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Understanding the piezoelectric properties in potassium-sodium niobate-based lead-free piezoceramics: Interrelationship between intrinsic and extrinsic factors

Fernando Rubio-Marcos [a,*,1], José F. Fernandez [a], Diego A. Ochoa [b], José E. García [b], Rocio E. Rojas-Hernandez [a], Miriam Castro [c], Leandro Ramajo [c,*,1]

[a] Electroceramic Department, Instituto de Cerámica y Vidrio, CSIC, Kelsen 5, 28049, Madrid, Spain
[b] Department of Physics, Universitat Politècnica de Catalunya—BarcelonaTech, Jordi Girona 1-3, 08034 Barcelona, Spain
[c] Institute of Research in Materials Science and Technology (INTEMA) (CONICET—University of Mar del Plata), J. B. Justo 4302, B7608FDQ Mar del Plata, Argentina

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ABSTRACT

Lead zirconate titanate (PZT) based ceramics are currently enjoying a wide use in piezoelectric devices despite lead toxicity. Due to growing environmental concerns, the attention on piezoelectric ceramics has been moving to lead-free materials, in particular to (K,Na)NbO_3-based ceramics. Here we report a systematic evaluation of the effects of the compositional modifications on $[(K_{0.44}Na_{0.52}Li_{0.04})][(Nb_{0.86}Ta_{0.10}Sb_{0.04})_{1-x}Zr_{5x/4}]O_3$ lead–free piezoceramics. We show that an interrelationship between the intrinsic and extrinsic factors is the linchpin for the development of good piezoelectric properties. Hence, the stabilization of the tetragonal symmetry on the orthorhombic-tetragonal polymorphic phase boundary facilities the poling process of the system, thereby enhancing the piezoelectric response. Additionally, the microstructure appears to be related to the piezoelectric properties; i.e., the improved piezoelectric properties correlate to the increase in grain size. The results of this work could help to understand the origin of piezoelectricity in potassium–sodium niobate-based ceramics.

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1. Introduction

Lead titanate-zirconate (PZT) ceramics are the most widely used piezoelectric materials. However, legal restrictions on the use of lead in electrical and electronic devices have led to greater efforts being made to develop lead-free alternatives to PZT-based materials [1–6]. Hence, many researchers have attempted to present materials capable of replacing lead-based ceramics [4–26]. Among these attempts, potassium–sodium niobate, $K_xNa_{1-x}NbO_3$ (KNN), ceramics have become one of the most investigated systems over the past ten years [10–26], ever since an exceptionally high piezoelectric constant (d_{33}) of ~400 pC N^{-1} was reported by *Saito* et al. in 2004 [12]. This findings were based on chemical modifications by complex simultaneous substitutions into the A (Li) and B (Ta and Sb) sites of the perovskite crystal lattice for a composition close to the morphotropic phase boundary (MPB) of the KNN system. In addition to these chemical modifications, a novel processing route for producing textured polycrystals has been carried out in this work. However, the inhomogeneous distribution of Nb, Ta and Sb on the B-site of the perovskite lattice is rather difficult to avoid because of the phase segregation of end members over a wide temperature interval [27]. Furthermore, apparent compositional segregation is evidenced in KNN ceramics annealed for a long time [10,27–29].

More recently, Zhuís group chemically designed a series of KNN-based ternary ceramic systems that effectively enhance the piezoelectric properties by tuning phase boundaries [24,30,31]. In this context, the polymorphic phase boundary (PPB) in lead-free piezoelectric materials, and particularly in KNN-based compositions, has attracted significant interest because of the unique properties found in their vicinity. However, in order to harness the full potential of these materials as micro-nanoscale functional entities, it is essential to achieve a reliable and precise control of the macroscopic response in the PPB. The enhancement of the macroscopic properties in a PPB is due to two contributions, which are known as intrinsic and extrinsic contributions. On the one hand,

* Corresponding authors.
E-mail addresses: frmarcos@icv.csic.es (F. Rubio-Marcos), lramajo@fi.mdp.edu.ar (L. Ramajo).
[1] F. Rubio-Marcos and L. Ramajo contributed equally.

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the intrinsic contribution is related to the linear lattice distortion, and is associated with the change in the polarization of the unit cell. As a result of the phase coexistence, the polarization rotation enhances at the PPB region, thereby improving the piezoelectric properties. Moreover, the property enhancement at PPB has been reported as a consequence of an electric field-induced phase transition; i.e. a polarization extension phenomenon [32]. Thus, PPB is a region where material response is apparently enhanced owing to polarization rotation and polarization extension. On the other hand, the extrinsic contribution is easily defined as all responses different from the intrinsic one. Ochoa et al. [33] have recently reported that, in addition to the intrinsic contribution, the extrinsic contribution (domain wall contribution) also maximizes in a PPB region. Thus, the extrinsic contribution is also responsible for improving the functional properties at the PPB [33]. Despite the progress achieved recently, a fundamental question nevertheless arises: What is the balance between the intrinsic and extrinsic contribution within a PPB? An attempt to answer this question is provided in this work.

Compositional engineering by doping is a classic approach in the field of piezoelectric materials to modify the structure and microstructure of materials, and therefore to tailor the piezoelectric response. Many aliovalent compositional modifications to KNN-based system have been studied, either with higher valence substitutions (donors) or with lower valence ions (acceptors) [24,34–38]. From this perspective, the (K,Na)NbO_3–$LiTaO_3$–$LiSbO_3$ system was synthesized by replacing the B-sites with Zr^{4+} ions, thereby engendering an evolution of the polymorphic behaviour containing tetragonal (***T***) and orthorhombic (***O***) symmetries. Through this compositional design, we have found that a balance between the intrinsic and extrinsic contributions constitutes a linchpin in the development of good piezoelectric properties. The stabilization of the rich ***T*** region into the PPB seems to be crucial for promoting the piezoelectric response.

