Electronic Materials Letters, Vol. 8, No. 1 (2012), pp. 43-45
DOI: 10.1007/s13391-011-1063-1

Electrical Properties of Lead-free $0.98(Na_{0.5}K_{0.5}Li_x)NbO_3$-$0.02Ba(Zr_{0.52}Ti_{0.48})O_3$ Ceramics

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(received date: 29 September 2011 / accepted date: 17 November 2011)

Lead-free $0.98(Na_{0.5}K_{0.5}Li_x)NbO_3$-$0.02Ba(Zr_{0.52}Ti_{0.48})O_3$ piezoelectric ceramics were investigated. The experimental results show that Li content strongly affects the orthorhombic-tetragonal morphotropic phase boundary (MPB) which results in different piezoelectric properties. The phase transition composition shows a range from 0.05 to 0.1. The sample with a composition of x = 0.1 showed the maximum values of piezoelectric coefficient (d_{33} = 201 ρC/N), electromechanical coupling coefficient (k_p = 39%), and remnant polarization (P_r = 21 μC/cm^2).

Keywords: piezoelectric properties, dielectric properties, NKLN-BZT, MPB

1. INTRODUCTION

Recently, the most widely used piezoelectric materials are PZT-based ceramics, owing to their superior piezoelectric properties. The Pb-based perovskite ferroelectric ceramics and single crystals have been generally investigated for piezoelectric applications. These materials have a high piezoelectric response, which is related to the Morphotropic Phase Boundary (MPB), between the rhombohedral and tetragonal phases. Lead materials have been considered to be a big threat to our environment, so an urgent task for the scientific community is to search for alternative lead-free piezoelectric compositions with electrical properties comparable to those of commercial $Pb(Zr,Ti)O_3$ (PZT) ceramics. However, the best properties from the currently studied lead-free piezoelectric candidates are still not as good as expected. The focus of this field so far is still on the search for new lead-free ferroelectric ceramics with a so-called morphotropic phase boundary (MPB) where it is considered that the materials will show superior dielectric, ferroelectric, piezoelectric, and electromechanical properties.

By comparison, the sodium potassium niobate (NKN) ceramic was considered to be more promising because of its high Curie point and adjustable electrical properties, particularly for NKN ceramics modified with Li. However NKN ceramics showed inferior electrical and structural properties with difficulty in connection with the high volatility of the alkaline elements at high sintering temperature. Therefore, the improvement or modification of these high-performance lead-free piezoelectric ceramics would prove definitely essential for final industrial application. Consequently, the approach to NKN ceramics has shifted to new NKN-based ceramics, such as NKN-$BaTiO_3$, NKN-$Li(Sb,Ta)O_3$, NKN-$LiNbO_3$ etc. Many researches on NKN ceramics doped with Li have been conducted. As a result of these, it can be inferred that Li doped NKN ceramics show relatively high Curie temperatures (T_c) and good electrical properties. In this paper, we report electrical and structural properties of $0.98(Na_{0.5}K_{0.5}Li_x)NbO_3$-$0.02Ba(Zr_{0.52}Ti_{0.48})O_3$(abbreviated NKLN-BZT) ceramics.

2. EXPERIMENTAL

NKLN-BZT ceramics with x-mol% Li_2CO_3 content ($0 \le x \le 0.2$) were fabricated by a conventional mixed oxide method with Na_2CO_3, K_2CO_3, Li_2CO_3, and Nb_2O_5 as the starting materials. These powders were separately dried in an oven at 100°C for 4 h. They were ball-milled for 12 h using zirconia balls in alcohol. After being dried at 100°C for 24 h, the powders were calcined at 850°C for 4 h. After re-milling with $BaCO_3$, ZrO_2, TiO_2 the powders were dried and pressed into disk samples of 12 mm diameter. The samples were sintered at 1090°C for 6 h. After the samples were polished to 1 mm thickness, silver paste was screen-printed on the surfaces as electrodes and then fired at 400°C for 10 minutes.

