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Ferroelectric Bi(Na,K)TiO_3-based materials for lead-free piezoelectrics

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Abstract

A lead-free piezoelectric materials of Cu-doped $Bi_{0.5}(Na_{0.79}K_{0.21})TiO_3$ (BNKT–*x*Cu) have been synthesized using a conventional ceramic process. The addition of a small amount of CuO increased the d_{33}-value up to 156 pC/N for BNKT–0.6Cu, while the large amout of CuO (>0.6 mol%) decreased it down to 80 pC/N for BNKT–2.0CuO. However, it was found that the mechanical quality factor (Q_m) was not increased until the CuO content was less then 0.6 mol%, but it was significantly increased when CuO exceeded 0.6 mol%, resulting from the development of small defect. The inverse dielectric permittivity followed the Curie–Weiss law above the deviation temperature ($T_{dev.}$) at high temperatures for the BNKT–*x*Cu. The thermal hysteresis for BNKT–*x*Cu confirmed that with an increase in the amount of CuO addition, the variation of the temperature in dielectric permittivity maximum (T_m) increased gradually while the depolarization temperature (T_d) decreased during the heating and the cooling cycles.

Keywords: A. Sintering; C. Dielectric properties; C. Piezoelectric properties; D. Perovskites

1. Introduction

Piezoelectric Pb(Zr,Ti)O_3 (PZT) has dominated the commercial market for electromechanical devices because of its superior piezoelectric and electromechanical properties near the morphotropic phase boundary composition [1]. However, upcoming environmental regulations in Europe may eliminate the use of lead-based materials because of their toxicity, such as the waste electrical and electronic equipment (WEEE) directive and the restriction of hazardous substances (RoHS). Therefore, it is desired that alternative lead-free piezoelectric systems analogous to the PZT will be found [2].

As new materials for replacing the PZT, lead-free piezoelectric materials have been attracting considerable. Recent reports on lead-free piezo-ceramics can be categorized into two main perovskite families: (K,Na)NbO_3 (KNN) and (Na,Bi)-TiO_3 (NBT)- or (K,Bi)TiO_3 (KBT)-based materials [3–5]. The KNN was first reported in the late 1950s with a piezoelectric coefficient (d_{33}) of the order of 80 pC/N with a Curie temperature of 420 °C and orthorhombic to tetragonal transition at ∼195 °C [5]. In addition, many works using various additives and optimum processing techniques have been reported for the improvement of the mechanical quality factor and the enhancement of the d_{33} by shifting the PPT downward to near room temperature. Even though the NBT–KBT system exhibited relatively high piezoelectric and dielectric properties near the MPB, on the other hand, there have been few studies on the effects of doping on this system [6].

In this study, Cu-doped Bi(Na,K)TiO_3 (BNKT–*x*Cu) was synthesized and the effect of CuO doping was investigated in relation to the piezoelectric properties and the relaxor behavior as a function of temperature. It was hoped that such investigations would provide a better understanding of relaxor behavior in ferroelectrics.

2. Experimental

Conventional ceramic processing was used for preparing the $Bi_{0.5}(Na_{0.79}K_{0.21})_{0.5}TiO_3$ (BNKT) solid–solution system. All the samples were fabricated with high-purity Aldrich Chemical oxide powders(>99.5%): Bi_2O_3, Na_2CO_3, K_2CO_3, and TiO_2. The BNKT powders were stoichiometrically weighed and mixed for 24 h in an anhydrous ethanol solution with stabilized zirconia media. These mixtures were then dried and calcined at

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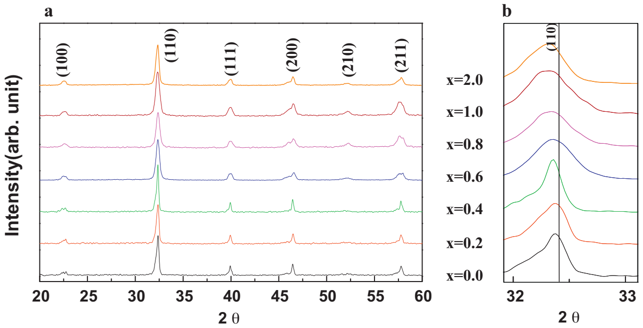

Fig. 1. XRD patterns for the BNKT–*x*Cu with $0.0\ \text{mol\%} \leq x \leq 2.0\ \text{mol\%}$ sintered at 1125 °C for 2 h. 2θ degrees (a) from 20° to 60° and (b) from 32° to 33°, respectively.

800 °C for 2. The CuO (99.0%) was added to the calcined BNKT powders, remixed, and then sintered at 1125 °C for 2 h.

The phase purity and the microstructure were examined by X-ray powder diffraction (PAD V diffractometer, Cupertino, CA) and scanning electron microscopy (S-3500N, Hitachi). The densities of the sintered samples were measured by the Archimedes method, which were found to be >96% of theoretical density. The dielectric permittivity and the dielectric loss were determined using an impedance analyzer (4294A, Agilent Tech. Ltd., Japan).

