Paper

Electrical Reliability and Segregated Manganese Behavior on Multilayered (Li,Na,K)NbO₃ Piezoceramics with Pd Electrodes

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Received November 9, 2017; Revised January 1, 2018; Accepted January 9, 2018

ABSTRACT

Multilayered (Li,Na,K)NbO₃ lead-free piezoceramics with Pd inner-electrodes were fabricated by controlling the additive amounts of x mol% MnCO₃ ($x = 0.0, 0.5, 1.0$, and 2.0) together with other additives. The multilayered samples containing the Mn compound had a markedly increase in electric resistivity from the order of 10^7 to 10^{11} $\Omega \cdot \text{cm}$ at 100°C . Moreover, the normalized electric-field-induced strains for $x = 1.0$ were over 350 pm/V at 5 kV/mm. The Mn distributions in several multilayered samples were investigated using a scanning electron microscope with an energy dispersive X-ray spectrometry. The segregated Mn phases were observed almost in the vicinity of Pd inner electrodes. In addition, mapping of Mn content for $x = 2.0$ indicated that segregated Mn phases existed in the ceramic layers. We hypothesize that this complex Mn distribution was related to the results of a continuous driving fatigue test. The multilayered sample with $x = 2.0$ only maintained a stable state of driving current for fatigue tests over 10^6 cycles using $0\sim 6$ kV/mm triangle wave form at 100°C . This significant electrical reliability was provided by the segregated Mn phases in the ceramic layers.

KEY WORDS

lead-free, alkaline niobate ceramics, multilayered structure, electrical reliability, energy dispersive X-ray spectrometry

1 Introduction

Lead containing piezoceramics, such as Pb(Zr_{1-x}Ti_x)O₃ (PZT) are still major compounds for producing piezoelectric devices, including sensors, actuators, and motors. The continued use of PZT based piezoceramic materials is because of their outstanding piezoelectric properties compared to other piezoceramics. However, lead compounds are toxic to humans, and laws regulating lead compounds have been established in every country. Thus, many researchers have continued to explore lead-free piezoceramics in an attempt to obtain the piezoelectricity of PZT.

In 2005, Y. Guo et al¹⁾ reported an Li_{0.06}Na_{0.47}K_{0.47}NbO₃ (LNKN) perovskite compound, which is a promising candidate for lead-free piezoceramic because of its high Curie temperature ($T_c = 470^\circ\text{C}$) and high piezoelectric constant ($d_{33} = 235$ pC/N). Y. Saito et al²⁾ found extremely high piezoelectric properties ($d_{33} = 416$ pC/N, $T_c = 253^\circ\text{C}$) for (Li,Na,K)(Nb,Ta,Sb)O₃ using the reactive template grain growth method. This year, innovative research and development on alkaline niobate perovskite oxides was initiated³⁾ since then (Na,K)NbO₃ compounds were first studied^{4,5)}. Many previous studies⁶⁻¹⁶⁾

had concentrated on improving piezoelectric coefficients, especially the longitudinal-mode piezoelectric coefficient (d_{33}). Consequently, the high T_c of LNKN decreased to a temperature lower than the T_c of basic PZT, around 370°C , owing to an improvement in the dielectric constant and piezoelectric coefficients at room temperature.

The described T_c and d_{33} for LNKN have values that are sufficiently comparable to PZT-based piezoceramics. Therefore, we concentrated on developing improved LNKN electrical and mechanical reliability using microstructural control^{17,18)}, and mechanical fatigue evaluations^{19,20)}. Notably, multilayered LNKN piezoceramics with Pd inner-electrodes showed remarkable displacement values with increasing applied voltage over 4 kV/mm in our previous study²¹⁾. Moreover, this multilayered piezoceramic continued to drive over 10^6 cycles with a unipolar triangle wave at 8 kV/mm and 100°C . These results indicate that multilayered LNKN piezoceramics will be able to replace PZT-based piezoceramics in the future, but significant issues remain to be resolved from a cost perspective. First, Ag/Pd, Ni, or Cu inner electrodes should be employed²²⁻²⁷⁾, however, these electrodes have several problems. The alkaline niobate perovskite ceramics with Ag/Pd electrodes require controlling the Ag elemental diffusion to the matrix²²⁾. Furthermore, Ni or Cu inner electrodes must be regulated in a reduced atmosphere to control oxygen vacancies²⁴⁻²⁷⁾.

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** The content of this article had been presented at JSPMIC2017.

For these reasons, the multilayered LNKN piezoceramics in this study used Pd inner electrodes. Second, niobate oxides are more costly compared to titanium and zirconium oxides, therefore, detailed comparisons should be made between multilayered LNKN piezoceramics and multilayered PZT piezoceramics.

