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Effect of Na_2O additions on the sinterability and piezoelectric properties of lead-free $95(Na_{0.5}K_{0.5})NbO_3$–$5LiTaO_3$ ceramics

Min-Soo Kim *, Dae-Su Lee, Eon-Cheol Park, Soon-Jong Jeong, Jae-Sung Song

Electric and Magnetic Devices Group, Korea Electrotechnology Research Institute, 28-1 Seongju-dong, Changwon 641-120, Republic of Korea

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Abstract

As a candidate for lead-free piezoelectric materials, Na_2O excess $95(Na_{0.5}K_{0.5})NbO_3$–$5LiTaO_3$ (NKN–5LT) ceramics were developed by conventional sintering process. Sintering temperature was lowered by adding Na_2O as a sintering aid. Abnormal grain growth in NKN–5LT ceramics was observed with varying Na_2O contents. This grain growth behavior was explained in terms of interface reaction-controlled nucleation and growth. The electrical properties of NKN–5LT ceramics were investigated as a function of Na_2O concentration. In the 1 mol% Na_2O excess NKN–5LT samples sintered at 1050 °C for 4 h in air, electromechanical coupling factor and piezoelectric constant of NKN–5LT ceramics were found to reach the highest values of 0.43 and 230 pC/N, respectively.

Keywords: Sintering; Microstructure; Piezoelectric properties; Niobates; Tantalates

1. Introduction

Lead-based piezoelectric ceramics such as $Pb(Zr_xTi_{1-x})O_3$ (PZT) have excellent piezoelectric properties and are applied to many piezoelectric devices today.[1,2] Though these ceramics possess high properties, they cause serious environmental problems due to containing lead to over 60 wt%. Therefore, to develop lead-free piezoelectrics with superior piezoelectric properties has been urged by the practical usage. Among several candidates for lead-free materials, alkali niobate-based materials, such as $Na_{0.5}K_{0.5}NbO_3$ (NKN), are well-known harmless materials and promising candidates for PZT alternative materials because of their excellent piezoelectric properties.[3–11] Because potassium niobate-based ceramics are difficult to sinter, many researches have been done on hot press and spark plasma sintering of NKN based ceramics.[3–5] The hot pressed NKN ceramics have been reported to possess high Curie temperature (420 °C), large piezoelectric longitudinal response (160 pC/N) and high planar electromechanical coupling factor (0.45).[3,4] In addition, synthesizing by spark plasma sintering has been found to produce lead-free materials suitable for industrial applications.[5]

NKN ceramics fabricated by ordinary sintering show relatively lower electrical properties ($d_{33} \sim 80$ pC/N, $k_P \sim 0.36$).[6] In order to improve the sinterability of the NKN ceramics, many studies have been carried out.[7–10] However, it was found that sintering of NKN ceramics under atmospheric pressure is difficult, in general, and the piezoelectric properties of NKN ceramics are not sufficient for applications. The volatility of the potassium component and its high reactivity with moisture make it difficult to carry out the conventional sintering of NKN ceramics. From the industrial point of view, atmospheric sintering is required for mass production. Recently, Guo et al. reported that was able to obtain excellent piezoelectric and electromechanical response with the composition near the morphotropic phase boundary [$0.95Na_{0.5}K_{0.5}NbO_3$–$0.5LiTaO_3$] (NKN–5LT) through the conventional sintering.[11] However, the sintering process of this system is still inefficient because the sintering temperature is too high (1110 °C) to inhibit the volatilization of cations.

In this study, synthesis process was confined to the ordinary sintering process. In order to achieve higher density and also lower sintering temperature of NKN–5LT ceramics, Na_2O additions were used as a sintering aid. The effect of Na_2O additions on the microstructures and piezoelectric properties of the NKN–5LT ceramics was investigated.

2. Experimental procedure

The material compositions used in this study are x mol% Na_2O excess NKN–5LT. NKN–5LT powders were prepared

* Corresponding author. Tel.: +82 55 280 1641; fax: +82 55 280 1590.
E-mail address: minsoo@keri.re.kr (M.-S. Kim).

