Dielectric and piezoelectric properties of sodium lithium niobate $Na_{1-x}Li_xNbO_3$ lead free ferroelectric ceramics

G. R. Li · Q. R. Yin · L. Y. Zheng · Y. Y. Guo · W. W. Cao

Abstract High density sodium lithium niobate lead free ceramics near the morphtropic phase boundary [$Na_xLi_{1-x}NbO_3$, (LNN), $x=0.12$] were prepared by the solid state reaction method. XRD patterns showed that the lattice structures were changed after polarization. The temperature dependence of the dielectric constant and dielectric loss, pyroelectric coefficient and DSC curves of LNN ceramics showed that there exist three phase transitions from room temperature up to the Curie temperature. The hysteresis loop and piezoelectric properties were measured and discussed.

Keywords $Na_xLi_{1-x}NbO_3$ · Piezoelectric · Dielectric · Ferroelectric · Phase transition

1 Introduction

Sodium Niobate, $NaNbO_3$ is in the orthorhombic phase at room temperature and its antiferroelectric-to-paraelectric phase transition (tetragonal) takes place at about 354 °C (Curie temperature). Lithium Niobate $LiNbO_3$ has a trigonal symmetry at room temperature and shows a second-order phase transition at about 1200 °C. The solid solution $Na_xLi_{1-x}NbO_3$ (LNN) ceramics is a very interesting material due to its lead free composition and high acoustic velocity, which is useful in high frequency applications. However, phase structures of LNN are very complex, they are strongly dependent on the Li^{+1} substitution ratio. It is know that the orthorhombic phase and trigonal phase co-exist in the morphtropic phase boundary (MPB) composition of LNN ($x=0.12$). Many papers have reported the limitation of Li^{1+} in LNN solid solutions [1, 2] and the related phase diagram [3, 4], but only a few papers dealt with dielectric, piezoelectric, and ferroelectric properties, and the correlation of these properties to the phase transitions [5]. Recently, there is an increasing demand for lead-free piezoelectric ceramics, hence, it is important to gain a better understanding on the dielectric and piezoelectric properties of LNN ceramics and the structure-property relation [6, 7]. In this paper, we report the fabrication of dense LNN ceramics by the solid reaction process, and give the dielectric, piezoelectric, ferroelectric properties. Related phase transitions will also be discussed.

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2 Experimental

LNN (compositions with $x=0.06$, 0.10, 0.12, 0.15, and 0.20, are abbreviated as LNN6, LNN10, LNN12, LNN15, and LNN20, respectively) ceramics were prepared by the conventional mixed oxide method. High purity powders were weighted according to the stoichiometric ratio of the composition and mixed in a ball mill, calcined at 850–1000 °C. The ceramic specimens were finally sintered at 1160–1360 °C. Ag electrodes were printed on the sintered samples and fired at 750 °C. These samples were poled under an electric field of 6 kV/mm in a silicone oil bath at 120 °C for half an hour.

The shrinkage of ceramics was measured by the high temperature shrinkage instrument. Structural phases were characterized by X-ray diffraction using a Guinier-Hägg camera with Cu Kα1 radiation. Hysteresis loops were measured by the Sawyer-Toywer circuit. The temperature dependence of the dielectric constant and loss tan δ was measured at a frequency of 1 kHz with a measuring field of about 1 V/mm using an automated dielectric measurement system with an LCR meter (Tonghui Electric TH2817). Piezoelectric constant d_{33} was measured by a quasi-static d_{33} meter (Institute of Acoustics, Academia Sinica, ZJ-2).

3 Results and discussion

The sintering temperatures of LNN ceramics were found to be strongly dependent on the Li^{+1} ratio. Figure 1 is the shrinkage of LNN ceramics (x=0.10, 0.12, and 0.15). These sintering behaviors is due to the smaller radii of Li^{+1} (0.82 A) compared to that of Na^{1+} (1.10 A), which causes lattice distortion and/or produces defects in the structure of LNN, resulting in the decreasing of diffuse active energy. The liquid phase occurred at lower temperatures as the ratio of $LiNbO_3$ increases, which makes the grain grow easer. Dense LNN ceramics have been obtained.

