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Sensors and Actuators A 136 (2007) 267–272
SENSORS AND ACTUATORS A PHYSICAL
www.elsevier.com/locate/sna

Properties of $(Na_{0.5}K_{0.5})NbO_3$–$SrTiO_3$ based lead-free ceramics and surface acoustic wave devices

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Received 22 June 2006; received in revised form 26 September 2006; accepted 6 November 2006
Available online 4 December 2006

Abstract

Lead-free $(1-x)[(Na_{0.5}K_{0.5})NbO_3]$–$xSrTiO_3$ ceramics, where x = 0–3 mol%, have been prepared by the conventional mixed oxide method in this paper. All of the $SrTiO_3$ doped $(Na_{0.5}K_{0.5})NbO_3$ specimens do not deliquesce as exposed to water for a long time. The samples are characterized by X-ray diffraction analysis, scanning electron microscopy, and atomic force microscopy measurements. The dielectric, piezoelectric and ferroelectric properties are also investigated. Our results show that the addition of $SrTiO_3$ is very effective in preventing the deliquescence and in improving the electric properties of $(Na_{0.5}K_{0.5})NbO_3$ ceramics. Finally, surface acoustic wave devices based on lead-free ceramics have been successfully fabricated and their characterization is presented.

Keywords: NKN; STO; Lead-free; Ceramics; SAW

1. Introduction

Single crystals and thin films for piezoelectric applications are generally produced by special techniques, requiring increased process optimization and high cost. Modified ceramics have good potential due to their lower processing cost and ability to facilitate a desirable combination of properties, such as high surface phase velocity, electromechanical coupling coefficient (k^2) and low temperature coefficient of frequency (TCF). Lead oxide (PbO) based ceramics have been widely investigated and used for transducers, piezoelectric actuators, surface acoustic wave (SAW) filters and sensors because of their excellent piezoelectric properties [1,2]. We have reported many researches about modified lead titanate (PT) and lead zirconate titanate (PZT) ceramics used for SAW applications [3,4]. However, high volatilization of PbO may pollute alternative lead-free material during firing process, and its toxicity can contaminate the environment and damage human health. With the raise of environmental consciousness, therefore, it is the present tendency to develop excellent lead-free materials replacing Pb-based piezoelectric ceramics.

Sodium potassium niobate ($Na_xK_{1-x}NbO_3$, NKN) ceramic is an attractive material as a result of its high k^2 and high phase transition temperature ($T_c \sim 420\,^{\circ}C$), especially near the morphotropic phase boundary (MPB) [5]. It has received a lot of attention and been thoroughly investigated [6,7]. Nevertheless, dense NKN ceramics are difficultly obtained since their phase stability is limited to 1140 °C close to the melting point [8]. Moreover, they would deliquesce once exposed to humidity due to the formation of extra phases. The main problem is the volatilization of potassium oxide (K_2O) at 800 °C making the stoichiometry difficult to control. Oxygen deficiency has been another problem in the preparation, which results from high-temperature processing and gives rise to electronic conductivity [9]. Many researchers used hot pressing or spark plasma sintering (SPS) techniques to yield better quality ceramics [10]. Recently, an efficient solution to improve foregoing problems is realized by utilizing some additives in NKN ceramics. Tashiro et al. [11] have used two-stage mixing method to obtain (K, Na, Pb)NbO_3 ceramics; however, the incorporation of PbO damages lead-free material. Park et al. [12] reported the addition of ZnO was effective in both improving the piezoelectric properties

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doi:10.1016/j.sna.2006.11.002

and preventing the deliquescence of NKN ceramics. The relaxorlike dielectric properties of $Na_{0.5}K_{0.5}NbO_3$–$SrTiO_3$ system have been investigated by Bobnar et al. [13,14] and Guo et al. [8,13–17] reported the structure and electrical properties of NKN ceramics by doping $SrTiO_3$, $BaTiO_3$, $LiNbO_3$ and $LiTaO_3$, respectively.

We have investigated the lead-free materials of (Li, Na, K)NbO_3 based perovskite system [9,18]. At present, the aim of our work is not only to synthesize NKN–STO ceramics by the conventional mixed oxide method and measure their properties, but also to fabricate surface acoustic wave (SAW) devices further.

2. Experimental

The raw materials of $(1-x)[(Na_{0.5}K_{0.5})NbO_3]$–$xSrTiO_3$ samples processed by a conventional mixed oxide method were pure reagent K_2CO_3, Na_2CO_3, Nb_2O_5, $SrCO_3$ and TiO_2 powders (>99.0% purity). First, K_2CO_3, Na_2CO_3 and Nb_2O_5 powders were ball-milled in polyethylene jar for 10 h with ZrO_2 balls using ethanol as medium. The same procedure was applied to ball-mill $SrCO_3$ and TiO_2 powders. Then, these slurries were separately dried and calcined at 950 °C in air for 10 h, respectively. After pulverization and weighting according to the stoichiometric formula, the two powder batches were ball-milled together. The resulting slurry was dried, calcined and pulverized sequentially. These powders, milled with 8 wt.% of PVA aqueous solution, were pressed into a disk of 12 mm diameter, at pressure of 25 kg/cm^2 and subsequently sintered in air with a heating rate of 5 °C/min at 1060–1220 °C, depending on the $SrTiO_3$ contents. A K_2O rich atmosphere was maintained with NKN–STO powder to minimize the potassium loss during sintering.

