Effect of Li_2O Addition on Piezoelectric Properties of NKN-5LT Ceramics

Min-Soo Kim [a], Dae-Su Lee[b], Eon-Cheol Park[c], Soon-Jong Jeong[d], In-Sung Kim[e] and Jae-Sung Song[f]

Electric and Magnetic Devices Group, Korea Electrotechnology Research Institute,
28-1 Seongju-dong, Changwon 641-120, Korea
[a]minsoo@keri.re.kr, [b]leeds@keri.re.kr, [c]ecpark@keri.re.kr, [d]sjjeong@keri.re.kr,
[e]kimis@keri.re.kr, [f]jssong@keri.re.kr

Abstract

As a candidate for lead-free piezoelectric materials, dense 95($Na_{0.5}K_{0.5}$)NbO_3-5$LiTaO_3$ (NKN-5LT) ceramics were developed by conventional sintering process. Sintering temperature was lowered by adding Li_2O as a sintering aid. The electrical properties of NKN-5LT ceramics were investigated as a function of Li_2O concentration. At the addition of 1 mol% Li_2O, electromechanical coupling factor (k_P) and piezoelectric coefficient (d_{33}) of NKN-5LT ceramics were found to reach the highest values of 0.37 and 250 pC/N, respectively.

Keywords : piezoelectric, lead-free, sodium potassium niobate, Lithium oxide

1. Introduction

Alkali oxide materials, including sodium - potassium niobate are considered as promising candidates for a piezoelectric lead-free system. Many researches have been done on hot press, hot isostatic press and spark-plasma sintering of NKN-based ceramics. The hot pressed NKN ceramics have been reported to possess high Curie temperature, large piezoelectric longitudinal response, and high planar coupling coefficient. In addition, synthesizing by Spark Plasma Sintering has been found to produce lead-free materials suitable for industrial applications. However, NKN ceramics fabricated by ordinary sintering show relatively lower electrical properties. 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 this study, synthesis process was confined to the conventional sintering process. In order to achieve higher density and also lower sintering temperature of 95($Na_{0.5}K_{0.5}$)NbO_3-5$LiTaO_3$ ceramics, Li_2O additions were used as a sintering aid. The effect of Li_2O additions on the microstructures and piezoelectric properties of the NKN-5LT ceramics was investigated.

2. Experimental and Results

NKN-5LT powders were prepared from the constituent oxides and carbonates by a conventional solid-state reaction. Na_2CO_3 and particularly K_2CO_3 are hygroscopic and so had to be given extra care to avoid water. The powder was calcined in an alumina crucible at 850°C for 5 hours twice. The calcined powder and Li_2CO_3 additions were ball milled again for 24 hours. 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 microscope and the crystal structure was determined by using X-ray diffraction.

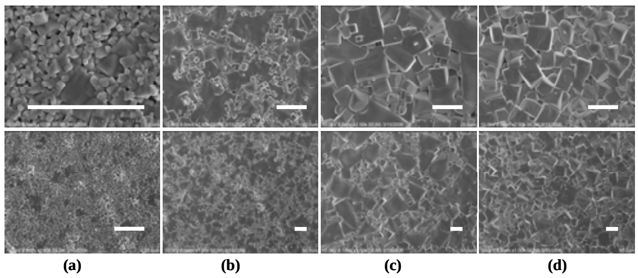

Fig. 1. Microstructures of the x mol% Li_2O excess NKN-5LT samples sintered at 1000°C for 4h in air. ((x = 0(a), 0.5(b), 1(c), 7(d)). scale bar: 10 μm.

It is reported that it is difficult to form a complete solid solution with NKN and LT. As reported, a phase with pure perovskite structure can be obtained only for composition NKN-5LT. In this study, the typical orthorhombic symmetry was observed at room temperature when 5 mol% $LiTaO_3$ was added, but other phases could not be detected in all of the samples.

Figure 1 shows the microstructures of the samples sintered at 1000°C for 4h in air. The effect of Li_2O additions on grain growth in NKN-5LT ceramics was observed. The samples were well densified, having a relative density of ~95% after sintering at 1000°C for 4h in air, as shown in Fig. 1. The samples with 0 mol% Li_2O 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 (the abnormal and the matrix 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 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. The various microstructures can be shown according to the critical driving force, - bimodal size distribution, impingement or suppression of growth.

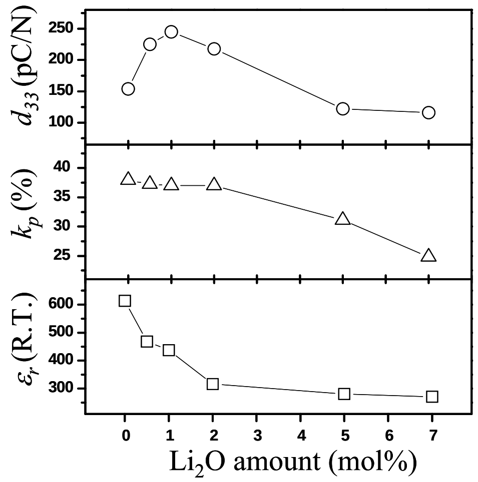

Fig. 2. Electrical properties of Li_2O excess NKN-5LT ceramics.

The electrical properties of NKN ceramics were evaluated as to the Li_2O additions. 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 150°C for 30 min. Piezoelectric constant was measured by a quasi-static meter of Berlincourt type. The electromechanical coupling coefficients were determined from resonance-antiresonance methods on the basis of IEEE standards by using an impedance analyzer.

Figure 2 shows the dielectric constant (ε_r) of NKN-5LT ceramics as a function of Li_2O contents. The dielectric constant of pure NKN-5LT in this study was approximately 620, which is higher than that of pure NKN ceramics sintered at 1110°C. 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 Li_2O addition. In addition, the piezoelectric properties were evaluated by the resonance-antiresonance method. Figure 2 also shows the planar mode electromechanical coupling factor (k_P) of NKN-5LT ceramics as a function of Li_2O content. The figures shows that k_P values 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 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%. Piezoelectric constants (d_{33}) of the samples are shown in Fig. 2. From this figure, it can be seen that the 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.

3. Summary

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. Excellent piezoelectric and electromechanical responses, d_{33}~250 pC/N, k_P~0.37, were obtained for the samples with 1 mol% Li_2O additions. 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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