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Lead-free NKN-5LT piezoelectric materials for multilayer ceramic actuator

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Abstract As a candidate for lead-free piezoelectric materials, Li_2O excess $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05LiTaO_3$ (NKN-5LT) ceramics were developed by conventional sintering process. Sintering temperature was lowered by adding Li_2O as a sintering aid. Abnormal grain growth in NKN-5LT ceramics was observed with varying Li_2O content. In the 1 mol% Li_2O excess NKN-5LT samples sintered at 1000°C for 4 h in air, electromechanical coupling factor and piezoelectric constant of NKN-5LT ceramics were found to reach the highest values of 0.37 and 250 pC/N, respectively. Lead-free piezoelectric ceramic, Li_2O excess NKN-5LT, multilayer ceramic actuators (MLCA) were fabricated. $10\times10\times1$ mm^3 size MLCAs were fabricated by conventional tape casting method. The displacement of Li_2O excess NKN-5LT MLCA with 3 mm thickness was ~1 μm at 150 V.

Keywords Lead-free · Piezoelectric · Actuator

1 Introduction

Piezoelectric materials for actuators are widely used in applications requiring precision displacement control or high generative force [1]. In particular, multilayer piezoelectric ceramic actuators (MLCA) have been widely studied because the assets of MLCA are a rapid operation, low power consumption, high precision control and no noise compared with the electromagnetic actuators [2, 3]. The most widely used piezoelectric ceramics are lead based materials because of their superior piezoelectric properties [4]. However, when considering lead toxicity, there is now greater interest in developing piezoelectric materials that are biocompatible and environmentally friendlier [5–9]. Recently alkali oxide materials, including sodium - potassium niobate, have drawn greater attention due to their ultrasonic applicability and are also considered as promising candidates for a piezoelectric lead-free system [5–9].

Many researches have been done on hot press and spark-plasma sintering (SPS) of NKN-based ceramics [6–8]. The hot pressed NKN ceramics with high density have been reported to possess high Curie temperature ~420 °C, large piezoelectric longitudinal response ~160 pC/N, and high planar coupling coefficient ~0.45 [6, 7]. In addition, synthesizing by SPS has been found to produce lead-free materials suitable for industrial applications [8]. However, NKN ceramics sintered by ordinary sintering show relatively lower electrical properties [6]. The volatility of the potassium component and its high reactivity with moisture make it difficult to carry out the conventional sintering of NKN ceramics.

In order to improve the sinterability of the NKN ceramics, many studies have been carried out. Recently, Guo et al. [9] reported that was able to obtain excellent piezoelectric and electromechanical response, d_{33} ~200 pC/N, k_P ~0.36 with the composition near the MPB [0.95$(Na_{0.5}K_{0.5})NbO_3$–$0.05LiTaO_3$] (NKN-5LT) through the conventional sintering. However, the sintering process of this system is still inefficient in that the sintering temperature is too high (1110 °C) to inhibit the volatilization of cations.

In this study, to manufacture lead-free MLCAs, we chose a composition of NKN-5LT with high electro-mechanical properties. For the ceramic compositions developed, to

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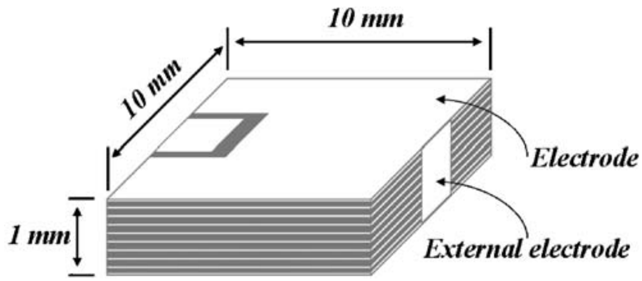

Fig. 1 Design of the MLCAs

achieve high density and also lower sintering temperature of NKN-5LT ceramics, Li_2O additions were used as a sintering aid. Li^+ is one of the A-site ions in NKN-5LT. The synthesis process was confined to the conventional sintering process. The effect of Li_2O additions on the microstructures and piezoelectric properties of the NKN-5LT ceramics was investigated. In addition, $10\times10\times1$ mm^3 size 1 mol% Li_2O excess NKN-5LT MLCAs were fabricated by tape casting methods. The electromechanical properties of the MLCA were studied. The pseudo-piezoelectric constant d_{33}^* was calculated and discussed.