To demonstrate the potential of thinner ceramic layers in multilayered LNKN piezoceramic structures, the amounts of manganese in the multilayered LNKN piezoceramic were increased in a controlled manner, with the expectation that it would improve the electric reliabilities, such as resistivity and continuous driving fatigue tests. The Mn addition technique is a conventional method for improving sinter-ability and resistivity^{11,12,18,24}. In addition, we observed Mn distributions in the ceramic matrix using a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDS) to characterize the cross-section surfaces in our multilayered alkaline niobate perovskite ceramics with additives. In this study, the relationship between electric reliabilities and Mn distributions in multilayered LNKN piezoceramics were demonstrated by addition with an Mn compound.

2 Experimental procedures

2.1 Synthesis of lead-free ceramic powder

A detailed description of the preparation procedure for ceramic powder and our motivation for the additive preferences has been described in our previous study¹⁸. Here, the experimental procedures to synthesize $\text{Li}_{0.06}\text{Na}_{0.52}\text{K}_{0.48}\text{NbO}_3$ (LNKN) containing 0.65 mol% Li_2CO_3 , 1.3 mol% SiO_2 , 0.5 mol% SrZrO_3 , and x mol% MnCO_3 ($x = 0.0, 0.5, 1.0$, and 2.0) are shown. The raw materials for the main phase were reagent-grade Li_2CO_3 , Na_2CO_3 , K_2CO_3 , and Nb_2O_5 (> 99.5% purity). The milling powders were subjected to a solid-state reaction at 900°C for 3 h. After that, the reaction products were separated into different batches, and were crushed with our preferred additives [reagent-grade Li_2CO_3 , SiO_2 , MnCO_3 , and SrZrO_3 (> 99.5% purity)] by ball milling for 24 h using ethanol and zirconia balls. The crushed mixture dried after the milling balls were removed.

2.2 Fabrication of multilayered piezoceramics

Next, the crushed powers were mixed together with a polyvinyl butyral based binder to prepare a tape-casting slurry. These slurries were spread into green sheets using a doctor blade, and dried sufficiently. Then, the Pd electrodes pastes were printed on the ceramic powder sheets by screen printing. The sheets were stacked alternately in a structure consisting of 10 ceramic layers and 11 inner electrode layers, together with top and bottom layer covers. The stacked laminates were pressed using a uniaxial pressing machine. After pressing, the stacked laminates were cut into $4 \times 2 \times 1 \text{ mm}^3$ multilayered LNKN piezoceramic samples using a chopping machine before sintering. These green multilayered piezoceramics samples were then sintered at 1000°C for 2 h. Finally, the outer Ag electrodes were printed on the termination sides of the sintered

samples at 800°C, and the poling electric fields of 3 kV/mm was applied at 100°C for 5 min in a thermostatic chamber.

2.3 Characterization of multilayer piezoceramics

To evaluate the densification and measure the thickness of one layer ceramic between electrodes, the cross-section polished surfaces of each multilayer structure were characterized using an SEM (ZEISS, MERLIN). The surfaces were polished to a buff finish with a 1 μm diamond slurry. To evaluate displacement performance of the multilayered LNKN piezoceramic, the unipolar strain–electric field (S–E) curves were measured at room temperature (25°C) using a laser displacement meter. In addition, the electric resistivities in the electric field of 3 kV/mm were measured using an ultrahigh-resistance meter (ADCMT 5451) at 100°C for 5 min. After confirming their plenary displacement performances and electric resistivity, continuous driving fatigue tests were conducted using a modified Sawyer–Tower circuit with a ferroelectric measurement module (aixACCT Systems TF Analyzer 2000). This test used a unipolar triangle wave form with a maximum electric field and frequency of 6 kV/mm and 200 Hz, respectively. Tests were conducted in an ambient air atmosphere at 100°C. Lastly, the SEM-EDS analyses were carried out to estimate the distributions of Mn and Si additives in the micro structures of the multilayer piezoceramics. The Mn and Si additives were measured as Mn-K (5.8951 Å) and Si-K (1.7398 Å) spectra, but the measurement of Sr-K (1.8066 Å) and Zr-K (2.0424 Å) spectra were difficult because these ion specimens had a uniform diffusion in the LNKN compound and formed a solid solution. This phenomenon was observed in previous TEM-EDS analysis¹⁸.