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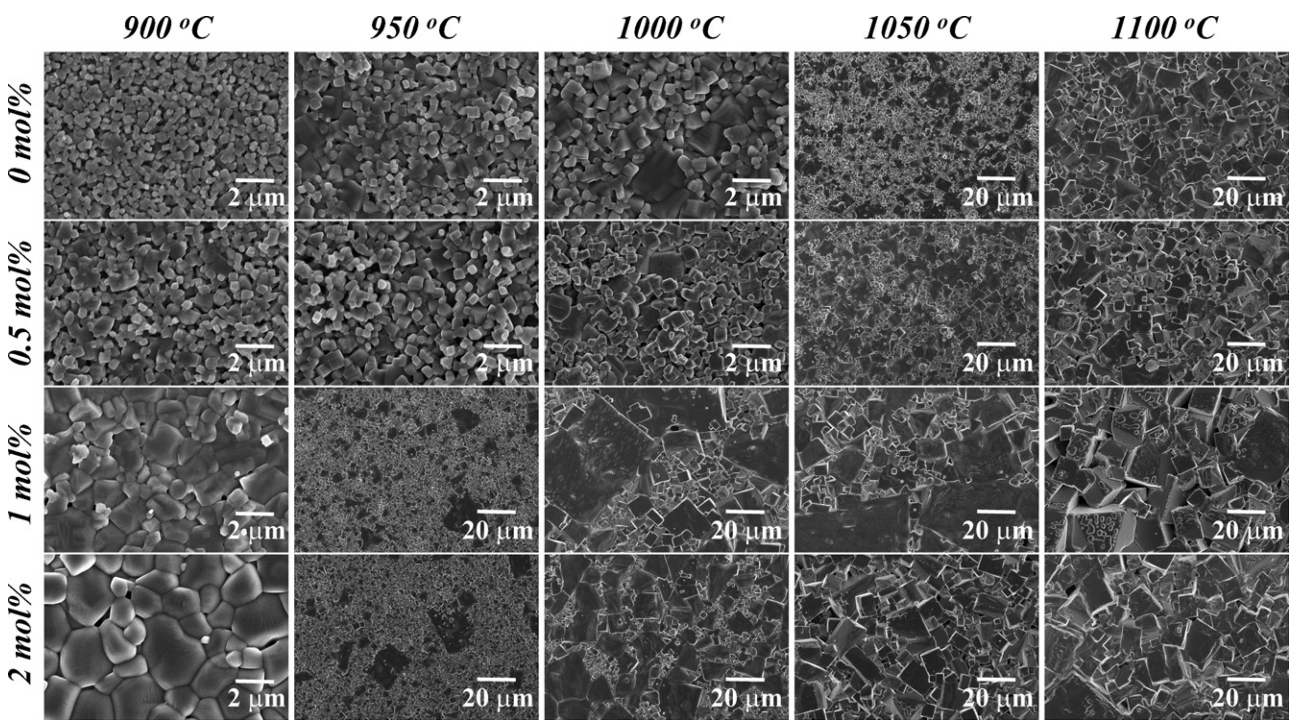

Fig. 1. Microstructures of Na_2O excess NKN–5LT samples sintered for 4 h in air at 900, 950, 1000, 1050 and 1100 °C, respectively, as a function of Na_2O contents.

from the constituent oxides and carbonates by a conventional solid-state reaction. Reagent grade metal oxide or carbonate powders, Na_2CO_3, K_2CO_3, Li_2CO_3, Nb_2O_5 and Ta_2O_5, were used as starting raw materials. After weighing to the corresponding composition the powders were mixed by ball milling in ethanol for 24 h with stabilized ZrO_2 media. In order to enhance the uniformity of the composition, the mixture was twice calcined at 850 °C for 5 h and ground. The calcined powder and Na_2CO_3 additions were ball milled again for 24 h. After milling, the slurry was again dried, crushed and passed through a 100 μm sieve. Na_2CO_3 and particularly K_2CO_3 are hygroscopic and so had to be given extra care to avoid water. These powders were granulated by adding PVA as a binder and subsequently pressed into disks under 300 MPa.

These powder compacts were fired in air. The microstructure was observed with a scanning electron microscopy and crystal structure was determined by using X-ray diffraction. For electrical characterization, samples were polished and painted with silver paste on the sample surfaces. Samples were immersed in silicon oil and poled in a 30 kV/cm field. The electric field was applied at a temperature of 150 °C for 30 min. The piezoelectric constant was measured by a quasi-static meter of Berlincourt type. The electromechanical coupling coefficients were determined from resonance–antiresonance methods by using an impedance analyzer. Ferroelectric measurement was carried out a maximum electric field of 30 kV/cm applied using an amplified bipolar waveform at 60 Hz.

