Sintering behavior, dielectric and piezoelectric properties of sodium potassium niobate-based ceramics prepared by single step and two-step sintering

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Abstract

In this work (1−x)K0.48Na0.48Li0.04Nb0.96Ta0.04O3−xSrTiO3 (0.0 ≤ x ≤ 0.10) ceramics were fabricated via single step sintering (SSS) as well as two-step sintering (TSS) methods. Investigation of the sintering behavior of ceramics revealed that TSS could reduce sintering temperature effectively and it enhances densification. The relative densities of TSSed ceramics were about 3% higher than SSSed ones. Coexistence of orthorhombic and tetragonal symmetries in ceramic containing 1% SrTiO3, resulted in maximum piezoelectric constant compared to others. Higher density and lower alkali elements loss in TSSed ceramics improved dielectric and piezoelectric properties compared to SSSed ceramics. Piezoelectric constant of the 0.99KNNLT–0.01ST ceramic sintered via SSS and TSS was measured at 208 and 278 pC/N, respectively.

Keywords: A. Sintering; C. Dielectric properties; Piezoelectricity; Piezoceramics

1. Introduction

Sodium potassium niobate (KNN)-based piezoceramics because of their high Curie temperature and relatively good piezoelectric properties, are considered as suitable candidates for replacement of lead-based piezoceramics, whose applications have been restricted due to lead toxicity [1]. This consideration was intensified especially after the work of Saito et al. [2] which reported comparable piezoelectric properties of KNN-based ceramics with lead-based ones. Unfortunately low sinterability of KNN-based ceramics and difficulty of their fabrication with high density via conventional sintering method under atmospheric pressure [3] have restricted their mass production and applications. Insufficient density of KNN-based ceramics, possibility of compositional deviation of sintered ceramic from stoichiometry composition and formation of secondary phases due to volatilization of alkali elements during sintering [4,5] are all results of low sinterability of KNN-based compounds and result in decline of piezoelectric properties of sintered ceramic.

So far many research works have been carried out to improve sintering behavior of KNN-based compounds via doping [6,7,8], modification [2,9,10] and using sintering aids [11,12]. Considerable improvements in piezoelectric properties of fabricated ceramics have been observed. Some investigators were able to fabricate dense ceramics with better properties using other sintering methods such as hot pressing [13] and spark plasma sintering [14], instead of conventional methods. However the complexity and expensiveness of these methods restrict their industrial applications. Therefore using a relatively simple and effective method to improve sintering behavior and piezoelectric properties of KNN-based compounds besides doping and modification of composition seems essential. One of the sintering methods which is capable of fabricating dense structure as well as fine microstructure is
two-step sintering (TSS). This novel method was introduced in 2000 by Chen and Wang [15] and it has been used to sinter different compounds such as Al2O3 [16], ZrO2 [17] and Y2O3 [18]. In first step of TSS, the sample is kept at a higher temperature (T1) for a short time to reach a critical density and then rapidly cooled down to lower temperature (T2) and is soaked for relatively prolonged time for densification without grain growth. Due to TSS, the potential to decrease the required sintering temperature effectivly using this method for sintering compounds containing volatile elements, eliminates or at least decreases loss of volatile elements and enhances densification. So far, the use of TSS for sintering KNN-based compounds has not been studied so much. Therefore, in this work, sintering of K0.48Na0.48Li0.04Nb0.96Ta0.04O3 (KNNLT) modified with different amounts of SrTiO3 (ST) via TSS was investigated. Moreover the conventional method (single step sintering) was also used. Sintering behavior, dielectric and piezoelectric properties of ceramics produced by two different sintering procedures were studied and compared.

