Lead-free Li-modified (Na,K)NbO₃ piezoelectric ceramics fabricated by two-step sintering method

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Two-step sintering method has been applied to (Li₀.₀₆Na₀.₄₇K₀.₄₇)NbO₃ (LNKN) ceramics in order to obtain a homogeneous microstructure and high density (96.1 % TD). The effects of the sintering temperature on the microstructure and electrical properties of LNKN ceramics were investigated. The two-step sintering has provided better densification at relatively lower temperature (≤950°C) than that of one-step sintering (1082°C), which suppresses the abnormal grain growth. In addition, the more homogeneous microstructure has been obtained by two-step sintering. The measured dielectric constant, dielectric loss and Curie temperature of the sample for two-step sintering were 666, 2.0 % and 454°C, respectively, similar to the values obtained with one-step sintering. Nevertheless, LNKN ceramics prepared by two-step sintering showed higher coercive electric field (=18.8 kV/cm) than that revealed by one-step sintering (=13.0 kV/cm).

1. Introduction

In recent years, a large number of lead-free piezoelectric ceramics have been investigated in order to preserve environmental harmony as well as to avoid the potential health risk. Alkali niobate ceramics based on solid solutions of NaNbO₃–KNbO₃ (NKN) systems have attracted considerable attention as a leading candidate for lead-free piezoelectric ceramics because of their excellent piezoelectric properties and high Curie temperature. However, in conventional solid-state synthesis route, the volatilization of alkaline elements (Na and K) during the firing process causes a compositional variation in the ceramics, which often results in the heterogeneous microstructures and abnormal grain growth. To overcome this problem, various processing techniques for NKN-based ceramics have been investigated such as the citrate precursor route, wet-type centrifugal separation technique, and spark plasma sintering method. These techniques provide homogenous microstructure of NKN-based ceramics, and consequently, improved ferroelectric and piezoelectric properties.

Since the ferroelectric and piezoelectric properties of the ceramics are closely associated with their microstructure, the textural control of ceramics has been investigated extensively on many systems using various processing techniques. Recently, Chen et al. formulated a two-step sintering method to achieve full density without grain growth. Figure 1 shows a typical heating schedule of two-step sintering method. The first step sintering is performed at a higher temperature (T₁) for rapid densification, caused by the rearrangement of particle, and then the sample was cooled down and held at a lower temperature (T₂) for complete densification. In order to obtain fully densified ceramics, a sufficiently high relative density (> 70%) is required at a first step. This method has been applied to various ceramics such as Y₂O₃, Al₂O₃, SiC, and BaTiO₃. Alkaline niobate ceramics have also been investigated using such a two-step sintering method. Wang et al. reported that pure NKN ceramics prepared with this method showed enhanced piezoelectric properties. Fang et al. have reported that Li and Ta/Sb modified NKN ceramics with superior properties can be prepared by two-step sintering. They also mentioned that the two-step sintering provides wider process window for firing temperature than the one-step sintering. These results suggested that two-step sintering method is more effective to prepare NKN-based ceramics with better performance. However, the microstructural studies on the two-step sintering of NKN-based ceramics are limited, which make it difficult to prepare NKN-based ceramics with homogeneous microstructure. In this study, the sintering behavior at 1st and 2nd step of two-step sintering is investigated in terms of the microstructure using Li-modified NKN (LNKN) in order to realize the fine and homogenous microstructure.

2. Experimental procedure

LNKN powders were prepared by conventional solid state reaction route. Reagent grade Li₂CO₃, Na₂CO₃, K₂CO₃ and Nb₂O₅ powders were used as the starting materials.
powders were weighed to synthesize the chemical composition according to \((\text{Li}_{0.06}\text{Na}_{0.47}\text{K}_{0.47})\text{NbO}_3\). The weighed powders were mixed with EtOH and ZrO\(_2\) media by ball milling, and calcined at 900°C for 3 h in air. The calcined powders were crushed and dried at 120°C in drying furnace. The powders were pressed into disks with 12 mm diameter using uni-axial press which was followed by the cold-isostatic-pressing (CIP) at 300 MPa and then sintered at various heating schedules such as temperature and holding times.

