Preparation and Characterization of (Na0.48K0.52)(Nb0.90Sb0.10)O3 Lead-free Ferroelectric Ceramics With MnO2 Sintering Aids

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Abstract: Lead-free (Na0.48K0.52)(Nb0.90Sb0.10)O3-xwt% MnO2(x=0.2, 0.8) ferroelectric ceramics were prepared by solid state sintering methods with MnO2 aids. The X-ray diffraction analysis revealed that the (020) peak shifts to higher angles at x=0.8 suggested that the lattice parameters decreased. The reason is that the Mn4+ may entering the Nb5+ sites. The largest maximum strain Smax was 0.13% under 40 kV/cm at room temperature.

1. Introduction

Pb(Zr1-xTix)O3 (PZT) based-ferroelectric ceramics can be widely used in actuators, ultrasonic motors and transducers[1]. Due to the toxicity of lead, Na0.5Bi0.5TiO3 and (K,Na)NbO3 based lead-free ceramics were extensively explored[2-5]. Among them, KNN-based ceramics have been deemed as potential candidates according to relatively good comprehensive performance, such as large strain (~0.32 %) under low electric field (~4 kV/mm) and high Curie temperature TC[4-5]. It was surprising that Jian Fu et al. reported (Na0.52K0.48)(Nb0.88Sb0.12)O3 ceramic generating a high strain value (~0.32%) under 4 kV/mm electric field with CuO sintering aid. The reason was that a low field phase transition contribution (~0.2%) and the enhanced domain switching contribution (~0.12%)[6]. The (Na1-xKx)(Nb1-ySby)O3+z mol% MnO2 ceramics were formed, but the strain of them have not been researched, and the result showed that MnO2 doping and Sb substitution lead to significant improvements in ferroelectric[7].

In this work, we developed the (Na0.48K0.52)(Nb0.90Sb0.10)O3+x wt% MnO2 (x=0.2, 0.8) ceramics in order to attain a low hysteresis and high strain. The result showed that the KNNS ceramics with R phase exhibit low strain. The largest maximum strain Smax was 0.13% under 40 kV/cm at room temperature at x=0.8.

2. Experimental

The (Na0.48K0.52)(Nb0.90Sb0.10)O3+x wt% MnO2 (x=0.2, 0.8) (KNNS0.10-xMn) ferroelectric ceramics were synthesized via the conventional solid-state process. The raw materials were K2CO3 (99.0%), Nb2O5 (99.5%), Sb2O3 (99.5%), Na2CO3 (99.8%), and MnO2 (97.5%). The raw materials were weighted and then were ball milled for 12 h in teflon-jar with ZrO2 balls and alcohol medium. The powders after drying were calcined at 850 °C for 5 h in air. Later, the calcined powders were mixed with 7 wt% polyvinyl alcohol (PVA) as the binder, and then pressed into green disks under a pressure of 20 MPa. After burning off the PVA under 600 °C for 30 min. The pellets were sintered at 1140 °C for 3 h in the calcined powder with the same composition in order to reduce the evaporation of...
potassium and sodium elements. After polishing the sintered pellets into 0.5 mm, silver paste was attached on both sides of pellets and then they were fired at 750 °C for 30 min.

The crystal structure of the ceramics were measured by X-ray diffraction at a scanning rate of 5°/min in the range of 20° from 20° to 60°(dx2700, China). The fracture microstructural observations of the ceramics were performed by scanning electron microscopy (SEM, JSM-6510, JEOL, Japan) thermally etched at 940 °C for 30 min. The electric-field-induced polarization hysteresis loops, bipolar strain curves were measured at 1 Hz in a silicone oil bath using an instrument (Precision Premier II, Radiant Technology, USA).