2. Experimental procedure

(1–x)KNNLT–xST (0.0 ≤ x ≤ 0.10) powders were synthesized by a conventional solid state reaction method using Na2CO3, K2CO3, Li2CO3, Nb2O5, Ta2O5, SrO and TiO2 with more than 99% purity as raw materials. At first, these powders were dried in an oven at 100 °C for 24 h and then were weighted for each composition according to a 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 the composition, the calcination was carried out twice, separated by 24 h ball milling. Calcined powders were mixed with polyvinyl alcohol as a binder and then pressed into green disks with a diameter of 12 mm at 50 MPa. The green disks were sintered via TSS and single step sintering (SSS). Time and temperature conditions as well as heating and cooling rates in TSS and SSS procedures are compared in Fig. 1. For TSS, samples were sintered in the range 1060–1150 °C with a 10 °C interval. 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. The crystal structure of the samples was determined using an X-ray diffractometer (XRD, X’pert PRO MRD, Philips). The microstructure of ceramics was observed using a scanning electron microscope (FE-SEM, JEOL, JSM-650FF, Japan). For electrical measurements, silver paste was applied on the lapped surfaces of the disks to serve as the electrodes. The density considerably due to domination of grain growth over mass transport is the probable reason for this observation. Increasing the temperature in the third step does not increase the density considerably due to domination of grain growth over densification. In this step, the driving force for sintering is consumed mainly for grain growth without having a considerable effect on densification of samples. At temperatures higher than 1140 °C a sharp drop in densities of all compositions occurs which is due to the loss of Na and K volatile elements resulting in reduction of the sample’s mass. Appearance of such behavior during sintering of KNN-based compounds results in

3. Results and discussion

3.1. Densification

3.1.1. Single step sintered samples

Variation of relative density (RD) of SSS (1–x)KNNLT–xST ceramics for 2 h versus sintering temperature is shown in Fig. 2. As can be seen, for all compositions variation of RD follows a four-step trend. In the first step, density increases with a relatively slow rate while in the second step a sharp increase can be seen. Mechanism change, from solid state to partial liquid phase sintering [19,20], which enhances diffusion and mass transport is the probable reason for this observation. Increasing the temperature in the third step does not increase the density considerably due to domination of grain growth over densification. In this step, the driving force for sintering is consumed mainly for grain growth without having a considerable effect on densification of samples. At temperatures higher than 1140 °C a sharp drop in densities of all compositions occurs which is due to the loss of Na and K volatile elements resulting in reduction of the sample’s mass. Appearance of such behavior during sintering of KNN-based compounds results in
difficulty and narrowness of proper sintering temperature range for these materials [21,22,23]. The onset temperature of the third step in Fig. 2 was chosen as optimum sintering temperature for each compound. At higher temperatures, not only it is impossible to reach higher density, but there is also the risk of alkali elements loss. According to Fig. 2 by increasing ST content, the sintering temperature decreases and proper sintering temperature range is broadened, indicating the ease of sintering compounds with higher ST content.

3.1.2. Two-step sintered samples

To succeed in TSS (reaching dense and fine microstructure) proper selection of first step temperature ($T_1$) as well as second step temperature ($T_2$) is very important. In the first step, a relatively dense microstructure is needed in which supercritical pores in the sample are removed and other pores become thermodynamically unstable so that they can be shrunk and removed in the second step. Reaching this state requires a temperature ($T_1$) higher than a critical value. The criterion for determination of this critical temperature is obtaining a critical density which is usually higher than 75% of the theoretical density (TD) [15]. Thus for TSS, first of all a proper $T_1$ should be determined. For this purpose, temperatures in the range 1090–1140 °C with 10 °C interval were chosen and the KNNLT compound was kept at these temperatures for 10 min and then cooled down to room temperature. The variations of sintered ceramics RD are shown in Fig. 3. According to this figure, by keeping samples for 10 min at temperatures higher than 1000 °C ceramics with RD values higher than 75% of TD values can be obtained. Moreover increment of density at 1140 °C was not considerable; so, the temperatures 1110, 1120, and 1130 °C were selected as candidate temperatures for further investigation. TSS was performed according to the temperature–time profile which is shown in Fig. 1, with $T_1$ within the above-mentioned temperature range and $T_2$ within 1000–1040 °C with 10 °C intervals and soaking time of 6, 8 and 10 h. The variations of RD versus $T_1$ and $T_2$ with different soaking times in the second step are shown in Fig. 4. According to this figure necessity of obtaining a critical density after first step in order to perform successful TSS can obviously be seen. If $T_1=1110$ °C (RD about 75% of TD, according to Fig. 3), by holding samples at different temperatures in the second step even for 10 h, an RD value higher than 83% of TD cannot be achieved. For 1120 and 1130 °C as $T_1$, the variation of RD versus $T_2$ shows an almost similar trend for different soaking
times, and the final values for obtained densities are identical. Thus 1120 °C as $T_2$ was preferred rather than 1130 °C. In order to determine the optimum soaking time in the second step of TSS, the RD values of KNNLT ceramics sintered at $T_1 = 1120$, 1130 °C and $T_2 = 1030$ °C with different soaking times are listed in Table 1. According to this table, the maximum RD obtained by sintering at $T_1 = 1120$ °C and $T_2 = 1030$ °C with 8 h holding time is about 96% of TD. While for SSS KNNLT at optimum temperature, the maximum RD is about 93% of TD (Fig. 2).