XRD patterns were used to investigate the crystal structure of non-poled and poled LNN ceramics. Results showed that relative peak intensities and lattice structures were quite different before and after poling. Figure 2 is the XRD patterns of the non-poled and poled LNN10 ceramics. Intensities of (020) and (112) peaks are quite different, in addition, (220) and (004) peaks of the non-poled LNN10 merged into one peak after poling. These differences indicated that domains were switched during poling, resulting in the change of peak intensities. The merging of (220) and (004) peaks may imply that a structural phase transition occurred under high electric fields.
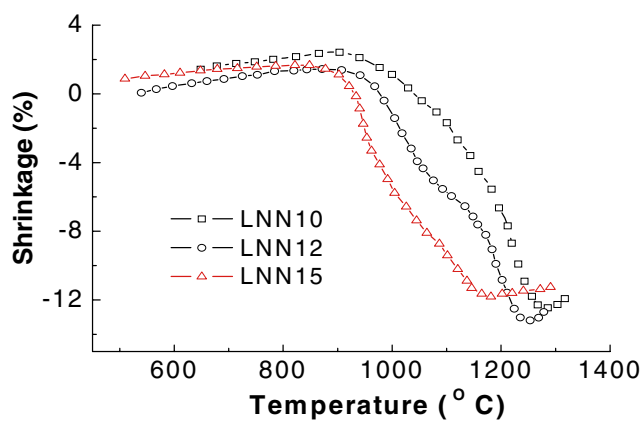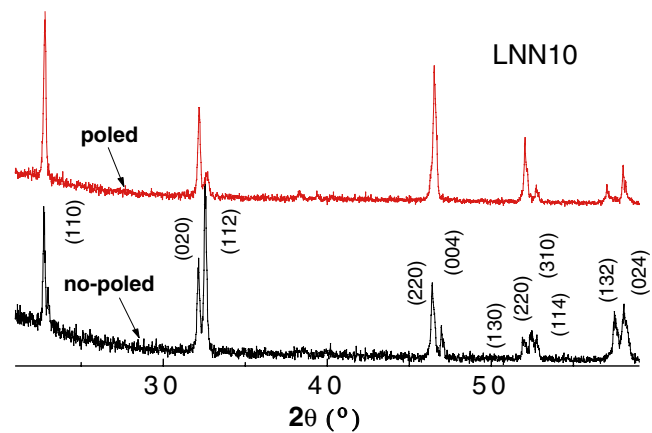
Fig. 2 The XRD pattern of LNN10 ceramics

Figure 3 shows the temperature dependence of the dielectric constant and loss for non-poled LNN ceramics near the MBP (i.e., LNN10, LNN12, and LNN15). One phase transition peak appeared for each case in the temperature range from 280 to 400 °C. Specifically, the peak temperatures were 359, 374 and 376 °C for LNN10, LNN12, and LNN15, respectively. There were no peaks in the temperature range from room temperature to 280 °C. However, a shoulder could be found at a temperature lower than the Curie temperature, the locations of the shoulder were in the temperature ranges of 325–350 °C, 345–358 °C, and 282–354 °C for LNN10, LNN12, and LNN15, respectively. The dielectric loss peak temperatures were 324, 344 and 328 °C for LNN10, LNN12 and LNN15, respectively, close to the corresponding beginning points of the shoulders.

