



# Improving the functional properties of $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ piezoceramics by acceptor doping

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## Abstract

ZrO<sub>2</sub> and TiO<sub>2</sub> modified lead-free  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$  (KNN) piezoelectric ceramics are prepared by a conventional solid-state reaction. The effect of acceptor doping on structural and functional properties is investigated. A decrease in the Curie temperature and an increase in the dielectric constant values are observed when doping. More interestingly, an increase in the coercive field  $E_c$  and remanent polarization  $P_r$  is observed. The piezoelectric properties are greatly increased when doping with small concentrations dopants. ZrO<sub>2</sub> doped ceramic exhibits good piezoelectric properties with piezoelectric coefficient  $d_{33} = 134$  pC/N and electromechanical coupling factor  $k_p = 35\%$ . It is verified that nonlinearity is significantly reduced. Thus, the creation of complex defects capable of pinning the domain wall motion is enhanced with doping, probably due to the formation of oxygen vacancies. These results strongly suggest that compositional engineering using low concentrations of acceptor doping is a good means of improving the functional properties of KNN lead-free piezoceramic system.

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## 1. Introduction

The most widely used piezoelectric ceramics are  $\text{Pb}(\text{Ti},\text{Zr})\text{O}_3$  (PZT)-based materials, on account of their high piezoelectric response, large-scale production capability and the tailoring of their properties through composition. Due to the high toxicity of lead, a wide range of strict regulations concerning environmental preservation are increasingly being introduced worldwide. Many governments have therefore established legislation regarding waste electric equipment (WEEE), restrictions on hazardous substances (RoHS), and end-of-life vehicles (ELV) to introduce directives regarding environmental pollutants.<sup>1</sup> The search for alternative lead-free piezoelectric materials is currently focused on modified bismuth titanates, alkaline niobates (KNN) and other systems in which a morphotropic phase boundary (MPB) occurs.<sup>2–4</sup>

Among the available lead-free piezoelectric materials under study, much attention has been paid over the last few years to  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  (KNN)-based ceramics as a result of the breakthrough made by Saito et al.,<sup>5</sup> who obtained high  $d_{33}$  ( $\sim 400$  pC/N) in the Li–Ta–Sb modified KNN. However, the major drawback of KNN ceramics is the need for special handling of the starting powders, sensitivity of properties to non-stoichiometry, and especially a complex densification process.<sup>6</sup> As regards PZT, sintering aids such as CuO, SnO<sub>2</sub>, ZnO or MnO<sub>2</sub> may improve sinterability and modify the dielectric and piezoelectric behaviour of the KNN materials.<sup>7–11</sup>

Compositional modification by doping is a very active research line for obtaining piezoceramics with enhanced properties. The  $(\text{K},\text{Na})\text{NbO}_3\text{--LiTaO}_3\text{--LiSbO}_3$ , particularly the composition  $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})(\text{Nb}_{0.86}\text{Ta}_{0.10}\text{Sb}_{0.04})\text{O}_3$ , is probably the most workable lead-free piezoelectric system known to date. However, its properties are not suitable for all end use, e.g. for power devices where piezoceramics with low losses and stable properties are required. In this perspective, good results are expected by means of hardener substitutions,

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such as those that occur in other perovskites,<sup>12</sup> although some structural and electrical aspects remain controversial as regards the role of dopants in the KNN system. It has recently been shown that Cu-doped KNN-modified compounds may exhibit typical characteristics of hard behaviour.<sup>13–16</sup> Hardener ions in a perovskite compound (e.g. Cu<sup>2+</sup> ions replace Nb<sup>5+</sup> ions in Cu-doped KNN) are most often acceptors, the introduction of which leads to the creation of oxygen vacancies, thereby forming the so-called complex defects.<sup>17</sup> These defects operate as pinning centres by hampering the motion of the domain walls. This domain wall pinning effect is responsible for the reduction in dielectric losses and stabilization of properties in ferroelectrics.<sup>18</sup> The goal of this study is thus to test the influence of Zr<sup>4+</sup> and Ti<sup>4+</sup> acceptor-doping in (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> on the structural, dielectric, piezoelectric and nonlinear properties. The addition of ZrO<sub>2</sub> and TiO<sub>2</sub> is expected to improve functional properties of KNN ceramics for power application, i.e. reduce the losses and increase the properties stability.

