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Low temperature sintering of lead-free $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ piezoelectric ceramics by co-doping with CuO and Nb_2O_5

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Abstract

Effect of excess CuO additive on the sintering behavior and piezoelectric properties of $Bi_{0.5}(Na_{82}K_{0.18})_{0.5}TiO_3$ ceramics was investigated. The addition of small amount of excess CuO as low as 1 mol% was quite effective to lower the sintering temperature (T_s) of BNKT ceramics down to 975 °C while their piezoelectric properties were degraded by Cu doping. However, the electric field-induced strain was markedly enhanced by further addition of Nb_2O_5 with CuO without elevating T_s. The normalized strain S_{max}/E_{max} of 427 pm/V was obtained with a specimen sintered with 0.02 mol CuO and 0.03 mol Nb_2O_5 in excess.

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

1. Introduction

Multilayer actuators (MLAs) become increasingly important in high precision mechatronic systems [1,2]. Currently most MLAs adopt expensive AgPd alloys as internal electrodes due to their thermal stability between piezoelectric ceramic layers throughout high temperature firing process. Provided that low temperature co-firing of piezoceramic/metal multilayer laminates is established without significant degradation in piezoelectric properties, a cheaper conductor such as silver or low Pd concentration alloy can be used as an inner electrode material for low cost MLAs [3,4].

Recently lead-free piezoelectric ceramics are extensively explored to expel environmentally harmful PZT-based ceramics that have been predominantly used as piezoelectric sensors and actuators last five decades. Among various candidates, Bi-based ceramics now attract great attention because of their giant field-induced strains of 400–614 pm/V [5–8]. However, Bi-based systems require a high sintering temperature (T_s) over 1150 °C for sufficient densification. On the other hand CuO was known as a good sintering aid for lowering T_s in case of PZT-based ceramics [9] and KNN ceramics [10,11] while its effect on the sintering behavior of Bi-based ceramics has been little reported so far. Therefore this study investigates the sintering behavior and strain properties of $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ (BNKT) ceramics co-doped with CuO and Nb_2O_5. In this work, the Na/K ratio was chosen as 82/18 because Sasaki et al. [12] reported that the piezoelectric properties reach highest when $x = 0.16–0.20$ in $(1 - x)(Bi_{0.5}Na_{0.5})TiO_3–x(Bi_{0.5}K_{0.5})TiO_3$ ceramics.

2. Experimental

A conventional solid state reaction route was applied to prepare the powders with compositions of $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3–xCuO–yNb_2O_5$ ($x = 0$, 0.01, 0.02, 0.03, 0.04 and 0.05; $y = 0$, 0.01, 0.02, 0.03 and 0.04). Powders of Bi_2O_3, K_2CO_3, Nb_2O_5, TiO_2, CuO (99.9%, Kojundo Chemical), and Na_2CO_3 (99.9%, Cerac Specialty Inorganics) were used raw materials. The powders were weighed according to the chemical formula, ball-milled for 24 h in ethanol, and calcined at 800 °C for 2 h. The calcined powder was pressed into circular disks with a diameter of 12 mm at 100 MPa. The green compacts were sintered in covered alumina crucibles at 975 °C for 2 h in air.

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The crystal structure was analyzed using an X-ray diffractometer (XRD, RAD III, Rigaku, Japan), and the surface morphology was examined 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 electric-field-induced strain (*S–E*) measurement was carried out using a linear variable differential transducer. The piezoelectric constant d_{33} was determined using a Berlincourt d_{33}-meter after poling samples under an electric field of 5 kV/mm at 80 °C for 15 min. The dielectric constant, loss tangent, planar piezoelectric coupling coefficient k_p, and mechanical quality factor Q_m of poled specimens were characterized with an impedance analyzer (HP4194A) on the basis of IEEE standards [13].

3. Results and discussion

3.1. Sintering behavior and piezoelectric properties of CuO-doped BNKT ceramics

Fig. 1 shows the surface SEM micrographs of undoped and CuO-doped BNKT ceramics sintered at 975 °C for 2 h in air. Undoped samples exhibit little grain growth with poor densification at such low T_s, however, both the average grain size and relative density increase up to 1.14 μm and 96% respectively, by adding excess CuO even as low as 1 mol%. Further increase in the amount of CuO aid only results in slight enhancement in the average grain size. It should be noted that the secondary phases are observed at grain boundaries and corners as indicated by arrows on the figures, which strongly suggests the presence of a liquid phase during sintering similarly to CuO added KNN ceramics [11]. However, XRD analysis detected little secondary phases, implying that the observed unwanted phase between grains is amorphous.

