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# Synthesis and properties of $Bi_{0.5}(Na_{1-x-y}K_xAg_y)_{0.5}TiO_3$ lead-free piezoelectric ceramics

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**Abstract**

$Bi_{0.5}(Na_{1-x-y}K_xAg_y)_{0.5}TiO_3$ piezoelectric ceramics were prepared by conventional ceramic processes. X-ray diffraction patterns show a pure perovskite structure, indicating that the $K^+$ and $Ag^+$ ions substitute for the $Na^+$ ions in $Bi_{0.5}Na_{0.5}TiO_3$. The temperature dependence of the dielectric constant and dissipation factor shows all ceramics to experience two phase transitions: from ferroelectric to anti-ferroelectric and from anti-ferroelectric to paraelectric. The transition temperature from ferroelectric to anti-ferroelectric and the temperature at which the dielectric constant reaches its maximum value decrease with the increase of $K^+$ amount. At room temperature, the ceramics containing 17.5–20 mol% $K^+$ and 2 mol% $Ag^+$ exhibit high piezoelectric constant ($d_{33}$ = 180 pC/N) and high electromechanical coupling factor ($k_p$ = 35%).


*Keywords:* Dielectric property; Piezoelectric property; $Bi_{0.5}Na_{0.5}TiO_3$; $Bi_{0.5}(Na_{1-x-y}K_xAg_y)_{0.5}TiO_3$

## 1. Introduction

Lead-based piezoelectric $Pb(Zr,Ti)O_3$ (PZT) ceramics, are widely used for actuators, sensors and transducers due to their excellent piezoelectric properties [1]. However, volatilization of toxic PbO during high-temperature sintering requires an appropriate treatment of lead-contained wastes to avoid environmental problems. Therefore, in order to eliminate lead pollution it is necessary to develop environment-friendly lead-free piezoelectric ceramics to replace PZT-based ceramics [2,3].

Sodium bismuth titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) discovered by Smolenskii et al. [4] is considered to be an excellent candidate as a lead-free piezoelectric ceramic with a large remnant polarization ($P_r$ = 38 μC/cm$^2$). However, BNT itself provides low piezoelectric properties due to its high coercive field ($E_c$ = 7.3 kV/mm) and high conductivity which cause difficulties in poling process. Recent investigations brought to BNT systems such as BNT–$BaTiO_3$, BNT–$Bi_{0.5}K_{0.5}TiO_3$, BNT–$Bi_{0.5}K_{0.5}TiO_3$–$BaTiO_3$, $[Bi_{0.5}(Na_{1-x-y}Li_xK_y)_{0.5}]TiO_3$, and so on [5–13] that can be poled easily.

The binary BNT–BKT piezoelectric ceramics show relatively high piezoelectric and dielectric properties at the composition near the morphotropic phase boundary (MPB). $Bi_{0.5}Ag_{0.5}TiO_3$ is ferroelectric with a low dissipation factor [14]. In this paper, a new ternary BNT–BKT–$Bi_{0.5}Ag_{0.5}TiO_3$ piezoelectric material was synthesized by traditional processes for electronic ceramics, and its piezoelectric properties were investigated.

## 2. Experimental procedures

A conventional ceramic process was used to prepare $Bi_{0.5}(Na_{1-x-y}K_xAg_y)_{0.5}TiO_3$ (abbreviated as BNKAT($x$/$y$)) ceramics with $x$ = 0.1–0.225 and $y$ = 0.01–0.075. Reagent grade $Bi_2O_3$ (99%), $Na_2CO_3$ (99.8%), $K_2CO_3$ (98%), AgO (99%) and $TiO_2$ (99.5%) were used as starting materials. All the starting materials, mixed in the appropriate stoichiometry by ball milling, were calcined at 860–960 °C for 2 h. After calcination, the ball-milled powders were pressed into discs and sintered at 1150–1200 °C for 2 h in air atmosphere. The specimens coated with silver paste to form electrodes on both

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sides were annealed at 600–700 °C, then poled in stirred silicone oil bath with a dc field of 3–4 kV/mm at 60–120 °C for 15–30 min.

