Structure, dielectric, and piezoelectric properties of CuO-doped 
$K_{0.5}Na_{0.5}NbO_3–BaTiO_3$ lead-free ceramics

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Lead-free piezoelectric ceramics $(1-x)K_{0.5}Na_{0.5}NbO_3+x$BaTiO$_3$+y mol % CuO have been fabricated by an ordinary sintering technique. Our results show that the doping of CuO is effective in promoting the densification of the ceramics. With the doping of CuO, all the ceramics can be well sintered and exhibit a dense, pure perovskite structure. After the formation of a solid solution with BaTiO$_3$, both the paraelectric cubic–ferroelectric tetragonal and ferroelectric tetragonal–ferroelectric orthorhombic phase transition temperatures decrease and a relax behavior is induced. Coexistence of the orthorhombic and tetragonal phases is formed in the ceramics with $0.04\leq x \leq 0.06$ and $y=1.0$ at room temperature. Because of the more possible polarization states arising from the coexistence of the two phases and the improved densification, the piezoelectric and dielectric properties of the ceramics are enhanced significantly. The ceramic with $x=0.06$ and $y=1.0$ exhibits the optimum properties: $d_{33}=193$ pC/N, $k_p=0.43$, $k_t=0.40$, and $T_C=314$ °C. On the other hand, the ceramics with $0\leq x \leq 0.01$ and $y=1.0$ exhibit excellent “hard” piezoelectric characteristics: $k_p\sim 0.40$, $k_t\sim 0.47$, $Q_m\sim 1940$, $\varepsilon_r\sim 230$, and tan $\delta\sim 0.5$.

I. INTRODUCTION

Lead zirconate titanate (PZT) and PZT-based piezoelectric ceramics possess excellent piezoelectric properties and hence have widely been used in actuators, sensors, as well as microelectronic devices. However, the use of the lead-based ceramics has caused serious environmental problems because of the high toxicity of lead oxide. Therefore, there is an urgent need to develop lead-free ceramics with good piezoelectric properties for replacing the lead-containing ceramics. In recent years, a number of extensive studies on lead-free piezoelectric ceramics such as Bi$_{0.5}$Na$_{0.5}$TiO$_3$-based materials, Bi-layered structure materials, tungsten bronze-type materials, BaTiO$_3$-based ceramics, and alkaline niobate-based materials have been carried out.

Among the lead-free ceramics, $K_{0.5}Na_{0.5}NbO_3$ (KNN), the solid solution of ferroelectric KNbO$_3$ and antiferroelectric NaNbO$_3$, is considered a promising candidate for lead-free piezoelectric ceramics because of its high Curie temperature (above 400 °C), good ferroelectric properties ($P_r=33$ μC/cm$^2$), and large electromechanical coupling coefficients. For a KNN ceramic prepared by the hot-pressing technique, it has a high density ($\rho=4.46$ g/cm$^3$), and exhibits good piezoelectric properties ($d_{33}=160$ pC/N, $k_p=0.45$). However, there is severe degradation in piezoelectric properties ($d_{33}=80$ pC/N, $k_p=0.36$) and density ($\rho=4.25$ g/cm$^3$) for a KNN ceramic prepared by an ordinary sintering technique. In order to improve the sintering performance and piezoelectric properties of KNN ceramics, a number of studies have been carried out; these include the formation of solid solutions of KNN with other ferroelectrics or nonferroelectrics, e.g., KNN–LiNbO$_3$, KNN–SrTiO$_3$, KNN–LiTaO$_3$, KNN–Li(Nb,Ta,Sb)O$_3$, and KNN–LiSbO$_3$, as well as the use of sintering aids, e.g., $K_{5.4}Cu_{1.3}Ta_{0.9}O_{29}$ for the BaTiO$_3$ ceramics prepared by an ordinary sintering technique, a small increase in their piezoelectric properties ($d_{33}=104–134$ pC/N, $k_p=0.30–0.31$) has been reported. It has also been shown that a MnO$_2$ sintering aid and special arrangements, such as muffling the green samples with powders of the same compositions during sintering, can further improve their piezoelectric properties ($d_{33}=194–225$ pC/N). However, the electromechanical coupling coefficients are relatively low (0.31–0.36). In the present work, CuO-doped $(1-x)K_{0.5}Na_{0.5}NbO_3+x$BaTiO$_3$ ceramics were prepared by an ordinary solid-state sintering method, and their structure, dielectric, and piezoelectric properties were studied. The origin for the improved piezoelectricity was also investigated.