2. Experimental details

2.1. Preparation process

Bearing in mind the ionic radii, the Zr^{4+} ion (r_{Zr}^{4+}: 0.72 Å for a coordination number CN = 6) [39] is in the size range of the B-site ions (r_{Nb}^{5+}: 0.64 Å, r_{Ta}^{5+}: 0.64 Å, r_{Sb}^{5+}: 0.60 Å for CN = 6) [39] of the (K,Na)NbO_3–$LiTaO_3$–$LiSbO_3$ system. Considering its valence, Zr^{4+} can act as acceptor dopant if introduced into the B-site, thereby modifying the properties of the system. Therefore, B-site deficient Zr^{4+} doped $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$, with a global formula $(K_{0.44}Na_{0.52}Li_{0.04})[(Nb_{0.86}Ta_{0.10}Sb_{0.04})_{1-x}Zr_{5x/4}]O_3$, hereafter abbreviated as KNL–$(NTS)_{1-x}Zr_{5x/4}$, is selected as a PPB tunable system. Thus, KNL–$(NTS)_{1-x}Zr_{5x/4}$ ceramics with $x = 0$, 0.005, 0.01, 0.03, and 0.05 were prepared by conventional solid-state reaction from an adequate mixture of corresponding oxides and carbonates. Na_2CO_3, Li_2CO_3 (PANREAC, >99.5%), K_2CO_3 (Merck > 99%), ZrO_2, Nb_2O_5, Ta_2O_5, and Sb_2O_5 (SIGMA-ALDRICH, >99.9%, >99% and >99.995%, respectively) were used as starting raw materials and were individually milled in order to obtain an appropriate distribution of the particle size. Furthermore, the raw materials were dried at 200 °C for 4 h before use because of their hygroscopic nature [37]. Powders with different ZrO_2 concentrations were weighted and ball-milled for 3 h in an ethanol medium in a high-energy laboratory ball-mill with Zirconia balls. Subsequently, the resulting powders were dried, sieved and calcined at 700 °C for 2 h at 3 °C/min [40]. The calcined powders were ball-milled in a plastic jar with Zirconia grinding media for 3 h in ethanol and dried for 4 h at 150 °C. Samples of 10 mm in diameter and 1 mm in thickness were uniaxially pressed at 200 MPa and sintered in air at 1125 °C for 2 h. Bulk densities of the samples were determined using the Archimedes method.

2.2. X-ray diffraction (XRD) measurement

XRD (X'Pert PRO Theta/2theta of Panalytical, PANalytical, The Netherlands) measurements were performed by applying CuK_α ($\lambda = 0.154056$ nm) radiation on unpoled and poled sintered ceramics. The patterns were recorded over the angular range 10–70° (2θ) with a step size of 0.0334° and a time per step of 100 s. The working voltage and current were 40 kV and 100 mA, respectively. Structural refinement was performed using a tetragonal symmetry, (***T, P4mm***), and an orthorhombic symmetry, (***O, Amm2***). The cell parameters were then calculated by fitting the observed reflections with a least-squares method using the Checkcell program [41]. The relative volume fractions were calculated by using the integrated intensities of the tetragonal (002) and (200) and orthorhombic (022) and (200) degenerate reflections, which obtained from the line profile analysis [11,42]. Peak positions were fitted assuming a Lorentz peak shape using the Peakoc software [43]. (*More information about the phase volume fraction vs Zr content is shown in the* ***Supplementary Information, section A***). The intensities and the position of the maxima of the tetragonal (002) and (200) degenerate reflection were also used to calculate the relative percent of domain switching (extrinsic contribution) and the electric-field-induced lattice strain (intrinsic contribution) for each composition (*More information about the domain switching and the electric-field-induced lattice strain contributions are given in the* ***Supplementary Information, section B***).

2.3. Microstructural characterization

The microstructure was evaluated on polished and thermally etched samples (1000 °C for 5 min) using a Field Emission Scanning Electron Microscope, FE-SEM (Hitachi S-4700). The microscope was coupled with a Themo NORAN x-sight energy dispersive X-ray spectrometer (EDXS), from Thermo Scientific Instruments, for chemical elemental analysis. The grain size distributions (GSD) and the average grain size (AGS) were measured from the FE-SEM micrographs using an image analysis program (Leica Qwin, Leica Microsystems Ltd, Cambridge, England) considering more than 300 grains.

2.4. Electrical characterization

Silver paste was coated on both sides of the sintered samples for the electrical measurements. Room temperature ferroelectric properties were measured by using a hysteresis meter (RT 6000 HVS, RADIANT Technologies). The dielectric properties were determined at different temperatures and frequencies using an impedance analyzer HP4294A. In order to test the piezoelectric properties, the samples were polarized under a direct current (*dc*) electric field of 4 kV/mm in a silicone oil bath at 25 °C for 30 min [44]. The piezoelectric constant d_{33} was measured using a piezo d_{33} meter (YE2730A d_{33} METER, APC International, Ltd., USA) at room temperature.

3. Results and discussion

3.1. Evolution of the polymorphic behaviour

Fig. 1**a** shows the XRD patterns of KNL–$(NTS)_{1-x}Zr_{5x/4}$ ceramics. Diffraction patterns correspond to a perovskite structure without secondary impurity phases for x = 0.005, 0.01 and 0.03. However, the presence of two minor secondary phases has been detected in un-doped ceramics (x = 0.00) and in the high-doped ceramics (x = 0.05). These secondary impurity phases can be attributed to

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