The piezoelectric constant $d_{33}$ was measured using a ZJ-2 quasi-static $d_{33}$ analyzer. Piezoelectric properties were measured by the resonance–antiresonance method using an impedance analyzer (HP 4194A). The planar electromechanical coupling factor $k_p$ was calculated from the resonance and antiresonance frequencies by using Onoe's formula.

Dielectric properties were determined with a capacitancemeter (HP4278A) at 1 kHz. The temperature dependence of dielectric constant and dissipation factor at 1 kHz of the poled samples were examined using a programmable furnace with a LCR analyzer (TH2816). The crystalline phase of the sintered ceramics was analyzed by X-ray diffraction (XRD) using Cu Kα radiation. A scanning electron microscope (JEOL JSM-5900 SEM) was used to observe the microstructure of the sintered samples.

## 3. Results and discussion

### 3.1. XRD analysis

X-ray diffraction patterns shown in Fig. 1 indicate that the BNKAT($x$/$y$) ceramics with the composition of $x = 0.175$–$0.225$ and $y = 0.015$–$0.075$ possess pure perovskite phase with rhombohedral structure; no second phases were found, which shows that $K^+$ and $Ag^+$ substitute for $Na^+$ in the BNT lattice to form solid solutions. The XRD peaks in the range of $2\theta$ between 57–60° and 75–79° are used to calculate the lattice parameters (see Table 1). The lattice constant obtained by this way increases with the increase of $K^+$ and $Ag^+$ amount as $y$ is lower than 0.02. However, the lattice constant decreases when $y$ is over 0.02. As we know, the ionic radius of $K^+$ ($r_{K^+} = 133$ pm) is larger than that of $Na^+$ ($r_{Na^+} = 97$ pm) and $Bi^{3+}$ ($r_{Bi^{3+}} = 120$ pm), which results in lattice distortion and increases the lattice constant of the material.

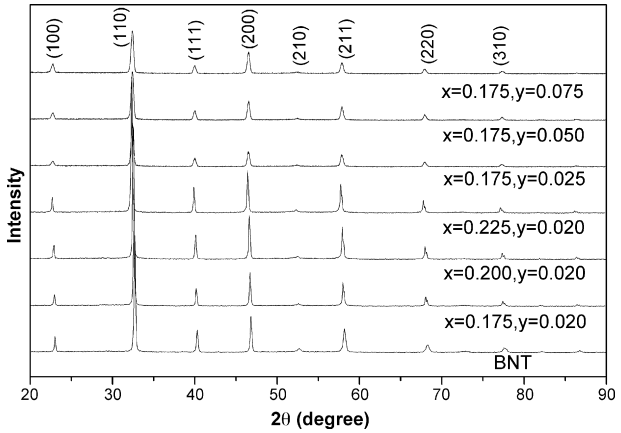


Fig. 1. XRD patterns of BNKAT($x$/$y$) ceramics with different $x$ and $y$ sintered at 1170 °C for 2 h.

Table 1
Lattice parameters of BNKAT($x$/$y$) ceramics

| Sample no. | $x$, $y$ | $a$ (nm) | $\alpha$ (°) |
|---|---|---|---|
| NKA-1 | $x = 0.175$, $y = 0.015$ | 0.389440 | 89.556 |
| NKA-2 | $x = 0.175$, $y = 0.02$ | 0.389503 | 89.592 |
| NKA-3 | $x = 0.20$, $y = 0.02$ | 0.389506 | 89.593 |
| NKA-4 | $x = 0.225$, $y = 0.02$ | 0.389515 | 89.597 |
| NKA-5 | $x = 0.175$, $y = 0.025$ | 0.389499 | 89.59 |
| NKA-6 | $x = 0.175$, $y = 0.05$ | 0.389497 | 89.59 |
| BNT | $x = 0$, $y = 0$ | 0.3886 | 89.36 |

### 3.2. SEM images

Fig. 2 shows the SEM images of BNKAT($x$/$y$) ceramics sintered at 1170 °C for 2 h in air atmosphere with (a) $x = 0.175$ and $y = 0.015$; (b) $x = 0.175$ and $y = 0.020$; (c) $x = 0.175$ and $y = 0.025$; and (d) $x = 0.225$ and $y = 0.020$, respectively. From Fig. 2 it can be seen that all the samples are very dense, with crystalline grains of regular square shape, evident grain boundary and uniform grain size. Moreover, the average grain size decreases with the increase of $K^+$ amount.

