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## Feature article

Defect control for enhanced piezoelectric properties in SnO<sub>2</sub> and ZrO<sub>2</sub> co-modified KNN ceramics fired under reducing atmosphereYu Huan<sup>a,\*</sup>, Xiaohui Wang<sup>b,\*</sup>, Tao Wei<sup>a</sup>, Peiyao Zhao<sup>b</sup>, Jing Xie<sup>b</sup>, Zifan Ye<sup>c</sup>, Longtu Li<sup>b</sup><sup>a</sup> School of Material Science and Engineering, University of Jinan, Jinan 250022, China<sup>b</sup> State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China<sup>c</sup> Department of Materials, Imperial College London, London SW7 2AZ, UK

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## ABSTRACT

The additions of SnO<sub>2</sub> and ZrO<sub>2</sub> are beneficial to improve the piezoelectric and dielectric properties of the reducing atmosphere fired (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub>-based ceramics. The degradation of electrical properties when the pure (Na<sub>0.52</sub>K<sub>0.45</sub>Li<sub>0.03</sub>)NbO<sub>3</sub> ceramics sintered in reducing atmosphere is mainly caused by the increasing of oxygen vacancy concentration, as low oxygen partial pressure promote the formation of oxygen vacancy. The 0.3 mol% SnO<sub>2</sub> and 0.3 mol% ZrO<sub>2</sub> co-modified ceramics sintered in reducing atmosphere exhibit excellent electrical properties ( $d_{33} = 198$  pC/N,  $k_p = 31.5\%$ ,  $\epsilon_{33}^T/\epsilon_0 = 304$ , and  $\tan\delta = 0.022$ ), which are comparable to the air fired ceramics with the same composition ( $d_{33} = 206$  pC/N,  $k_p = 32.6\%$ ,  $\epsilon_{33}^T/\epsilon_0 = 590$ , and  $\tan\delta = 0.020$ ). By thermally stimulated depolarization current technique, it can be demonstrated that the reduced fired doped ceramics have similar concentration of oxygen vacancy and defect dipole with the air fired ceramics due to the substitution of Sn and Zr into the A-sites and B-sites of perovskite structure. This study not only demonstrate the Sn and Zr co-doped KNN-based systems could possibly co-fire with base metal inner electrode but also broaden the selection of low-cost and eco-friendly materials for multilayer piezoelectric devices.

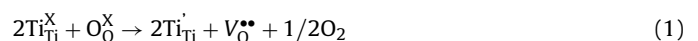
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## 1. Introduction

Lead oxide-based ceramics, such as PbZrO<sub>3</sub>-PbTiO<sub>3</sub>(PZT) and Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-Pb(Ni<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> systems, have been widely employed in actuator, sensor and transducer applications due to their excellent piezoelectric properties [1,2]. However, own to the toxic nature of lead, developing environmentally friendly lead-free materials is highly desirable [3]. Through years of extensive efforts, marginal success has been achieved on finding lead-free piezoelectric materials. Among the lead-free candidates, there are essentially three major subgroups based on perovskite structure, including (Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> (BNT)-based, BaTiO<sub>3</sub> (BT)-based, and (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> (KNN)-based systems [4–13]. As the electrical properties of all existing lead-free piezoelectric ceramics have not yet reached the level of traditional PZT-based materials, the multilayer structure has long been considered candidate solution to increase the total mechanical strain [14]. In order to reduce production cost, especially the cost of the inner electrodes, com-

paring with the precious metal, base metal inner electrode, such as Ni and Cu, is strongly recommended for multilayer piezoelectric device. The lead-free piezoelectric materials co-fired with base metal inner electrodes make it possible for designing low-cost lead-free piezoelectric devices whose properties could be comparable to the PZT-based devices.

