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Journal of the European Ceramic Society 24 (2004) 1693–1697
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Electrical properties of piezoelectric sodium-potassium niobate

M. Ichiki[a,*], L. Zhang[a], M. Tanaka[b], R. Maeda[a]

[a]Institute of Mechanical System Engineering, National Institute of Advanced Industrial Science and Technology, 1-2 Namiki, Tsukuba, Ibaraki, 305-8564, Japan
[b]Department of Precision Machinery, Nihon University, Funabashi, Chiba, 274-8564, Japan

Abstract

Piezoelectric material is one of the most important components of the micro-electro mechanical system (MEMS). Most piezoelectrics have useful multi-functions for MEMS, e.g. sensor, actuator and transducer. An AFM cantilever, scanning mirror device and pumping system for a micro-chamber, are the typical applications of piezoelectric material on MEMS. Lead-based materials, e.g. lead zirconate titanate and lead lanthanum zirconate titanate, have been most popular among many piezoelectric materials. Recently alkali oxide materials, including potassium sodium niobate, have been given attention in view of their ultrasonic application and also as promising candidates for a piezoelectric non lead-based system. But this material system has been reported difficult to sinter only in the conventional method and it is possible to sinter by use of the hot isostatic press (HIP) method. In this report the synthesis process is, however, limited to the conventional solid state reaction method for the wide use of this material system. Several kinds of impurity doping into the base material is carried out in the sample preparation procedure. The physical, electrical properties and crystal structure of the several kinds of sodium-potassium niobate materials will be shown.

Keywords: Alkali oxide; Electrical properties; Impurities; Perovskite; Powders–solid state reaction

1. Introduction

There has been an increase in the various kinds of micro fabrication technologies for MEMS including device design, film formation, structure and system integration. Ferroelectrics are one of the promising materials, which have piezoelectric, pyroelectric, dielectric, electro optic and ferroelectric properties and are applicable to key components of MEMS including sensing and/or actuation, e.g. printer head, micro pump,[1] micro scanning mirror,[2] atomic force microscopy (AFM) cantilever,[3] ferroelectric non-voltaic memory, surface elastic wave device and infrared sensor. There has been also increasing development of ferroelectric films formation technology for high performance MEMS, in that miniaturization of size and weight, energy-saving of the manufactured device and multi-functional performances are realized simultaneously.

Lead system compounds, including lead zirconate titanate, have been used widely as one of the most popular ferroelectrics. Lead zirconate titanate, which is $Pb(Zr_yTi_z)O_3$ abbreviated as PZT or PZT(Y/Z), where $Y=100y$ and $Z=100z$, is also a ferroelectric solid solution that has wide-ranging material properties which depend on its composition. The crystal structure of PZT system is structurally based on perovskite phase. Such a perovskite film has been formed in use of micro fabrication technologies, e.g., sol-gel process,[4] laser ablation,[5] sputtering[6] and jet-printing deposition.[7] Some compositions of PZT near the morphotropic phase boundary are applicable for micro electro-mechanical system (MEMS) for its high piezoelectric constant, electro-mechanical coupling constant and its related ferroelectric properties.

In view of the environmental point, the accumulation of lead compounds has been developed into a social problem on the earth; e.g. the volatilization of lead during firing process and the final disposal of electronic parts including lead compounds. The exclusion of electronic parts including lead compound has been restricted gradually and will be prohibited by WEEE (Waste Electrical Electronic Equipment) in the EU in the near future. Such electrical parts have to be disposed of after the lead is removed perfectly in future. But it is, in practice, considered to be impossible to collect all lead

* Correponding author. Tel.: +81-298-61-7140; fax: +81-298-61-7169.
E-mail address: ichiki-m@aist.go.jp (M. Ichiki).