The d_{33} and k_p were determined for CuO added specimens and the results are shown in Fig. 2. The piezoelectric parameters for high temperature (HT) fired BNKT ceramics are also given for comparison because the piezoelectric properties of low temperature (LT) fired BNKT ceramics without CuO sintering aid cannot be measured due to their poor density. The d_{33} and k_p of HT fired specimen with $x = 0$ are 146 pC/N and 34%, respectively, which are higher than those of LT fired specimens that moreover show degradations in the piezoelectric properties with increasing CuO content. These results seem to be arisen from the experimental evidence that Cu ions generally act as acceptors in ABO_3 type perovskite structures [14], which is also supported by the fact that the ionic radius of a Cu^{2+} is closer to that of Ti^{4+} than those of Bi^{3+}, Na^+, or K^+ ions [15].

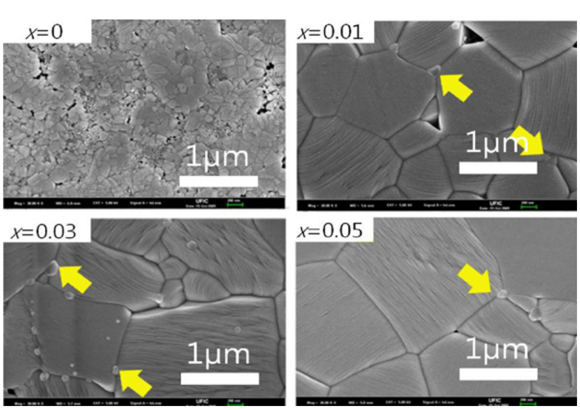

Fig. 1. The surface SEM micrographs of undoped and *x* mol CuO doped BNKT ceramics sintered at 975 °C for 2 h in air.

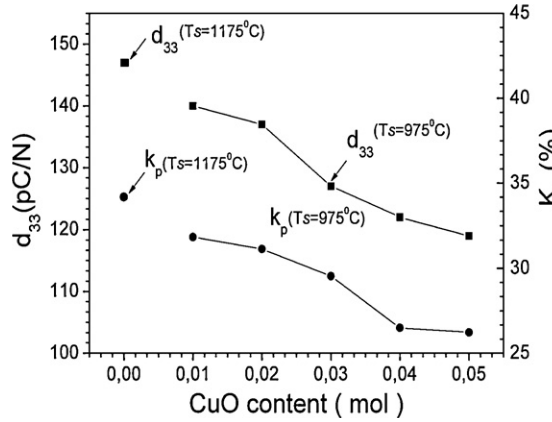

Fig. 2. The d_{33} and k_p of *x* mol CuO doped BNKT ceramics.

3.2. Effects of further Nb_2O_5 doping on the sintering behavior and piezoelectric properties of CuO-added BNKT ceramics

To improve the piezoelectric properties of CuO added BNKT ceramics, Nb was co-doped with CuO. Fig. 3 shows SEM photographs of BNKT ceramics sintered with 0.02 mol CuO and *y* mol Nb_2O_5 simultaneously. The sintering was also carried out 975 °C for 2 h in air. Comparison of microstructures between specimens with and without Nb_2O_5 elucidates that the addition of Nb_2O_5 results in faceted grain morphology as well

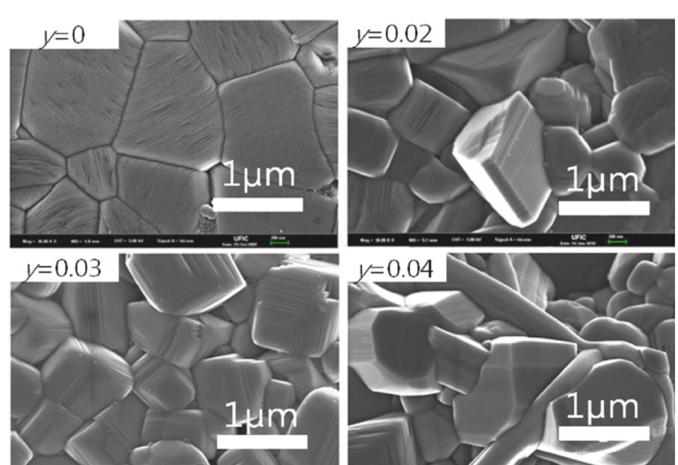

Fig. 3. The effect of further addition of *y* mol Nb_2O_5 on the microstructure of 0.02 mol CuO added BNKT ceramics sintered at 975 °C for 2 h in air.

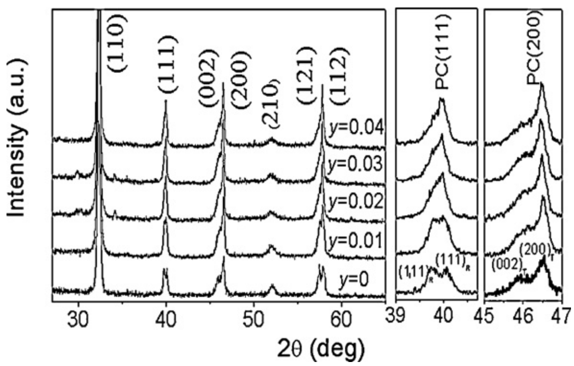

Fig. 4. X-ray diffraction patterns of BNKT ceramics sintered with both 0.02 mol CuO and y mol Nb_2O_5 in excess.

as reduced grain sizes, however, the sintered density is little deteriorated by Nb_2O_5 doping. The relative densities of specimens with $y = 0–0.04$ were in the range of 96.2–96.5%.