II. EXPERIMENTAL

A conventional ceramic fabrication technique was used to prepare $(1-x)K_{0.5}Na_{0.5}NbO_3+x$BaTiO$_3+y$ mol % CuO (KNNBT–Cu–x/y) ceramics. Analytical-grade metal oxides or carbonate powders K$_2$CO$_3$ (99.9%), Na$_2$CO$_3$ (99.8%), Nb$_2$O$_5$ (99.95%), BaCO$_3$ (99%), TiO$_2$ (99.9%), and CuO (99%) were used as raw materials. $K_{0.5}Na_{0.5}NbO_3$ and BaTiO$_3$ powders were first synthesized at 880 °C for 6 h...
and 1000 °C for 8 h, respectively, using a solid-state reaction method. After the calcination, K$_{0.5}$Na$_{0.5}$NbO$_3$, BaTiO$_3$, and CuO powders were weighted according to the formula of KNNBT–Cu$_{x}$/1.00 and ball-milled in ethanol using zirconia balls for 8 h. The resulting mixture was further mixed with a polyvinyl alcohol (PVA) binder solution thoroughly and then pressed into disk samples. The disk samples were sintered at 1090–1170 °C for 4 h in air. Silver electrodes were fired on the top and bottom surfaces of the samples. The ceramics were poled under a dc field of 4–5 kV/mm at 180 °C in a silicone oil bath for 30 min.

The crystalline structure of the sintered samples was examined using x-ray diffraction (XRD) analysis with CuKα radiation (Bruker D8 advance). The microstructure was observed using a scanning electron microscopy (SEM) (Leica Stereoscan 440). The bulk density $\rho$ was measured by the Archimedes method. The relative permittivity $\varepsilon_r$ and loss tangent $\tan \delta$ were measured as a function of temperature using an impedance analyzer (HP 4192A). A conventional Sawyer-Tower circuit was used to measure the polarization hysteresis ($P$-$E$) loop at 100 Hz. The electromechanical coupling factors $k_p$ and $k_t$ and mechanical quality factor $Q_m$ were determined by the resonance method according to IEEE Standard 176 using an impedance analyzer (HP 4294A). The piezoelectric coefficient $d_{33}$ was measured using a piezo-$d_{33}$ meter (ZJ-3A, China).

III. RESULTS AND DISCUSSION

The XRD patterns of the KNNBT–Cu$_{x}$/1.00 ceramics are shown in Fig. 1. All the ceramics possess a pure perovskite structure, and no secondary phase is observed. This suggests that BaTiO$_3$ has diffused into the KNN lattices to form a new homogeneous solid solution, with Ba$^{2+}$ entering the (Na$_{0.5}$K$_{0.5}$)$^{+}$ sites and Ti$^{4+}$ occupying the Nb$^{5+}$ sites. Together with the enlarged XRD patterns in the range of 2θ from 20° to 70° and (b) from 43° to 48°.

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from 43° to 48°, as shown in Fig. 1(b), it can be seen that the ceramics with \( x = 0.04 \) has an orthorhombic structure (see Ref. 29). As \( x \) (the molar fraction of BaTiO\(_3\)) increases, a tetragonal phase appears and increases continuously in volume. At \( x = 0.06 \), the ceramic possesses the tetragonal phase only (see Ref. 30). These suggest that the orthorhombic and tetragonal phases coexist in the ceramics with \( 0.04 \leq x \leq 0.06 \).

Figures 2(a)–2(c) show the SEM micrographs of the KNNBT–Cu-\( x/1.00 \) ceramics with \( x = 0.00, 0.03, \) and 0.06. All the ceramics are well sintered. As shown in Fig. 2(a), the KNNBT–Cu-0/1.00 ceramic sintered at 1090 °C for 4 h is dense and well crystallized. As \( x \) increases to 0.03, the sintering temperature increases to 1120 °C and the grains become slightly larger [Fig. 2(b)]. At \( x = 0.06 \), the sintering temperature is higher (1140 °C) but the grains become slightly smaller and more uniform [Fig. 2(c)]. The increase in sintering temperature with increasing \( x \) may be attributed to the high sintering temperature of BaTiO\(_3\) ceramics (~1300 °C). On the other hand, the sintering of the ceramics without doping of CuO is not very effective and complete. Figure 2(d) shows, as an example, the SEM micrograph of the KNNBT–Cu-0.06/0 ceramic sintered at 1150 °C for 4 h. It can be seen that the ceramic is porous and the grains are very small. As shown in Fig. 3 for the KNNBT–Cu-0.06/y ceramics, the density \( \rho \) increases significantly from 4.20 g/cm\(^3\) (relative density of 91%) to 4.45 g/cm\(^3\) (relative density of 97%) as \( y \) increases from 0.0 to 0.5, and then remains almost unchanged. Together with the SEM observation [Fig. 2(d)], it is clearly seen that a small amount of CuO doping (~0.5 mol %) can assist the densification effectively and improve the sintering performance of the KNNBT ceramics.