2 Experimental procedure

The material compositions used in this study are x mol% Li_2O excess NKN-5LT (x=0~7). NKN-5LT powders were prepared from the constituent oxides and carbonates by a conventional solid-state reaction. Appropriate mixtures of Na_2CO_3, K_2CO_3, Li_2CO_3, Nb_2O_5 and Ta_2O_5 were ball milled for 24 h. After milling, the slurry was dried, crushed and passed through a 100 μm sieve. The powder was calcined twice in an alumina crucible at 850 °C for 5 hours. These powders were granulated by adding PVA as a binder and subsequently pressed into disks under 300 MPa. These powder compacts were sintered for 4 h in air. The microstructure was observed with a SEM, and the crystal structure was determined by using an XRD. For electrical characterization, samples were polished and painted with silver paste on the sample surfaces. They were immersed in silicon oil and poled in a 3 kV/mm field. The electric field was applied at 150 °C for 30 min. The piezoelectric constant was measured by a quasi-static meter of Berlincourt type and indicated with the dimension of (pC/N). The electromechanical coupling coefficients were determined from resonance-antiresonance methods by using an impedance analyzer.

For the MLCAs, a tape-casting method was employed to fabricate devices from the 1 mol% Li_2O excess NKN-5LT powder. Figure 1 shows the design of the MLCA. Modified interdigital type electrode was designed for this actuator fabrication. 70Ag-30Pd electrode was printed on the 100 μm-thick piezoelectric green sheet, and 10 layers of the sheets were then laminated. $10\times10\times1$ mm^3 MLCAs were fabricated by a sintering process at an elevated temperature 1000 °C. All alternative electrodes were

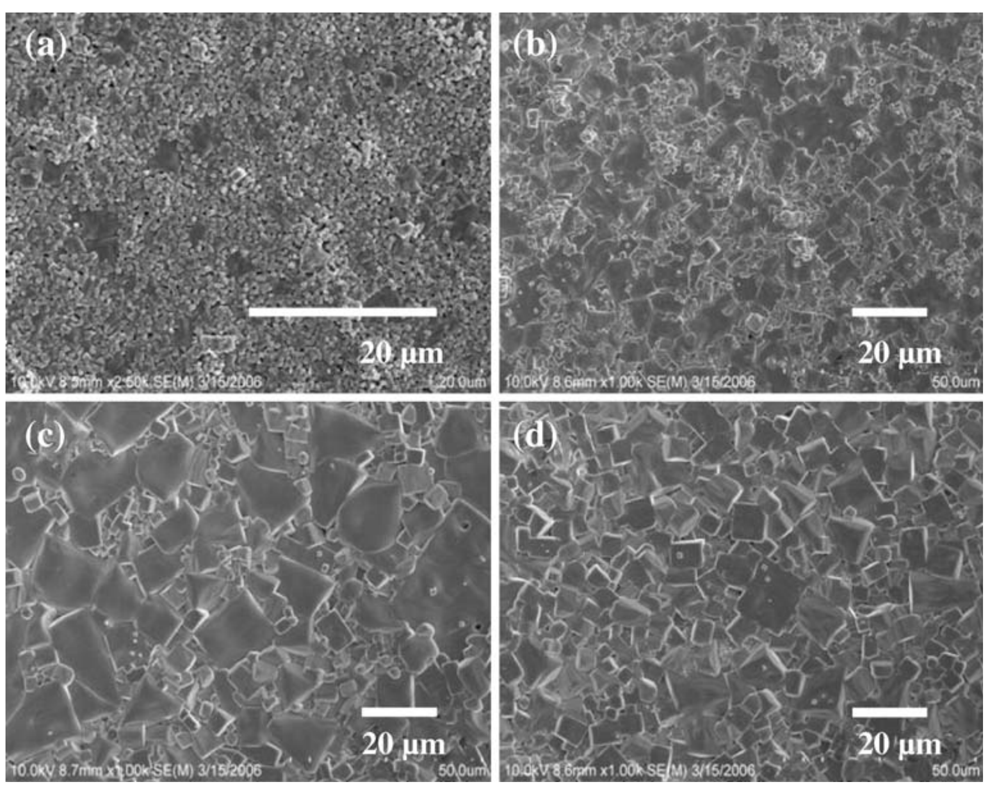

Fig. 2 Microstructures of the x mol% Li_2O excess NKN-5LT samples sintered at 1000 °C for 4 h in air [(x=0 (**a**), 0.5 (**b**), 1 (**c**), 7 (**d**)]

connected to the external electrode. An Ag-based external lead was applied through a screen printing method. To measure their displacement characteristics, the curve of displacement versus electric field was made by the laser vibrometer (Graphtec Demodulator AT 3700). The laser vibrometer with a resolution of 1 nm was employed to measure d^*_{33} piezoelectric displacement indicated with the dimension of (pm/V).