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We used X-ray diffraction (XRD) to analyze the crystallinity and microstructures. The dielectric properties were measured using an LCR meter (PM6306, Pluke). Hysteresis loops of the samples were measured by a Sawyer-Tower circuit. The samples were poled under a DC field of 4 kV/mm for 20 minutes. The piezoelectric strain constant d_{33} was measured by a d_{33} meter (Channel Product DT-3300). The electromechanical coupling factor k_p was calculated by measuring the anti-resonance and resonance frequencies.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray patterns in the range of 2θ from 20° to 60° of pure NKLN-BZT ceramics with different x values sintered at 1090°C for 4 h. The $\{(Na_{0.5}K_{0.5})\ Li_x\}Nb_{0.84}O_3$-$Ba(Zr_{0.52}Ti_{0.48})O_3$ ceramics have single phase perovskite structures with Li content x up to 0.2. Fig. 1(b) shows the enlarged XRD patterns in the range of 2θ from 40° to 50°; the ceramics show a phase transition from an orthorhombic symmetry ($x \leq 0.05$) to a tetragonal ($x \geq 0.1$). The Li content x should be expected as more confirmation for a phase transition from an orthorhombic symmetry to a tetragonal one, as analyzed. With Li doping the structural lattice distortion should increase by increasing the Li content within the solubility. So a small amount of Li inserted in the lattice of the NKN perovskite tends to induce a distortion of the oxygen octahedral of NKN. This kind of structure distortion may enhance the phase structure transition. Also Li tends to promote sintering, and influence grain growth. Li is usually considered to be an effective sintering aid for a few material systems because of the low melting point of Li_2CO_3.

Figure 2 shows the temperature-dependent dielectric properties of NKLN-BZT ceramics at 1 kHz. The NKLN-BZT ceramics exhibit two phase transitions; a ferroelectric phase

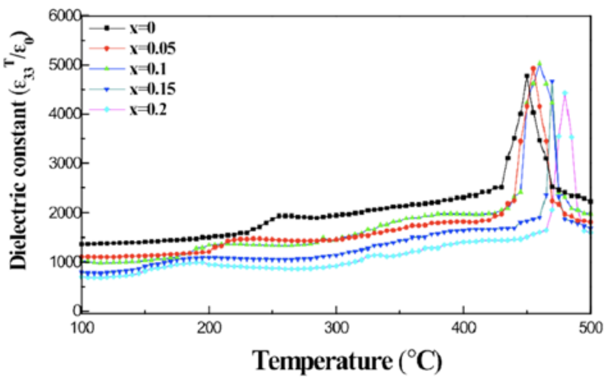

Fig. 2. Dielectric constant at 1 kHz versus temperature curves of $0.98(Na_{0.5}K_{0.5}Li_x)NbO_3$-$0.02Ba(Zr_{0.52}Ti_{0.48})O_3$ ceramics.

transition of tetragonal-cubic (T_c), and an orthorhombic-tetragonal ($T_{o\text{-}t}$) when $x = 0.1$. The T_c shifts upward with the increasing of Li content, and $x = 0.1$ may possess a T_c of 470°C. Mostly Li replaces Na and K sites to form a solid solution and leads to the linear shift of Curie point T_c to a higher temperature. The dielectric properties of NKN based ceramics can be improved greatly by doping with Li, which is a potential Pb-free candidate for the replacement of PZT-based ceramics.

Figure 3 shows the polarization-electric field hysteresis loops of NKLN-BZT ceramics with different Li content. The NKLN-BZT (x = o) ceramics show a lower P_r value and with increasing Li content, the P_r of NKLN-BZT ceramics increase. The remnant polarization of the NKLN-BZT ceramics shows a maximum remnant polarization (P_r = 21 μC/cm^2) is obtained when Li content is 0.1 mol%. However when increasing Li content exceeds 0.1, the remnant polarization P_r decreases, while the coercive field E_c increases. Particularly, E_c's rapid growth could be considered to be the phase structure changing from orthorhombic to tet-

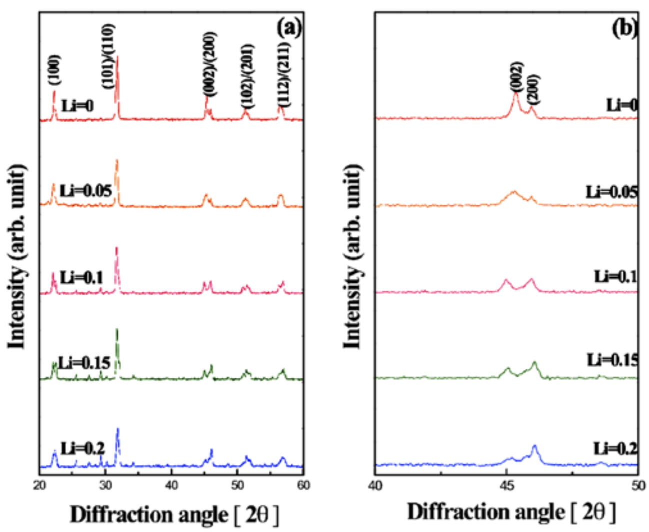

Fig. 1. XRD patterns of $0.98(Na_{0.5}K_{0.5}Li_x)NbO_3$-$0.02Ba(Zr_{0.52}Ti_{0.48})O_3$ ceramics from 20° to 60° and (b) from 40° to 50°.