3. Results and discussion

Fig. 1 shows the XRD patterns for the BNKT–*x*Cu. All prepared BNKT had perovskite structures and no secondary phases related to CuO (Fig. 1(a)). Fig. 1(b) shows the enlarged diffraction patterns from 31.8° to 33°. As a small amount of CuO addition (<0.4 mol%), the diffraction peaks of BNKT were not changed by the CuO content. However, with a further increase in the CuO addition ($x \geq 0.4$ mol%), peaks of BNKT were found to shift toward a lower angle; this shift could be attributed to the substitution of Cu^{2+} for Ti^{4+}, leading to the creation of an oxygen vacancy. Because the oxygen ions in the perovskite structure came into contact with the metal ions, it was found that a small amount of oxygen vacancies could be formed without any secondary phase [7]. Therefore, it suggests that oxygen vacancies and the difference in the ionic radius between Cu^{2+} and Ti^{4+} in the B-site induced the structural distortion and the change in the lattice volume of BNKT.

Fig. 2 illustrated piezoelectric properties for BNKT as a function of the CuO content. In Fig. 2(a), the d_{33} for pure BNKT was 144 pC/N, while the dielectric permittivity (ε_r) was 1237. When a small amount of CuO was added, both the d_{33} and ε_r were slightly increased and saturated until 1.0 mol% of CuO. With a further increase in the amount of CuO (>1.0 mol%), they were decreased suddenly, which is probably due to the large amount of the secondary phase (liquid phase). In Fig. 2(b), no variation of the mechanical quality factor (Q_m) was found when less than 0.6 mol% of CuO was added. As the CuO was further increased to >0.6 mol%, the Q_m started increasing and reached the maximum of 110 for BNKT–1.2Cu, and then decreased. From the increase in Q_m, it could be inferred that the oxygen vacancy formed in order to compensate for the charge in the B-site due to the substitution of Cu^{2+} for Ti^{4+}, leading to the occurrence of the domain pinning effect [7]. The variation of the electromechanical coupling factor k_p was observed, but it was not significant.

Fig. 3 shows the ε_r for BNKT–*x*Cu measured at 100 kHz against temperatures. As the increase of CuO, the temperature at maximum of ε_r (T_m) decreased, and the corresponding ε_r decreased, while the depolarization temperature (T_d) increased. From these results, it can be considered that the curves of ε_r for BNKT–*x*Cu were obviously broad as in the case of typical relaxor ferroelectrics [8]. The inset of Fig. 3 shows the inverse relative permittivity ($1/\varepsilon_r$) for BNKT–0.6Cu, which measured at 1 MHz to avoid the contribution of the space-charge polarization at high temperatures and lower measurement frequency, resulting in no space-charge polarization contribution detected. As shown, $1/\varepsilon_r$ of BNKT–0.6Cu followed the Curie–Weiss law above the deviation temperature ($T_{dev.}$), while the $1/\varepsilon_r$ exhibited a large deviation below $T_{dev.}$. The diffuseness of the permittivity maxima (ε_{max}) can be described by an empirical expression previously developed by Smolenskii and

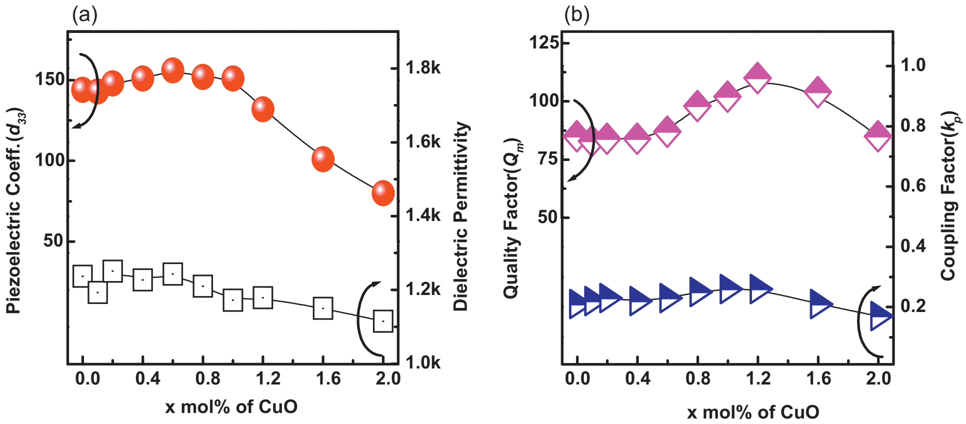

Fig. 2. Variations in dielectric and piezoelectric properties (a) d_{33} with dielectric permittivity and (b) Q_m with k_p for BNKT as a function of the CuO contents.

