Enhanced electric field induced strain in SrTiO$_3$ modified (K,Na)NbO$_3$-based piezoceramics

Mohammad Reza Bafandeh a,⇑, Raziyeh Gharakhani b, Jae-Shin Lee c

a Department of Metallurgy, University of Kashan, Kashan, Iran
b Department of Materials Engineering, Isfahan University of Technology (IUT), Isfahan 84156-83111, Iran
c School of Materials Science and Engineering, University of Ulsan, Ulsan, Republic of Korea

Abstract

Lead-free 0.96K$_{0.5}$Na$_{0.5}$NbO$_3$–0.04LiTaO$_3$ ceramics modified with different amounts of SrTiO$_3$ (ST) from zero to 10 mol% were prepared by normal sintering. It was found that ST modification changed the crystal structure from orthorhombic to tetragonal and for ceramics with 10 mol% ST, pseudocubic structure was formed which was nonpolar. Investigation of bipolar strain revealed that with increasing ST content to 7.5 mol%, the negative strain decreased. This observation was attributed to the existence of nonpolar regions with local composition close to that of the ceramic containing 10 mol% ST. This phenomenon was accompanied with strain enhancement in unipolar strain curve because of the contribution of strain due to electric field-induced transition from nonpolar to ferroelectric phase, in addition to electric field induced strain.

Keywords: Piezoceramics Sintering Piezoelectricity

1. Introduction

Piezoelectric ceramics are widely used as actuators, sensors, transducers and generators due to their electromechanical behavior [1]. Environmental regulations have limited using piezoceramics containing lead due to their toxicity. One of the potential candidates as an alternative for lead-based piezoceramics is (K,Na)NbO$_3$ (KNN). KNN has high Curie temperature and its piezoelectric properties are relatively high [2]. In recent years many papers have been published about KNN-based ceramics. In order to provide a solid background about KNN ceramics, some of recent papers are briefly introduced.

One of recent researches which reported sintering behavior of KNN-based ceramics has been carried out by Li et al. [3]. It was found that ceramic with 1.0 wt.% of frit (BaO–CuO–B$_2$O$_3$–MnO$_2$) doping could be sintered at temperature about 100 °C lower than sintering temperature of undoped ceramic and consequently exhibited optimal electrical properties. Using CuTa$_2$O$_6$ (CT) as sintering aid of KNN ceramics revealed that Nb– sites were replaced by Cu and Ta ions causing the expansion of the lattice volume. As another result of this modification, density and electromechanical coupling factor of sintered ceramics were enhanced [4]. Sol–gel derived KNN powders exhibited low sintering temperature (1020 °C) and excellent electrical properties. The enhanced electric properties were related to coexistence of orthorhombic and tetragonal phases in the samples at room temperature as well as homogenous microstructure with fine grains and high density [5].

The influences of SrZrO$_3$ (SZ) on (1–x)(K$_{0.45}$Na$_{0.55}$)Li$_{1-x}$ (Nb$_{0.90}$Ti$_{0.04}$)O$_3$–xSrZrO$_3$ ceramics revealed that crystal growth and the densification of the ceramics were promoted by increasing SZ content. The coexistence of orthorhombic–tetragonal phases was found to transform from the phase boundary near tetragonal side to orthorhombic side as SZ content increased from 1 mol% to 4 mol%, and a pseudocubic phase was formed when 5 mol% SZ was added [6].

Investigation of the effects of Li and La doping on the phase structure and electrical properties of (K$_{0.5}$Na$_{0.5}$)$_2$Li$_2$La$_2$NbO$_7$ ceramics revealed that ferroelectric–paraelectric phase transition temperature decreased with increasing doping level. La-doping in the ceramics displayed a relatively low loss tangent (tan δ) from room temperature up to 350 °C. Detailed studies of dielectric and electrical properties indicated that the Curie temperature shifted to lower temperature with the increase in Li and La doping [7]. The effects of K/Na ratio on the phase structure, microstructure and electrical properties of (K$_{0.45}$Na$_{0.55}$)Li$_{1-x}$NbO$_3$ (K,NL, x = 0.34–0.61) lead-free piezoelectric ceramics were studied by Hao et al. [8]. Results showed that samples with x = 0.46–0.52 had a coexisted crystal structure with both orthorhombic and...
tetragonal phases, separating orthorhombic phase on both sides of this composition and corresponding to a polymorphic phase transition near room temperature. In this region, enhanced electrical properties were obtained. The approach of two-step sintering obviously broadened the sintering temperature range of the ceramics and further improved piezoelectric properties by ~10%, indicating it is a promising way for fabricating (K,Na)NbO3-based ceramics [8]. 

