



## Piezoelectric and dielectric properties of $\text{Sm}_2\text{O}_3$ -doped $0.82\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – $0.18\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ ceramics

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### ABSTRACT

$\text{Sm}_2\text{O}_3$  (0–0.7 wt.%)–doped lead-free  $0.82\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – $0.18\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$  (abbreviated to 0.82BNT–0.18BKT) piezoelectric ceramics were synthesized by the conventional mixed-oxide method, and the effect of  $\text{Sm}_2\text{O}_3$  addition on the dielectric and piezoelectric properties was investigated. X-ray diffraction (XRD) patterns show that  $\text{Sm}_2\text{O}_3$  diffuses into the lattice of the 0.82BNT–0.18BKT ceramics to form a solid solution with a pure perovskite structure. SEM images indicate that the microstructure become uniform by doping a small amount of  $\text{Sm}_2\text{O}_3$ . The electrical properties of 0.82BNT–0.18BKT ceramics have been greatly improved by certain amount of  $\text{Sm}_2\text{O}_3$  substitutions. At room temperature, the 0.82BNT–0.18BKT ceramics doped with 0.3 wt.%  $\text{Sm}_2\text{O}_3$  exhibited the optimum properties with high piezoelectric constant ( $d_{33} = 147$  pC/N) and high planar coupling factor ( $k_p = 22.4\%$ ).

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### 1. Introduction

Nowadays,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) and PZT-based multi-component materials are widely applied in electronic and microelectronic devices due to their excellent piezoelectric properties [1–3]. However, because of the detrimental environmental effects of lead, lead-free piezoelectric ceramics have received much attention over the past decades [4–6].

Bismuth sodium titanate,  $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$  (abbreviated as BNT), is considered as an excellent lead-free piezoelectric ceramic candidate because of its large remanent polarization ( $P_r = 38$   $\mu\text{C}/\text{cm}^2$ ) and high Curie temperature ( $T_c = 320$  °C) [7]. However, high conductivity and high coercive field ( $E_c = 73$  kV/cm) can cause problems in the poling process, and thus limit its practical application [7–9]. To improve its properties, several BNT-based solid solutions have been developed. BNT– $\text{BaTiO}_3$  [10], BNT– $\text{NaNbO}_3$  [11], BNT– $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$  [12,13,14], or combination of multiple additives [15–18] have been studied. Among them, the (1– $x$ ) BNT– $x$ BKT ceramics have attracted considerable attention for

the existence of a tetragonal–rhombohedral morphotropic phase boundary (MPB) located at  $x = 0.16$ – $0.20$  [13,14]. Compared with pure BNT, the BNT–BKT compositions near the MPB provide excellent piezoelectric properties. However, for practical applications, the piezoelectric and dielectric properties of BNT–BKT ceramic need to be further enhanced.

Li et al. [19] reported that  $\text{CeO}_2$  doping could reduce the coercive field  $E_c$  and improve the piezoelectric properties of  $\text{Bi}_{0.5}\text{Na}_{0.44}\text{K}_{0.06}\text{TiO}_3$  ceramics. Yoo et al. [20] demonstrated that the piezoelectric properties could be improved significantly by doping appropriate amount of Sr into 0.84BNT–0.16BKT system. Yang et al. [21] found that at a low  $\text{Nd}_2\text{O}_3$  concentration, the Nd doped 0.82BNT–0.18BKT ceramics show a high piezoelectric constant. It can be concluded that these rare earth elements were effective additives in enhancing the electrical properties of the BNT-based system. However, few researchers have reported the effects of  $\text{Sm}_2\text{O}_3$  on electrical properties of BNT-based system.

Due to the good piezoelectric and ferroelectric properties, we have focused our studies on the 0.82BNT–0.18BKT system to examine the effect of  $\text{Sm}_2\text{O}_3$  on BNT-based ceramics [14]. In this paper, the  $\text{Sm}_2\text{O}_3$ -doped 0.82BNT–0.18BKT ceramics were synthesized by the conventional solid-state reaction method. The effects of  $\text{Sm}_2\text{O}_3$  additives on the phase composition, microstructure, dielectric and piezoelectric properties were investigated.

