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Structural dependence of piezoelectric, dielectric and ferroelectric properties of $K_{0.5}Na_{0.5}(Nb_{1-2x/5}Cu_x)O_3$ lead-free ceramics with high Q_m

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ABSTRACT

$(K_{0.5}Na_{0.5})(Nb_{1-2x/5}Cu_x)O_3$ (abbreviated as KNNC, $x = 0–2\%$) lead-free ceramics were synthetized by the solid state solution method. Pure perovskite phase with orthorhombic symmetry was observed. The evolution of the structure of KNNC was examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman scattering spectra techniques. Our results revealed that, defect dipoles $(Cu_{Nb}'''-V_O^{\bullet\bullet})'$ were formed and provided a restoring force to reverse the switched polarization, which resulted in double $P–E$ hysteresis loops in KNNC with Cu doping at $x = 0.75\%$ and 1%. However, non-polar defect complex $(V_O^{\bullet\bullet}-Cu_{Nb}'''-V_O^{\bullet\bullet})^{\bullet}$ caused a lattice shrinkage and the observed square shaped $P–E$ loops in KNNC ceramics under high doping levels ($x > 1\%$).

1. Introduction

In the past decade, perovskite potassium sodium niobate $(K,Na)NbO_3$ (KNN) family has attracted much attention as a promising candidate of lead-free piezoelectric materials. Good piezoelectric properties, such as a large piezoelectric constant, $d_{33} = 416$ pC/N, and a large planar coupling factor, $k_p = 0.61$, have been observed in textured $K_{0.5}Na_{0.5}NbO_3$-based ceramics [1]. Since then, a number of studies have been carried out to develop "soft" and/or "hard" KNN-based piezoelectric ceramics for various practical applications.

Generally, soft piezoelectrics exhibit square hysteresis, large dielectric constant, large electromechanical coupling factor k, high piezoelectric constant d_{33} and high dielectric losses $\tan\delta$, while hard piezoelectrics have lower k, d_{33}, $\tan\delta$ and high mechanical quality factor Q_m [2]. Actually, hard piezoelectrics with high Q_m are essentially required by many high-power and high-voltage devices, such as ultrasonic motors and transformers [3]. Although the mechanism of softening and hardening of the piezoelectric properties is still not clearly understood, perovskite piezoelectric ceramics can generally be hardened if doped with acceptor-type dopants, such as $Fe^{3+, 2+}$ substituted onto Zr^{4+}/Ti^{4+} sites [4,5]. It has been reported that the addition of small amount of Cu compounds, e.g. CuO [6–8], $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ [10], and $K_4CuNb_8O_{23}$ [11], where Cu^{2+} substitutes onto Nb^{5+} site as an acceptor, were effective in improving the Q_m of KNN ceramics. For KNN-based lead-free ceramics, a high mechanical quality factor ($Q_m = 2500$) has been reported in CuO-doped $K_{0.5}Na_{0.5}NbO_3$ [6], which is much higher than that of lead zirconium titanate (PZT).

In this paper, we present results of an experimental study on the structure and property evolution of the Cu-substituted $K_{0.5}Na_{0.5}NbO_3$ ceramics with high mechanical quality factor. Typically, there are three types of formula for Cu doping: (1) $K_{0.5}Na_{0.5}NbO_3–x\%CuO$, where CuO is directly mixed with KNN, (2) $K_{0.5}Na_{0.5}(Nb_{1-2x/5}Cu_x)O_3$, and (3) $K_{0.5}Na_{0.5}(Nb_{1-x}Cu_x)O_{3-\delta}$. In the latter two types, Nb^{5+} is substituted by Cu^{2+}. However, only the first and the third dopant type were reported in the literatures [6–9]. We, instead, focused on the second type formula in this work and prepared the ceramic samples by conventional solid state reaction process. The structural dependence of the ferroelectric, piezoelectric and dielectric properties was investigated and discussed in details.

2. Experimental

Ceramics with nominal composition $(K_{0.5}Na_{0.5})(Nb_{1-2x/5}Cu_x)O_3$ (abbreviated as KNNC, $x = 0$, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00%, respectively,) were synthetized by conventional solid state solution process. Analytical reagents of K_2CO_3, Na_2CO_3,

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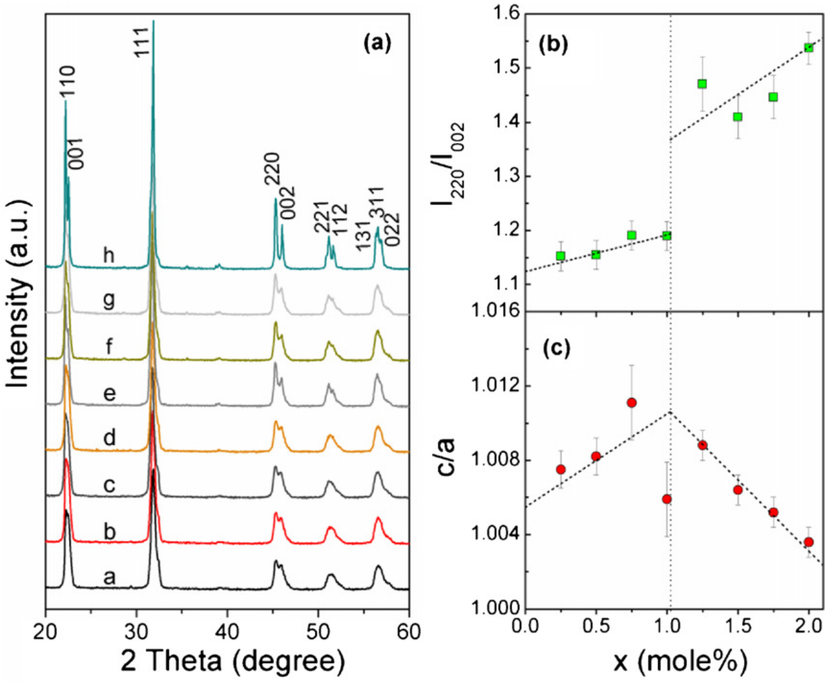

