite $(A_{m-1}B_mO_{3m+1})^{2-}$ blocks. The pseudo-perovskite blocks can offer large possibilities in terms of compositional flexibility, which allow mono-, di-, trivalent element (e.g., Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Bi^{3+} and La^{3+}), or a mixture of them on the A-site and a transition element (e.g., Fe^{3+}, Cr^{3+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, Mo^{6+} and W^{6+}) on the B-site [6]. The number of $[BO_6]$ octahedra in the pseudo-perovskite blocks *m* (basically from 1 to 6) strongly affects the dielectric and ferroelectric properties of BLSF, because the spontaneous polarization arises from different modes of $[BO_6]$ octahedral rotation, where the displacement of the ions on the B-site dominates the polarization component in the *a*–*b* plane of the pseudo-perovskite layers.

$CaBi_4Ti_4O_{15}$ (CBT) belongs to the family of BLSF with *m* = 4, where Ca^{2+} and Bi^{3+} located at A-site, while Ti^{4+} occupied the B-site of the pseudo-perovskite blocks. Compared to other extensively studied BLSF ceramics with *m* = 4, such as $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (T_c = 668 °C, d_{33} = 17 pC/N) [7] and $K_{0.5}Bi_{4.5}Ti_4O_{15}$ (T_c = 555 °C, d_{33} = 21.2 pC/N) [8], CBT was reported to possess higher Curie temperature (T_c = 790 °C) but much lower piezoelectric coefficient (d_{33} = 8 pC/N) [9]. It was reported that $(MCe)^{2+}$ (M = Li, Na, K) doped CBT ceramics can effectively enhance the piezoelectric coefficient up to 20 pC/N without sacrificing the Curie temperature [10,11]. However, the B-site modification of CBT ceramics, being expected to possess substantially increased d_{33} (>20 pC/N), has not yet been reported, which is the topic of this research.

The structure and properties of B-site Nb-doped and Nb/Mn co-doped CBT ceramics were investigated and compared with pure CBT counterpart. Enhanced piezoelectric coefficient (d_{33} = 23 pC/N) was obtained in Nb/Mn co-doped CBT ceramics. Of particular importance is that the B-site modified CBT ceramics do not contain the alkali metals, such as in $Na_{0.5}Bi_{4.5}Ti_4O_{15}$, $K_{0.5}Bi_{4.5}Ti_4O_{15}$, and A-site $(MCe)^{2+}$ (M = Li, Na, K) doped CBT, making the ceramic fabrication process easier.

2. Experimental procedures

Ceramic samples of $CaBi_4Ti_4O_{15}$ (CBT), $CaBi_4Ti_{3.95}Nb_{0.05}O_{15}$ (CBTN), and $CaBi_4Ti_{3.95}Nb_{0.05}O_{15}$ + 0.2 wt% MnO_2 (CBTN–Mn) were prepared by the solid state reaction method. Reagent-grade $CaCO_3$ (99.9%), Bi_2O_3 (99.9%), TiO_2 (99.9%), Nb_2O_5 (99.5%), and MnO_2 (99.9%) were selected as the starting raw materials. The raw

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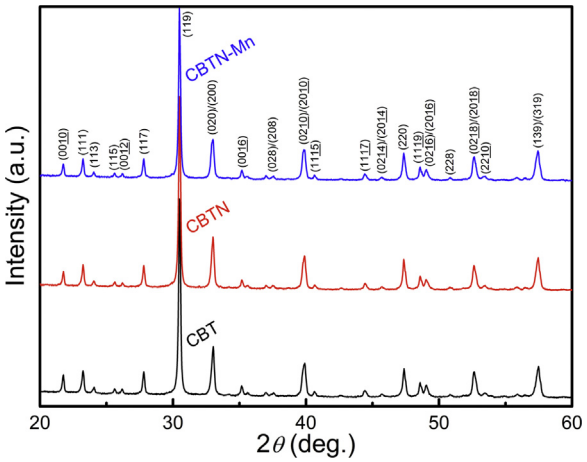

Fig. 1. XRD patterns of the CBT, CBTN, and CBTN–Mn ceramics.

powders were mixed by ball milling with ethanol for 24 h, then dried and calcined at 800 °C for 2 h. A small amount of Rhoplex binder (1.0 wt%) was added in the calcined powders and milled again, dried and pressed into pellets. After the binder burn-out, the pellets were cold isostatic pressed and subsequently sintered at 1075–1175 °C for 2 h in air. The phase structure was determined by X-ray diffraction (XRD: X'Pert Pro PANalytical, CuKα radiation), which was analyzed by X'Pert HighScore software. The microstructure features of the polished and thermally-etched surfaces, as well as the fractured surfaces of the sintered ceramics were characterized by the field emission scanning electron microscopy (FE-SEM, JSM-5610LV; JEOL, Japan).