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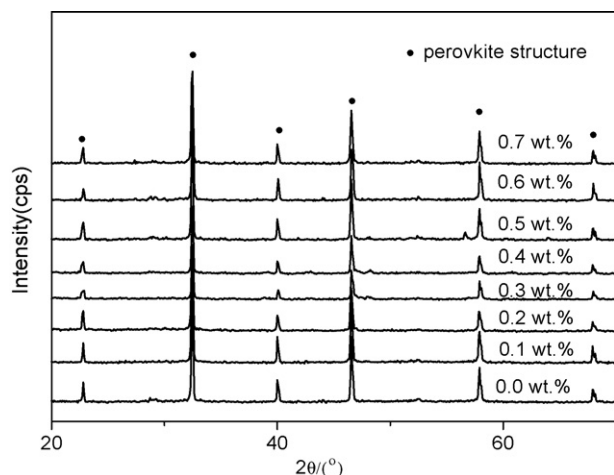


Fig. 1. XRD pattern of the 0.82BNT–0.18BKT ceramics with various amounts of added Sm<sub>2</sub>O<sub>3</sub>.

## 2. Experimental

Powders with a nominal composition of 0.82Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>–0.18Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub> + *x* wt.% Sm<sub>2</sub>O<sub>3</sub> (*x* = 0–0.7) (abbreviated to 0.82BNT–0.18BKT–*x*) were synthesized by a conventional solid-state reaction method. Reagent grade oxide or carbonate powders of Na<sub>2</sub>CO<sub>3</sub> (99.8%), K<sub>2</sub>CO<sub>3</sub> (99%), TiO<sub>2</sub> (99.5%), Bi<sub>2</sub>O<sub>3</sub> (99.64%) and Sm<sub>2</sub>O<sub>3</sub> (99.9%) (All raw materials were made by Sinopharm Chemical Reagent Co., Ltds) were used as starting materials. All the starting materials were mixed by ball milling for 8 h and then were calcined at 850 °C for 2 h. After calcination, the mixture was ball milled again and mixed thoroughly with a poly vinylbutyral (PVB) binder solution and then pressed into 12 mm diameter and 1.5 mm thickness disks. After burning off PVB, the pellets were embedded into pre-prepared powder with similar composition and sintered in air in the temperature range of 1140–1160 °C for 2 h. The bulk density of the sintered samples was determined by the Archimedes method. The phase structure was examined by X-ray diffraction (XRD) analysis using a Cu Kα radiation (λ = 1.54178 Å) (D8 Advance, Bruker Inc., Germany). The surface morphology of the ceramics was studied by scanning electron microscope (SEM) (JSM-5900, Japan).

For the electrical measurements, silver paste was coated on both sides of the sintered samples and fired at 740 °C for 20 min to form electrodes. Dielectric properties were measured using an Agilent 4294A precision impedance analyzer (Agilent Inc., USA) in the temperature range from room temperature to 500 °C. *P*–*E* hysteresis loops were recorded using an aix-ACCT TF2000FE-HV ferroelectric test unit (aix-ACCT Inc., Germany). For the measurement of piezoelectric properties, samples were poled in silicon oil at room temperature under 70–100 kV/cm for 15 min. The piezoelectric constant *d*<sub>33</sub> was measured using a quasi-static *d*<sub>33</sub> meter (YE2730 SINOCERA, China). The planar electromechanical coupling factor *k*<sub>p</sub> and mechanical quality factor *Q*<sub>m</sub> were obtained by a resonance–antiresonance method through an impedance analyzer (HP 4294A) on the basis of IEEE standards.

## 3. Results and discussion

The X-ray diffraction (XRD) patterns of 0.82BNT–0.18BKT ceramics with different addition of Sm<sub>2</sub>O<sub>3</sub> have been shown in Fig. 1. All ceramics exhibit a pure perovskite structure and no second phases can be detected, which implies that the Sm<sup>3+</sup> has diffused into the 0.82BNT–0.18BKT lattices to form a solid solution. Further XRD analysis is performed in the 2θ ranges from 38° to 48° as shown in Fig. 2. The reflection (1 1 1) appeared at 40° splits into (0 0 3)/(0 2 1) reflection and similar splitting is observed at 46°, which suggest the tetragonal–rhombohedral phase structure exists in all the ceramics.

Fig. 3 shows the SEM micrographs of the 0.82BNT–0.18BKT ceramics as a function of the Sm<sub>2</sub>O<sub>3</sub> contents. As can be seen in Fig. 3, all the ceramics are very dense, with a relative density (measured by the Archimedes method) larger than 95%. For the undoped 0.82BNT–0.18BKT ceramics, the average grain size is about 2 μm and the ceramics are inhomogeneous. As the amount of Sm<sub>2</sub>O<sub>3</sub> increases to 0.3 wt.%, a relatively uniform grain size (2.5 μm) is obtained. However, when *x* > 0.3 wt.%, the grain size becomes small

