Short communication

Effects of SrTiO₃ on dielectric and piezoelectric properties of K₀.₄₈Na₀.₄₈Li₀.₀₄Nb₀.₉₆Ta₀.₀₄O₃-based piezoceramics

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A B S T R A C T

In this study, (100 − x) K₀.₄₈Na₀.₄₈Li₀.₀₄Nb₀.₉₆Ta₀.₀₄O₃ − xSrTiO₃ (0 ≤ x ≤ 10) ceramics were fabricated via normal sintering of synthesized powder by using solid state reaction. All ceramics revealed pure perovskite structure, indicating formation of solid solution between KNNLT and ST up to 10%. With increasing x, the crystal structure of ceramics changed from orthorhombic to tetragonal and finally pseudocubic symmetry when x = 10. Ceramic containing 1% ST had orthorhombic and tetragonal symmetries, simultaneously. Investigation of the variation of dielectric constant of ceramics versus temperature revealed that for ceramic with x = 1, polymorphic phase transition (PPT) temperature between orthorhombic and tetragonal is less than room temperature. Thus coexistence of two different structures in this ceramic is due to vicinity of its composition to morphotropic phase boundary (MPB). As a result, the maximum piezoelectric constant was measured for this ceramic. Ceramics containing 5 and 7.5% ST tend to appear relaxor ferroelectric behavior which is because of chemical inhomogeneities in both A- and B-sites of the ABO₃ perovskite structure.

1. Introduction

Piezoelectric ceramics because of having electromechanical behavior could be used in many applications such as actuators, transducers and sensors [1]. So far lead-based piezocermics especially Pb(Zr,Ti)O₃ (PZT) due to their excellent electromechanical properties have been predominant in the market of piezocermics [2]. PZT contains lead as a toxic element so its application is harmful for environment either within processing or during disposal of waste counterparts. In recent years, approval of restricting regulations such as Waste from Electrical and Electronic Equipment (WEEE) accelerated the search for lead-free piezocermics [3]. One of the potential candidates as an alternative for PZT family is sodium potassium niobate (KNN) because of its high Curie temperature and relatively good piezoelectric properties [4]. Unfortunately sinterability of KNN is low and results in decrease of properties of sintered ceramic as well as its reproducibility. Thus in many researches by doping and or modification of chemical composition have been tried to improve sinterability and consequently piezoelectric properties of KNN-based ceramics. Improvement of properties is not only due to the higher sinterability but also due to coexistence of two different crystal structures in the ceramic. The reason of coexistence of two structures in a piezocermic could be the vicinity of polymorphic phase transition (PPT) temperature to room temperature or closeness of chemical composition to morphotropic phase boundary (MPB). One of promising modifiers, in which its positive effect on electric properties of KNN has been proved, is LiTaO₃ (LT). For example Guo et al. [5] investigated (1 − x)KNN − xLT system and found at x = 0.05, the crystal structure changes from orthorhombic to tetragonal and ceramic containing 5% LT has a mixture of orthorhombic and tetragonal symmetries and as a result, the maximum piezoelectric constant was measured for this composition. They attributed the improvement of properties to the vicinity of chemical composition to MPB as well as closeness of PPT temperature to room temperature. As a result, temperature dependence of piezoelectric properties of ceramic containing 5% LT was predicted. In this work, with the aim to improve the piezoelectric properties of KNN-based ceramics as well as to increase thermal stability of properties, 0.96KNN−0.04LT was selected as a based composition and addition of SrTiO₃ (ST) to it was investigated, for which its PPT temperature is far enough from room temperature so that thermal stability of its properties within a relative broad temperature range is guaranteed. Therefore in this study, K₀.₄₈Na₀.₄₈Li₀.₀₄Nb₀.₉₆Ta₀.₀₄O₃ (abbreviated as KNNLT) ceramics modified with different amounts of ST (0–10 mol%) were fabricated and phase structure, microstructure as well as dielectric and piezoelectric properties of sintered ceramics were studied.
2. Experimental procedure

(100 − x)KNNLT − xST (0 ≤ x ≤ 10) powders were synthesized by a conventional solid state reaction method using Na2CO3 (99%), K2CO3 (99%), Li2CO3 (99.9%), Nb2O5 (99.9%), Ta2O5 (99.9%), SrO (99%) and TiO2 (99.9%) as raw materials. At first, 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. Each composition was fabricated via solid state reaction, i.e. calcination. In order to remove carbon dioxide from carbonate raw materials and formation of solid solution with perovskite structure, calcination was performed at 880 °C for 6 h.

In order to increase 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 1060–1150 °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 density of all sintered ceramics was measured by the Archimedes method and the temperature that yielded the maximum relative density for each composition was chosen as an 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). The microstructure of ceramics was observed using scanning electron microscopy (FE-SEM, JEOL, JSM-650FF, Japan). Before SEM observation, the samples were thermally etched by keeping polished samples for 1 h at temperature 100 °C lower than sintering temperature.

