Preparation and characterization of Pb-free (Na, K)NbO_3-based ceramics for eco-friendly piezoelectric device

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Introduction

The Pb(Zr, Ti)O_3[PZT] materials have been widely utilized in practical applications for many years because of their excellent electrical properties. However, PZT materials based on Pb($Zr_{0.5}$ $Ti_{0.5}$)O_3 with over 60wt% lead can cause of environmental pollution. Currently the use of PZT materials be tightened up by environmental regulations : the European Union established directives concerning waste electrical and electric equipment (WEEE), restrictions on hazardous substances (RoHS), and end-of-life vehicles (ELV) etc.[1]

Therefore the study on lead-free piezoelectric material has been investigated for replacing PZT materials. Recently, significant progress has been reached in NKN-based ceramics. ($Na_{0.5}$ $K_{0.5}$)NbO_3 piezoelectric ceramics characterized by high piezoelectricity are specially attracting attention as lead-free piezoelectric ceramics. However, since they have serious problems such as high reactivity with water containing K_2O, the volatilization of K_2O and Na_2O during sintering, and difficulty in sintering an elaborate shape, the volatilization of K_2O and Na_2O cause considerable pores, which decrease the electrical properties.[2]

Therefore, this paper introduces an innovative technique that uses NKN thin film to cover NKN-based ceramics to decrease the amount of pores. This technique will characterize the feasibility of using single crystal PZT cubes to enhance the piezoelectric properties of PZT ceramic. Added NKN thin film on NKN-based ceramics tends to be higher piezoelectric coefficient (d_{33}) than NKN-based ceramics prepared by conventional powder processing.

Experimental

NKN ceramics with x=0.40–0.60 were prepared by the conventional solid-state reaction technique, using starting materials of Na_2CO_3 99.8%, K_2CO_3 99.0%, and Nb_2O_5 99.5%. Then, they were weighed according to the stoichiometric ratio, ball mixed for 24 h in methanol, and calcined at 750-950 ℃ for 2 h. The calcined mixture was again ball milled for 24 h and pressed into pellet disks of 20 mm diameter and 2.0 mm thickness. Sintering was carried out at the sintering temperature between 1040 and 1120 ℃ for 2 h.

Precursor solutions were prepared from ethoxide of sodium (CH_3CH_2ONa), potassium (CH_3CH_2OK) and niobium [$(CH_3CH_2O)_5Nb$] (Aldrich). The individual ethoxide of sodium and potassium in 2-MOE were mixed and stirred for 2 h to show a yellow color solution. These chemicals were added to a a calculated amount of niobium ethoxide and then mixed for 2 h. The mixed solution was maintained at 120 ℃, with slow stirring for 2 h. A sticky resinous gel formed after standing for a further 8 h at room temperature. Then the NKN precursor solution was deposited on prepared bulk-type NKN ceramics for decreasing the amount of pores by spin coater in ambient atmosphere at 3000 rpm for 30 s. The process of spin-coating and pyrolysis treatments was repeated two times to achieve a total thickness of about 0.5 μm. Then the pyrolyzed films were annealed at various temperatures from 600 to 900 ℃ for 10 min by direct insert method to form perovskite structures.

For electrical characterization, they were coated with silver paste on the upper and lower surfaces and sintered at 600 ℃

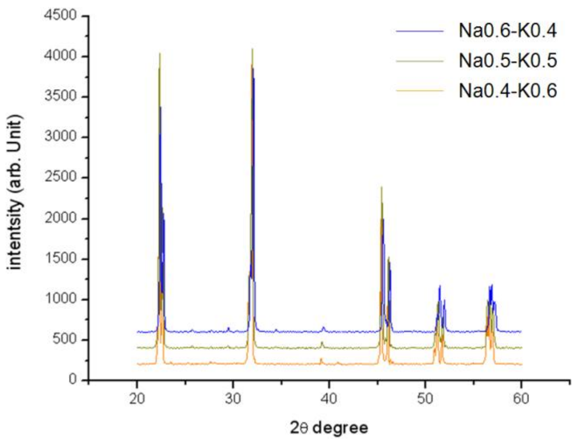

Figure 1 XRD profiles for the (Na_xK_{1-x})NbO_3 ceramics with various x ratio.

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for 30 min. The microstructures were characterized by a scanning electronic microscope (SEM, JEOL Co.). The crystal structure of NKN-based ceramics and thin film were measured by a x-ray diffraction (XRD, Rigaku Co.) at room temperature using Cu-Kα radiation. The bulk density was determined by measuring the mass, the volume and dimensions. For piezoelectric measurements, poling was accomplished in silicon oil bath using a dc power supply under 5.5 kV/mm for 50 min at 120 ℃. The piezoelectric coefficient (d_{33}) was measured with a Piezoelectric d_{33} meter (YE 2730A, Sinocera Piezotronics).