3. Results and discussion

As reported, it is difficult to form a complete solid solution with NKN and LT.[11] A phase with pure perovskite structure can be obtained only for composition NKN–5LT. In this study, XRD analysis for the as-used NKN–5LT powder and sintered NKN–5LT samples showed that a single NKN–5LT phase with the perovskite structure had formed but other phases could not be detected in all of the samples.

Fig. 1 shows microstructures of the samples sintered for 4 h in air. Higher density of NKN–5LT ceramics were achieved by adding Na_2O and increasing heat-treatment temperature as shown in Fig. 1. In addition, the optimum sintering temperature was lowered by Na_2O addition. However, when the sintering temperature was 1100 °C, the relative densities were lowered as shown in Fig. 1. These densification behaviors may be affected by volatility of the cations at high temperatures.

The effect of Na_2O additions on grain growth in NKN–5LT ceramics was observed in Fig. 1. The samples with 0 mol% Na_2O sintered at 900, 950 and 1000 °C, respectively, consisted of mostly equiaxed grains with submicron-size. The microstructure of the sample with 0 mol% Na_2O sintered at 1050 °C showed mostly equiaxed matrix grains and some large abnormal grains, square or rectangular in appearance. As the sintering temperature increases up to 1100 °C, the number of abnormal grains increases. As the Na_2O was added to 0.5 mol%, grain growth behavior and microstructures were similar to 0 mol% Na_2O excess samples but the number and the size of abnormal grains were increased. Addition of 0.5 mol% Na_2O causes an increase in the number of abnormal grains. All the grains (the abnormal and the matrix grains) have faceted interfaces. At 1100 °C, all of the large grains impinged upon each other, limiting further growth, in the samples. As the Na_2O was added up to a maximum of 1 mol%, the number and the size of abnormal grains were increased much. At 950 °C, there was some grain growth with a few grains apparently beginning to grow abnormally. At

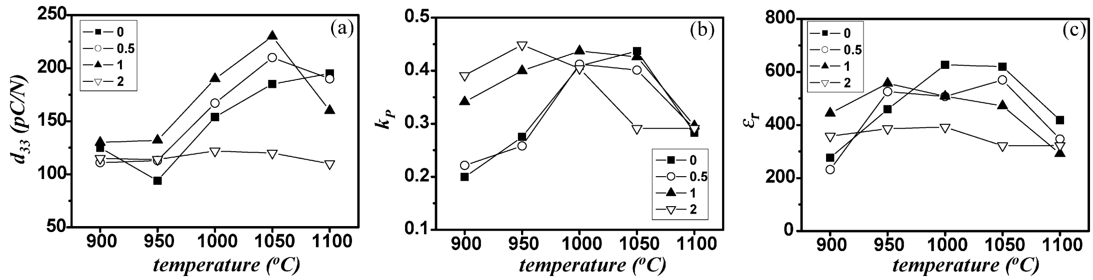

Fig. 2. Electrical properties of Na_2O excess NKN–5LT ceramics: (a) piezoelectric constant, (b) electromechanical coupling factor, and (c) relative dielectric constant.

1000 °C some large grains appeared, and at 1050 °C the large grains impinged on each other deterring further growth and consequently decreasing abnormal grain size. The sample sintered at 1100 °C consisted mostly of equiaxed grains and no abnormal grains are present. When more Na_2O was added, grain growth behavior and microstructures were similar to 1 mol% Na_2O excess samples but the large grain impinged on each other even at 1000 °C. In the samples with 2 mol% Na_2O sintered at 1050 °C, no abnormal grain growth takes place.

