



Piezoelectric Properties of Ta (≤ 5 (mole)%) Doped in $\text{Na}_{0.685}\text{K}_{0.315}\text{NbO}_3$

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To explore the piezoelectric potential of Ta doping on the MPB-like composition $\text{Na}_{0.685}\text{K}_{0.315}\text{NbO}_3$, ceramic pellets of $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$) were arranged by solid-state reaction method. For piezoelectric measurements, sintered pellets were electroded, in parallel capacitor configuration, with silver coating deposited by direct current (dc) magnetron sputtering of a silver target. Polarization and piezoelectric parameters were measured using a ferroelectric (PE-loop tracer) and piezo-meter (AixACCT Systems, GmbH). Composition (y) variation of remnant polarization, coercive field, converse piezoelectric coefficient (d_{33}^*), and polarization current measurements were carried out in the prepared compositions. The remnant polarization (P_r) is $18.439 \mu\text{C}/\text{cm}^2$ with a coercive field (E_c) of $8 \text{ kV}/\text{cm}$ for NKN single crystals. d_{33}^* was observed $300.76 \text{ pm}/\text{V}$ for $y = 0.04$ at the applied field of $22 \text{ kV}/\text{cm}$.

Keywords: NKN, Ferroelectrics, Piezoelectric.

1 Introduction

Over the past decade, a notable event in the field of piezoelectric materials may be that increasing attention has been paid to lead-free compositions as a replacement of conventional Pb-based compounds.

The elevated piezoelectric properties of lead zirconate titanate (PZT) ceramics are considered because of the coexistence of two structural phases in the morphotropic phase boundary (MPB)¹. For example, $\text{Pb}(\text{ZrTi})\text{O}_3$ ceramics contain at least 70% of lead oxides and have been applied commercially for nearly half a century. They remain the main piezoelectric materials until now for various actuators, sensors, and transducers applications.¹ These lead-containing materials have caused serious environmental problems during high-temperature fabrication or post-use disposal.

Among numerous alternatives, due to their relatively good ferroelectric properties, the high temperature of Curie (T_c), and the high electromechanical coupling coefficient², sodium-potassium niobate-based piezoceramics (NKN) could replace lead-based ceramics. Therefore, ferroelectric perovskites are generally chosen preferably as lead-free candidate materials. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) and $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN) are currently two main lead-free piezoelectric compositions with perovskite structures³. Although NKN-based compositions

exhibit better piezoelectric and electromechanical properties⁴⁻⁶.

However, pure KNN ceramics have very poor dielectric and piezoelectric properties, whose representative d_{33} data is $\sim 80 \text{ pC}/\text{N}$ for the normally sintered KNN ceramics⁷ and $\sim 148 \text{ pC}/\text{N}$ even for its counterpart prepared by spark plasma sintering with high density⁸. Many studies to date revealed that Li, Sb, and Ta are effective elements for enhancing the piezoelectric properties of KNN ceramics⁹.

By substituting elements, Saito *et al.*⁵ found an improvement in the piezoelectric properties of NKN. In the vicinity of the MR, two or several phases coexist and the Ferro ceramic exhibits extremal electro-physical behavior^{1,5}. The dielectric and piezoelectric properties anomaly show ferroceramics close to these compositions as the polarization rotation becomes easy due to the coupling between two equivalent energy states of two existing structural phases¹⁰. Electrical properties and temperature-dependent dielectric properties of Ta ($y \leq 0.05$) doping in NKN which is discussed in an earlier publication^{11,12}. This behaviour demonstrates the technological potential that makes it interesting to study the electrical properties of ferroelectric solid solutions, near the MPB. In the year of 2004, Saito *et al.* reported a giant piezoelectric coefficient d_{33} of $416 \text{ pC}/\text{N}$ in highly textured (K, Na)NbO₃ (KNN) ceramics⁵, which sparked worldwide enthusiasm for intense research on KNN-based lead-free piezoelectric materials¹³⁻¹⁵.