Fig. 1. (a) XRD patterns of the KNNC ceramics, (b) intensity ratio of diffraction peak $I_{(2\,2\,0)}/I_{(0\,0\,2)}$ and (c) evolution of the lattice parameter ratio c/a with $x = 0.25$–2.0%.

Nb_2O_5, and CuO were mixed by a planetary ball mill using anhydrous ethanol as the media, and then calcined at 850 °C for 2.5 h. After calcination, the mixture was ball milled again and then pressed into disks of 15 mm in diameter and 1.5 mm in thickness under a cold-isostatic pressure of 300 MPa for 90 s. These Cu-doped green pallets were sintered at 1070 °C for 4 h, while pure KNN pellets were sintered at 1090 °C for 4 h, and all in a K/Na rich ambient.

The crystalline structure of KNNC ceramics was determined by X-ray diffraction (XRD; D/Max2550VB+/PC, Rigaku Co., Tokyo, Japan) with Cu K_α radiation on powder samples. The structure of KNNC ceramics was studied by scanning electron microscope (SEM; 6700F, JEOL, Tokyo, Japan). Micro-Raman spectrum measurements were performed on a Raman spectrometer under backscattering geometry (HR800, Jobin Yvon, Paris, France). An Argon ion laser was used as the excitation source with an output powder of 15 mW at 488 nm.

Top and bottom electrodes were made by coating silver paint on both sides of the sintered and polished ceramic disks, followed by annealing at 550 °C for 20 min. For piezoelectric measurement, the ceramics were poled under a dc field of 3 kV/mm at 130 °C in a silicone oil bath for 20 min. Temperature dependences of the complex dielectric permittivity as well as the dc conductivity of KNNC ceramics were measured using a precision impedance analyzer (4294A, Agilent, Santa Clara, CA, USA) and a high-resistance meter (4339B, Agilent, Santa Clara, CA, USA) in a temperature range of 25–480 °C controlled by a program controller (TP-95, Linkam, Surrey, UK). The ferroelectric hysteresis loops (P–E loops) as well as electrostrictive strains (S–E loops) were examined by using a standard ferroelectric analyzer (TF-2000, aixACCT, Aachen, Germany). The piezoelectric coefficient (d_{33}) was measured by a piezoelectric d-meter (ZJ-4NA, Institute of Acoustics, Chinese Academy of Science, Beijing, China). The electromechanical coupling factor (k_p) and the mechanical quality factor (Q_m) were obtained by the resonance method according to the IEEE Standard 176 using a precision impedance analyzer (4294A, Agilent, Santa Clara, CA, USA).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the KNNC samples. It can be seen that all the KNNC ceramics present a pure perovskite phase at room temperature and no secondary phase can be detected. The crystalline structure was orthorhombic (JCPDS-32-0822), featured by the splitting of the (1 1 0)/(0 0 1) and (2 2 0)/(0 0 2) peaks with higher intensity counts for the (1 1 0) and (2 2 0) reflections. With increasing Cu^{2+} concentration, the splitting of (1 1 0)/(0 0 1) and (2 2 0)/(0 0 2) orthorhombic reflections became more significant, implying that the dopant was incorporated into the perovskite lattice to form a solid solution. It can be concluded that the solubility limit of Cu in KNN is more than 2%.

Fig. 1(b) and (c) presents the evolution of the intensity ratio of the two characteristic diffraction peaks $I_{(2\,2\,0)}/I_{(0\,0\,2)}$ and the lattice parameters ratio c/a. The c/a ratio, as well as the unit-cell volume V, increases with increasing amount of Cu^{2+} for $x < 1\%$. They start to decrease with Cu increasing to higher concentration. The evolution in c/a and V suggests a transition behavior in the incorporation of

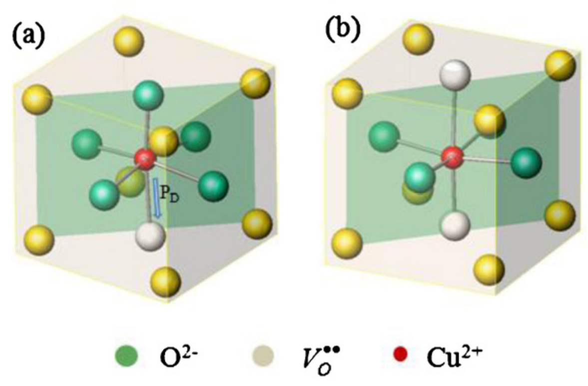

Fig. 2. Schematic representation of the defect structure in KNNC: (a) $(Cu_{Nb}'''-V_O^{\bullet\bullet})'$ with a lower Cu concentration and (b) $(V_O^{\bullet\bullet}-Cu_{Nb}'''-V_O^{\bullet\bullet})^{\bullet}$ with a higher Cu concentration. P_D is the polarization associated with the $(Cu_{Nb}'''-V_O^{\bullet\bullet})'$ complex.