When the interfaces or boundaries are faceted, abnormal grain growth can occur, while normal grain growth occurs only in systems with rounded interfaces or boundaries.[12–18] The various microstructures can be shown according to the critical driving force for rapid grain growth–bimodal size distribution, impingement or suppression of growth.[12–16] The observed abnormal grain growth behavior shown in Fig. 1 appears to be qualitatively consistent with two-dimensional nucleation of steps as proposed earlier.[17,18] The small matrix grains undergo slow stagnant growth, and apparently some large grains grow rapidly to form the abnormally large grains. The observed dependence of abnormal grain growth on heat-treatment temperature is shown in Fig. 1. The series of microstructures at increasing temperatures in Fig. 1 shows that the rates of formation of abnormal grains and their growth increase with temperature as expected from the previous works and two-dimensional nucleation theories.[17,18]

These microstructural changes as Na_2O contents show the typical grain growth behavior due to the change in critical driving force for rapid grain growth with the faceted interfaces or boundaries.[12–18] The results in Fig. 1 can be explained in terms of a reduction of the critical driving force for rapid grain growth by addition of Na_2O. It can be seen that the number of abnormal grains increases with Na_2O addition. By adding Na_2O the critical driving force for rapid grain growth is lowered. Therefore, the number of grains that show abnormal growth is increased. An increase in the sintering temperature also lowers the critical driving force, resulting in an increase in the number of abnormal grains. Further reduction in the critical driving force, the number of abnormal grains increases more with increasing sintering temperature. Reduce the critical driving force by Na_2O addition to the point where the majority of grains can grow, resulting in impingement, as shown in the case of the samples sintered at 1100 °C with 1 mol% Na_2O and at 1050 °C with 2 mol% Na_2O. Similar behavior has been observed in the alumina–anorthite system with the addition of MgO.[13]

The electrical properties of the samples were evaluated. Piezoelectric constants (d_{33}) of the samples are shown in Fig. 2(a). The piezoelectric coefficients show strong dependences for compositions and sintering temperatures. The d_{33} increases with sintering temperatures up to 1050 °C, and then decrease. At 1000 and 1050 °C, it can be seen that the d_{33} increases with increasing Na_2O content of up to a 1 mol% addition, and then decreases. One mole percent of Na_2O excess NKN–5LT samples sintered at 1050 °C show the largest values of piezoelectric coefficients. This value of the sample is a remarkable result in comparison with the results reported in previous studies.[11] Fig. 2(b) shows the planar mode electromechanical coupling factor (k_P) of the samples. The figures shows that k_P values of the samples sintered at 1050 °C did not change even when the Na_2O content increased up to 1 mol%, and then decreased when Na_2O was added to 2 mol%. Fig. 2(c) shows the dielectric constant (ε_r) of NKN–5LT ceramics as functions of temperatures and Na_2O contents. The dielectric constant of pure NKN–5LT sintered at 1000 °C in this study was approximately 620, which is higher than that of pure NKN ceramics sintered at 1110 °C.[11] The high dielectric constant of pure NKN–5LT ceramics may be related to densified microstructures as shown in Fig. 1. The ε_r decreased with Na_2O addition. P-E hysteresis loops were observed by a ferroelectric test unit. Na_2O excess NKN–5LT shows a typical ferroelectric polarization hysteresis loops. Of all the samples investigated, the 1 mol% Na_2O excess NKN–5LT ceramics sintered at 1050 °C for 4 h demonstrated d_{33} of 230 pC/N, k_P of 0.43 and ε_r of 470, with remnant polarization $P_r = 11.7\ \mu C/cm^2$ and coercive electric field $E_C = 11.8$ kV/cm.

These electrical properties may be related to the microstructures including densification, grain shape, grain size and size distribution. One mole percent of Na_2O excess NKN–5LT samples sintered at 1050 °C which show the excellent electrical properties have high relative density and impinged angular large grains with a few small matrix grains. These results show that the electrical properties can be improved by control of the microstructures. Further investigation of the electrical properties related to microstructures will be carried out in future studies.

4. Conclusions

Na_2O excess NKN–5LT ceramics synthesized by ordinary sintering technique was investigated. Sintering temperature was lowered by Na_2O additions and the phases with perovskite structure were observed. Doping with Na_2O caused an increase in the number of abnormal grains in the samples. The changes in grain growth behavior can be explained by lowering the critical driving force needed for rapid grain growth by addition of Na_2O, and therefore an increase in the number of abnormal grains. In the samples with further Na_2O additions, the critical driving force becomes low enough to permit all the grains to grow so abnormal grain growth is suppressed. Excellent piezoelectric and electromechanical responses, $d_{33} \sim 230$ pC/N, $k_P \sim 0.43$, were obtained for the samples with 1 mol% Na_2O addition sintered at 1050 °C for 4 h in air. These excellent piezoelectric and electromechanical properties indicate that this system is potentially good candidate as lead-free material for a wide range of electro-mechanical transducer applications.

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