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doi:10.1016/S0955-2219(03)00475-8

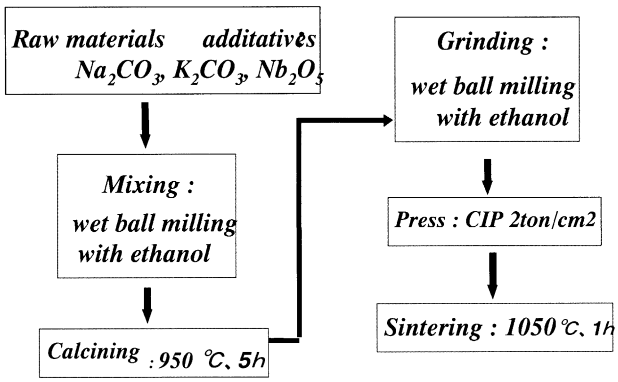


Fig. 1. Sample preparation procedure of NKN.

compounds from disposed electronic devices with the present technology. In electronic parts, it is just in piezoelectric materials that concentration of lead compounds is the highest, and the majority of those are PZT system. This is because PZT system includes lead as its main component at more than 50 wt.%. There is, therefore, a strong demand to develop a substitution of PZT system material.

Several kinds of non-lead based materials have been reported; $BaTiO_3$,[8] (Na, K)NbO_3 (NKN) system,[9–11] (Bi,Na)TiO_3 system,[12,13] Bi-layered structural ferroelectrics (BLSF),[14,15] langasite system.[16] However there is no suitable material that could perfectly substitute PZT, which has many useful properties. At present some kinds of the material are going to be introduced for partial substitution of PZT. Among them NKN system has a similar Curie temperature Tc and high electro-mechanical coupling constant compared with PZT. NKN has two phase transition temperatures as follows; NKN has a Curie temperature at 420 °C and phase transition temperature from orthorhombic to tetragonal at around 200 °C. NKN system is, however, reported to be very difficult to synthesise in the conventional solid-state reaction method. NKN materials have been reported as an application device for tunable microwave.[17] NKN film grown using PLAD on high resistive SiO_2/Si has been successfully prepared and estimated its microwave loss.[17] The obtained results are useful enough for tunable millimeter-wave devices.

This paper will show mainly the material preparation and characteristics of NKN. Some physical properties, including density, dielectric constant, crystal structure and ferroelectric hysteresis, are examined with use of standard estimation method. Impurity addition of some materials to NKN is also investigated.

2. Sample preparation and properties

Sample materials are synthesized in the conventional solid-state reaction method.[18,19] The procedure is summarized in Fig. 1. Raw materials are potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3) and niobium oxide (Nb_2O_5) in the case of NKN. CuO, Ta_2O_5 and Al_2O_3 are used as impurity into NKN. The