Figures 4(a) and 4(b) show, as example, the temperature dependences of \( \varepsilon_r \) at 10 kHz for the KNNBT–Cu-\( x/1.00 \) ceramics with \( x = 0.00, 0.04, 0.06, \) and 0.07, while the variations of the phase transition temperatures \( T_C \) and \( T_{O-T} \) with \( x \) are summarized in Fig. 4(c). Similar to a pure KNN ceramic, the KNNBT–Cu-0/1.00 ceramic (i.e., a pure KNN ceramic with 1 mol % CuO doping) undergoes two phase transitions: the paraelectric cubic–ferroelectric tetragonal phase transition at 421 °C (\( T_C \)) and the ferroelectric tetragonal–ferroelectric orthorhombic phase transition at 201 °C (\( T_{O-T} \)). After the addition of BaTiO\(_3\), the ceramics with \( x \leq 0.06 \) exhibit similar phase transitions at different \( T_C \) and \( T_{O-T} \). However, only the cubic-tetragonal phase transition is observed in the temperature range of ~200 to 550 °C for the ceramics with \( x > 0.06 \). As shown in Fig. 4(c), both \( T_C \) and \( T_{O-T} \) decrease linearly, at a rate of ~22 °C/0.01 mol and ~25 °C/0.01 mol, respectively, with increasing \( x \). For the ceramic with \( x = 0.06 \), the observed \( T_{O-T} \) is close to room temperature, suggesting that the orthorhombic and tetragonal phases coexist in the ceramic. This is in agreement with the results of x-ray diffraction (Fig. 1). It can also be seen that the transition peak associated with the cubic-tetragonal phase transition becomes broadened considerably at \( x > 0.06 \) [Fig. 4(a)]. This implies that the transition has become a diffuse phase transition, which will be discussed more in the following paragraphs.

To provide more information on the phase transition, the temperature dependences \( \varepsilon_r \) of at 10 kHz, 100 kHz, and 1 MHz were measured, giving the results shown in Fig. 5. It can be seen that the cubic-tetragonal phase transition peak for the ceramic with \( x = 0 \) is sharp and frequency independent, suggesting that the ceramic is a normal ferroelectric (Fig. 5(a)). As \( x \) increases to 0.06, the peak becomes slightly broadened and frequency dependent. However, at \( x = 0.07 \) and 0.10, the transition peak becomes broadened significantly and more frequency dependent. This suggests that a
diffuse phase transition is induced and the ceramics have transformed gradually from a normal ferroelectric to a relaxor ferroelectric.

The diffuseness of a phase transition can be determined from the modified Curie-Weiss law \(1/\varepsilon_r-1/\varepsilon_m=C^{-1}(T-T_m)^\gamma\) where \(\varepsilon_m\) is the maximum value of dielectric constant at the phase transition temperature \(T_m\). \(\gamma\) is the degree of diffuseness, and \(C\) is the Curie-like constant. \(\gamma\) can have a value ranging from 1 for a normal ferroelectric to 2 for an ideal relaxor ferroelectric. Based on the temperature plots of \(\varepsilon_r\) at 100 kHz, the graphs of \(\ln(1/\varepsilon_r-1/\varepsilon_m)\) vs \(\ln(T-T_m)\) for the KNNBT–Cu-x/1.00 ceramics with \(x=0.00, 0.06, 0.07,\) and 0.10 were plotted, giving the results shown in Fig. 6. All the samples exhibit a linear relationship. By least-squared fitting the experimental data to the modified Curie-Weiss law, \(\gamma\) was determined. The calculated \(\gamma\) for the KNNBT–Cu-0.00/1.00 ceramic is 1.02, revealing the normal ferroelectric characteristics. As \(x\) increases, \(\gamma\) increases gradually from 1.25 at \(x=0.06\) to 1.80 at \(x=0.10\). This clearly shows that the ceramic has transformed gradually from a normal ferroelectric to a relaxor ferroelectric.

