Electrical Properties and Polarization Reversal in (Li,Na)NbO_3 Lead-Free Piezoelectric Ceramics

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Keywords: lead-free piezoelectric ceramics, (Li,Na)NbO_3, electrical properties, polarization reversal

Abstract. In this study, the relationships between the electrical properties and polarization switching of lead-free ($Li_{0.06}Na_{0.94}$)NbO_3 (LNN6) ceramics were investigated. The electrical properties of stoichiometric LNN6 did not change with polarization switching. On the other hand, the frequency dependence of the impedance of Na-deficient LNN decreased with polarization switching, and the coupling factor k_p, the piezoelecric constant d_{33} and the dielectric constant $\varepsilon_{33}{}^{T}/\varepsilon_0$ decreased with polarization switching. Moreover, the dielectric curve of Na-deficient LNN6 after 10 switchings showed peaks at approximately 330, 400 and 500 °C

Introduction

Lithium-modified sodium niobates, (Li,Na)NbO_3 (LNN), are candidate materials for lead-free piezoelectric ceramics. LNNs are very useful in high-frequency applications owing to their high frequency constants and low dielectric constants. In addition, the composition of $Li_{0.12}Na_{0.88}NbO_3$ has morphotropic phase boundaries, and this material has a large electromechanical coupling factor [1]. However, the thermal properties of LNNs show thermal hysteresis at around 100 °C due to the presence of tetragonal-rhombohedral phase boundaries, which is a problem crucial for applications of LNNs. Recently, Kimura *et al*. [2,3] have succeeded in improving the thermal stability of LNNs by thermal treatment at 400 °C. The properties and phase transitions of LNNs are unknown and are of great interest.

We have recently investigated the compositions and electrical properties of LNNs [4,5]. We discovered that the depolarization temperature of LNNs increases from approximately 330 °C to 400 °C by high electric field poling [4,5]. In addition, we found that the peak of the temperature dependence of the dielectric constant of Na-deficient LNN is at approximately 400 °C. In this paper, the relationships between the electrical properties and polarization reversal of LNNs were investigated.

Experimental

($Li_{0.06}Na_{0.94}$)NbO_3 (LNN6) samples were prepared by a conventional solid-state process. The starting compositions were stoichiometric [LNN6] and Na (1%)-deficient [LNN6-Na]. Oxide Nb_2O_5 and carbonate Li_2CO_3 powders of 99.9% purity and Na_2CO_3 of 99.95% purity were used as starting materials. These powders were mixed in ethanol with zirconium balls by ball milling for 15 h. After calcination at 950 °C for 2 h, the calcined powders were ball-milled again for 20 h and dried, and then polyvinyl alcohol (PVA) was added as a binder. These powders were pressed into disks of 13 mm diameter and 1.1-1.3 mm thickness. Sintering was carried out at various temperatures from 1180 to 1240 °C for 2 h in air. The sintered samples were polished to a thickness of 1 mm and then silver paste was applied to form electrodes. The dielectric constant of the sintered sample was measured using the LCR meters (NF Corporation, ZM 2353 and HIOKI E. E. Corporation, 3532-50). The piezoelectric properties were evaluated using a piezoelectric d_{33} meter (Institute of Acoustics Chinese Academy of

Sciences, ZJ-3B) and the resonance-antiresonance method with an impedance analyzer (Schlumberger, SI 1260). Poling treatment was performed in a silicone oil bath by applying a DC electric field of 6 kV/mm for 5 min at 120 °C. The flow of polarization switching is shown in Fig. 1. Polarization reversal was performed by applying the electric field in the reversal direction and confirmed by a reversal of sign in the d_{33} meter. After polarization reversal, the dielectric and piezoelectric properties were measured at room temperature.

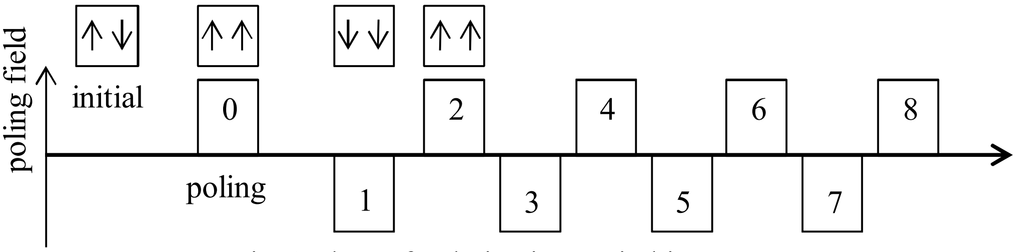


Fig. 1 Flow of polarization switching.