The crystal structure of BNKT ceramics co-doped with 0.02 mol CuO and y mol Nb_2O_5 was analyzed using X-ray diffractometry and the results are given in Fig. 4. All specimens demonstrate a perovskite structure without any noticeable secondary phase. The rhombohedral phase is characterized by (1 1 1)/(1 −1 1) peak splitting at 40° while the tetragonal phase is done by (0 0 2)/(2 0 0) peak splitting at around 46° [14]. According to Fig. 4, therefore, at room temperature, CuO-added BNKT ceramics reveal the coexistence of rhombohedral and tetragonal phases, and then both phases gradually transform to a pseudocubic phase as the amount of excess Nb_2O_5 increases. The transition from crystallographically anisotropic rhombohedral and tetragonal phases to a more symmetric pseudocubic phase might be attributed to the lattice distortion caused by the difference in ionic radii between matrix atoms and dopants [16]. Considering the fact that the ionic radii of Bi, Na, K, Ti, Cu and Nb ions are 1.17 Å, 1.18, 1.33, 0.61, 0.68, and 0.64, respectively [14], both Cu and Nb ions seem to replace smaller Ti ions.

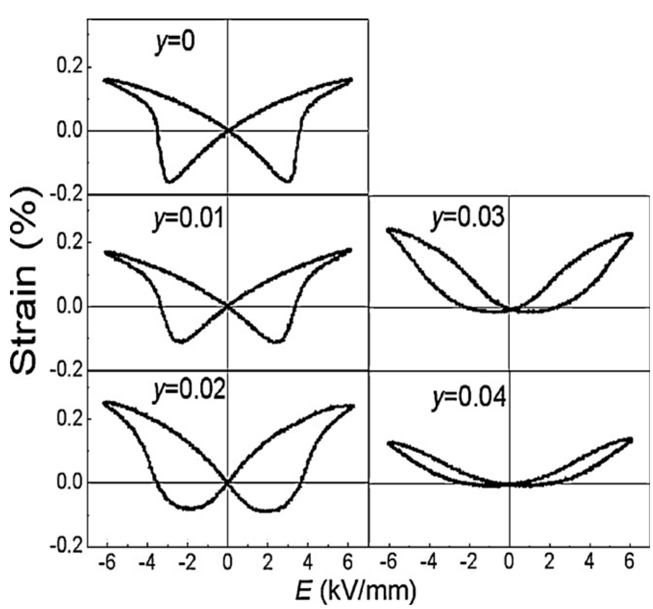

Fig. 5. Bipolar $S–E$ curves of BNKT ceramics sintered with both 0.02 mol CuO and y mol Nb_2O_5 in excess.

An interesting result was found from bipolar strain measurements as represented in Fig. 5. When Nb_2O_5 was doped by 0.02–0.04 mol in addition to 0.02 mol CuO, the electric field-induced strain was remarkably increased. The normalized strain S_{max}/E_{max} of a specimen with $x = 0.02$ and $y = 0$ was 214 pm/V, but it increased up to 427 pm/V when $y = 0.02$. Further addition of Nb_2O_5 up to $y = 0.04$ leads to not only a decrease in the S_{max}/E_{max} but smaller hysteresis in $S–E$ loop. In this case, a parabolic $S–E$ relationship with little negative strain is observed, suggesting that the pseudocubic phase is not piezoelectric but electrostrictive like relaxors such as PMN-PT [17]. This result is very similar to recently reported antiferroelectrics (BNT-BT-KNN) [18] that also revealed very low $S–E$ hysteresis and high electrostriction coefficients. It should be noted that the S_{max}/E_{max} of LT fired BNKT (427 pm/V) obtained in this work is still lower than that of HT fired Nb-doped BNKT ceramics (641 pm/V) [19] sintered at 1175 °C for 2 h without CuO sintering aid.

4. Conclusions

Low temperature sintering of BNKT ceramics was examined by doping CuO as a sintering aid. It was found that the addition of excess CuO was quite effective to lower T_s of BNKT ceramics by 200 °C even at a doping level as low as 1 mol% although their piezoelectric properties were degraded with CuO doping. However, the electric-field-induced strain was markedly enhanced by further addition of Nb_2O_5 with CuO even at a low T_s of 975 °C. A large normalized strain S_{max}/E_{max} of 427 pm/V was observed in a specimen co-doped with 0.02 mol CuO and 0.02 mol Nb_2O_5 in excess, which is very promising for its application to low cost MLAs.

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