3. Results and discussion

Fig. 1. XRD patterns of the KNNS0.10-xMn ceramics

Fig. 1 shows the X-ray diffraction patterns of KNNS0.1-xMn ceramics measured at room temperature. The results suggest that the MnO₂ dopants completely diffuse into the KNN matrix, and all of the obtained ceramics show a typical perovskite structure in Fig. 1(a). To characterize the evolution of the phase composition of the ceramics, the magnified XRD patterns with 2θ between 45° and 47° are plotted in Fig. 1(b). It shows only a single (020) peak indicating R phase[8]. The (020) peak of KNNS0.1-0.2Mn ceramic is in agreement with the KNNS0.1 ceramic[8]. The (020) peak shifts to higher angles at x=0.8 suggests that the lattice parameters decrease. Some of the Mn⁴⁺ (0.67 Å) ions are reduced to Mn³⁺ (0.66 Å) ions stably existing at high temperatures at 1100~1200 °C[9-10]. Part of Mn³⁺ and Mn⁴⁺ ions may enter the Nb⁵⁺ (0.78 Å) sites (acceptor-type doping) according to similar valence state[11]. The formation of oxygen vacancies during process of the entering generates the lattice parameters decrease[12].

The scanning electron microscopy micrographs of (1-x)KNNS0.10-xMn samples are shown in Fig. 2. All of the samples exhibit a dense microstructure. The grain size of KNNS0.10-0.2Mn ceramics is homogeneous (see Fig. 2(a)). However, the grain size of KNNS0.10-0.8Mn ceramics (see Fig. 2(c)) precipitate a clear bimodal distribution, with many small grains being located at the boundaries of coarse grains. The coarse grains in KNNS0.10-0.8Mn ceramics have square or tetragonal cross sections. As reported in previous works, an increase in grain growth takes place with a liquid phase to enhance atomic mobility[13-14]. It is thought that the low melting point MnO₂ are formed liquid phase. The grains are indistinct in fracture surface of KNNS0.10-0.8Mn ceramics (see Fig.2(d))through thermal etching, it may be KNNS0.10-0.8Mn with low-melting-point, while KNNS0.10-0.2Mn ceramics exhibit clear grain with high-melting-point.
Fig. 2. SEM images of the KNNS$_{0.10-x}$Mn ceramics with different compositions:
(a)-(b) $x=0.2$; (c)-(d) $x=0.8$.

Fig. 3 shows the P-E loops and S-E loops of KNNS$_{0.10-x}$Mn ceramics at 40 kV/cm. The S-E loop of the ceramics has a butterfly shape with an asymmetric feature, owing to the presence of an internal bias field. This is a common feature in lead-free oxides caused by being sintered at higher temperature and longer time\cite{15}. The S-E loop presents ferroelectric characteristics (see Fig. 3(b)). The ceramics at $x=0.8$ exhibit higher strain and negative strain values (Sneg) than it of ceramics at $x=0.2$. The phenomenon is consistent with the ferroelectric behavior of the ceramics (see Fig. 3(a)). The reason is that the use of the MnO$_2$ sintering aid can improve the ferroelectric properties of the ceramics\cite{17}. Accordingly, for the NKNSb-0.8Mn ceramic, $P_r$ reaches a value of 14.7 $\mu$C/cm$^2$ while $E_c$ has value of 5.9 kV/cm. The KNNS$_{0.10}$-0.8Mn ceramics exhibit 38% hysteretic ($H = \Delta S/S_{max}$) estimated higher than KNNS$_{0.10}$\cite{8}. 
4. Conclusion

We developed the (Na_{0.48}K_{0.52})(Nb_{0.90}Sb_{0.10})O_3 + x wt% MnO_2 (x=0.2, 0.8) ceramics. The result showed that the KNNS ceramics with R phase exhibit low strain. The ceramics at x=0.8 present ferroelectric behavior than it at x=0.2, since Mn^{4+} ions may enter the Nb^{5+} sites. XRD patterns of the KNNS_{0.10-0.8}Mn ceramics reflect the reason.

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