3 Results and discussion

Fig. 1 shows SEM images of the cross-section polished surfaces of the multilayered structure of our fabricated piezoceramics. As shown, the multilayered LNKN piezoceramics with Pd electrodes obtained a dense ceramic and continuous inner-layer structure. Several sub-micrometer particles, dark gray in color, were observed in the ceramic layers and in the vicinity of the Pd electrodes. There were aggregate phases of additives, such as Si-glass and Mn

Fig. 1 Polished cross-section surface images of multilayered LNKN piezoceramic with Mn contents of (a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 1.0$, and (d) $x = 2.0$ mol%.

phases. Their function will be described in the later discussion of SEM-EDS analysis. The inner-layer thickness of the piezoceramics with Mn contents of $x = 0.0, 0.5, 1.0$, and 2.0 were 42, 36, 35, and 36 μm , respectively. The electric fields in each following experiment were based on the ratio of the voltage to their thickness values.

The S-E curves for the multilayered LNKN piezoceramics with differing Mn contents are shown in Fig. 2. As shown, these are typical multilayered LNKN piezoceramic curves, despite the decreasing thickness of the inner-layer ceramics; the maximum electric-field-induced strains with Mn contents of $x = 0.0, 0.5, 1.0$, and 2.0 were 0.24%, 0.28%, 0.30%, and 0.28%, respectively. In particular, the strain value for the Mn content of $x = 1.0$ improved significantly. To clarify the relationship between strain value and electric field, the normalized electric-field-induced strains ($S_{\text{max}}/E_{\text{max}}$, often termed the large signal piezoelectric coefficient, d_{33}^*) with electric fields of 5, 8, and 10 kV/mm, are included in Fig. 3. In our previous study, we investigated the multilayered LNKN piezoceramics with an inner-layer thickness of 50 μm , and the $S_{\text{max}}/E_{\text{max}}$ values at 5 kV/mm were over 330 pm/V²¹⁾. The multilayered LNKN piezoceramics with Mn amounts of $x = 0.0, 0.5$, and 2.0 had almost identical performances of the samples in the previous study, i.e., their $S_{\text{max}}/E_{\text{max}}$ values were 311, 335, and 329 pm/V at 5 kV/mm. Moreover, the $x = 1.0$ multilayered LNKN piezoceramic sample had the largest value of 356 pm/V. In addition, the $x = 1.0$ sample retained the remarkably high $S_{\text{max}}/E_{\text{max}}$ over 300 pm/V until an electric field value of 10 kV/mm.

These changes in the $S_{\text{max}}/E_{\text{max}}$ values are also related to electric resistivity, which provides a measure of electrical reliability. Fig. 4 shows the relationship between electric resistivity in 3 kV/mm at 100°C and Mn amount. The sample without Mn additive, $x = 0.0$, had a very low electric resistivity of $6.0 \times 10^7 \Omega\cdot\text{cm}$. The others containing Mn additives had increasing electric resistivity with increasing Mn content. The resistivity improved slightly from $x = 0.5$ to 2.0 , with values of 1.7×10^{11} , 2.9×10^{11} , and $6.2 \times 10^{11} \Omega\cdot\text{cm}$, respectively. This suggests that the increase in $S_{\text{max}}/E_{\text{max}}$ from $x = 0.0$ to 1.0 was caused by the increase in electric resistivity. However, the multilayered LNKN piezoceramic with an Mn content of $x = 2.0$ had a lower $S_{\text{max}}/E_{\text{max}}$ value than that of $x = 1.0$. We hypothesize that the Mn contents of $x = 2.0$ were in excess of the optimum for achieving high displacement performance because manganese oxides do not have piezoelectricity.

The results from the continuous driving fatigue tests and final driving current behavior prior to breakdown are shown in Fig. 5. The multilayered LNKN piezoceramic with excess Mn content, $x = 2.0$, did not reach breakdown when the fatigue cycles were over 10^6 cycles. Therefore, the fatigue tests were ceased for these samples when 10^6 cycles was reached because of time constraints; nonetheless, this result indicates the remarkable electrical reliability despite the decreasing thickness from 50 μm to 36 μm in our previous test²¹⁾. For the other Mn contents, the number of cycles did not change significantly and remained roughly constant

Fig. 2 Unipolar strain–electric field (S–E) curves of multilayered LNKN piezoceramic with Mn contents of (a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 1.0$, and (d) $x = 2.0$ mol%. The arrows in (a) indicate the driving directions.

Fig. 3 Summary of each normalized electric-field-induced strain ($S_{\text{max}}/E_{\text{max}}$) with Mn contents of $x = 0.0, 0.5, 1.0$, and 2.0 , respectively. The electric fields were 5, 8, and 10 kV/mm.

