CuO as a sintering additive for $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$–$(K_{0.5}Na_{0.5})NbO_3$ lead-free piezoceramics

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Abstract

CuO as a sintering additive was utilized to explore a low-temperature sintering of $0.92(Bi_{1/2}Na_{1/2})TiO_3$–$0.06BaTiO_3$–$0.02(K_{0.5}Na_{0.5})NbO_3$ lead-free piezoceramic which has shown a promise for actuator applications due to its large strain. The sintering temperature guaranteeing the relative density of greater than 98% is drastically decreased with CuO addition, and saturates at a temperature as low as ∼930 °C when the addition level exceeds *ca.* 1 mol.%. Two distinguished features induced by the addition of CuO were noted. Firstly, the initially existing two-phase mixture gradually evolves into a rhombohedral single phase with an extremely small non-cubic distortion. Secondly, a liquid phase induced by the addition of CuO causes an abnormal grain growth, which can be attributed to the grain boundary reentrant edge mechanism. Based on these two observations, it is concluded that the added CuO not only forms a liquid phase but also diffuses into the lattice. In the meantime, temperature dependent permittivity measurements both on unpoled and poled samples suggest that the phase stability of the system is greatly influenced by the addition of CuO. Polarization and strain hysteresis measurements relate the changes in the phase stability closely to the stabilization of ferroelectric order, as exemplified by a significant increase in both the remanent strain and polarization values. Electron paramagnetic resonance (EPR) spectroscopic analysis revealed that the stabilization of ferroelectric order originates from a significant amount of Cu^{2+} diffusing into the lattice on B-site. There, it acts as an acceptor and forms a defect dipole in association with a charge balancing oxygen vacancy.
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1. Introduction

In response to the increasing concerns and regulations on the use of toxic materials for electric and electronic devices, the search for innocuous materials with competitive functional properties has been one of the hottest pursuits in the field of materials science and engineering over the last two decades.[1–7] This is especially true for the piezoelectric community, since widely used piezoceramics are highly dependent upon the presence of lead (Pb) that is listed among the six toxic materials to be abolished as early as possible. In addition, the research activities are largely driven by the exponentially increasing demand on high performance piezoceramics, which are essential to realize the desired technological achievements for the next generations, *e.g.* energy-effective, miniaturized, and integrated.[8] With a couple of breakthroughs,[9,10] two important classes of lead-free piezoceramics, *i.e.* $(K_{0.5}Na_{0.5})NbO_3$ (KNN)- and $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)-based materials, are now considered as the most promising in replacing lead-containing piezoceramics.[3–6]

In the case of actuator applications, large displacements are often facilitated using multilayer technology, where a piezoceramic as an active component and electrodes as passive

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ones are co-fired.[11] In this case, the total cost is significantly affected by the cost of the electrode material. Therefore, Ag/Pd alloys are utilized and their thermochemical reactions with the ubiquitous PZT have been studied[12] and recently also extended to include the reactions with BNT-based lead-free piezoceramics.[13] A significant cost reduction is feasible using copper as an electrode material.[11] More affordable electrode materials, however, hinge on a low sintering temperature, which should preferably lie below 1000 °C. Low temperature sintering has an additional advantage in the case of lead-free piezoceramics, because they normally contain highly volatile elements such as Na, K, and Bi. In the case of KNN-based materials, CuO as a sintering additive has been successfully utilized to bring the sintering temperature down to as low as ~950 °C.[14,15] However, beyond the reduction in sintering temperature, the doping with CuO as sintering additive is accompanied by a pronounced impact on defect structure owing to the formation of defect dipoles as well as on the piezoelectric properties.[16]

Recently, we reported that an electric-field-induced strain of as large as ~0.45% can be achieved in 0.96BNT–0.06BaTiO$_3$ (BT) ceramics, when a small amount of BNT is replaced by KNN.[17] The follow-up studies for the dependence of properties on composition[18] and temperature[19] revealed that the giant strain is a consequence of a polymorphic phase boundary (PPB) shifted to room temperature by the addition of KNN. In other words, the large strain originates from the fact that the inherently large poling strain of electrically induced low temperature phase is fully reflected in each unipolar cycle due to a 'depolarization' effect caused by a 'non-polar' high temperature phase at zero field.[20] This reversible transition between two polymorphs was clearly demonstrated by *in situ* transmission electron microscopy studies[21] as well as *in situ* high energy X-ray diffraction studies combined with *in situ* neutron diffraction.[22] Here, the initially assumed 'non-polar' high temperature phase[20] was identified as a ferroelectric tetragonal *P4bm* phase, the ferroelectricity of which is extremely weak due to the very small tetragonal distortion (*c/a* ~1.0003).[22,23]