### 3.3. Effect of $K^+$ and $Ag^+$ on piezoelectric properties

The dependence of the piezoelectric properties of BNKAT($x$/$y$) ceramics on the amount of $K^+$ and $Ag^+$ is shown in Fig. 3(a)–(c), respectively. Fig. 3(a) shows that regardless of the $Ag^+$ amount, the piezoelectric constant $d_{33}$ of the BNKAT($x$/$y$) ceramics increases with $K^+$ amount up to 20 mol% and then decreases with further increase. The variation of the electromechanical coupling coefficients $k_p$ and $k_{31}$ with $K^+$ amount is almost similar to that of $d_{33}$, but their maximum occur at $K^+$ 17.5 mol% (Fig. 3(b)). Fig. 3(a)–(c) shows that the piezoelectric constant $d_{33}$ and electromechanical coupling coefficient $k_p$ reach the maximum at $y = 0.02$ when $x = 0.175$. The mechanical quality factor $Q_m$ decreases with the increase of $K^+$ amount. When the $K^+$ amount is less than 0.15, the $d_{33}$, $k_p$, $k_{31}$ and $Q_m$ are slightly dependent on $Ag^+$ concentration. At room temperature, the samples show optimal $d_{33}$ of 180 pC/N when $x = 0.2$ and $y = 0.02$ and exhibit a high planar electromechanical coefficient $k_p$ of 35% when $x = 0.175$ and $y = 0.02$.

### 3.4. Effect of $K^+$ and $Ag^+$ on dielectric properties

Fig. 4 gives the dielectric properties of BNKAT($x$/$y$) ceramics as a function of $x$ and $y$. The room temperature dielectric constant $\varepsilon_r$ and dissipation factor tan $\delta$ at 1 kHz of the ceramics were found to increase with the increase of $K^+$ amount. For $K^+$ amount is lower than 0.175, the $Ag^+$ amount can hardly affect the dielectric constant and the dissipation factor.

Fig. 5 shows the temperature dependence of the relative dielectric constant $\varepsilon_r$ and dissipation factor tan $\delta$ of the BNKAT($x$/$y$) ceramics at 1 kHz. Compared to the results reported by Takennaka [5], all samples are characterized by the existence of three phases, i.e., ferroelectric, anti-ferroelectric and paraelectric states in different temperature ranges. In Fig. 5 $T_f$ refers to the temperature of the phase transition between the