Figure 4 is the temperature dependence of the dielectric constant and loss for poled LNN ceramics. Although their Curie temperatures were nearly unchanged compared to the non-poled cases, the shape of the shoulders changed greatly. The shoulder in the dielectric peak of LNN15 even became a peak and its intensity exceeds the peak at the Curie temperature. The temperature dependence of dielectric loss for all LNN ceramics showed two peaks, corresponding to the shoulder temperature and the Curie temperature. In addition, both dielectric constant and loss
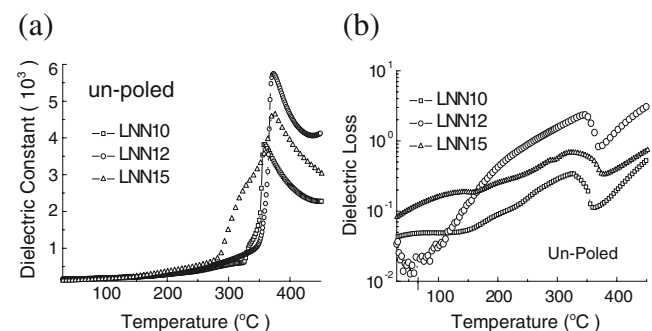
Fig. 1 Shrinkage of the LNN ceramics

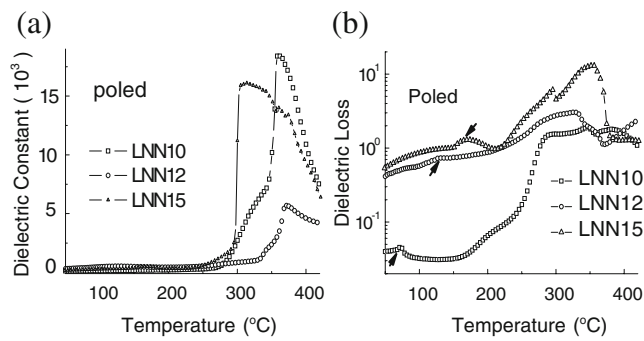**Fig. 3** Temperature dependence of dielectric constant (**a**) and dielectric loss (**b**) for non-poled LNN ceramics

Fig. 4 Temperature dependence of dielectric constant (a) and dielectric loss (b) for poled LNN ceramics

Fig. 6 Temperature dependence of pyroelectric coefficient

showed a peak in the temperature range from room temperature to 280 °C for poled LNN ceramics. Thus, three peaks were observed in poled LNN ceramics, while there were only two for non-poled LNN ceramics.

Figure 5 shows the DSC curves for poled LNN ceramics, the DSC curve for the non-poled LNN12 was also plotted in the figure for comparison. It was clear that all of LNN ceramics showed two peaks, indicating that there exist two first order phase transitions. The Curie temperature corresponding to the second peak was the same for non-poled and poled LNN12. Comparing the poled and non-poled LNN12, the area under the curve, reflecting the phase transition energy, in the first peak was little larger than that of the second peak. These results were consistent with the temperature dependence of dielectric properties of LNN ceramics. However, a phase transition in the temperature range from room temperature to 280 °C was not observed by the DSC measurement.

Figure 6 is the temperature dependence of the pyro-electric coefficient of LNN12. It shows a peak at about 50 °C, close to its dielectric loss peak temperature. To confirm the characteristic of this peak, piezoelectric property was checked using a poled LNN10 ceramics with d_{33}=42 pC/N. The sample was annealed at 165 °C
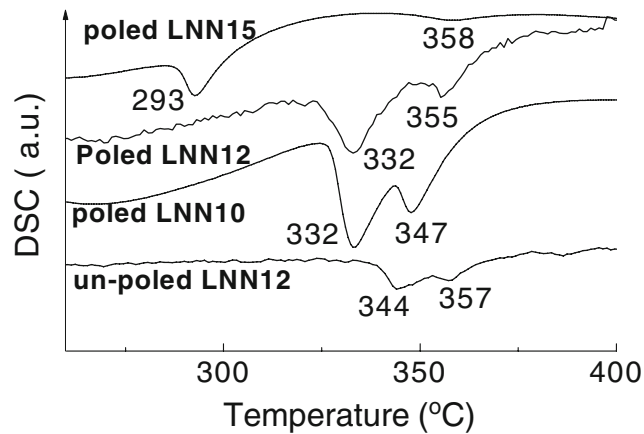
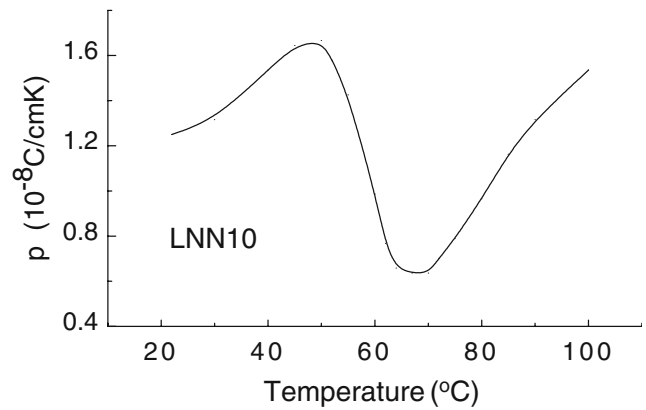for several hours and the d_{33} value was not changed. Thus, this peak corresponds to a ferroelectric-to-ferroelectric phase transition.