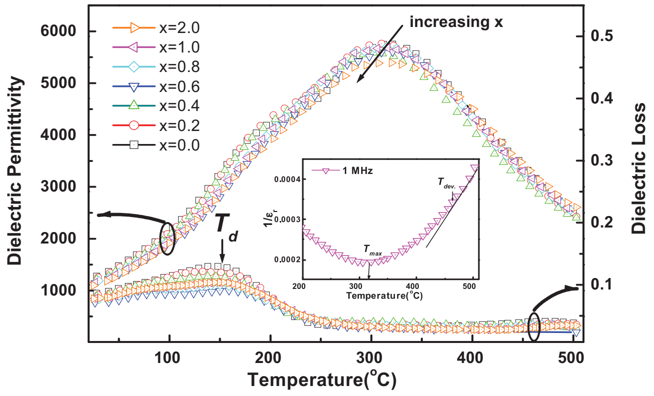

Fig. 3. Temperature dependence of the dielectric permittivity with (a) the amount of CuO measured at 100 kHz. The inset shows the inverse dielectric permittivity of BNKT–0.6Cu.

Table 1
Summary of the ε_{max}, T_m, $T_{dev.}$, and γ for BNKT–xCu with 0.0 mol% $\leq x \leq$ 1.0 mol% measured at 1 MHz.

Composition	$\varepsilon_{\max}$	T_m(°C)	$T_{dev.}$ (°C)	γ
BNKT–0.0Cu	5277	316	165	1.67
BNKT–0.2Cu	5764	310	167	1.58
BNKT–0.4Cu	5584	302	156	1.57
BNKT–0.6C11	5158	315	174	1.87
BNKT–0.8C11	5593	305	155	1.83
BNKT–1.0Cu	5681	311	169	1.64

Kirillov [9,10] as:

$$\frac{1}{\varepsilon_r}-\frac{1}{\varepsilon_{\max}}=\frac{(T_{dev.}-T_m)^{\gamma}}{2\varepsilon_{\max}\delta^{\gamma}} \tag{1}$$

where δ is the diffuse parameter, and γ is the critical exponent that varies from $\gamma = 1$ for a normal ferroelectric to $\gamma = 2$ for a relaxor ferroelectric [11]. In the high temperature region, $1/\varepsilon_r$ for BNKT–0.6Cu followed the C–W behavior from ~500 °C to $T_{dev.}$ with $\gamma = 1.87$. It can be considered that the high temperature-paraelectric phase above $T_{dev.}$ was driven by a soft optic mode condensation or a displacive transition [12]. Table 1 shows a summary of the ε_{max}, T_m, $T_{dev.}$, and γ values for BNKT–xCu.

Fig. 4 shows the thermal hysteresis (TH) of T_m and T_d measured at 100 kHz under heating and cooling. For pure BNKT in Fig. 4(a), T_m was not changed, which implied the absence of TH. On the other hand, when CuO was added, T_m shift slightly toward a low temperature. The difference in TH for T_m between the heating and the cooling cycles increased slightly with increasing the content of CuO. Fig. 4(b) shows TH on T_d. As the CuO addition increased, T_d decreased gradually upon heating, being in the range from 132 °C to 125 °C; there was a relatively small variation upon cooling. In general, TH was well known to be attributed to a large structural distortion [13]. Therefore, it can be explained that Cu^{2+} having a large ionic radius was substituted for Ti^{4+}, which led to the structural changes, resulting in TH during the heating and the cooling cycles. Moreover, a study on TH needs further experimental work in order to better understand the relaxor materials.

4. Summary

A lead-free BNKT–xCu system with 0.0 mol% $\leq x \leq$ 2.0 mol% was synthesized using a conventional method. Upon the addition of a small amount of CuO (<0.6 mol%), a dense microstructure with a relatively large grain size was formed, which is caused by the formation of liquid phase. $1/\varepsilon_r$ followed the Curie–Weiss law above $T_{dev.}$, provided that there was no a space-charge polarization contribution at high temperatures. TH for BNKT–xCu was found to exhibit a different behavior during the heating and the cooling cycles, which was caused by the structural distortion of BNKT.

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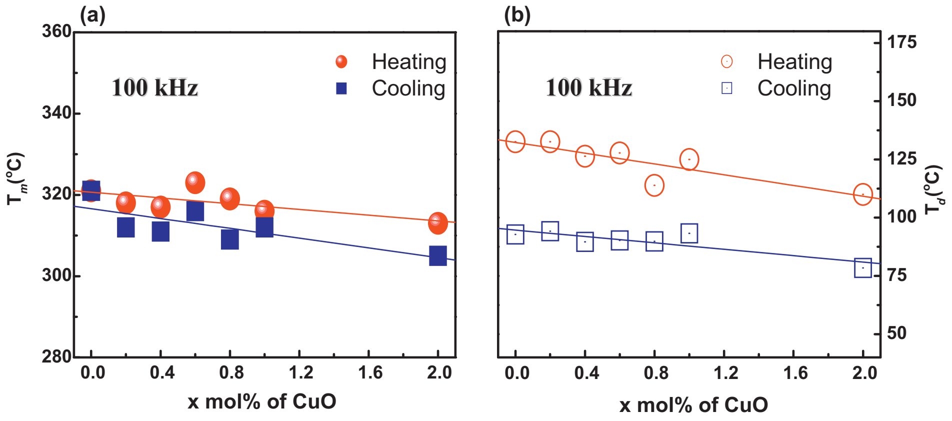

Fig. 4. Thermal hysteresis of (a) T_m and (b) T_d under heating and cooling measured at 100 kHz as a function of the amount of CuO.

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