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This article is focused on the structural, dielectric, and piezoelectric behavior, near the Morphotropic-like region¹⁶. Solid solutions of $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$) were prepared with solid-state reaction route using double sintering, in the composition range $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$). The observed remnant polarization, coercive field and converse piezoelectric coefficient (d_{33}^*) at room temperature under an applied electric field of 22 kV/cm and 1 Hz were carried out in the prepared samples. For the composition with $y = 0$ value of d_{33}^* was observed 166.52 pm/V; which decreases to 88.55 pm/V, for $y = 0.02$, and abruptly increases up to 300.76 pm/V for $y = 0.04$, and thereafter decreases with increasing y , in the measured range.

2 Experimental procedure

$\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$) pellet samples were using solid-state reaction method, from the powders of Na_2CO_3 , K_2CO_3 , Nb_2O_5 , Ta_2O_5 (all with purity $\geq 99.9\%$, from MERK, Germany). In the beginning, raw powders were dried separately, at 200 °C for 2 hours, to eliminate the absorbed moisture and weighed in stoichiometric ratio. The preparation method of $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($0 \leq y \leq 0.05$) ceramic pellets has been described in an earlier publication^{5,6}. The calcined mixture was further ground for half an hour and then pressed into pellets of 8 mm diameter and about 2 mm thickness, using 0.4 GPa uniaxial pressure. These pellets, with $y = 0, 0.01, 0.02, 0.03, 0.04$, and 0.05, were double sintered, each composition for 4 hours in the order of their melting points respectively, in a high temperature muffle furnace. Measuring Polarization characteristics and piezoelectric parameters of the prepared samples, with a ferroelectric- (PE loop tracer) and piezo- meter (AixACCT Systems, GmbH).

3 Results and Discussion

The polarization - electric field hysteresis (PE) loops observed at ambient temperature and 1 Hz for samples $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$) were shown in Fig 1. All samples have a standard hysteresis loop confirming the ferroelectric nature of all preparations $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$), NKNT ceramics. The area of the hysteresis loop was observed increasing with increasing Ta content (y value), up to $y = 0.02$, and afterward, with further increase in y , the area of the loop was observed decreasing, in the measured range. The observed strain [S(%)] vs. electric field (E) behavior for NKN

ceramics, measured at 1 Hz and room temperature, is shown in Fig 2. The S(%)- E loops show the largest strain, for the composition with $y = 0.01$, among the prepared samples, at the applied field of 22kV/cm.

Figure 3 shows the variation of remnant polarization (P_r) and coercive field (E_c) of the prepared samples with composition (y). The P_r value of the ceramics for $y = 0.02$ is found to be 4.67 $\mu\text{C}/\text{cm}^2$, which increases up to 18.439 $\mu\text{C}/\text{cm}^2$, for $y = 0.03$, in the measured range. The E_c value is also found to increase from 8.076 to 10.183 kV/cm, for $y = 0.03$ and 0.05. The presence of internal bias field, and the asymmetric shape and horizontal offset of coercive field, may be associated with the observed behavior, with varying composition. The increased distortion in the cell by decreasing the volume of

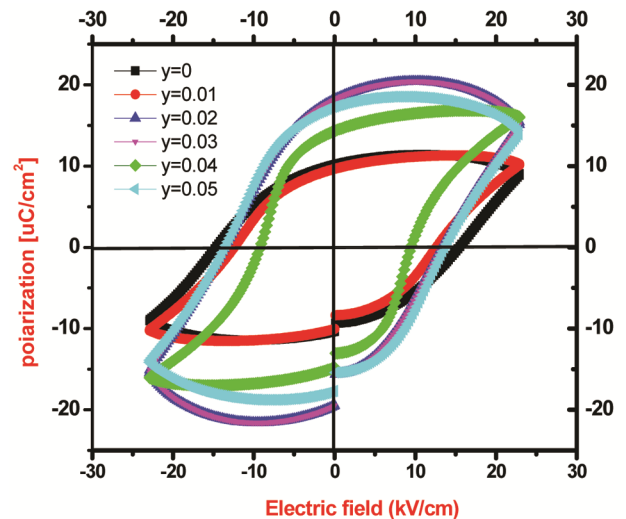


Fig. 1 — P-E loop for different compositions (y) of $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$), at applied field 22 kV/cm.

