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Nanoscale ferroelectric/relaxor composites: Origin of large strain in lead–free Bi–based incipient piezoelectric ceramics

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ABSTRACT

La–doped $(Bi_{0.5}Na_{0.41}K_{0.09})TiO_3$ ceramics were synthesized using a conventional solid–state reaction route. X–ray diffraction and electric–field–induced polarization studies revealed a phase transformation from a ferroelectric to a relaxor with increasing La content. Piezoresponse force microscopy and transmission electron microscopy indicated the coexistence of ferroelectric and relaxor phases at the morphotropic phase boundary (MPB). A normalized strain of 857 pm/V was observed at the MPB at 4 kV/mm, which is comparable to that of other macro ferroelectric/relaxor composite materials. We propose that the inherent nanoscale ferroelectric/relaxor composite in the La–doped $(Bi_{0.5}Na_{0.41}K_{0.09})TiO_3$ ceramic be the origin of such giant electric–field–induced strain.

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1. Introduction

Piezoelectric ceramics play an important role in electronic device applications, especially lead oxide–based piezoelectric ceramics, such as $Pb(Zr,Ti)O_3$, $(Pb,La)(Zr,Ti)O_3$, and $Pb(Mg_{1/3}Nb_{2/3})O_3$ [1,2]. On the other hand, these materials contain more than 60 *wt.%* lead [3], which is toxic and causes damage to the kidneys, brain, and nervous system. The volatilization of lead oxide (PbO) during high–temperature sintering not only causes environmental pollution but also generates instability in the composition and electromechanical properties of the final products. In recent years, for environmental protection and human health, many countries (European Union, Japan, USA, Korea, etc.) have regulated all of their new electronic products to be lead–free [4–6]. Therefore, there is a need to develop lead–free piezoelectric ceramics that are environmentally–friendly and possess comparable electromechanical properties to those of existing lead–based materials.

Among the various lead–free piezoelectric candidates, binary $(Bi,Na)TiO_3$–$(Bi,K)TiO_3$ (BNKT) solid solutions are considered to be promising owing to their enhanced electromechanical properties near the morphotropic phase boundary (MPB) [7–9]. Many studies have reported that the electromechanical properties of BNKT at the MPB composition can be improved further by modification with various dopants or modifiers [10]. For example, BNKT modified with $BiAlO_3$ [11], $LiSbO_3$ [12], or $BaTiO_3$ [13] exhibits excellent ferroelectric and piezoelectric properties. A temperature–insensitive electrostrictive coefficient was also found in $(K,Na)NbO_3$ [14]- or $BaZrO_3$ [15]–modified BNKT. Moreover, Nb [16], $Sr(K_{0.25}Nb_{0.75})O_3$ [17], Sn [18], Nb and $(Ba_{0.7}Sr_{0.3})TiO_3$ [19] doped/modified BNKT were found to exhibit giant electric–field–induced strain (EFIS).

Ferroelectricity in piezoelectric crystals is characterized by their non centro–symmetric or polar structures. With the application of an electric field, ions undergo asymmetric displacement that results in a small change in the crystal dimensions, which is defined as the EFIS [20,21]. The mechanism of EFIS in piezoelectric ceramics was first considered in lead–based materials with the composition of $(Pb,La)(Zr,Ti,Sn)O_3$ [22,23], which showed a large strain due to an electric–field–induced antiferroelectric to ferroelectric phase transition. In lead–free piezoelectric ceramics, a giant EFIS was reported by Zhang et al. in $Bi_{1/2}Na_{1/2}TiO_3$–$BaTiO_3$–$K_{0.5}Na_{0.5}NbO_3$ ceramics [24,25]. Initially, the origin of this giant strain was believed to be a significant volume change due to a field–induced phase transformation. Whereas, later studies highlighted that the origin of large EFIS in Bi–based piezoceramics was the electric–field–induced

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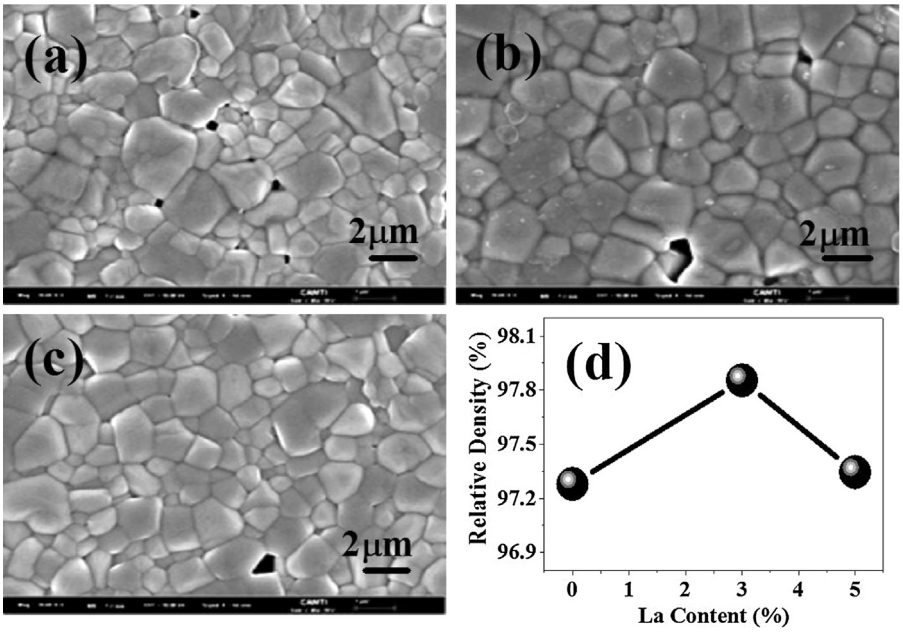