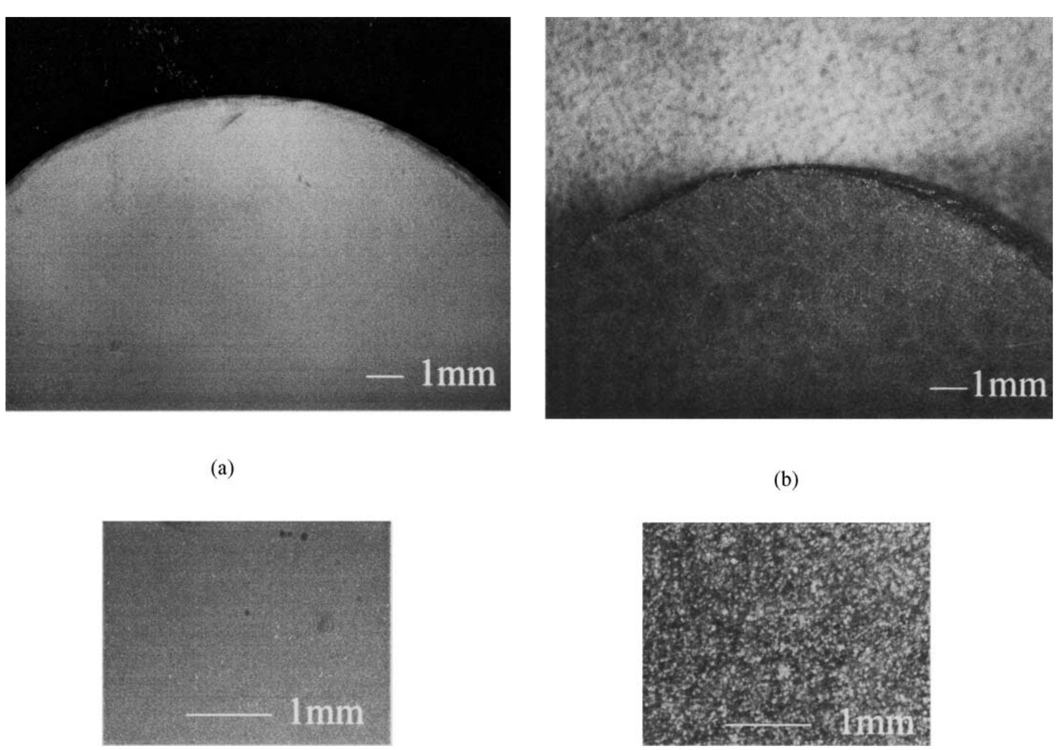
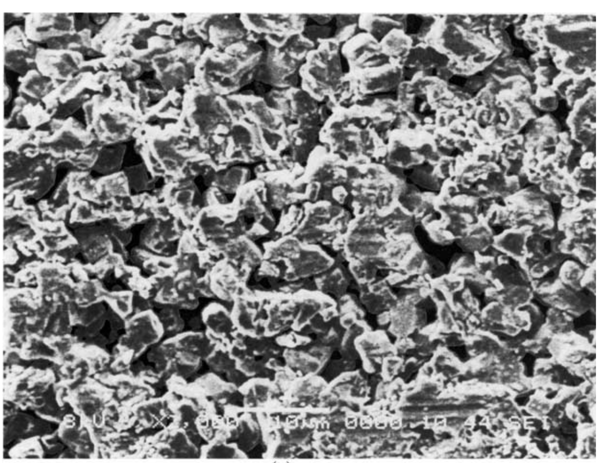


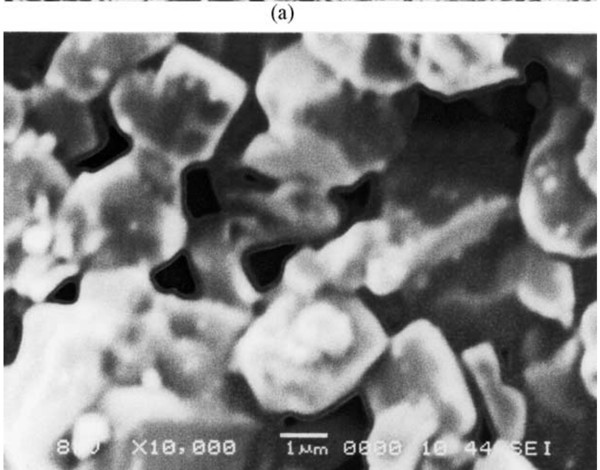
Fig. 2. OM image of NKN (a) and (b) for pure NKN, and (c) and (d) for Cu-doped NKN.

quantity of additional material is 1 mol% to the based material. These powders are weighed precisely for their stoichometric composition in use of electro balance. Excess addition for vapor compensation is not carried out in this production process. The purity of all-raw powders is over 99.9% (3 N) and these particle sizes are under 50 μm. The mixing and grinding process are carried out in wet ball milling with ethanol. Pressed powder was sintered in the air at around 1050 °C for 1 h after cold-isostatic press (CIP) process. The resulting block was cut into 20 mm in diameter and around 4 mm in thickness. Small plate sample, 5 mm×5 mm×0.5 mm (thickness), is also prepared for ferroelectric estimation.