Results and Discussion

Polarization switching was performed in LNN6 and LNN6-Na. Over 40 switchings were possible for LNN6, whereas it was impossible to realize over 10 switchings in the case of LNN6-Na. Fig. 2 shows the frequency dependence of the impedances of LNN6 and LNN6-Na after poling (0 switchings) and after 10 switchings. The phase θ_{max} of LNN6 was approximately 80° after poling, which did not change with polarization switching. On the other hand, the θ_{max} of LNN6-Na decreased from approximately 80° to approximately -40° after 10 switchings. These results reveal that the frequency dependence of the impedance of LNN6-Na decreased with polarization switching.

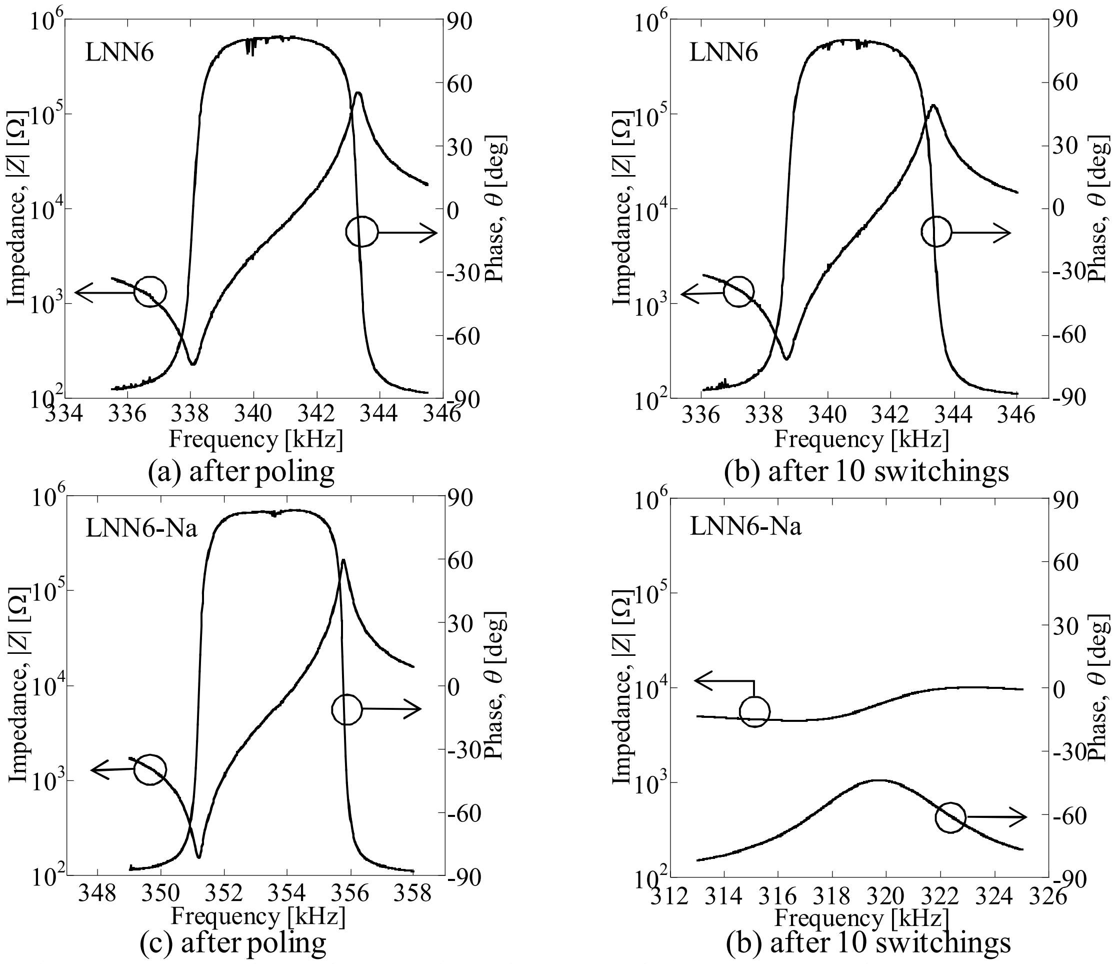
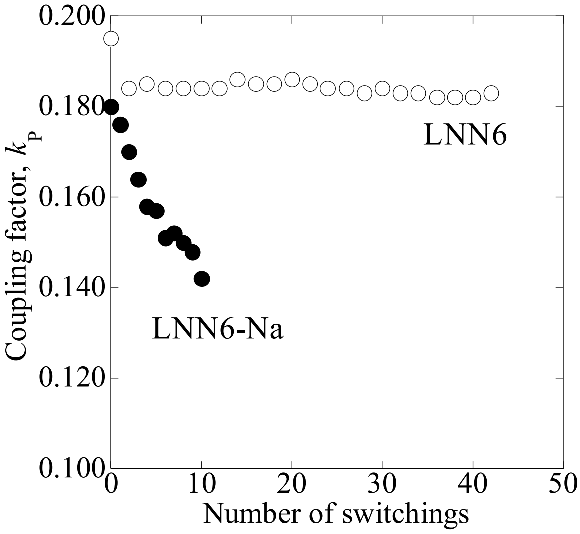
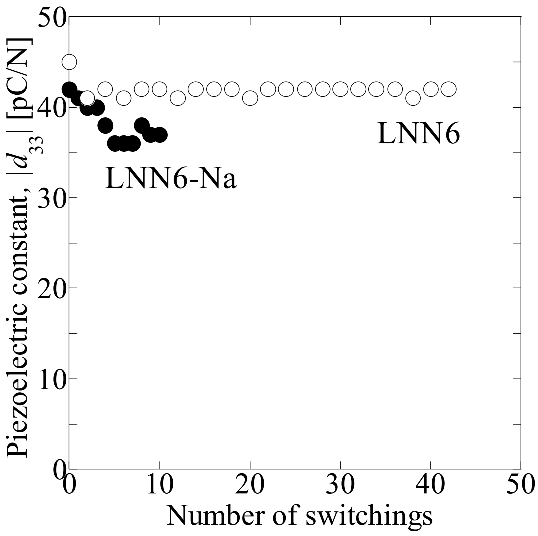