Fig. 1. FE–SEM images of polished and thermally etched cross–sections of La0 (a), La3 (b), and La5 (c) ceramics, and the relative density as a function of La content (d).

reversible phase transformation from polar (or ferroelectric) to nonpolar (or relaxor) phases [16–19,26,27]. Bi–based ceramics exhibiting large EFIS were recently considered to be incipient piezoceramics [27,28], in which the materials become macroscopically piezoelectric under an applied electric field. Incipient piezoceramics, however, require high electric fields for inducing a phase transformation to obtain the giant strain. This can be ameliorated by using composites consisting of a relaxor (matrix) and a ferroelectric phase (seed). Through this approach, the critical electric field to initiate a giant EFIS was reported to be lowered in some Bi–based composites [29–32].

For lead–based piezoceramics, enhanced properties near the MPB are generally attributed not only to polarization rotation and extension, [22,23] but also to the substantial contributions from nanodomains [33]. Analogous results have also been reported in lead–free systems close to the MPB [34] or polymorphic phase transition (PPT) [35] regions. *In situ* high–energy X–ray [36–38], transmission electron microscopy (TEM) [30,33,35,39], and piezoresponse force microscopy (PFM) [34,40,41] are powerful tools for providing perspicuous picture of the crystal structure and domain morphology, which is helpful for further uncovering the origin of the improved electromechanical properties. In this study, a new mechanism of giant EFIS in a La–doped $(Bi_{0.5}Na_{0.41}K_{0.09})TiO_3$ ceramic was proposed on the basis of analyzed data from PFM and TEM.

2. Experimental procedure

Ceramic specimens were prepared via a conventional solid–state reaction route. The starting powders were weighed according to the compositions of $[Bi_{0.5}Na_{0.41}K_{0.09}]_{1-x}La_xTiO_3$ (abbreviated as La100*x*; $x = 0$, 0.03, and 0.05). The powder mixture was ball–milled for 24 h in ethanol with zirconia balls as milling media. The slurries were dried and then calcined at 850 °C for 2 h. The calcined powder was mixed with polyvinyl alcohol as a binder and pressed into green discs of 12 mm diameter at 110 MPa. Sintering was performed in covered alumina crucibles at 1175 °C for 2 h in air.

The sintered discs were first lapped to a thickness of 1 mm and annealed at 250 °C for 30 min to remove any residual stress from the mechanical treatments. A silver paste was screen–printed on both sides of the specimen and then fired at 700 °C for 30 min. The sample was then poled in a silicone oil bath at room temperature under a direct current field of 50 kV/cm for 15 min (poled samples). To remove the poling effect, a group of samples were anealed at 350 °C for 5 h (unpoled samples).

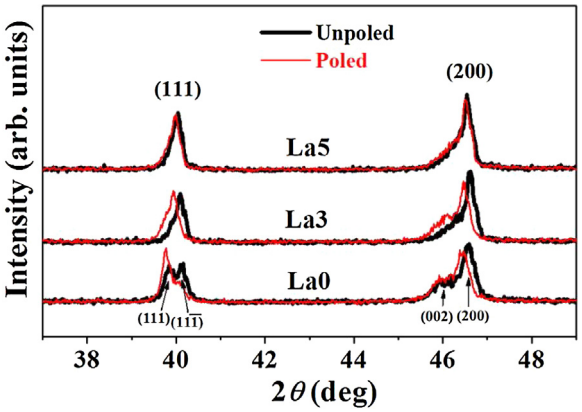

Fig. 2. X–ray diffraction patterns of the {111} and {200} reflections of the unpoled and poled La100*x* specimens with $x = 0$, 0.03, and 0.05.

The density of the sintered samples was determined using an Archimedes method and the surface morphology was observed by a field–emission scanning electron microscopy (FE–SEM, JEOL, JSM-65OFF, Japan). The crystal structures were analyzed by X–ray diffraction (XRD, RAD III, Rigaku, Japan) at room temperature. The dependence of the switching current (I) was measured in a commercial apparatus, aixPES (aixACCT Systems GmbH, Aachen, UNIST). The polarization hysteresis (P) and strain (S) on the electric field (E) were measured at 300 mHz with a 15 μF measurement capacitance using a Sawyer–Tower circuit equipped with an optical sensor (Philtec, Inc., Annapolis, MD, USA).

For PFM observations, the sintered samples were ground to approximately 60 μm and then polished to approximately 20 μm in thickness using a polycrystalline diamond paste with abrasive particles of 3.5, 1.0, and 0.25 μm (DP–Paste P by Struers A/S, Ballerup, Denmark) for 1 h each. The PFM experiments were carried out using

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