Surface morphology of the prepared sample is observed with use of optical micrograph (OM) and scanning electron microscopy (SEM). Material characteristics of the prepared samples are examined with several kinds of estimation, i.e. density, dielectric constant, crystal structure and ferroelectric hysteresis. Density is examined with use of Archimedes method, in which density is calculated from the weight difference between two conditions e.g. in dry and in water condition. Dielectric constant is obtained by use of LCR meter at 1 kHz frequency. Crystal structure is investigated by X-ray diffraction (XRD). The output intensity of XRD is 1.2 kW which is consists of 40 kV and 30 mA. Ferroelectric hysteresis loop is measured with use of ferroelectric test system (RT6000), which has the maximum applied electrical voltage of 4 kV.



(a)



(b)

Fig. 3. SEM observation of NKN. (b) is enlarged image of (a).

3. Results and discussions

Fig. 2 shows the OM image of surface morphology of NKN and Cu-doped NKN. It shows that NKN has a relatively flat surface, and no large crack and heterogeneous phase. Fig. 3 shows the surface structure on NKN observed in use of SEM. Magnification ratio of (a) is 2000 times and (b) is 10 000 times to its original scale. NKN consists of small particles, which average size 3–5 μm and has a square appearance.

Table 1 is a summary of the experimental results of prepared sample. Some of the impurity effect is examined with use of Cu^{2+}, Ta^{5+} and Al^{3+}. All samples are relatively high density from 4.14 to 4.40 g/cm^3 in spite of using conventional synthesized method. Impurity doping is sensitive to dielectric constant. NKN without impurity has the highest value of both density and dielectric constant. On the other hand NKN with Cu doping has lowest value of density and dielectrics. Fig. 4 shows the crystal structure of pure and impurity doped NKN. All NKN samples have perovskite single phase and little difference among them. (100) (110) (200) (210)

Table 1
Experimental results of synthesized NKN and its doping effect

Material and its impurity	Density (g/cm^3)	Dielectric constant
NKN	4.40	1164
NKN + Cu^{2+}	4.14	576
NKN + Ta^{5+}	4.31	968
NKN + Al^{3+}	4.20	994
NKN[9]	4.25	290
NKN (HIP process)[10]	4.46	420

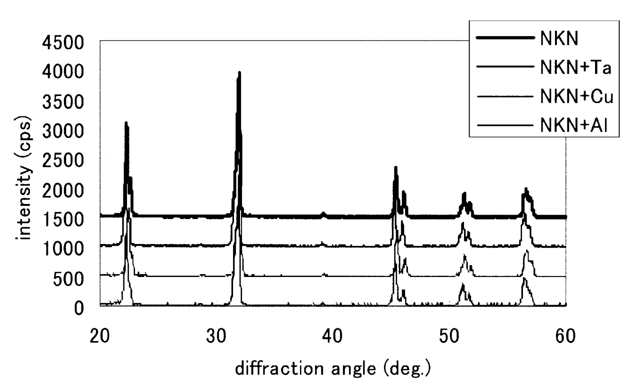


Fig. 4. Crystal structure of prepared pure and doped NKN.

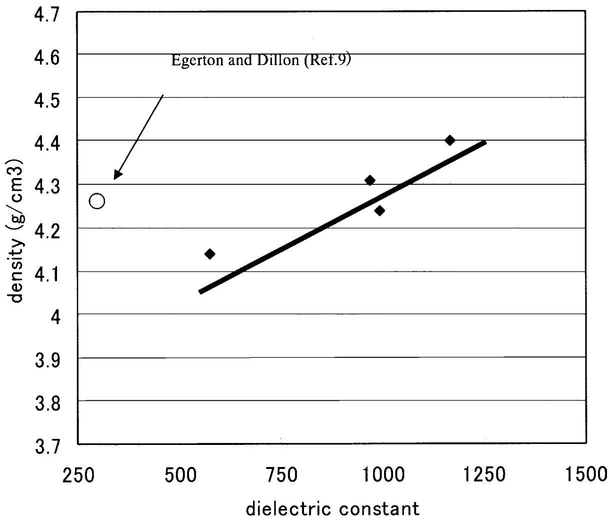


Fig. 5. Relationships between density and dielectric constant.