\[ \text{K}_x\text{Na}_{3-x}\text{Nb}_2\text{O}_7-x \text{ mol CuO (KNN–xCu) sintered in air atmosphere and argon atmosphere, respectively and the corresponding hardening characteristics were investigated by Wang et al. [9]}. \]

Results indicated that the Cu\(^{2+}\) ions can play different roles on the hardening mechanism in air atmosphere and argon atmosphere. The Cu\(^{2+}\) ions were considered to replace the Nb\(^{5+}\) ions for forming O\(^{2-}\) vacancies, and act as a hardener when sintered in air. However, when sintered in argon atmosphere, a large portion of Cu\(^{2+}\) ions could be reduced into Cu\(^{+}\) ions and then replaced by Na\(^{+}\) [9].

In order to determine the piezoceramic potential for actuator applications, electric field-induced strain (EFIS) is one of the most important parameters. So far, EFIS behavior of KNN-based ceramics has not been studied so much and there are few papers on this topic. Among them it can be referred to Hollenstein et al. [10] who reported converse piezoelectric constant, \(d_{33}=310 \text{ pm/V for } \text{K}_0.45\text{Na}_0.55\text{Li}_0.05\text{Nb}_2\text{O}_7\text{, Li}_0\text{ et al. [11]} \) that measured \(d_{33}=252 \text{ pm/V for KNN modified with LiNbO}_3, \text{SrTiO}_3 \text{ and BiFe}_3 \text{ and Matsubara et al. [12]} \) that reported \(d_{33}=280 \text{ pm/V for } 0.5 \text{ mol } \text{K} \text{ (as sintering aid)-added } \text{K}_0.5\text{Na}_0.5\text{Li}_0.0\text{Nb}_2\text{O}_7\text{. In contrast, in some } \text{B}_x\text{Na}_{3-x}\text{TiO}_3 \text{(BNT)-based systems by doping and modification, giant converse piezoelectric constant higher than 600 \text{ pm/V have been reported [13–15]}} \). Therefore it seems that lack of enough studies exist on improving EFIS behavior of KNN-based piezoceramics. Therefore the \(\text{K}_0.45\text{Na}_0.55\text{Li}_0.05\text{Nb}_2\text{O}_7\text{Ta}_0.05\text{O}_3\text{ (abbreviated as KNNLT) composition due to its relatively good piezoelectric properties and also its polymorphic phase transition temperature which is far enough from room temperature [16] that can guarantee stability of its properties within a relatively broad temperature range, was chosen as a base composition in this study. Due to positive effects of \text{SrTiO}_3 \text{ in KNN-based ceramics, in this study (100–x)KNNLT – xST } (0 \leq x \leq 10) \text{ ceramics were fabricated using solid state reaction and subsequent normal sintering in air and the effects of different amounts of ST on phase structure, ferroelectric properties as well as electric field-induced strain behavior of sintered ceramics were investigated.}

### 2. Experimental procedures

(100–x)KNNLT – xST \((0 \leq x \leq 10)\) powders were synthesized by a conventional solid state reaction method using \text{Na}_2\text{CO}_3, \text{K}_2\text{CO}_3, \text{Li}_2\text{CO}_3, \text{Nb}_2\text{O}_5, \text{Ta}_2\text{O}_5, \text{SrO} \text{ and TiO}_2 \text{ with more than 99% purity as raw materials. These powders were dried in oven at 100 °C for 24 h and then were weighed for each composition according to stoichiometric formula. Each powder mixture was ball-milled for 24 h with zirconia balls using ethanol media. The dried slurries were calcined at 880 °C for 6 h. In order to increase the homogeneity of composition, the calcination was carried out twice separating by 24 h ball milling. Calcined powders were mixed with poly vinyl alcohol as a binder and then pressed into green disks with a diameter of 12 mm at 50 MPa. Green disks were sintered in the temperature range 1960–1150 °C. In order to minimize the alkali elements loss during sintering, the green disks were buried under the calcined powder with the same composition in a covered alumina crucible. The densities of all sintered ceramics were measured by the Archimedes method and the temperature that yielded the maximum relative density for each composition was chosen as the optimum sintering temperature. Specimens sintered at these temperatures were used for electrical characterization. The crystal structure of ceramics was determined using an X-ray diffractometer (XRD, X’pert PRO MRD, Philips). For electrical measurements, silver paste was applied on the lapped surfaces of the disks to serve as the electrodes. The ferroelectric hysteresis loops were measured using a Sawyer-Tower circuit to apply an electric field with a triangular waveform. The electric field induced strain was measured using a linear variable differential transducer (LVDT, Mitutoyo MCH-331 & M401). The voltage was supplied using a high voltage amplifier (Trek, 610E) driven by waveform generator (Agilent 33250A).
ions. In addition, it is obvious that diffraction peaks shift toward a higher angle with increasing the amount of ST, indicating ST addition decreases the lattice parameter. According to valence of Sr and Ti ions which are +2 and +4, respectively as well as closeness of ionic radius of Sr$^{2+}$ ions to that of Na$^+$ and K$^+$ ions and also closeness of ionic radius of Ti$^{4+}$ to that of Nb$^{5+}$, it can be expected that Sr$^{2+}$ ions substitute instead of Na$^+$ and K$^+$ ions in A-sites and Ti$^{4+}$ ions substitute instead of Nb$^{5+}$ ions in B-sites of ABO$_3$ perovskite structure. Considering these substitutions, smaller ionic radius of Sr$^{2+}$ ions (1.44 Å, CN = 12) compared to the average ionic radius of A-site matrix ions, i.e. Na$^+$ (1.39 Å, CN = 12) and K$^+$ (1.64 Å, CN = 12), as well as the smaller Ti$^{4+}$ ion (0.61 Å, CN = 6) compared to Nb$^{5+}$ (0.64 Å, CN = 6) which is the matrix B-site ion in the ABO$_3$ perovskite structure, results in decrease of lattice parameters with increasing ST content. The lattice parameters of ceramic with different amounts of ST, are as follows:

- $x = 0$, $a = c = 4.005$ Å, $b = 3.945$ Å;
- $x = 1$, $a = c = 4.003$ Å, $b = 3.942$ Å;
- $x = 3$, $a = b = 3.948$ Å, $c = 4.046$ Å;
- $x = 5$, $a = b = 3.945$ Å, $c = 4.043$ Å;
- $x = 7.5$, $a = b = 3.942$ Å, $c = 4.040$ Å;
- $x = 10$, $a = b = c = 3.968$ Å.

The tetragonality factor of pure tetragonal ceramics, i.e. ceramics containing 3%, 5%, 7.5% ST were calculated to be almost equal to 1.025.

3.2. Electrical characterization

3.2.1. Ferroelectric properties

Fig. 3 shows polarization versus electric field for (100–x)KNNLT – xST ceramics. As can be seen in the figure, all samples except $x = 10$ exhibit well saturated $P$–$E$ loop which is one of the characteristics of ferroelectric materials. Two important parameters that can be extracted from $P$–$E$ loops are remnant polarization ($P_r$) and coercive field ($E_c$) which are cross sections of polarization and electric field axes, respectively. The $P_r$ corresponds to the remained aligned dipoles after removing electric field and the $E_c$ indicates the electric field required for domain switching. Therefore $P_r$ and $E_c$ values versus ST content are plotted in Figs. 4 and 5, respectively. As shown in Fig. 4, $P_r$ increases abruptly for $x = 1$ ceramic. Coexistence of orthorhombic and tetragonal structures in this sample that results in higher domain switching orientations on applying electric fields is responsible for this behavior. By more addition of ST from 3% to 7.5%, a continuous increase in $P_r$ is observed, indicating the positive effect of ST addition on ferroelectric behavior of ceramics. For ceramic with $x = 10$ a sharp drop in $P_r$ is seen which is due to its symmetric pseudocubic structure showing small dipole moment. A similar observation has been reported in KNN–LiSbO$_3$ system by Wu et al. [18]. The variation of $E_c$ versus ST content is almost reverse of $P_r$ versus ST content which indicates ST addition and coexistence of two symmetries facilitates domain switching.

3.2.2. Electric field-induced strain (EFIS)

Bipolar electric field-induced strain curves of (100–x)KNNLT – xST ceramics as a function of composition, are shown in Fig. 6. All specimens except $x = 10$ exhibit typical butterfly shape strain curves as a characteristic of the ferroelectric materials. For the specimen with $x = 10$, the “negative strain” which is defined as the difference between zero-field strain and the lowest strain [19] is close to zero and the strain loop exhibits a drastic deviation from those of typical ferroelectric materials. This behavior can be attributed to a phase transition from ferroelectric to a nonpolar...
phase [20]. Such a phenomenon has not been reported in KNN-based systems, however it can be found in many BNKT-based systems [13–15,21]. The maximum negative strain was observed in the specimen with \( x = 1 \), which is believed to be due to the well developed ferroelectric domains in the specimen as evidenced in the \( P-E \) loop in Fig. 3.