For electrical measurements, silver paste was applied on the lapped surfaces of the disks to serve as the electrodes. The temperature dependence of dielectric properties was measured using an impedance analyzer (HP 4192A) in a temperature range of 25–500 °C. Some samples were poled at 100 °C in silicon oil bath by applying an electric field of 3–4 kV/mm for 30 min. The piezoelectric constant d33 was measured using a piezo-d33 meter (ZJ-6B, Institute of Acoustics, Beijing, China).

3. Results and discussion

3.1. Structure and phase determination

X-ray diffraction (XRD) patterns of (100 − x)KNNLT − xST ceramics sintered at optimum sintering temperature are shown in Fig. 1. By comparing XRD patterns with JCPDS pattern 01-071-2171 (corresponding to orthorhombic KNbO3) and 01-071-0945 (corresponding to tetragonal KNbO3) it can be recognized that all samples show pure perovskite structure without any secondary phase, indicating the formation of solid solution between KNNLT and ST within the studied range 0 ≤ x ≤ 10. Crystalline type of perovskite structure is usually determined based on the relative intensities of split peaks around 2θ = 46°. Therefore the magnified XRD patterns of ceramics in the range 44° < 2θ < 47° are shown in Fig. 2. It can be seen that XRD patterns of ceramic with x = 0.0 shows (20 0)(0 2 0) peak splitting around 2θ = 46°, confirming the orthorhombic symmetry. This observation is in good agreement with reported results by Guo et al. [5]. For ceramics with 3 ≤ x ≤ 7.5, XRD patterns show (0 0 2)/(0 2 0) peak splitting, indicating the tetragonal symmetry. The split peaks around 2θ = 46° in XRD pattern of ceramic with x = 1 have equal intensities which is due to coexistence of orthorhombic and tetragonal structures. Such as this justification to determine crystalline structure of KNN-based ceramics has been reported in many researches such as [6–9]. The merging the split peaks together for ceramic with x = 10 indicates formation of pseudocubic structure for this composition. Changing of crystalline structure with increasing the amount of ST is due to introduced distortion in unit cell as a result of difference in the ionic size between the substituent’s and lattice ions.

In addition, it is obvious that diffraction peaks shift toward a higher angle with increasing the amount of ST, indicating ST addition decreases lattice parameter. According to valence of Sr and Ti ions which are +2 and +4, respectively as well as closeness of ionic radius of Sr2+ ions to ionic radius of Na+ and K+ ions and also closeness of ionic radius of Ti4+ to that of Nb5+, it can be expected that Sr2+ ions substitute instead of Na+ and K+ ions in A-sites and Ti4+ ions substitute instead of Nb5+ ions in B-sites of ABO3 perovskite structure. Considering these substitutions, smaller ionic radius of Sr2+ 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 Ti4+ ion (0.61 Å, CN = 6) compared to Nb5+ (0.64 Å, CN = 6) which is the matrix B-site ion in the ABO3 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 = 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.
3.2. Microstructure analysis

Fig. 3 shows the microstructure of (100–x)KNNLT–xST specimens sintered at the optimum sintering temperature. It can be seen that composition modification with ST changes microstructure, especially grain size of ceramics. Addition of ST up to 5 mol% promotes grain growth, while further addition of ST inhibits grain growth and results in fine microstructure. In KNN-based ceramics, partial formation of liquid phase during sintering has been reported as auxiliary sintering mechanism [10–12]. Wang and Li [13] also reported formation of liquid phase during sintering of (1 – x)KNN–xLiNbO3 due to excess amount of Na2O. They observed an abrupt increase in shrinkage rate at 930 °C and this observation was attributed to formation of some liquid phase at this temperature.

The temperature that yielded the maximum relative density for each composition was chosen as an optimum sintering temperature. The optimum sintering temperature for ceramics with 0, 1, 3, 5, 7.5 and 10% ST were determined 1130, 1130, 1120, 1110, 1090 and 1090 °C, respectively. The relative density which is ratio between measured density and theoretical density of optimally sintered samples with 0, 1, 3, 5, 7.5 and 10 mol% ST, were calculated 94.2, 94.4, 94.7, 95.3, 95.5 and 95.8%, respectively, indicating ST modification enhanced densification.