Two-step sintering was carried out at various temperatures to obtain LNKN samples with high density. The disk samples were fired at high temperature \((T_1 = 900–1000°C)\) for 1 min with rapid heating rate of 40°C/min, and then cooled down to lower temperature \((T_2 = 900–920°C)\) and held for long time \((t_2 = 10–15\,\text{h})\). The ceramics density and microstructure at the 1st step were examined to investigate the sintering behavior. The ceramics heated at \(T_1\) for 1 min was taken out of a furnace and quenched to room temperature immediately. For comparison, a conventional one-step sintering were also performed at 1082°C for 2 h LNKN samples obtained by both sintering methods were grind by diamond cutter and polished with diamond paste. Thermal-etched surfaces were observed using scanning electron microscopy (SEM; Technex Tiny-SEM). The crystal structure was evaluated by X-ray diffraction (XRD; Philips X’pert MPD) with Cu Kα radiation. For electric measurements, Ag electrodes were formed on both surfaces of disks. Resistivity was measured on various temperatures between 900 and 1000°C. At \(T_1 = 950°C\), the density and average grain size were 73\% TD and 0.56 \(\mu\text{m}\) in average. The difference of the density and average grain size between 950 and 1000°C is shown in Figs. 2 and 3, respectively. For comparison, the microstructure of one-step sintering at 1082°C for 2 h LNKN ceramics quenched from (b) 900°C, (c) 940°C, (d) 950°C, (e) 960°C, and (f) 1000°C.

3. Results and discussion

3.1 Microstructure and densification

The microstructure and relative density of green compact and the ceramics quenched from various temperatures \((T_1 = 900–1000°C)\) are shown in Figs. 2 and 3, respectively. The green compact showed less than 60\% of theoretical density (TD) and the average grain size was 0.36\(\mu\text{m}\). In consequence of the quenching experiments to determine temperature \(T_1\), it was found that the density and the grain size increased significantly at temperatures between \(T_1 = 960\) and 1000°C. At \(T_1 = 950°C\), the density and average grain size were 73\% TD and 0.56\(\mu\text{m}\), respectively. At \(T_1 = 960°C\), however, the density was improved to 78\% TD with the grain size of 0.68 \(\mu\text{m}\) in average. The difference of the density and average grain size between 950 and 960°C is relatively large. The neck formation and growth were well recognized at temperature above 950°C, and consequently the average grain size was increased up to 1 \(\mu\text{m}\) at \(T_1 = 1000°C\).

These turning points imply the different sintering mechanisms. Hoshina et al.\(^{19}\) have examined the sintering mechanism on BaTiO\(_3\) by estimation of shrinkage rates. They observed that the turning points of shrinkage rates were caused by different sintering mechanisms such as grain boundary diffusion, volume diffusion and grain rearrangement in the range from 900 to 1360°C. Additionally, it have been concluded that the grain rearrangement at higher temperature is need to eliminate the large pores which inhibit the densification in 2nd step. However, our results suggested that the densification and the grain growth of LNKN ceramics are sensitive against a slight variation of temperature as compared to BaTiO\(_3\). The density significantly changed from 60\% TD to 88\% TD with narrow temperature range from 900 to 1000°C, and such temperature dependence is in good agreement with the previous reports about sintering behavior of NKN-based ceramics.\(^{24,25}\) This indicates that the sintering mechanisms on NKN-based ceramics are mixture of grain boundary diffusion, volume diffusion, and grain rearrangement, and then grain growth can easily occur at lower temperature. In particular, the relatively large difference between 950 and 960°C seems to imply that the dominant mechanism varies from grain boundary diffusion to volume diffusion, which can accelerate the grain growth. For the above reason, we fixed \(T_1\) at 950°C as suitable temperature to improve the bulk density without significant grain growth after two-step sintering.

Using \(T_1 = 950°C\) as the fixed temperature at 1st step, two parameters in 2nd step, temperature \(T_2\) and holding time \(t_2\), were examined. The SEM images and densities are shown in Figs. 4 and 5, respectively. For comparison, the microstructure of one-step sintering at 1082°C for 2 h is also shown in Fig. 3.\(^6\) The densities are also listed in Table 1. The samples prepared by two-step sintering showed higher density and homogeneous
microstructure compared to that prepared by one-step sintering. Whereas the grain size distribution obtained by one-step sintering was relatively wide with coarse grains of over 14 μm in size, all the samples sintered by two-step sintering were composed of smaller grains less than 9 μm in size without abnormal grain growth. The average grain size depends on the holding temperature \( T_2 \). Compared at the same holding time, LNKN sample sintered at 920°C showed 1.5 times larger grain size than that sintered at 900°C. The densities of the ceramics prepared by two-step sintering were higher than that prepared by one-step sintering, as shown in Table 1. These results clearly demonstrate that the two-step sintering provides higher density and microstructure-controlled LNKN ceramics. The highest density (96.1% TD) was obtained by two-step sintering with \( T_1 = 950°C, T_2 = 920°C \), and \( t_2 = 10 h \). The sintering schedule adopted in the present study provided the dense and homogeneous microstructure, even at relatively lower sintering temperatures by 100°C~ than the one-step sintering.