The crystallographic study was confirmed by X-ray diffraction (XRD) using Cu Kα ($\lambda = 0.154$ nm) radiation with a Seimens D-5000 diffractometer operated at 40 kV and 40 mA. The microstructure was observed by field emission scanning electron microscopy (FESEM) with a Hitachi S-4100 microscope. Bulk densities were measured by the Archimedes method using distilled water as medium. The dielectric (measured from 30 °C to 520 °C at 1 kHz) and piezoelectric properties were measured with an HP 4294A precision impedance analyzer. To measure the electrical properties, silver paste was painted on both sides of the samples to form electrodes, and then subsequently fired at 150 °C for 20 min. After that, samples were poled under 40 kV/cm dc field at 150 °C in a silicone oil bath for 20 min. The electromechanical coupling factor in thickness (k_t) and planar (k_p) mode was calculated from the resonance–antiresonance method. Ferroelectric hysteresis loops (P–E) were obtained under 50 kV/cm ac field at 60 Hz by a modified Sawyer–Tower circuit [19]. The samples were also submerged in 150 °C silicon oil to prevent arcing. In order to fabricate the SAW devices, the pellets were polished to a mirror finish on one side. Then, the interdigital transducer (IDT) electrodes, made of 200 nm aluminum by thermal evaporation method, were patterned onto the polished surface using the lift-off photolithographic process. The surface roughness of polished ceramics was examined by atomic force microscopy (AFM) with a NT-MDT P7LS microscope using the tapping mode. The device characterization was measured with an HP 8714ES network analyzer (Agilent Technologies, Palo Alto, CA).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the $(1-x)$NKN–xSTO ceramics. The NKN–STO ceramics are composed of orthorhombic NKN and cubic STO [13]. The main identified phase matches the JCPDS 742454 of orthorhombic $NaNbO_3$ and the JCPDS 710946 of orthorhombic $KNbO_3$, and the results reveal that the orthorhombic structure is preserved. As increasing the STO content, the peaks shift toward a higher angle slightly because the host Na^+ (ionic radius 1.39 Å) and K^+ (1.64 Å) are replaced by doped Sr^{2+} (1.44 Å) and Nb^{5+} (0.64 Å) is replaced by Ti^{4+} (0.61 Å), respectively [13]. Kosec et al. [13] reported when STO excesses 25 mol%, the STO peak would clearly appear. And Guo et al. [8] indicated with $x > 3$ mol%, the structure will change from orthorhombic to tetragonal at room temperature. Therefore, we focus our research on the characterization with the STO dopants less than 3 mol%.

Fig. 2 shows the SEM images of $(1-x)$NKN–xSTO ceramics. The sintering temperature increases with the addition of STO resulting from the melting point of NKN at 1130 ± 10 °C and STO at 1910 °C [13]. It is distinct that the grain size becomes smaller gradually, and the values of average gain size (D) are listed in Table 1. In addition, the bulk densities (ρ) of the doped ceramics reach up to 4.4–4.5 g/cm^3 (the theoretical density is 4.51 g/cm^3) [7], equivalent to the relative densities (ρ_r) 97–99%. None of the doped samples exhibit deliquescence against water, indicating that the STO addition can reduce the formation of unstable secondary phases enhancing the stability.

Antiferroelectric $NaNbO_3$ possesses many phase transitions in wide temperature range (−100–643 °C), but ferroelectric $KNbO_3$ combined with $NaNbO_3$ produces a new ferroelectric phase and displays two phase transitions around 200 °C and 420 °C, corresponding to the transition temperatures of orthorhombic to tetragonal and tetragonal (ferroelectric) to cubic

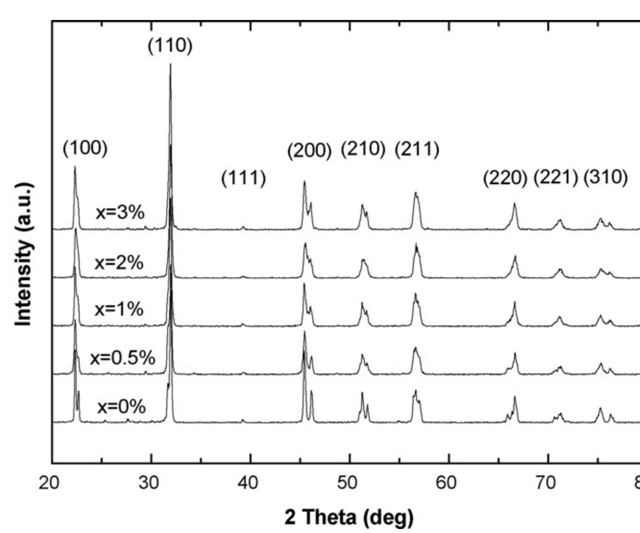

Fig. 1. X-ray diffraction patterns of the $(1-x)$NKN–xSTO ceramics.