Results and Discussion

Figure 1 typically shows the XRD profiles for the NKN ceramics with different Na/K ratios. It suggests that the single phase of the orthorhombic perovskite structure is formed in the NKN ceramics within the wide compositional range of x=0.40–0.60. In addition, the main diffraction peaks are observed to slightly shift to lower diffraction angles with increasing Na compositions, which could be readily understood by the fact that K^+ has a larger ionic radius than Na^+.

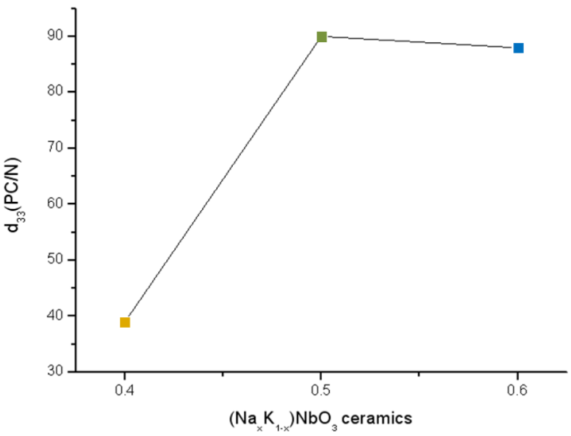

Figure 2 Dependence on piezoelectric coefficient (d_{33}) for the $(Na_xK_{1-x})NbO_3$ ceramics with various x ratio.

Figure 2 describes the alkali compositional dependence of piezoelectric coefficient (d_{33}) measured at room temperature. Obviously, the d_{33} values are almost dependent on the sodium ratio in the compositional range of x=0.40–0.60. For the ceramics with x=0.50, the d_{33} value is 95 pC/N, which is similar with the earlier result of 91 pC/N in the conventionally prepared KNN ceramics.

XRD profiles of the 10% excess of $(Na_{0.5}\ K_{0.5})NbO_3$ thin film are shown in Figure 3. There was no evidence of second phases in the wide sintering temperatures. The NKN film showed a tendency to become a distorted tetragonal structure with increasing sintering temperature.

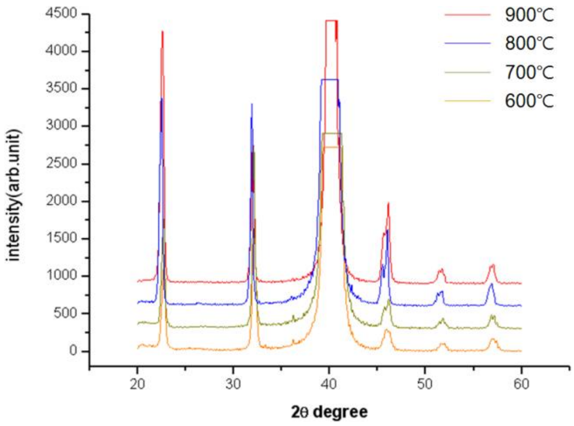

Figure 3 XRD profiles for the 10% excess of $(Na_{0.5}\ K_{0.5})NbO_3$ thin film on $Pt/Ti/SiO_2/Si$ with different sintering temperatures.

Conclusion

Single perovskite phase NKN piezoelectric ceramics with few secondary phases were prepared within a wide range of Na/K ratio. The piezoelectric constants larger than 90 pC/N could be obtained at the regime of high Na/K ratios. Also, crack-free NKN films with a pure perovskite structure were fabricated using sol-gel method that employed ethoxide-based precursors. In addition, the NKN sol-gel surface coating on the prepared NKN ceramics are expected to lead to smooth and stable interfaces, resulting in improved electrical properties. The demonstrated NKN ceramics are very promising for use as eco-friendly piezoelectric devices.

References

1. L. Wu, J. L. Zhang, C. L. Wang, J. C. Li, "Influence of compositional ratio K/Na on physical properties in $(K_xNa_{1-x})NbO_3$ ceramics" J. Appl. Phys. 103, 084116 (2008)
2. Ye-Jing Dai, Xiao-Wen Zhang, Ke-Pi Chen, "Morphotropic phase boundary and electrical properties of $K_xNa_{1-x}NbO$ lead-free ceramics" Appl. Phys. Lett. 94, 042905 (2009)
3. Yong-hyun Lee, Jeong-ho Cho, Byung-ik Kim, Duck-kyun Choi, "Piezoelectric Properties and Densification Based on Control of Volatile Mass of Potassium and Sodium in $(K_{0.5}Na_{0.5})NbO_3$ Ceramics" Jpn. J. Appl. Phys., 47, 4620 (2008)
4. Yirong Lin, Clark Andrews, and Henry A. Sodano, "Enhanced piezoelectric properties of lead zirconate titanate sol-gel derived ceramics using single crystal $PbZr_{0.52}Ti_{0.48}O_3$ cubes" J. Appl. Phys. 108, 064108 (2010)