3.2 Phase evaluation, dielectric and electrical characterizations

The influence of sintering process on the basic properties has been investigated with comparison between LNKN samples obtained by one-step and two-step sintering methods. The properties of LNKN ceramics obtained by both one-step sintering and two-step sintering methods are summarized in Table 1. LNKN ceramics obtained by two-step sintering showed a high density as compared to one-step sintering. Similarly, there is no difference in electrical resistivity, dielectric properties, and Curie temperature among the samples obtained by different sintering methods. Figure 6 shows the XRD pattern of each sample. Both patterns revealed the peaks of LNKN composition with a perovskite structure. The temperature dependence of dielectric properties is shown in Fig. 7. The relative permittivity and dielectric loss of each sample showed almost same temperature

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<p>| Table 1. Characteristic properties of LNKN ceramics sintered by two-step sintering and one-step sintering |
|----------------------------------------------------------|----------------|-------------|---------------|----------------|---------------|---------------|</p>
<table>
<thead>
<tr>
<th>Sintering condition</th>
<th>Density (TD)</th>
<th>Resistivity ( 10^9 (, \Omega , m) )</th>
<th>Dielectric constant</th>
<th>Dielectric loss (%)</th>
<th>( T_c ) (°C)</th>
<th>( P_e ) (μC/cm(^2))</th>
<th>( E_c ) (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-step</td>
<td>920~950°C 10 h</td>
<td>96.1</td>
<td>4.8</td>
<td>666</td>
<td>2.0</td>
<td>454</td>
<td>13.7</td>
</tr>
<tr>
<td>One-step</td>
<td>1082°C 2 h</td>
<td>94.3</td>
<td>3.7</td>
<td>728</td>
<td>2.5</td>
<td>454</td>
<td>20.2</td>
</tr>
</tbody>
</table>

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Fig. 4. SEM images of (a) 900°C/10 h, (b) 900°C/15 h, (c) 920°C/10 h, (d) 920°C/15 h, and (e) one-step sintering.

Fig. 5. Comparison of relative density and average grain size between various sintering conditions.

Fig. 6. XRD pattern of LNKN samples prepared by one-step sintering and two-step sintering.

Fig. 7. Dielectric constant (left) and dielectric loss (right axis) of LNKN samples prepared by one-step and two-step sintering as function of temperature.
dependence. There is a dielectric anomaly at 454°C corresponding to the Curie temperature $T_C$ of LNKN ceramics during cooling from a high temperature for each sample. These results suggest that two-step sintering can decrease the sintering temperature and homogenize the microstructure without significant degradation of basic properties. Figure 8 shows ferroelectric $P$-$E$ hysteresis loops of one-step and two-step sintered ceramics. The differences were found in polarization and coercive electric field. The remnant polarization ($P_r$) and coercive electric field ($E_c$) of the ceramics prepared by one-step sintering were 20.2 μC/cm$^2$ and 13.0 kV/cm, respectively. On the other hand, in case of two-step sintering, $P_r$ and $E_c$ were 13.7 μC/cm$^2$ and 18.8 kV/cm, respectively.

It should be noted that LNKN ceramics obtained by two-step sintering showed a higher $E_c$ as compared to one-step sintering. It is widely accepted that the dielectric properties of ceramics strongly depend on the grain size. It has been reported that such effect can be also recognized in the ferroelectric properties of NKN-based ceramics. These reports have suggested that the coercive electric field is increased with decreasing the grain size due to the expansion of grain boundary region, which could inhibit domain switching. Thus, further investigation on domain switching and evaluation of piezoelectric properties would be one of motivation in our future work.

4. Conclusion

In this study, two-step sintering method was applied to prepare dense LNKN ceramics. The density and microstructure were evaluated at each stage of $T_1$ and $T_2$ in order to control the microstructure. The neck growth with rapid grain growth was recognized at temperature range from 960 to 1000°C. LNKN ceramics with the highest density of 96.1% TD was obtained for the sample sintered with the holding temperature of $T_1 = 950°C$ and $T_2 = 920°C$ for 1 min and 10 h, respectively in two-step sintering. Two-step sintering can reduce the sintering temperature and provide the homogeneous microstructure without abnormal grain growth, as recognized in one-step sintering. LNKN ceramics prepared by two-step sintering showed higher $E_c$ (= 18.8 kV/cm) than that obtained by one-step sintering (= 13.0 kV/cm). The measured dielectric constant, dielectric loss, and Curie temperature were 666, 2.0% and 454°C, respectively.

References


Fig. 8. Ferroelectric P-E hysteresis loops of LNKN samples prepared by one-step sintering and two-step sintering.