Fig. 4 Relationship between Mn contents and electric resistivity at 3 kV/mm and 100°C.

until Mn contents of $x = 1.0$. Notably, the driving currents clearly changed regardless of the amount of Mn additive contained in the ceramic. The typical current loops before breakdown are shown

Fig. 5 Results of a continuous driving fatigue test for each Mn content sample. Measurement conditions were a unipolar-triangle wave of 0–6 kV/mm and 200 Hz at 100°C. The arrows in (a) and (b) indicate the driving directions.

in Fig. 5 (a) and (b). The multilayered LNKN piezoceramic with an Mn content of $x = 0.0$ indicated a strained driving current loop (Fig. 5 (a)), which suggested a reduction in electric resistivity in a high electric field around the top of the current. This behavior implies that oxygen vacancies and alkaline cations were conducted in the LNKN ceramic. For Mn contents of $x = 0.5$ and 1.0 , the current loop in Fig. 5 (b) did not increase around the maximum electric field, although the number of surviving cycles was almost identical to that for $x = 0.0$. This difference suggests that samples with $x = 0.5$ and 1.0 had sudden breakdowns in continuous driving fatigue test despite having improved high resistivity compared with an Mn content of $x = 0.0$. Mn is often added in a ceramic to prevent oxygen vacancies from conducting in the ceramic, but this phenomenon of sudden breakdowns should be evaluated in more detail. Given that a more detailed analysis was needed to understand these current loop changes and the survival over 10^6 cycles for the sample with $x = 2.0$, SEM-EDS analyses were conducted.

The EDS mapping results for Mn-K and Si-K spectra are shown in Fig. 6. These results are presented for the complex Mn distributions for all contents, and for the Si distributions with ordinary aggregate particles showing Si and K elemental reactions¹⁸⁾. Most segregations of the Mn phase were measured in the vicinity of the Pd inner electrodes. The mapping result with Mn contents of $x = 2.0$ indicated that other Mn segregates were found in the LNKN piezoceramic layers.

In comparison with the results of continuous driving fatigue test, the segregated Mn phases around the inner electrodes were associated improved electric resistivity on the electrode interfaces,

Fig. 6 Element mapping results for Mn and Si using a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDS).

and this state would prevent an increase in electric current during continuous driving, such as $x = 0.5$ and 1.0 . The multilayered LNKN piezoceramic with an Mn content of $x = 2.0$ could drive only over 10^6 cycles. This significantly high electrical reliability implies that the segregated Mn phases in the ceramic layers increased the electric resistivity and/or mechanical strength of the ceramic layers, which prevented sudden breakdowns. The Mn additive effects in one layered bulk ceramic were evaluated in a previous study, which demonstrated the improved electric resistivity¹⁸⁾ and mechanical strength¹⁹⁾.

These phenomena suggest that the liquid-like Mn phases were separated and extracted from the piezoceramic inner layer sheet during the sintering process. The addition of the Mn phase provided a liquid-phase sintering process. Many previous reports^{12,28-30)} discussed the solid solution of Mn element in this composition. It would be difficult for the Mn compound to react with LNKN due to a low sintering temperature at 1000°C. If Mn elements were substituted into the Nb sites, one might expect the sintering temperature of the LNKN ceramic to be higher than 1000°C.

A more detailed investigation of the relationship between segregated Mn phases and continuous driving fatigue behavior is needed for a more complete characterization of these materials; tools for these next steps include the alternating-current impedance

method and analysis of electrode interfaces by TEM-EDS. These results will be reported in the near future.

4 Summary

We successfully fabricated multilayered LNKN piezoceramics with additives of 0.65 mol% Li_2CO_3 , 1.3 mol% SiO_2 , 0.5 mol% SrZrO_3 , and x mol% MnCO_3 ($x = 0.0, 0.5, 1.0$, and 2.0). The multilayered sample with an Mn content of $x = 2.0$, with a one layer thickness of 36 μm , was subjected to a continuous driving fatigue test with a 0–6 kV/mm unipolar-triangle wave form at 100°C, and performed for over 1 million cycles (10^6 cycles). The multilayered samples had remarkable $S_{\text{max}}/E_{\text{max}}$ values, over 300 pm/V, and was especially high for an Mn content of $x = 1.0$, 356 pm/V at 5 kV/mm. A more detailed analysis was necessary to understand the current loop change and sample survival over 10^6 cycles for $x = 2.0$, thus SEM-EDS analyses were conducted.

The segregated Mn phase was distributed in the vicinity of the Pd inner electrodes when Mn contents were $x = 0.5$ and 1.0 . One potential explanation for this distribution is that the aggregation of Mn phase increased the resistivity of the electrode interfaces. When the Mn reached 2.0 mol%, the segregated Mn phase was also detected in the ceramic matrix. The significantly high electrical reliability, e.g., over 10^6 continuous driving cycles, implied that the segregated Mn phases in the ceramic layers increased the electric resistivity and/or mechanical strength of the ceramic layers. The detailed implications of this Mn distribution required additional clarification; we need more detailed analyses, such as the alternating-current impedance method and analysis of electrode interfaces by TEM-EDS.

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