3.3. Electrical characterization

3.3.1. Dielectric constant of ceramics as a function of temperature and measuring frequency

The variation of dielectric constant of (100–x)KNNLT–xST ceramics versus temperature during heating cycle from 25 to 500 °C under 1 kHz measuring frequency is plotted in Fig. 4. Pure KNN undergoes three polymorphic phase transitions (PPTs) on heating; rhombohedral to orthorhombic (r–o) transition at around –123 °C, orthorhombic to tetragonal (o–t) transition at around 200 °C and tetragonal to cubic (t–c) transition at around 410 °C [14]. Doping and/or modification of KNN can change PPT temperatures. Such as this behavior has been reported in KNN-LiTaO3 [5], KNN-Ba(Zr0.05Ti0.95)O3 [15] and KNN-BaAlO3 [16] among many other papers. According to Fig. 4 for 0ST, there exist two peaks in the range of 25–500 °C. The lower temperature peak is related to T_o–t and higher one corresponds to the Curie temperature (T_C). The T_C and T_o–t of KNNLT were found to be 419 and 79 °C, respectively. In ceramics with x = 1 and x = 3 just one peak were revealed.
corresponding to $T_c$ around 393 and 355 °C, respectively. Thus for these two compositions, orthorhombic–tetragonal phase transition temperature is lower than 25 °C. Based on XRD results (Section 3.1) 1ST ceramic has orthorhombic and tetragonal structures, simultaneously. In some researches coexistence of orthorhombic and tetragonal structures in KNN-based ceramics is related to the close composition to MPB [5,7,17,18]. However some investigators interpret this observation as the vicinity of orthorhombic–tetragonal phase transition temperature to room temperature. Considering coexistence of two different structures in 1ST sample and also its PPT temperature which is lower than room temperature, it can be concluded that 1ST composition is near to MPB composition of $(100 - x)\text{KNNLT} - x\text{ST}$ system. Thus it can be suggested that coexistence of orthorhombic and tetragonal structures in 1ST is related to MPB phenomenon not to PPT phenomenon. Further increasing $x$ up to 7.5 caused broadening of $T_c$ peak and the tetragonal–cubic phase transition became more diffuse, which has been typically observed in relaxor ferroelectrics [19]. Ceramic with $x = 10$ showed a flat and broad peak in Fig. 4 that is a result of its pseudocubic structure.

In order to further investigate the dielectric behavior of ceramics with $x = 3, 5$ and 7.5, the variation of dielectric constant versus temperature under different measuring frequencies from 1 to 100 kHz was characterized and the results are given in Fig. 5. It is seen that 3ST reveals weak frequency dependence while both 5ST and 7.5ST show strong frequency dispersions, that is, the maximum dielectric constant decreases and its corresponding temperature increases with increasing frequency. This observation further proves relaxor like behavior of 95KNNLT-5ST and 92.5KNNLT-7.5ST ceramics. So it can be concluded that with increasing $x$ from 3 up to 7.5, tetragonal–cubic transition becomes more and more diffuse. A modified Curie–Weiss law [20] was suggested to determine the diffuseness of ferroelectric phase transitions:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C}$$

(1)

where $\gamma$ is the diffuseness of phase transition, $C$ is a constant, $\varepsilon_m$ is the maximum dielectric constant and $T_m$ is its corresponding temperature in $\varepsilon$–$T$ diagram. The $\gamma$ value varies from 1 to 2. The limiting values $\gamma = 1$ and $\gamma = 2$ indicate a normal ferroelectric and relaxor ferroelectric, respectively. The relation between $\log(1/\varepsilon - 1/\varepsilon_m)$ and $\log(T - T_m)$ for $x = 3, 5$ and 7.5 are displayed in Fig. 6. According to the modified Curie–Weiss law [20] the slope of the curve corresponds to the diffuseness ($\gamma$). By linear fitting of experimental data in Fig. 6, the $\gamma$ values for $x = 3, 5$ and 7.5 were determined to be 1.11, 1.58 and 1.85, respectively, indicating that there is a gradual change from a normal ferroelectric state to a relaxor in $(100 - x)\text{KNNLT} - x\text{ST}$ ceramics with increasing $x$.

The relaxor behavior can be induced by many reasons such as microscopic composition fluctuation, merging of micropolar regions into macropolar regions, or a coupling of the order parameter and local disorder mode thorough the local strain [19]. Cationic disorder in the same crystallographic site can also induce relaxor behavior [21]. In $(100 - x)\text{KNNLT} - x\text{ST}$ ceramics, Sr$^{2+}$, K$^+$, Na$^+$ and
Further, the vs... ceramic is finer than 95KNNLT-5ST ceramic. Since grain boundaries can act as barriers for domain switching, a mixture of relaxor microstructure is more difficult than coarser one and results in lower $d_{33}$. The 90KNNLT-10ST ceramic showed an abrupt drop in $d_{33}$ value due to its pseudocubic structure, which is without dipoles, so this ceramic should be considered as non-polar.

4. Conclusions

In this work, (100 – $x$)KNNLT–xST ceramics were prepared by normal sintering in air. The ceramics did not show secondary phase, indicating formation of solid solution between KNNLT and up to 10 mole% ST. Crystalline structure of KNNLT was orthorhombic and that of ceramics with $x \geq 3$ was tetragonal. 99KNNLT-1ST exhibited mixture of orthorhombic and tetragonal phases and due to higher number of switching orientations showed maximum $d_{33}$ at 208 pC/N. From temperature and frequency dependence of dielectric constant measurements, it was found that ST modification gradually induced a transition from normal behavior to relaxor behavior. 10ST sample exhibited a pseudocubic structure with a negligible piezoelectric constant, indicating non-polar state at this level of ST modification.

References