By comparing RD of KNNLT sintered via SSS and TSS, it can be concluded that TSS results in sintering temperature decrease as well as an increase in the density of ceramics. This observation can be attributed to the difference in contribution of grain growth and densification as the main processes during sintering. Indeed during TSS the driving force of sintering (reduction of interface energy), is spent mainly on densification. Moreover activation of a triple junction drag mechanism due to rapid cooling of the sample from $T_1$ to $T_2$, prevents grain growth within second step of sintering [17]. In a fine microstructure the number of grain boundaries is higher and grain boundary diffusion process as one of the densification mechanisms is enhanced. In addition, keeping sample for a short time (10 min) at high temperature ($T_1$) in TSS compared to a relatively prolonged time (120 min) in SSS and also a relatively low temperature of the second step (1030 °C) results in lower volatilization of volatile Na and K elements during TSS resulting in ceramics with higher densities compared to SSS.

TSS was also performed for other compounds with different amounts of ST. The survey of RD variation versus sintering conditions showed that 1030 °C as $T_2$ and 8 h of soaking time were optimum for all compositions. The determined optimum $T_1$ and obtained RD values for different compounds sintered via TSS are listed in Table 2.

### 3.2. Structure and phase determination

The X-ray diffraction (XRD) patterns of (1–$x$) KNNLT–$x$ST ceramics sintered at the optimum sintering temperature via SSS are shown in Fig. 5. By comparing the XRD patterns with the JCPDS patterns 01-071-2171 (corresponding to orthorhombic KNbO$_3$) and 01-071-0945 (corresponding to tetragonal KNbO$_3$) 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 $0.0 \leq x \leq 0.10$. The XRD pattern of the ceramic with $x=0.0$ shows the (202)/(020) peak splitting around $2\theta=46^\circ$, confirming the orthorhombic symmetry. This observation is in good agreement with reported results of Guo et al. [9]. For ceramics with $0.03 \leq x \leq 0.075$, XRD patterns show a (002)/(200) peak splitting, indicating the tetragonal symmetry. The split peaks around $2\theta=46^\circ$ in the XRD pattern of ceramic with $x=0.01$ have equal intensities, which is due to the coexistence of orthorhombic and tetragonal structures. The merging of the split peaks for the ceramic with $x=0.10$ indicates the formation of a pseudocubic structure for this composition. By comparing the peak angles of different compositions, it can be found that with increasing ST amount, the diffraction peaks shift toward higher angles, indicating the shrinkage of the unit cell. This result seems to be due to the smaller ionic radius of Sr$^{2+}$ ions (1.44 Å, CN=12) compared to the average ionic radius of the

### Table 1

Values of relative densities of TSSed KNNLT ceramics at $T_1 = 1120$, 1130 °C and $T_2 = 1030$ °C.