These phase transitions were observed by Nitta before [1], who used temperature dependence of XRD pattern to identify that the phase transition in the temperature range from room temperature up to the Curie temperature corresponds to a structural transition from rhombohedra-to-orthorhombic phase. Our results showed that this is a ferroelectric-to-ferroelectric phase transition. The other two peaks in the temperature dependence of DSC and dielectric properties correspond to orthorhombic to tetragonal phase, and tetragonal to cubic phase transitions.

Figure 7 shows the hysteresis loops of LNN10. The shape of the hysteresis is typical for a ferroelectric material. An interesting point is the sudden change of the loop size passing a critical field level. The loops have almost the same coercive field for different applied voltages from 2,500 V up to 3,500 V, their residual polarization only changed slightly. However, when the voltage level is increased to 4,000 V, the size of hysteresis loop suddenly increased. Remanent polarization almost doubled (0.62 mC/m²) and the coercive field
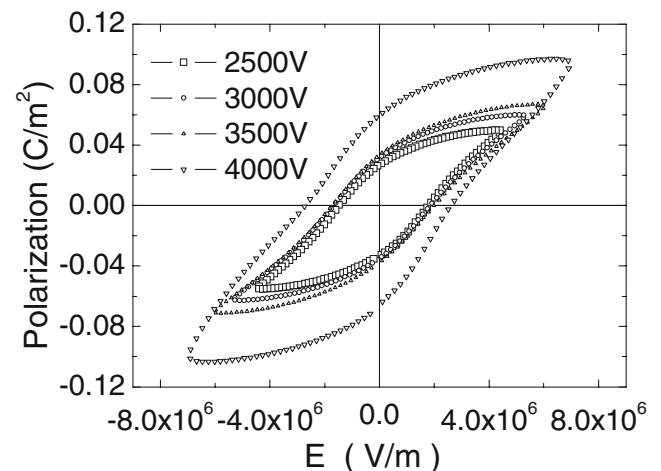

Fig. 5 DSC curves of LNN ceramics

Fig. 7 Hysteresis loop of LNN10 ceramics under different switching electric fields

increased about 50% (2,700 V/mm). The rapid change of hystersis loop implies that the lattice structure undergone a phase transition at this electric field. In case of LNN10, the structural phase transition occurs under an electric field higher than 2,700 V/mm.

4 Summary

High density LNN piezoelectric ceramics have been prepared and characterized. Results of dielectric, piezoelectric, pyroelectric, and DSC measurements showed that there exist three phase transitions. A structural phase transition was induced by high electric fields in the poled sample, which resulted in different XRD patterns, and different temperature dependence of the dielectric constant and loss for poled and non-poled LNN ceramics. From our preliminary analysis, this phase transition is between two

ferroelectric phases but the exact lattice structure change still needs to be identified.

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