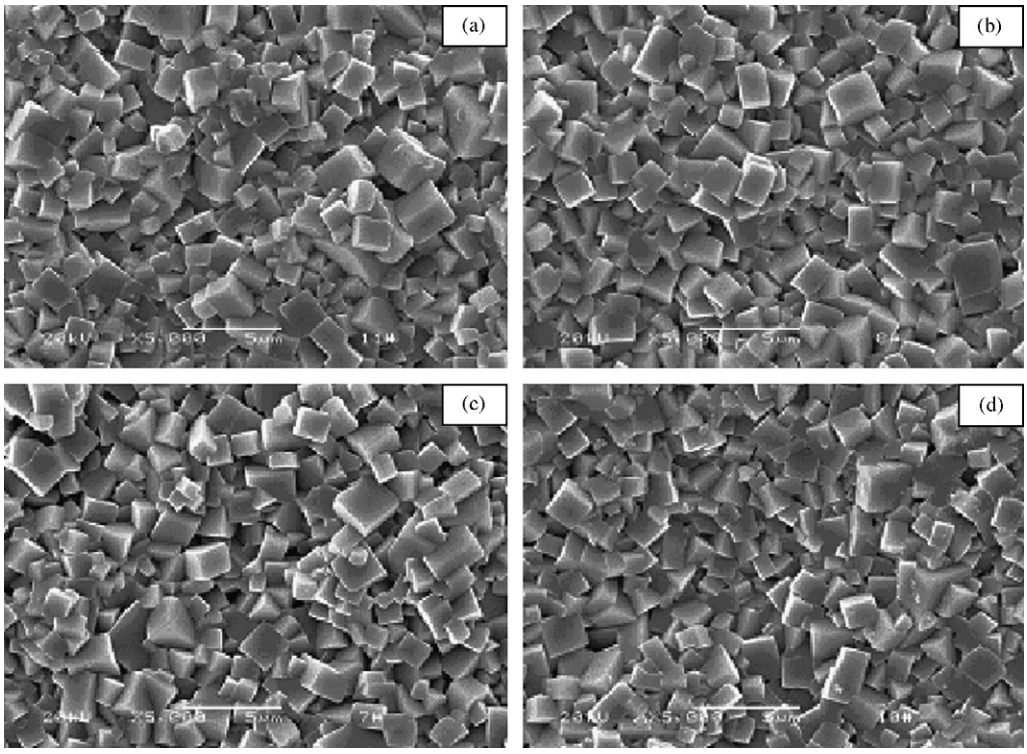


Fig. 2. SEM images of BNKAT($x$/$y$) ceramics sintered at 1170 °C for 2 h with (a) $x = 0.175$ and $y = 0.015$; (b) $x = 0.175$ and $y = 0.020$; (c) $x = 0.175$ and $y = 0.025$; (d) $x = 0.225$ and $y = 0.020$.

ferroelectric and anti-ferroelectric phases, and $T_m$ stands for the temperature at which the dielectric constant reaches its maximum value. The dielectric constant increases with the temperature with a sharp jump up to $T_f$ and reaches the maximum at $T_m$. The dissipation factor sharply increases with temperature up to $T_f$ where it reaches its maximum due to the ferroelectric to anti-ferroelectric phase transition, and then decreases with the temperature because of the less distortion in

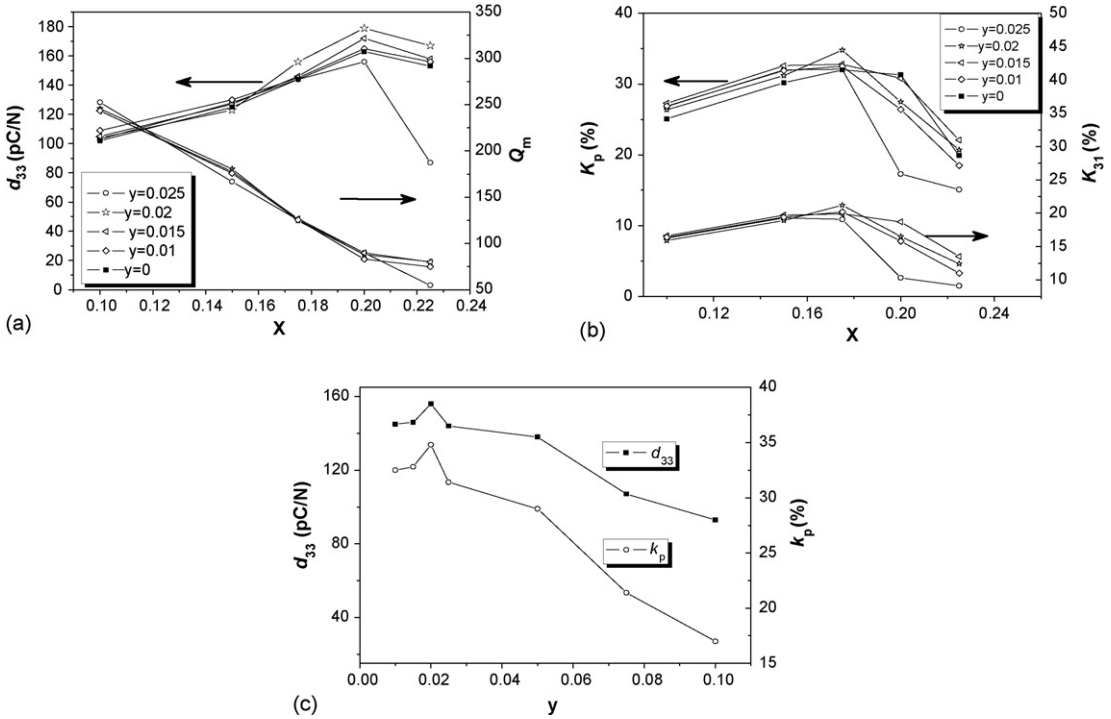


Fig. 3. Piezoelectric and dielectric properties of BNKAT($x$/$y$) ceramics as a function of $x$ and $y$: (a) the dependence of $d_{33}$ and $Q_m$ on $x$; (b) the dependence of $k_p$ and $k_{31}$ on $x$; (c) the dependence of $d_{33}$ and $k_p$ on $y$ when $x = 0.175$.