In this study, we have conducted a low temperature sintering of 0.92BNT–0.06BT–0.02KNN[20] using CuO as a sintering additive to see if the material is suitable for the fabrication of multilayered structures. In the meantime, a possible alteration in the electrical properties due to an incorporation of Cu^{2+} ions into the lattice was checked in consideration of the fact that Cu^{2+} replacing the B-site ions in the ABO$_3$-type perovskite structure is a well-known acceptor.[24] Note that in the case of the lead-free systems that normally contain several volatile elements, it is highly possible that the added copper, though in excess, could diffuse into the lattice. In fact, it was reported in KNN that the effect of copper diffusing into the lattice is so pronounced that once sintered at above 1000 °C, where the distribution of Cu^{2+} incorporated into the lattice is expected to be more homogeneous, KNN exhibits the characteristic features that define a 'hard' piezoceramic with a significant aging characteristic[25] and increased mechanical quality factor.[26]

2. Experimental procedure

0.92(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$–0.06BaTiO$_3$–0.02(K$_{0.5}$Na$_{0.5}$)NbO$_3$–*x*CuO (100*x*CuO, *x* in mole fraction) was prepared through solid oxide route with reagent grade oxides and carbonates from the commercial powder manufacturer (Alfa Aesar). Firstly, properly weighed 0CuO powder based on its stoichiometric formula was ball-milled with a planetary mill (Frisch) using ethanol as a milling medium and yttria-stabilized zirconia balls for 24 h. Dried powders were calcined in a covered alumina crucible at 900 °C for 3 h. Then, an excess amount of CuO in mol.% of 0, 0.1, 0.2, 0.4, 0.8, 1.0, 1.6, 2.0, 4.0, and 8.0 was introduced to the calcined 0CuO, and the mixed powders were ball-milled again in a planetary mill with the same conditions used for the initial milling step. The obtained powders of each composition were uniaxially shaped into pellets and compacted hydrostatically at 150 MPa. To find the temperature where the relative density determined by Archimedes method reaches ~98%, sintering was performed from 900 °C up to 1150 °C with about a 20 °C step, while the sintering time was kept constant at 3 h. The compositions will be abbreviated hereafter as 100*x*CuL or 100*x*CuH depending on the sintering temperature adopted. Any sintering temperature lower than 1150 °C was termed as L and 1150 °C as H. Specimens were heated up to each sintering temperature at a rate of 5 °C/min.

The purity and the formation of the desired phase were monitored for crushed and thermally annealed sintered samples by powder X-ray diffraction (XRD; D8 Advance, Bruker, Germany) using CuKα_1 radiation and an inductively coupled-plasma (ICP) spectroscopy. As consistent with our previous report,[27] ICP analysis revealed that the composition of sintered 0CuO has no deviation from that intended within the resolution limit. For the XRD, strain-free silicon standard powder (640C, NIST, Gaithersburg, U.S.A.) was used as an internal standard. The instrumental broadening and zero shift were corrected from a profile fitting for patterns of the standard silicon powder. Diffraction patterns were refined using the software package Fullprof software.[28] Refined lattice parameters were converted to the corresponding values for a basic perovskite unit cell using crystallographic relations. For the microstructure analyses, scanning electron microscopy (SEM, XL 30 FEG, Philips, Netherlands) equipped with TSL EBSD system was used on cross-sectioned surfaces of sintered specimens mirror-polished and thermally etched at 900–1000 °C for 30 min depending on the compositions. Stereological interpretation based on the linear intercept technique was used for the determination of size distribution and average grain size.

All samples were ground on both sides to remove the surface regions and electroded with a silver paint. For the temperature-dependent permittivity measurements, the electrodes were first fired at 550 °C for 30 min. Poling was achieved using two successive unipolar cycles at 8 kV/mm at the frequency of 50 mHz at room temperature. Permittivity values together with loss tangent were measured both on poled and unpoled samples, using an impedance analyzer (HP 4192A, Pala Alto, U.S.A.) in the frequency range of 100 Hz–1 MHz and in the temperature range of 25–350 °C. The mechanical quality factor, which has been