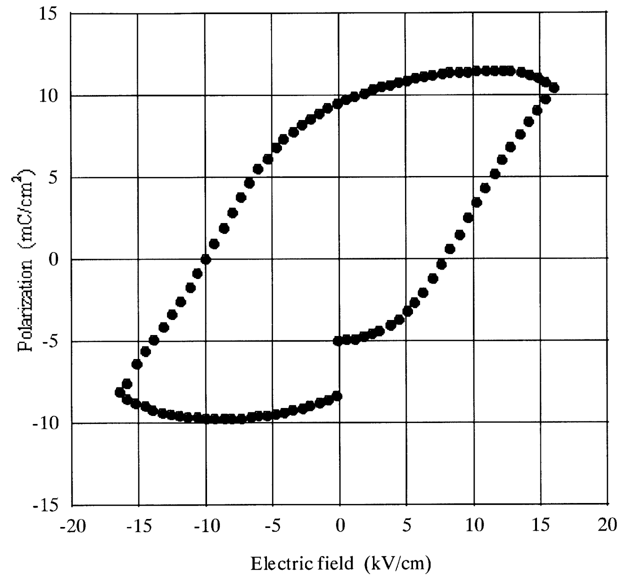


Fig. 6. Ferroelectric hysteresis loop of NKN.

and (211) spectra are observed sharply in diffraction angle from 20 to 60 degrees. There is very weak (111) orientation of crystal face in NKN in all cases.

Pure NKN with no impurity doping material has the highest characteristics of density and dielectric constant. A 1 mol% addition of Cu, Ta and Al to the NKN is not effective for the improvement of dense synthesis and also dielectric constant. The prepared NKN has high density and dielectric constant compared with a previous report.[9] The density on NKN (4.40 g/cm^3) is almost the same level with NKN with use of HIP process (4.46 g/cm^3).[11] These improvements of dielectric constant could be due to synthesis process, in particular heat treatment and grinding process. The sintering temperature and time of present and previous work[9] is almost the same. On the other hand the calcination time (5 h) is shorter than that of the previous (16 h).[9] CIP process is also introduced before sintering in addition to heat condition. It takes much more time for grinding in the present work compared with previous work.[9] The pre-sintered powder of present work could be, therefore, much more fine. By the way there is a linear relationship between density and dielectric constant, which is shown in Fig. 5. If the denser sample can be synthesized, high dielectric NKN will be realized. Impurity addition only has a disadvantage in the present condition and materials. On the other hand suitable processing condition can be obtained in case of the pure NKN. Fig. 6 is ferroelectric hysteresis loop of NKN without impurity. The measurement is carried out with high voltage mode (from 63 V to 4 kV). Ferroelectric measurement is carried out with applied voltage of 500 V. NKN shows the typical ferroelectric polarization reversal. Remanent polarization Pr is 8.9 μm/cm^2 (average value) and coercive electric field Ec is 9.0 kV/cm (average value). These values are same order and within few times compared with previous work[11]. Ferroelectric property is confirmed from Fig. 6. But it is necessary to make many more investigations in order to obtain the suitable poling conditions. A high dense sample of NKN can be synthesized even by use of the conventional method in present work. More improvement of process conditions will lead to the development of wider use of NKN.

4. Summary

Piezoelectric alkali oxide ceramics NKN is investigated in view of the material preparation and some physical properties. Density of synthesized NKN is high enough compared with NKN with use of HIP process. Dielectric constant is estimated in use of LCR meter at 1 kHz. Crystalline structure is obtained in use of XRD. Dielectrics and density have linear relationships. It shows that NKN has a relatively flat surface, and no large crack and heterogeneous phase. A ferroelectric property of NKN is confirmed through the P–E hysteresis measurement.

Acknowledgements

The authors thank Ms. K. Tanaka (AIST) for sample preparation and Ms. T. Imai (AIST) for manuscript preparation. The authors also thank Dr. Y. Tsutsui (AIST) for their encouragement with this work.

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