The obtained samples were parallel polished and painted with silver paste on both sides, then fired at 750 °C to form the electrodes. The electrical resistivity was calculated from the resistance, which was measured using a source meter (Keithley 2410C) by applying 100 V on the samples. The temperature dependence of the dielectric constant and loss at 100 kHz was determined by an LCR meter (HP4194A, Hewlett-Packard, CA) with the temperature increasing from 30 to 850 °C. For the piezoelectric

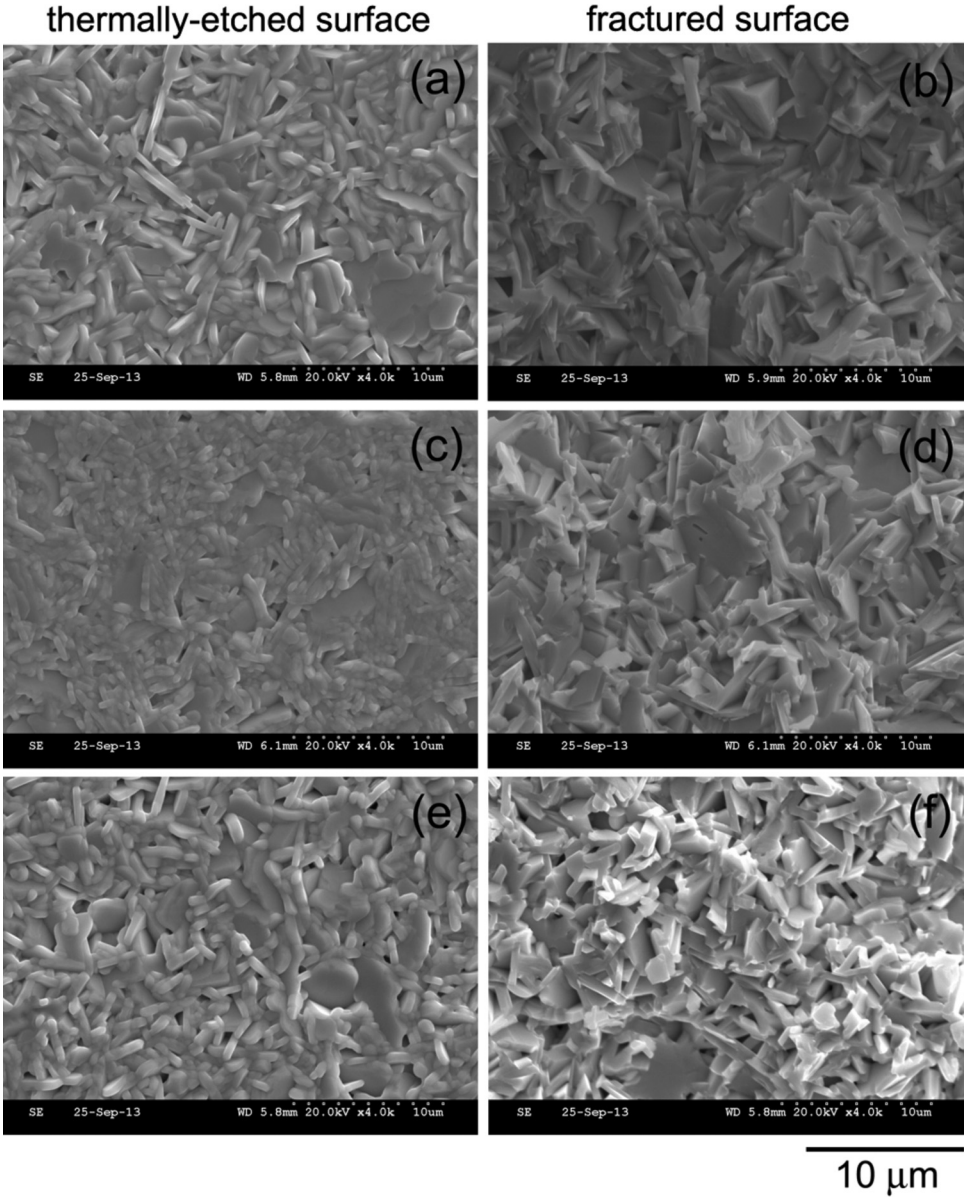

Fig. 2. SEM images of thermally-etched and fractured surfaces of the (a,b) CBT, (c,d) CBTN, and (e,f) CBTN–Mn ceramics.