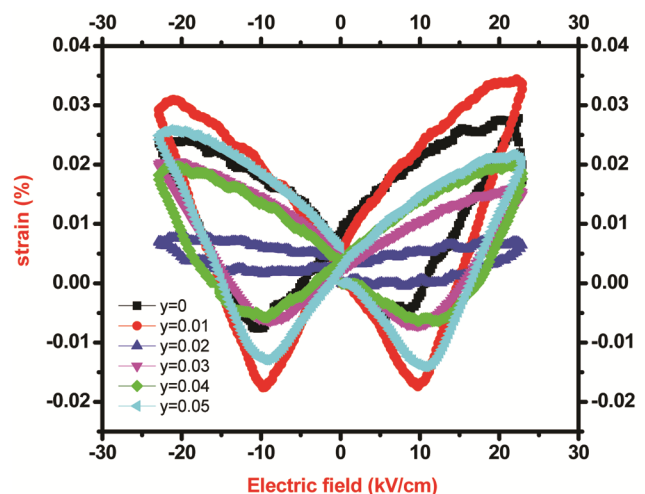


Fig. 2 — Variation of strain (%) with electric field (E), in $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$), at applied field 22 kV/cm.

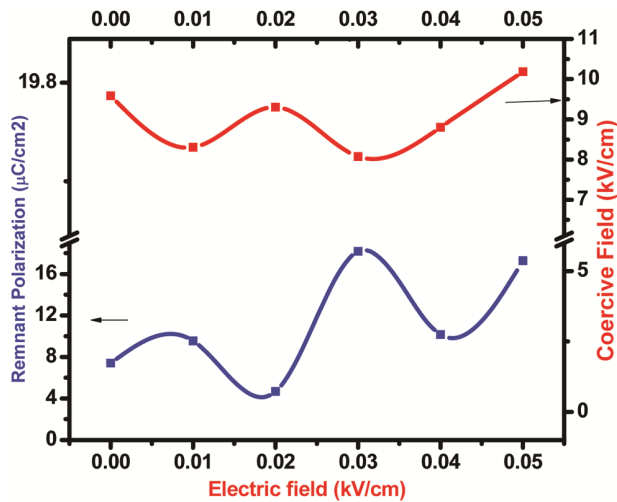


Fig. 3 — Variation of remnant polarization (P_r) and coercive field (E_c) with composition y , in $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$), at applied field 22 kV/cm.

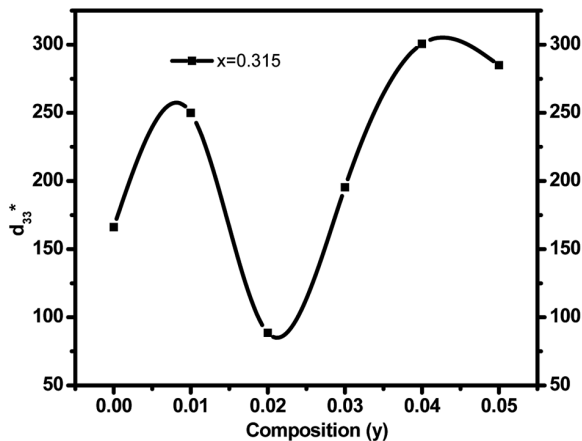


Fig. 4 — Variation of the converse piezoelectric coefficient (d_{33}^*) with composition y , in $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$), at applied field 22 kV/cm.

switchable domains may also increase E_c ¹⁷. The microstructure, stress, defects, and processing conditions of the material also affect the shape of the P-E hysteresis loop¹⁸.