3 Results and discussion

As mentioned, it is difficult to form a complete solid solution with NKN and LT [9]. A phase with pure perovskite structure can be obtained only for composition NKN-5LT. In this study, XRD analysis for the calcined NKN-5LT powder and sintered NKN-5LT samples showed that a single NKN-5LT phase with the perovskite structure formed but other phases could not be detected in all of the samples.

Figure 2 shows the microstructures of the samples sintered at 1000 °C for 4 h in air as a function of Li_2O contents. The samples were well densified, having a relative density of ~95% after sintering. Figure 2 also shows the effect of Li_2O additions on grain growth in NKN-5LT ceramics. The samples with 0 mol% Li_2O NKN-5LT consist of mostly equiaxed matrix grains with submicron-size and some abnormal grains, square or rectangular in appearance. As the Li_2O was added up to a maximum of 1 mol%, the number of abnormal grains and the grain size increased. All the grains have faceted boundaries. When more Li_2O was added, the abnormal grains impinged upon each other in the samples, deterring further growth and consequently decreasing abnormal grain size. The 7 mol% Li_2O sample consists mostly of equiaxed matrix grains and no abnormal grains are present. These microstructural changes show the typical grain growth

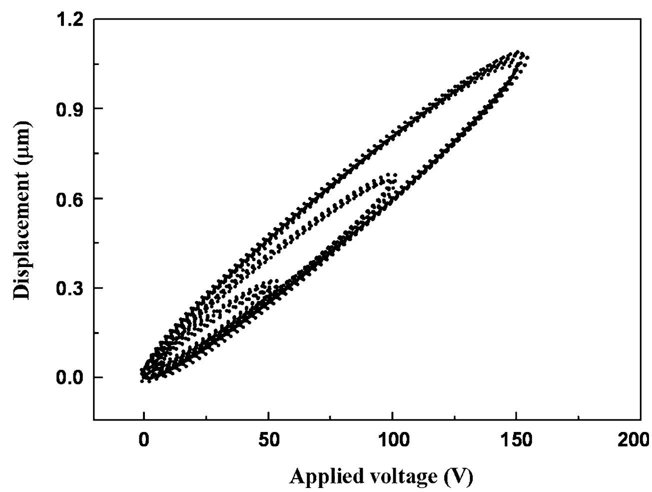

Fig. 4 Longitudinal displacement as a function of the AC voltage at 1 Hz for Li_2O excess NKN-5LT MLCA

behavior due to the change in critical driving force for rapid grain growth with the faceted interfaces or boundaries. 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 [10–13]. The various microstructures can be shown according to the critical driving force—bimodal size distribution [Fig. 2(b)], impingement [Fig. 2(c)] or suppression [Fig. 2(d)] of growth [14, 15]. Further investigation of the sintering behavior related to interface structure in NKN-5LT system will be carried out in future studies.

Figure 3 shows the electro-mechanical properties of NKN-5LT ceramics as a function of Li_2O contents. It can be seen that the piezoelectric constants (d_{33}) increases with increasing Li_2O content of up to a 1 mol% Li_2O addition, and then decreases above 1 mol% Li_2O. The piezoelectric coefficients show a strong compositional dependence. 1 mol% Li_2O excess NKN-5LT samples show the largest values of piezoelectric coefficients d_{33} ~250 pC/N. This value of the sample sintered at 1000 °C is a remarkable result in comparison with the results reported in previous studies [11]. The figures shows that the planar mode

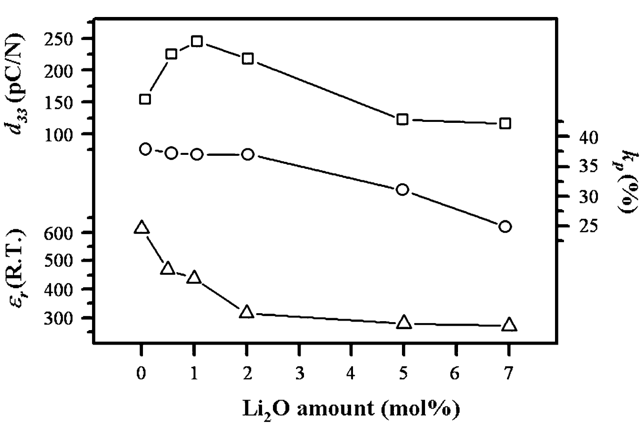

Fig. 3 Electrical properties of Li_2O excess NKN-5LT ceramics as a function of the Li_2O additions