Fig. 2 Frequency dependence of impedance Z values of LNN6 and LNN6-Na after poling (0 switchings) and after 10 switchings.

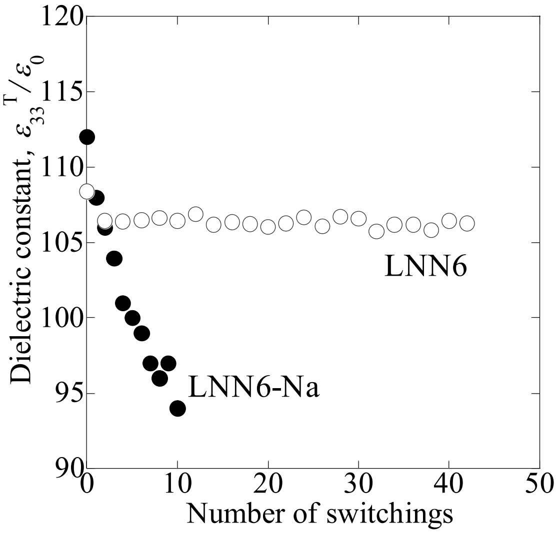
Fig. 3 shows (a) the electric coupling factor k_P, (b) the piezoelectric constant d_{33} and (c) the dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ as a function of the number of polarization switchings. In Figs. 3(a) and (b), the k_P and d_{33} of LNN6-Na decreased with polarization switching, while those of LNN6 did not change. This suggests that the piezoelectricity of LNN6-Na deteriorated with polarization switching. In Fig. 3(c), the $\varepsilon_{33}^T/\varepsilon_0$ of LNN6-Na decreased upon polarization switching. This indicates that a lower dielectric layer may be produced by polarization switching in LNN6-Na. Table 1 shows the electrical properties obtained after poling (0 switchings) and after 10 switchings.