The ratio of the maximum strain to the maximum field in the cycle is the converse piezoelectric coefficient (d_{33}^*), which was calculated as S_{\max}/E_{\max} ¹⁹. Figure 4 shows the variation of converse piezoelectric constant (d_{33}^*) of NKTN ceramics with y , at room temperature. For the composition with $y = 0$ value of d_{33}^* was observed 166.52 pm/V; which decreases to 88.55 pm/V, for $y = 0.02$, and abruptly increases up to 300.76 pm/V for $y = 0.04$, and thereafter decreases with increasing y , in the measured range.

Figure 5 shows the variation of polarization current with electric field. The magnitude of positive

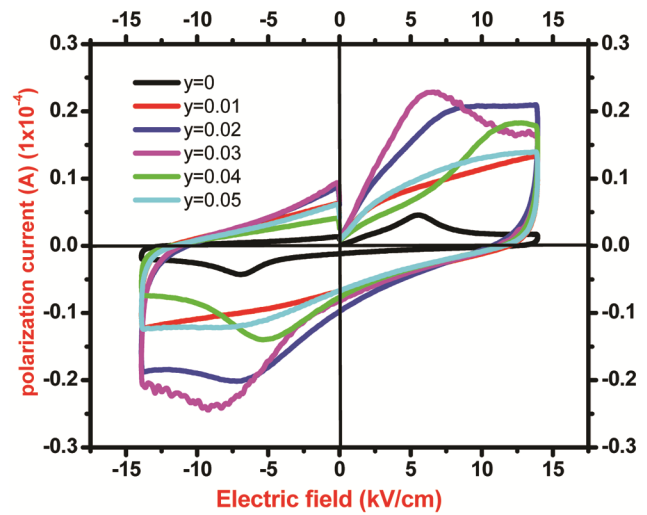


Fig. 5 — Variation of polarization current with electric field, in $\text{Na}_{0.685}\text{K}_{0.315}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$ ($y \leq 0.05$), at 22 kV/cm.

polarization current was found maximum for $y = 0.03$ (0.22×10^{-4} A) and minimum for $y = 0.00$ (0.04×10^{-4} A), and also the negative polarization current was found maximum for $y = 0.03$ (-0.23×10^{-4} A) and minimum for $y = 0.00$ (-0.04×10^{-4} A).

Piezoelectric properties and hysteresis loops significantly depend on crystal structure, grain size, and density of ceramics^{20,21}. In ferroelectric ceramics grain, the boundary is a low permittivity region, and therefore, at the grain boundary, the polarization may be quite low. Additionally, space charges within grain boundaries exclude polarization charge on the grain surface, which can cause polarization discontinuity on grain surface to form a depolarization field, and polarization decreases. As grain size increases, the number of grain boundaries decreases, resulting in an increase in remnant polarization as grain size increases²⁰. The processing affects the grain boundary properties and microstructure of a ceramic. The grain boundary resistivity affects the space-charge accumulation and thus the size-effect response is masked in the ferroelectric grains²²⁻²⁵. The observed variable piezo properties can be attributed to the control of grain boundary resistivity and grain size in this preparation procedure.

4 Conclusions

lead-free piezoelectric Tantalum doped $\text{Na}_{0.685}\text{K}_{0.315}\text{NbO}_3$ ceramics have been prepared by a conventional mixed oxide route. The effect of tantalum addition on the microstructure and various electrical properties has been studied. Due to the occupation of tantalum on the B side as a donor, the

material properties thus get softer electrically. The piezoelectric constants are slightly improved; however, the desirable working temperature for a piezoelectric ceramic is reduced. Reported and current observations indicate that the preparation process, composition, and structure significantly influence the piezoelectric properties of ceramics.

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