To prevent the oxidation of the base metal electrode, piezoelectric green pieces must be sintered in a reducing atmosphere [15]. However, under such condition, the Ti<sup>4+</sup> can be easily reduced to Ti<sup>3+</sup> and the oxygen vacancies with *n*-type carriers are inevitably generated by the following reactions:



These undesirable titanium ions at the lower valence state and oxygen vacancies could lead to the degradation of insulation resistance and piezoelectric properties [16–19]. Besides, Bi<sub>2</sub>O<sub>3</sub> and PbO can be readily reduced to their metallic state and form alloys with the base metal under low oxygen partial pressure. Therefore, PZT, BT and BNT-based piezoelectric systems are difficult to co-fire with base metal inner electrodes. In contrast, alkali and niobium ions in KNN-based systems have good chemical stability under the same

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condition. Recently, Kawada et al. [20–23] successfully fabricated the multilayer ceramics with Ni inner electrodes using  $\text{CaZrO}_3$  or LiF modified KNN materials under low oxygen partial pressure. Although the low piezoelectric properties (quasistatic piezoelectric coefficient  $d_{33} \sim 138$  pC/N for the ceramics; converse piezoelectric coefficient  $d_{33}^* \sim 200$  pm/V for 1 layer actuator at an electric field of 2.5 kV/mm) of these KNN-based ceramics are undesirable for actuator application [23]. Their finding demonstrates the possibility of KNN-based system can be identified as a potential lead-free piezoelectric candidate material for multilayer devices.

An important thing to be considered with reducing atmosphere fired typical perovskite ceramics is the formation of oxygen vacancies and free electrons on account of Eq. (2), which leads to high conductivity and degradation of electrical properties [24]. Furthermore, doping with donors or acceptors will inevitably introduce a large amount of defects (trap charges, dipoles, or vacancies), which have a significant effect on the electrical properties. Therefore, a detailed discussion on defect structures in reduced fired ceramics is required for designing the low-cost KNN-based piezoelectric applications. Until now, the studies about the effects of defect structure on the electrical properties of the KNN-based ceramics sintered in reducing atmosphere are limited [23,25]. The aim of this work is to investigate the effects of sintering atmosphere on the electrical properties and defect structure of  $\text{SnO}_2$  and  $\text{ZrO}_2$  co-modified  $(\text{Na}_{0.52}\text{K}_{0.45}\text{Li}_{0.03})\text{NbO}_3$  ceramics, by using various methods including thermally stimulated depolarization current (TSDC) analysis.

## 2. Experimental procedure

$(\text{Na}_{0.52}\text{K}_{0.45}\text{Li}_{0.03})\text{NbO}_3 + x\text{SnO}_2 + x\text{ZrO}_2$  ( $x=0, 0.003, 0.006, 0.009$ ) powders were prepared using the conventional mix-oxide method. Analytically pure powders of  $\text{Nb}_2\text{O}_5$  (99.5%),  $\text{SnO}_2$  (99.8%),  $\text{ZrO}_2$  (99%),  $\text{Na}_2\text{CO}_3$  (99.8%),  $\text{K}_2\text{CO}_3$  (99%), and  $\text{Li}_2\text{CO}_3$  (99%) were utilized as starting materials. All raw materials were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. The alkali carbonates were first dried at 80 °C and then homogenized with  $\text{Nb}_2\text{O}_5$ ,  $\text{SnO}_2$  and  $\text{ZrO}_2$  in a planetary mill for 8 h according to the nominal stoichiometric composition using ethyl alcohol as medium. The powder mixtures were calcined twice at 850 °C for 5 h with intermediate milling. Subsequently, the mixed powders were milled, dried, and sieved. The powders were then compacted into pellets with the diameter of 10 mm and the thickness of 1 mm by uniaxial pressing in a stainless-steel die using Polyvinyl Butyralas binder. The green pellets were sintered in two different conditions: (1) 1085 °C peak hold temperature for 2 h in air atmosphere; (2) 1085 °C for 2 h in reducing atmosphere with  $P_{\text{O}_2} = 10^{-13}$  atm followed by annealing in a weak oxidizing atmosphere at 950 °C for 2 h. The oxygen partial pressure of the ambient atmosphere during firing was controlled by  $\text{N}_2$  gas and 95 vol%  $\text{N}_2/5$  vol%  $\text{H}_2$  mixture gas. The heating and cooling rate was 3 °C/min. In addition, all the pellets were sintered in a sealed crucible to minimize the evaporation of alkaline metals. For electric measurement, the two main surfaces of the sintered disk samples were coated with silver paste and then heat-treated at 550 °C for 30 min. The disk samples were poled in silicon oil under a direct current electric field of 3 kV/mm at 70 °C for 30 min.