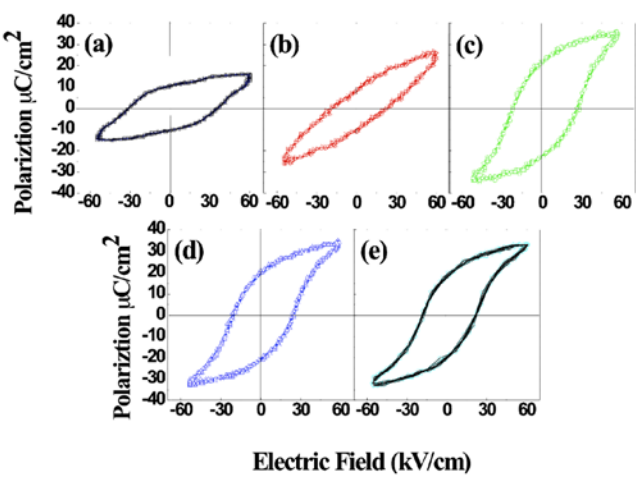

Fig. 3. Hysteresis loops of the $0.98(Na_{0.5}K_{0.5}Li_x)NbO_3$-$0.02Ba(Zr_{0.52}Ti_{0.48})O_3$ ceramics x = 0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.15, (e) x = 0.2.

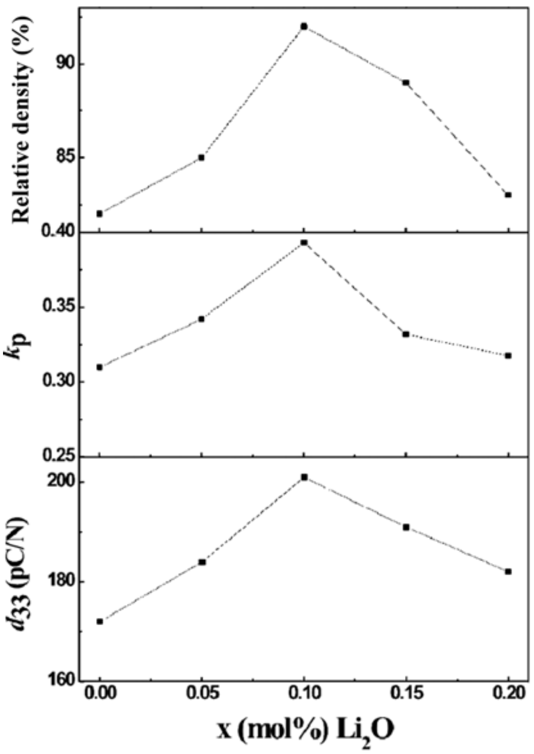

Fig. 4. Piezoelectric properties and relative density of 0.98($Na_{0.5}K_{0.5}Li_x$)NbO_3-0.02Ba($Zr_{0.52}$Ti0.$_{48}$)O_3 ceramics.

ragonal across this composition area with Li content 0.05 < x < 0.1.

Figure 4 shows the piezoelectric coefficient d_{33} and planar electro mechanical coefficient k_p of the NKLN-BZT ceramics with different Li content. Initially they go up slightly with an increase in x, reaching the peak at approximately 201, and then drop down with the further increase of Li content. The maximum d_{33} (201 ρC/N) and k_p (39%) can be obtained at a composition close to the tetragonal side ($0.05 \leq x \leq 0.1$) of the orthorhombic-tetragonal phase transition region, where two ferroelectric phases may coexist near room temperature. The increase in piezoelectric properties could be associated with bulk density.

4. CONCLUSIONS

In summary, NKLN-BZT lead-free piezoelectric ceramics were manufactured by ordinary sintering process. Their phase transition behavior, structural and electrical properties were investigated. The addition of Li enhances the piezoelectric properties as well as the sinterability of NKN-BZT ceramics. It was found that the electrical properties of NKLN-BZT (x = 0.1) ceramics sintered 1090°C for 4 h have a piezoelectric constant, a planar electromechanical coupling coefficient and a remnant polarization of d_{33} = 201 ρC/N, k_p = 39%, and P_r = 21 μC/cm^2, respectively. These results show that the piezoelectric properties of NKLN-BZT ceramics make them a potentially good candidate as a lead-free material for energy harvesting and transducer applications.

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