<table>
<thead>
<tr>
<th>Second step soaking time (h)</th>
<th>$T_1$ (°C)</th>
<th>$T_2$ (°C)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1030</td>
<td>1120</td>
<td>94.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>1130</td>
<td>94.9 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1030</td>
<td>1120</td>
<td>96.3 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>1130</td>
<td>96.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1030</td>
<td>1120</td>
<td>96.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>1130</td>
<td>96.5 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

The optimum $T_1$ and relative densities of TSSed (1–$x$) KNNLT–$x$ST ceramics.

<table>
<thead>
<tr>
<th>ST content (%)</th>
<th>$T_1$ (°C)</th>
<th>$T_2$ (°C)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1120</td>
<td>1030</td>
<td>96.3 ± 0.4</td>
</tr>
<tr>
<td>1</td>
<td>1120</td>
<td>1030</td>
<td>96.3 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>1110</td>
<td>1030</td>
<td>96.5 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>1100</td>
<td>1030</td>
<td>96.6 ± 0.3</td>
</tr>
<tr>
<td>7.5</td>
<td>1100</td>
<td>1030</td>
<td>96.8 ± 0.5</td>
</tr>
<tr>
<td>10</td>
<td>1090</td>
<td>1030</td>
<td>96.9 ± 0.5</td>
</tr>
</tbody>
</table>
A-site matrix ions, i.e. Na\(^{+}\) (1.39 Å, CN=12) and K\(^{+}\) ions (1.64 Å, CN=12), as well as the smaller Ti\(^{4+}\) ion (0.61 Å, CN=6) compared to the Nb\(^{5+}\) ion (0.64 Å, CN=6) which is the matrix B-site ion in the ABO\(_3\) perovskite structure.

It should be noted that XRD patterns of sintered ceramics via TSS were similar to those of their SSS counterparts. Therefore in this part, only XRD patterns of latter ceramics are shown.

3.3. Microstructure analysis

Microstructures of (1−\(x\)) KNNL−\(x\)ST ceramics sintered optimally via SSS and TSS are shown in Figs. 6 and 7, respectively. The dense, homogenous and fine microstructure of TSS ceramics compared to those fabricated via SSS is clear. Investigation of grain size for ceramics sintered via different procedures demonstrated the capability of TSS to
enhance densification as well as prevent grain growth. In SSS procedure, severe grain growth, diminishes densification. The growth ratio (grain size of sintered ceramic/particle size of calcined powder) for SSS and TSS were about 8 and 3, respectively, indicating the capability of the TSS procedure to prevent grain growth and yield fine and dense microstructure.

3.4. Variation of dielectric constant with temperature

Variations of the dielectric constant of (1–x) KNNLT–xST ceramics sintered via SSS and TSS, are shown in Figs. 8 and 9, respectively. As can be seen, by increasing the ST content, transition temperatures from ferroelectric to paraelectric (Curie

Fig. 7. SEM images of optimally TSSed (1–x) KNNLT–xST ceramics.
temperature, $T_C$) as well as orthorhombic to tetragonal ($T_{ot}$) decrease. For example, $T_C$ of SSSed ceramics with $x=0.0$ and 0.01 are 417 and 393°C and their $T_{ot}$ values are 78 and 40°C, respectively. Transition temperatures for TSSed ceramics are almost identical with those of SSSed ceramics. However as shown, the dielectric constants at room temperature and higher temperatures for TSSed ceramics are higher compared to SSSed ceramics. The higher density of TSSed ceramics as well as lower deviation of composition from stoichiometry as a result of lower alkali elements loss are responsible for this observation. The strong dependence of dielectric constant on density has also been observed and reported for other piezoceramics [24,25]. The insignificant dielectric constant of the ceramic with $x=0.10$ is due to its pseudocubic structure which is without dipole and could be considered as a non-polar material.