The sample with \( x = 7.5 \) compared to other compositions except \( x = 10 \) shows a lower negative strain. This result is probably due to the existence of regions inside this ceramic with local composition close to 90KNNLT–10ST composition. The result of this composition heterogeneity is formation of non-polar regions in ceramic which results in reduction in the negative strain. Decreased negative strain in 92.5KNNLT–7.5ST ceramic is accompanied with increase in positive strain. Although there are some nonpolar regions with pseudocubic structure in 92.5KNNLT–7.5ST ceramic, polar phase with tetragonal structure is predominant phase and responsible for EFIS. Moreover electric field-induced phase transition from pseudocubic to ferroelectric also contributes to the strain behavior, resulting in large positive strain in this ceramic. Enhanced strain in some BNK-based systems with composition separating ferroelectric and nonpolar phase have been reported before. The giant strain was first reported in a BNT–BaTiO\(_3\) (BT) single crystal. The reason of this behavior was related to huge volume change during electric-field-induced anti ferroelectric (AFE) to ferroelectric (FE) transition [22]. Later, it was also reported in BNT–BT ceramics when a small amount of (KNN) was added [23].

Succeeding compositional [24] and temperature-dependent studies [25] demonstrated that the giant strain appeared at a boundary dividing FE and AFE order and the AFE phase has its origin in the high-temperature polymorph of the BNT–BT system that Takenaka et al. [26] initially designated as AFE.

In ceramic with \( x = 10 \), nonpolar phase with pseudocubic structure is predominant. So in addition to drastic drop in remnant polarization (in Fig. 4), drastic deviation from typical butterfly strain loop (in Fig. 6) is observed.

Variations in the unipolar strain versus applied electric field for different compositions are shown in Fig. 7. As shown in this figure, with increasing \( x \) from zero to 5, the obtained strain increases slowly. This behavior could be attributed to the positive effect of ST addition on the piezoelectric behavior of ceramics. Further addition of \( x \) to 7.5 is accompanied with an abrupt jump in strain value. As mentioned above, reduced negative strain in specimen with \( x = 7.5 \) is evidence for existence of pseudocubic nonpolar regions, in this ceramic. So the main reason for unipolar strain enhancement in ceramic with \( x = 7.5 \) is existence of nonpolar regions. Electric field-induced phase transition from nonpolar to ferroelectric, contributes to EFIS and enhances obtained strain.

Dynamic piezoelectric constant or normalized strain (\( d_{33}^p \)) of ceramics was calculated from the ratio between the maximum strain in unipolar curve and its related electric field. As could be expected the maximum \( d_{33}^p \) occurs at \( x = 7.5 \) which is due to common effect of electric field-induced strain and electric field-induced phase transition from a nonpolar to a polar phase. Comparing dynamic piezoelectric constant of 92.5KNNLT–7.5ST ceramic (\( d_{33}^p = 400 \) pm/V) with reported values in other KNN-based ceramics such as 310 pm/V for K\(_{0.485}\)Na\(_{0.485}\)Li\(_{0.01}\)Nb\(_0.99\)O\(_3\) [10], 252 pm/V for KNN modified with LiNbO\(_3\), SrTiO\(_3\) and BiFeO\(_3\) [11] and 200 pm/V for 0.5mol\% KCT (as sintering aid)-added K\(_{0.3}\)Na\(_{0.48}\)Li\(_{0.02}\)NbO\(_3\) [12] reveals that 92.5KNNLT–7.5ST has good potential for actuator applications.

By comparison between measured values for \( d_{33} \) (which has been reported in our previous paper [17]) and calculated \( d_{33}^p \), it can be found that piezoelectric constants obtained from the converse measurement is higher than those obtained from direct measurement. A similar result has been also reported by Holleinstein et al. [10] in KNN modified with Li and Ta, which was attributed to the following two reasons.

First, the large applied fields during converse measurement (up to 4 kV/mm) may actually lead to an enhancement in poling of the samples. Second, the domain walls maybe more susceptible to migrate under large unipolar electric than under uniaxial and weak dynamic compressive pressure.

4. Conclusions

(100–\( x \))KNNLT – \( x \)ST ceramics were fabricated by normal sintering in air. XRD results revealed that pure KNN had orthorhombic structure while with increasing \( x \), crystalline structure changed from orthorhombic to tetragonal. In ceramics with \( x = 1 \) orthorhombic and tetragonal structures coexisted. Ceramics with \( x = 10 \) exhibited pseudocubic structure, so it can be considered as a nonpolar ceramic. The maximum unipolar strain was obtained in 92.5KNNLT–7.5ST ceramic and was attributed to electric field-induced strain as well as electric field-induced phase transition of pseudocubic regions in this ceramic to ferroelectric phase. According to high converse piezoelectric constant of 92.5KNNLT–7.5ST ceramic (\( d_{33}^p = 400 \) pm/V) it can be used for actuator applications.

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References