## 2. Experimental

The (K<sub>0.5</sub>Na<sub>0.5</sub>)(Nb<sub>1-x</sub>M<sub>x</sub>)O<sub>3-x</sub> compositions with  $x=0.0$  and 0.005 being M=Zr or Ti, hereafter abbreviated as KNN-M, were synthesized by a conventional solid-state reaction. The raw materials of analytical grade used in this study were K<sub>2</sub>CO<sub>3</sub> (99%), Na<sub>2</sub>CO<sub>3</sub> (99.5%), Nb<sub>2</sub>O<sub>5</sub> (99.9%), ZrO<sub>2</sub> (99%) and TiO<sub>2</sub> (99%). After separate milling, the powders were weighed and mixed by ball milling using ZrO<sub>2</sub> balls in absolute ethanol medium for 3 h, then dried and calcined twice at 700 °C for 2 h. The calcined powders were then milled again and cold-isostatically pressed at 750 MPa into 7 mm diameter pellets and sintered in air, without a binder, at 1125 °C for 2 h. Care was taken to ensure that a high alkaline element pressure is maintained during the process by surrounding the pellets with powder of the same composition, and the pellets were deposited on Pt foils to avoid reaction with alumina boats. All as-sintered ceramics showed relative densities over 95% measured by Archimedes' method.

X-ray diffractograms were recorded at room temperature (RT) on a Bruker D2 PHASER equipped with a XFlash detector. A two-axis diffractometer in Bragg-Brentano geometry with Cu K $\alpha_{1,2}$  radiation was used for the *in situ* XRD characterization. The control of temperature was provided by a furnace from 30 °C to 500 °C. The cell parameters and their evolution with temperature were refined by a LeBail fitting procedure as implemented in the Fullprof suite.<sup>19</sup> The Raman scattering spectra were obtained on a Labram (Horiba) spectrometer with a He–Ne excitation wavelength of 632.8 nm, coupled to a Linkam sample holder, with variable temperature from 30 °C to 500 °C. DSC measurements were performed on a Seiko apparatus covering the 100–1000 K temperature range. Microstructure was evaluated on polished and thermally etched samples (1000 °C for 5 min for pure KNN and 980 °C for 5 min for doped KNN) using a Field Emission Scanning Electro Microscope, FE-SEM (JEOL JSM-7001F). The micrographs were performed on the polished and thermally etched surfaces of the samples coated with graphite.

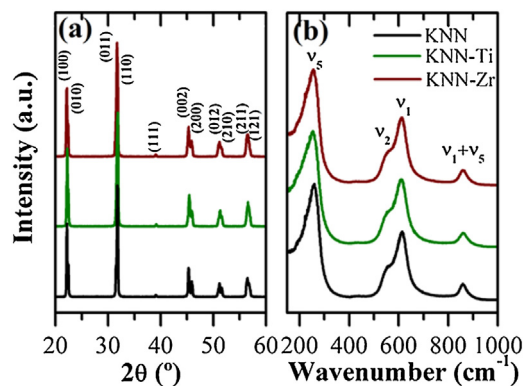


Fig. 1. XRD patterns (a) and Raman spectra (b) of the pure KNN and KNN-M ceramics measured at room temperature.

The voltage conditions were set at 20 kV and the work distance was established at 12 mm. In order to analyse the composition of the material, an energy dispersive spectroscopy (EDS) analysis was performed using an OXFORD X-Max<sup>N</sup> EDS detector provided with INCA Energy software. A pure Co sample was used as a reference material. The average grain size was determined from the SEM images using an image processing and analysis software (ImageJ). The grain size was expressed as Feret's diameter using more than 400 grains in each measurement. Electrical characterization was carried out on ceramic discs with sputtered gold–chromium electrodes on both parallel surfaces. The temperature dependence of the dielectric permittivity was measured on unpolled samples using an impedance analyzer (HP 4192A) from 30 °C to 600 °C. The measurements were done during the heating ramp at a rate of 2 °C/min. The permittivity dependence with a sub-switching AC electric field was measured at 1 kHz and at RT, by means of a capacitance. The hysteresis cycles were recorded using a modified Sawyer-Tower circuit, at 1 Hz and at RT. The samples were polled in silicon oil at 80 °C for 30 min under a 30 kV/cm DC electric field. Subsequently, the longitudinal piezoelectric coefficient was measured using a piezo- $d_{33}$  meter (YE2730A, APC International) at RT. The piezoelectric constant  $d_{31}$  and the electromechanical coupling factor  $k_p$  were determined at RT by the resonance/antiresonance method on the basis of the IEEE standards.

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns of the pure KNN and KNN-M ceramics measured at RT. For all ceramics, a pure perovskite phase indexed in the *Amm*2 orthorhombic space group is observed. In contrast to the results obtained by Ramajo et al.,<sup>20</sup> no parasitic phases are observed at low concentration of dopant. Our results suggest that taking special care of the reagents and of the synthesis method plays an important role to avoid the formation of parasitic phases. The cell parameters vary by less than 0.5%, indicating that the structure does not change significantly upon doping with ZrO<sub>2</sub> or TiO<sub>2</sub>. Since the Ti<sup>4+</sup> and Zr<sup>4+</sup> ionic radii, 0.61 Å and 0.72 Å, respectively, in a six-fold environment,<sup>21</sup> are close to that of Nb<sup>5+</sup> ion (0.64 Å), dopant atoms should essentially locate on the B-site, which by charge

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