Table 1 Displacement and pseudo piezoelectric constant (d^*_{33}) of the 1 mol% Li_2O excess NKN-5LT MLCA sintered at 1000 °C for 4 h in air.

Applied voltage (V)	Electric field (kV/mm)	Displacement (μm)	Strain (10^{-3})	d^*_{33} (pm/V)
50	0.5	0.29	0.121	242
100	1	0.64	0.267	267
150	1.5	1.05	0.437	292

The d^*_{33} values given are those evaluated using the electric field and strain.

electromechanical coupling factors (k_P) did not change even when the Li_2O content increased up to 2 mol%, and then gradually decreased when Li_2O was added to above 2 mol %. In order to synthesize NKN-5LT ceramics with high k_P, the excess Li_2O content should be lower than 2 mol%. The dielectric constant (ε_r) of pure NKN-5LT in this study was approximately 620, which is higher than that of pure NKN ceramics sintered at 1110 °C [9]. The high dielectric constant of pure NKN-5LT ceramics may be related to densified microstructures as shown in Fig. 2. The ε_r decreased with Li_2O addition. Ferroelectric measurement was carried out a maximum electric field of 30 kV/cm applied using an amplified bipolar waveform at 60 Hz. NKN-5LT shows a typical ferroelectric polarization hysteresis loops. The remnant polarization was P_r ~8.7 μC/cm^2 and coercive electric field was E_C ~12.8 kV/cm for 1 mol% Li_2O excess NKN-5LT ceramics. The hysteresis loops, P_r and E_C values, were not changed even with increasing Li_2O content. These values are the same as previous NKN-5LT work, and in fact much lower compared with hot-pressed NKN [6, 9].

The $10\times10\times1$ mm^3 size 1 mol% Li_2O excess NKN-5LT MLCAs were fabricated by tape casting methods. The design of the MLCA is shown in Fig. 1. For evaluating the properties of the MLCAs, 3 ea MLCAs were stacked and the total thickness was 3 mm. Figure 4 shows the longitudinal displacement of the Li_2O excess NKN-5LT MLCA as a function of AC voltage at 1 Hz at room temperature. Its displacements are 0.29 μm at 50 V, 0.64 μm at 100 V, 1.05 μm at 150 V, respectively. Strain of a MLCA is the ratio of its displacement over the total thickness of all active layers, while electric field is the ratio of the voltage applied over each active layer. For this MLCA, the total thickness of the 24 active layers is 2.4 mm (1 layer thickness=100 μm). Hence, the strain of the MLCA is about 0.267×10^{-3} under an AC electric field of 1 kV/mm. Table 1 shows the displacement and pseudo-piezoelectric constant of the 1 mol% Li_2O excess NKN-5LT MLCA. These excellent electro-mechanical properties indicate that this system is potentially good candidate for lead-free material for a wide range of electro-mechanical transducer applications.

4 Conclusions

Li_2O excess NKN-5LT ceramics synthesized by ordinary sintering technique was investigated. Sintering temperature was lowered by Li_2O additions and the phases with perovskite structure were observed. Abnormal grain growth in NKN-5LT ceramics was observed with varying Li_2O contents. Excellent piezoelectric and electromechanical responses, d_{33} ~250 pC/N, k_P ~0.37, were obtained for the samples with 1 mol% Li_2O addition sintered at 1000 °C for 4 h in air. The 1 mol% Li_2O excess NKN-5LT MLCAs with $10\times10\times1$ mm^3 size were fabricated by conventional tape casting method. Strain dependent on electric field was measured through laser vibrometer to extract displacement. The displacement of Li_2O excess NKN-5LT MLCA with 3 mm thickness was ~1 μm at 150 V. The pseudo-piezoelectric constant d_{33}^{*} was calculated and discussed. These excellent piezoelectric and electromechanical properties indicate that this system is potentially good candidate for lead-free material for a wide range of electro-mechanical transducer applications.

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