A diffuse phase transition has been observed in many \(ABO_3\)-type perovskites and Bi-layered structure compounds, e.g., \(Bi_0.5Na_0.5TiO_3\)-based ceramics, \(K_0.5La_0.5Bi_2Nb_2O_9\), \(Pb(Sr_0.7Ti_0.3)O_3\), and \(Pb(Mg_0.5Nb_2.5)O_3\). For those compounds, either \(A\) sites or \(B\) sites are occupied by more than two cations. It has been known that for the \(A\)-site complex \((A_1A_2)BO_3\) or \(B\)-site complex \((B_1B_2)O_3\) perovskite ferroelectrics, a large difference in ionic radii of the \(A\)-site cations or \(B\)-site cations is favorable for the formation of ordered structure. \(\gamma\) for the KNNBT–Cu-x/1.00 ceramics, Ba\(^{2+}\) (ion radius of 1.34 Å) substitutes the \(A\)-site Na\(^+\) and K\(^+\) (0.97 and 1.33 Å, respectively), while Ti\(^{4+}\) (0.68 Å) substitutes the \(B\)-site Nb\(^{5+}\) (0.69 Å). As the ions in each site have similar radii, the \(A\)-site and \(B\)-site disordered degrees and the local compositional fluctuation may increase, giving rise to a relaxor phase transition.

The variations of the piezoelectric coefficient \(d_{33}\), mechanical quality factor \(Q_m\), electromechanical coupling coefficients \(k_p\) and \(k_t\), relative permittivity \(\varepsilon_r\), and loss tangent \(\tan \delta\) with \(x\) for the KNNBT–Cu-x/1.00 ceramics are shown in Fig. 7. The observed \(d_{33}\) increases with increasing \(x\) and then decreases, giving a maximum value of 193 pC/N at \(x=0.06\). Unlike \(d_{33}\), \(Q_m\) decreases significantly from 1940 to 730 as \(x\) increases from 0.00 to 0.02; the decrease then becomes gradual at higher \(x\). The observed \(k_p\) and \(k_t\) remain almost unchanged at a large value of 0.46 and 0.47, respectively, with increasing \(x\) and then start to decrease at \(x=0.05\). On the other hand, as \(x\) increases from 0 to 0.10, \(\varepsilon_r\) increases largely from \(\sim 230\) to \(\sim 1200\) while \(\tan \delta\) increases slightly from \(\sim 0.5\% \) to \(\sim 3\%\). It should be noted that the ceramics with \(0<x<0.01\) exhibit excellent “hard” characteristics such as large \(k_p\) (\(\sim 0.40\)) and \(k_t\) (0.47), high \(Q_m\) (\(\sim 1940\)), and low \(\varepsilon_r\) (\(\sim 230\)) and \(\tan \delta\) (\(\sim 0.5\%\)).

Figure 8 shows the variations of \(d_{33}\), \(Q_m\), \(k_p\), \(k_t\), \(\varepsilon_r\), and \(\tan \delta\) with \(y\) (the molar concentration of CuO) for the KNNBT–Cu-x/0.06/y ceramics. As shown in Figs. 8(a) and 8(b), all the observed \(d_{33}\), \(Q_m\), \(k_p\), and \(k_t\) exhibit similar dependences on \(y\), i.e., increase first with increasing \(y\) and then decrease. At \(y=1.0\), they all reach a maximum value, being 193 pC/N, 286, 0.43, and 0.40, respectively. On the other hand, the observed \(\varepsilon_r\) decreases generally with increasing \(y\), while \(\tan \delta\) decreases significantly from 17\% to 2.5\% as \(y\) increases from 0.0 to 0.25 and then remains almost un-
changed [Fig. 8(c)]. The enhancement in both the piezoelectric and dielectric properties should be attributed to the improved densification of the ceramics (Fig. 3). On the other hand, the addition of CuO may cause hardening effects in the ceramics. The ionic radius of Cu$^{2+}$ is 0.73 Å, so it may substitute the B-site ions Nb$^{5+}$ (0.68 Å) and Ti$^{4+}$ (0.69 Å) as an acceptor-type dopant. Therefore, the excess of CuO may result in a decrease in $d_{33}$, $k_p$, and $k_t$.