The density of the samples was determined by the Archimedes method. The scanning electron microscopy (SEM; Leo-1530, Oberkochen, Germany) was used to examine their microstructure, element mapping, and composition analysis. The crystalline structure of the crushed sintered ceramics was determined by XRD (Rigaku 2500, Rigaku, Tokyo, Japan) with  $\text{Cu K}\alpha$  radiation. The quasistatic piezoelectric coefficient  $d_{33}$  of the poled samples was measured using a quasistatic piezoelectric coefficient meter (ZJ-3A, Insitute of Acoustics, Chinese Academy of Sciences, Bei-

jing, China). Dielectric permittivity  $\epsilon_{33}^T/\epsilon_0$ , dielectric loss  $\tan\delta$  at 1 kHz and the planar electromechanical coupling factor  $k_p$  of the poled ceramics at room temperature were measured using a capacitance meter (Agilent 4294A, Agilent, Santa Clara, CA, USA). The pA meter (Model HP4140B, Hewlett-Packard, Santa Clara, USA) was applied to measure the insulation resistance. The temperature-dependent dielectric properties at 1 kHz were measured using a capacitance meter (HP4278A, Hewlett-Packard, Santa Clara, USA) from  $-100$  °C to 400 °C with an automated temperature controller. The polarization-electric field ( $P$ - $E$ ) hysteresis loops and electric-field-induced strain ( $S$ - $E$ ) curves were obtained by the TFANALYZER 2000E ferroelectric measuring system (aixACCT Systems GmbH, Aachen, Germany).

For the TSDC spectra, the ceramics were electrically poled under a high direct current polarization electric field of 200 V/mm at different polarization temperatures ( $T_p$ ) for 10 min. After that, the direct current electric field was turned off, the ceramics was rapidly cooled down to  $-20$  °C. Finally, samples were heated from  $-20$  °C to 350 °C at a rate of 5 °C/min. The depolarization current density was recorded in the steady state condition by a pA meter (6517B, Keithley, Cleveland, USA) attached to the ceramics under short circuit conditions. Measurements as a function of temperature were performed using a quarto temperature controller of Novocontrol Technologies (Novocontrol GmbH, Montabaur, Germany).

## 3. Results

Fig. 1 presents the microstructure of the furnace atmosphere controlled as-sintered KNN-based ceramics. Significant differences in grain size can be observed from samples with pre determined compositions sintering in air or reducing atmospheres. The average grain size shrinks rapidly with the increasing of  $\text{SnO}_2$  and  $\text{ZrO}_2$  content  $x$ , especially when doping content exceeds 0.3 mol%. All the reduced fired ceramics have a larger average grain size than the air fired counterpart with the same composition. Such feature becomes more evident with  $x \geq 0.006$ . In addition, a bimodal microstructure emerges for the reduced fired samples. The grain morphology of the reduced fired ceramics are round-shaped, comparing with well-defined edges of the air fired ceramics. These differences might correlate to the free enthalpy increment induced by the defect structure in reduced fired samples. The distribution of element in the  $x=0.003$  air and reduced fired ceramics, which were polished and thermally etched at 1035 °C, is characterized by the element mapping using the energy-dispersive X-ray (EDX) analysis shown in Fig. 2. It can be seen that all the elements are homogeneously distributed in the ceramics. The Li element could not be detected using EDX technique due to its light weight. To further identify the chemical composition of grains and grain boundaries, we used the energy dispersion spectrum analysis (EDS) to reveal the atomic percentages of the elements of a single grain and a large region containing many grains and grain boundaries. The difference in composition is tiny, not only for the air fired  $x=0.003$  sample but also for the reduced fired  $x=0.003$  sample. EDS result further indicates that no element aggregates at the grain boundary and chemical compositions are homogeneously in the ceramics.

Fig. 3a and b show the XRD patterns of the samples with different compositions sintered in air and reducing atmosphere, respectively. All samples exhibit a pure perovskite phase structure. The crystal structure of the reduced and air fired ceramics exhibits similar change rule. The undoped ceramics have a pure monoclinic structure [26], and the crystal structure completely transforms to orthorhombic structure when  $x$  reaches 0.006 [27]. A two-phase coexistence zone composing of orthorhombic and monoclinic ferroelectric phases is formed at  $x=0.003$ , commonly called polymorphic phase transition (PPT) composition. The doped ele-

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