(a) coupling factor k_P



(b) piezoelectric constant d_{33}



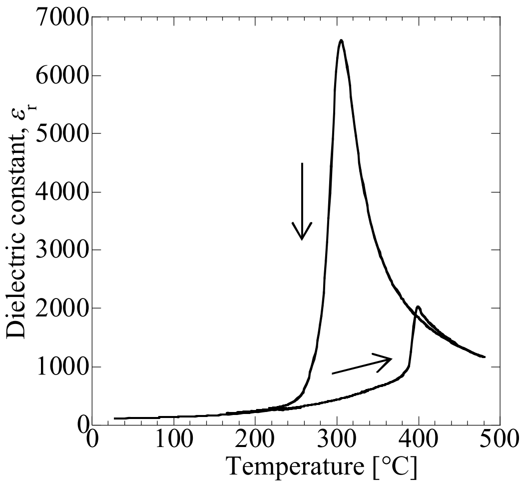
(c) dielectric constant $\varepsilon_{33}^T/\varepsilon_0$

Fig. 3 (a) Coupling factor k_P, (b) piezoelectric constant d_{33} and (c) dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ as a function of number of switchings at applied electric field of ±6 kV/mm.

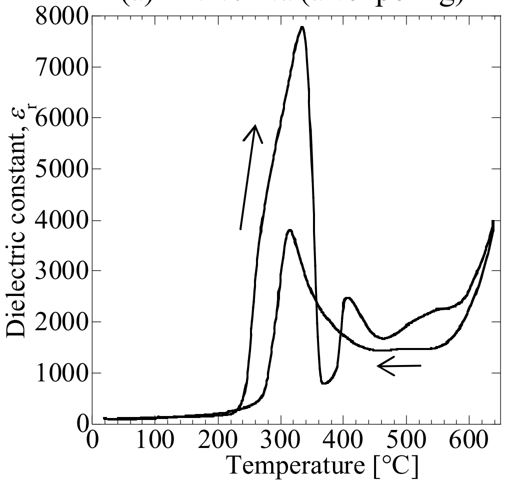
Table 1 Piezoelectric properties of LNN6 and LNN6-Na after poling (0 switchings) and 10 switchings.

	Number of switchings	$\varepsilon_{33}^T/\varepsilon_0$	k_P	Q_m	d_{33} [pC/N]
LNN6	0	108	0.195	850	45
LNN6	10	106	0.184	770	42
LNN6Na-1	0	112	0.180	1250	42
LNN6Na-1	10	94	0.142	--	37

Fig. 4 shows the temperature dependence of the dielectric constant for LNN6-Na (a) after poling (0 switchings) and (b) after 10 switchings measured at a frequency of 1 kHz. In Fig. 4(a), the peaks of the dielectric constant after poling were observed at approximately 400 °C on heating and at approximately 330 °C on cooling. This phenomenon in the LNN has been shown by high-electric-field poling [4,5]. On the other hand, in Fig. 4(b), some peaks were observed at approximately 330, 400 and 500 °C on heating after 10 switchings. The peaks in X-ray diffraction patterns of LNN6-Na after 10 switchings were not different from those of LNN6-Na after poling (0 switchings). Much more work is required to clarify these phenomena.



(a) LNN6-Na (after poling)



(b) LNN6-Na (after 10 switchings)

Fig. 4 Temperature dependence of dielectric constant for LNN6-Na (a) after poling (0 switchings) and (b) after 10 switchings.

Conclusion

The relationships between the electrical properties and polarization switching of LNN6 and LNN6-Na were investigated. The electrical properties of LNN6 did not change with polarization switching. On the other hand, the k_p and d_{33} of LNN6-Na decreased with polarization switching. This shows that the piezoelectricity of LNN6-Na deteriorated with polarization switching.

The $\varepsilon_{33}^T/\varepsilon_0$ of LNN6-Na decreased with polarization switching. From these results, we consider that a lower dielectric layer was produced by polarization switching in LNN6-Na.

The temperature dependence of the dielectric constant of LNN6-Na showed some peaks at approximately 330, 400 and 500 °C with heating after 10 switchings.

Acknowledgement

This work was supported in part by grants from the Murata Science Foundation and the Institute of Ceramics Research and Education, NITECH.

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