Except for $y=0$, all the KNNBT–Cu-$x/y$ ceramics exhibit a well-saturated $P$-$E$ loop under an electric field of about 6 kV/mm. Figure 9(a) shows, as examples, the $P$-$E$ hysteresis loops of the KNNBT–Cu-$x/1.00$ ceramics with $x=0.02$, 0.06, 0.08, and 0.10, while the loops for the KNNBT–Cu-$0.06/y$ ceramics with $y=0.50$, 1.00, and 1.75 are shown in Fig. 9(b). As shown in Fig. 9(a), the KNNBT–Cu-$x/1.00$ ceramic with $x=0.02$ exhibits a squarelike $P$-$E$ loop, giving a large remanent polarization $P_r$ (19.1 μC/cm$^2$) and a relatively low coercive field $E_c$ (1.15 kV/mm). As $x$ increases to 0.06, the ferroelectric properties are weakened, giving a smaller $P_r$ (14 μC/cm$^2$) and a higher $E_c$ (1.16 kV/mm). At $x=0.08$ and 0.10, the $P$-$E$ loop becomes slim and slanted, $P_r$ decreases to 7.9 and 5.4 μC/cm$^2$, respectively, and $E_c$ increases to 1.33 and 1.22 kV/mm. Similarly, both the KNNBT–Cu-$0.06/y$ ceramics with $y=0.50$ and 1.00 exhibit a squarelike $P$-$E$ loop, giving a large $P_r$ (16.7 and 14.0 μC/cm$^2$, respectively) and a low $E_c$ (1.25 and 1.16 kV/mm, respectively). At $y=1.75$, the $P$-$E$ loop becomes slim and slanted, $P_r$ decreases to 9.1 μC/cm$^2$, and $E_c$ increases to 1.27 kV/mm. These clearly show that a high molar fraction of BaTiO$_3$ (e.g., $>0.06$) and a high doping level of CuO (e.g., $>1.00$) would weaken the ferroelectric properties of the ceramics significantly.

It has been known that the morphotropic phase boundary (MPB) plays a very important role in the improvement of piezoelectric properties of perovskite piezoelectric ceramics, such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–BaTiO$_3$, PZT, and Pb$_{0.69}$Ba$_{0.31}$TiO$_3$–BaTiO$_3$. In general, the piezoelectric properties of the ceramics become optimum near the MPB region. A MPB is defined as an abrupt structural change for a solid solution with variation in composition. Typically, the change is nearly independent of temperature, giving a nearly vertical line in the phase diagram such as those for the PZT and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–BaTiO$_3$ systems. It is generally believed that the enhancement in piezoelectric properties of the ceramics near the MPB is mainly attributed to the more possible polarization states resulting from the coexistence of the two phases. Unlike PZT and other systems, the phase transitions for the KNNBT–Cu-$x/y$ ceramics depend not only on the compositions but also on the temperature [Fig. 4(c)]. Although the phase boundary between the orthorhombic and tetragonal phases may not be a MPB, it is believed to be the major origin for the enhancement in piezoelectric properties of the ceramics. Similar to the other systems with MPB, the KNNBT–Cu-$x/1.00$ ceramics with $x$ in the range of 0.04–0.06 contain both the orthorhombic and tetragonal phases near room temperature, and thus more possible polarization...
excellent hard piezoelectric characteristics: $kp$ both possess the largest $kt$ ceramics are enhanced significantly. Accordingly, the ceramic coexistence of the two phases and the improved densification of the orthorhombic phases coexist near room temperature. Because of the coexistence of the two phases and the improved densification, the piezoelectric and dielectric properties of the ceramics are enhanced significantly. Accordingly, the ceramic with $x=0.06$ and $y=1.00$ exhibits the optimum properties: $Q_m \sim 1940$, $e_r \sim 23.0$, and $\tan \delta \sim 0.5\%$.

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IV. CONCLUSIONS

Dense KNNBT–Cu-x/y piezoelectric ceramics have been prepared by a conventional sintering technique, and their microstructure, dielectric, piezoelectric, and ferroelectric behaviors have been studied in detail. Except for their microstructure, dielectric, piezoelectric, and ferroelectric behaviors have been studied in detail. Except for their microstructure, dielectric, piezoelectric, and ferroelectric behaviors have been studied in detail. Except for their microstructure, dielectric, piezoelectric, and ferroelectric behaviors have been studied in detail. Except for their microstructure, dielectric, piezoelectric, and ferroelectric behaviors have been studied in detail. Except for their microstructure, dielectric, piezoelectric, and ferroelectric behaviors have been studied in detail. Except for their microstructure, dielectric, piezoelectric, and ferroelectric behaviors have been studied in detail. Except for their microstructure, dielectric, piezoelectric, and ferroelectric behaviors have been studied in detail.