Figs. 8 and 9 show that for ceramics with $x=0.05$ and 0.075, peaks have become much broader compared to ceramics with lower ST content. Such an observation has also been reported by Guo et al. [26]. This behavior could be related to the appearance of relaxor-like behavior in 0.95KNNLT–0.05ST and 0.925KNNLT–0.075ST ceramics. The relaxor behavior can be induced by many reasons such as microscopic composition fluctuation, merging of micropolar regions into macropolar regions or coupling of the order parameter and local disorder mode through the local strain [27–29]. In the solid solution (1–$x$) KNNLT–$x$ST, K, Na, Li, and Sr ions occupy the A sites and Nb, Ta and Ti ions occupy the B sites of the ABO$_3$ perovskite structure. The cation disorder in perovskite unit cell could be one of the reasons for the appearance of relaxor behavior. Moreover, it is known that ST shows non-ferroelectric behavior at room temperature and higher temperatures due to the locating of Ti ions at the central equilibrium position of the ST lattice [27]. In this case, the macrodomains in pure KNNLT should be divided into microdomains with increasing ST, which also may result in the appearance of the relaxor behavior.

For ceramics containing 3%, 5% and 7.5% ST, only one peak corresponding to ferroelectric–paraelectric transition can be seen in Figs. 8 and 9, indicating that $T_{ot}$ values of these ceramics are less than room temperature and tetragonal symmetry is stable at room temperature.

3.5. Piezoelectric constant

Piezoelectric constants ($d_{33}$) of (1–$x$) KNNLT–$x$ST ceramics sintered via SSS and TSS are compared in Fig. 10. As can be seen, the $d_{33}$ values of TSS ceramics are higher than the SSS ones, which is due to higher density, more homogenous microstructure and lower alkali elements loss. The ceramic containing 10% ST, due to its pseudocubic structure, is non-polar and its $d_{33}$ is close to zero. The maximum $d_{33}$ corresponds to the ceramic with $x=0.01$. According to Fig. 5 this ceramic has orthorhombic and tetragonal symmetries simultaneously. Coexistence of two structures, results in increase in the number of possible orientations for domain switching during poling and consequently improvement of piezoelectric properties. Coexistence of two different crystalline structures in a piezoceramic could be due to two reasons: first, vicinity of chemical composition to the morphotropic phase boundary (MPB) and second, closeness of polymorphic

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**Fig. 8.** Temperature dependence of dielectric constant of SSSed (1–$x$) KNNLT–$x$ST ceramics.

**Fig. 9.** Temperature dependence of dielectric constant of TSSed (1–$x$) KNNLT–$x$ST ceramics.

**Fig. 10.** Piezoelectric constant of (1–$x$) KNNLT–$x$ST ceramics sintered via SSS and TSS as a function of ST content.
phase transition (PPT) temperature to room temperature. To find out the main reason for coexistence of two different structures in a ceramic, investigation of dielectric constant variations as a function of temperature could be helpful. According to Figs. 8 and 9, for the ceramic containing 1% ST, $T_{\text{on}}$ is close to room temperature. Therefore the vicinity of the PPT temperature to room temperature is the reason for the coexistence of two structures in this ceramic as well as the appearance of the maximum value of $d_{33}$.

According to Fig. 10, apart from ceramics containing 1% and 10% ST, for other ceramics, increasing ST increases $d_{33}$, indicating the positive effect of ST on improvement of $d_{33}$.

4. Conclusions

In this work, two-step as well as single step (conventional) sintering process have been used to fabricate KNNLT ceramics modified with different amounts of ST. The results showed that the TSS procedure could decrease sintering temperature effectively and increase density. Achieving a finer and more homogenous microstructure was also the other advantage of TSS. As a result, TSSed ceramics showed higher dielectric and piezoelectric properties compared to SSSed ones. Therefore it can be concluded that TSS can be used to sinter KNN-based compounds containing volatile alkali elements and because of the reduction of elements' loss and compositional deviation from stoichiometry, the electrical properties of sintered ceramics are improved.

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