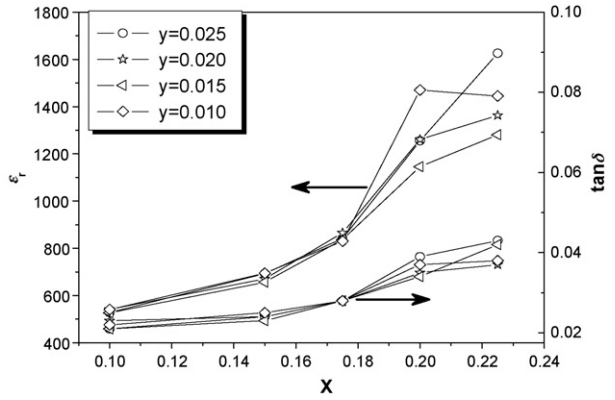


Fig. 4. Dielectric properties of BNKAT(*x*/*y*) ceramics as a function of *x* and *y*.

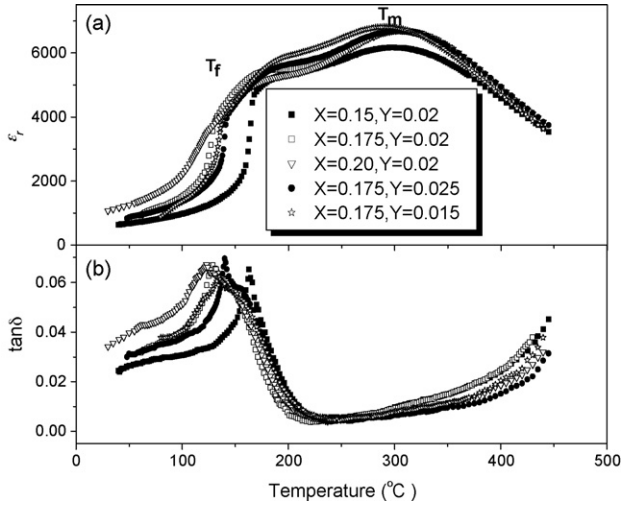


Fig. 5. Temperature dependence of the dielectric constant (a) and dissipation factor (b) of BNKAT(*x*/*y*) ceramics with different $K^+$ and $Ag^+$ concentration at 1 kHz.

the crystalline structure after depolarization until $T_m$ [15,16]. It may be observed in Fig. 5 that with the increase of $K^+$ there is an evident decrease in $T_f$ and a slight decrease in $T_m$, but $T_f$ remains above 135 °C when $x = 0.2$ and $y = 0.02$, whereas the effect of the $Ag^+$ amount on $T_f$ and $T_m$ is very slight.

## 4. Conclusions

BNKAT(*x*/*y*) ceramics ($x$ = 10–25 mol%, $y$ = 1–7.5 mol%) were synthesized by a conventional ceramics technique. Crystalline phases, microstructure, and dielectric and piezoelectric properties of these ceramics were studied. X-ray diffraction patterns show that the ceramics possess pure perovskite structure with a $K^+$ and $Ag^+$ ions substituting for $Na^+$ in the BNT lattice. The dependence of the dielectric constant and dissipation factor on temperature reveals two phase transitions in all the studied ceramics: from ferroelectric to anti-ferroelectric and from anti-ferroelectric to paraelectric. The transition temperature from ferroelectric to anti-ferroelectric phases and the temperature at which the dielectric constant reaches its maximum value decrease with the increase of the amount of $K^+$. Dielectric and piezoelectric properties measurements show that the addition of $K^+$ and $Ag^+$ improves the piezoelectric and dielectric properties. The composition with $x$ = 17.5–20% and $y$ = 2% performed satisfactorily with $d_{33}$ = 180 pC/N, $k_p$ = 35%, $Q_m$ = 125, and tan $\delta$ = 0.028.

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