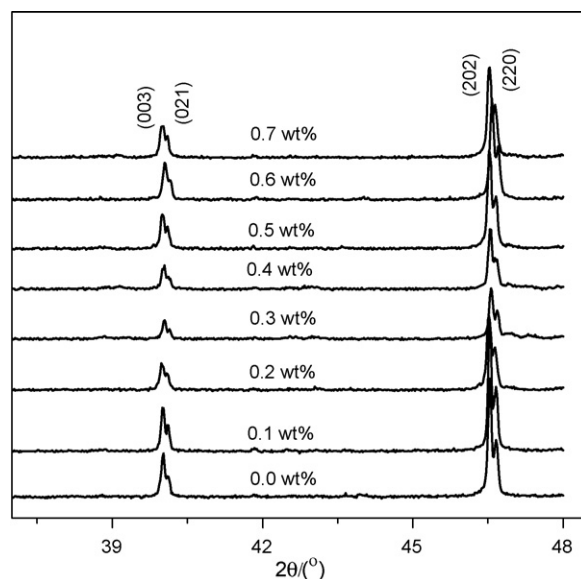


Fig. 2. XRD pattern of the 0.82BNT–0.18BKT ceramics with various Sm<sub>2</sub>O<sub>3</sub> amounts in the 2θ range of 38–48°.

and inhomogeneous again. Therefore, it is believed that a reasonable addition of Sm<sub>2</sub>O<sub>3</sub> to 0.82BNT–0.18BKT ceramics can modify the microstructure and the grain size of the sample.

The *P*–*E* ferroelectric property measurements for the specimens are summarized in Fig. 4. We can see from this figure that all the ceramics exhibit a typical and saturated *P*–*E* loop. The optimum values of the remanent polarization (*P*<sub>r</sub>) and the coercive field (*E*<sub>c</sub>) are 23.44 μC/cm<sup>2</sup> and 39.95 kV/cm, respectively, at 0.3% Sm<sub>2</sub>O<sub>3</sub> addition. As we have mentioned, pure BNT ceramics have a remanent polarization *P*<sub>r</sub> of 38 μC/cm<sup>2</sup> and relatively high coercive field *E*<sub>c</sub> of 73 kV/cm. Compared to pure BNT ceramics, the observed *E*<sub>c</sub> of 0.82BNT–0.18BKT ceramics with 0.3 wt.% Sm<sub>2</sub>O<sub>3</sub> addition is decreased by more than 40%. As is well-known, the low *E*<sub>c</sub> will facilitate the poling process, making the 0.82BNT–0.18BKT ceramics doped with 0.3 wt.% Sm<sub>2</sub>O<sub>3</sub> exhibit better piezoelectric properties. It is hence anticipated that the ceramics obtained at 0.3 wt.% Sm<sub>2</sub>O<sub>3</sub> additions are advantageous for piezoelectric ceramics applications.

The piezoelectric constant *d*<sub>33</sub>, electromechanical coupling factor *k*<sub>p</sub>, dielectric constant ε<sub>r</sub>, mechanical quality factor *Q*<sub>m</sub> and dissipation factor tan δ as a function of Sm<sub>2</sub>O<sub>3</sub> content are illustrated in Fig. 5. The observed *d*<sub>33</sub> and *k*<sub>p</sub> first increase and then decrease with the increasing Sm<sub>2</sub>O<sub>3</sub> content. The maximums of *d*<sub>33</sub> and *k*<sub>p</sub> are obtained at 0.3% Sm<sub>2</sub>O<sub>3</sub> addition, which are 147 pC/N and 0.22, respectively. This phenomenon is in accordance with the *P*–*E* loop results in Fig. 4. For ε<sub>r</sub> and tan δ, the same trends as *d*<sub>33</sub> are also shown in Fig. 5, excepting for the maximum values located at different concentration *x* (*x* = 0.2). The observed *Q*<sub>m</sub> decreases significantly as *x* increase from 0.0 to 0.2, and then increases promptly for 0.2 ≤ *x* ≤ 0.7. These results suggest that after the substitution of Sm<sup>3+</sup>, the ceramics become “soft”, thus giving rise to evident improvements in *d*<sub>33</sub>, *k*<sub>p</sub> and ε<sub>r</sub>. According to Shannon’s effective ionic radius [22], Sm<sup>3+</sup> (0.98 Å) can occupy the A-site of Bi<sup>3+</sup> (1.17 Å) or Na<sup>+</sup> (1.18 Å), but it cannot enter into the B-site because Ti<sup>4+</sup> is in the radius of 0.68 Å. The substitution of Sm<sup>3+</sup> for Bi<sup>3+</sup> causes a great distortion in the crystal lattice, which will enhance the motion of the ferroelectric domains and result in the improvement of piezoelectric properties. Additionally, the substitution of Sm<sup>3+</sup> for Na<sup>+</sup> can lead to some A-site vacancies in the lattice, which facilitate the movement of the domains and thus improve the piezoelectric properties significantly [23–25]. It is noteworthy that the

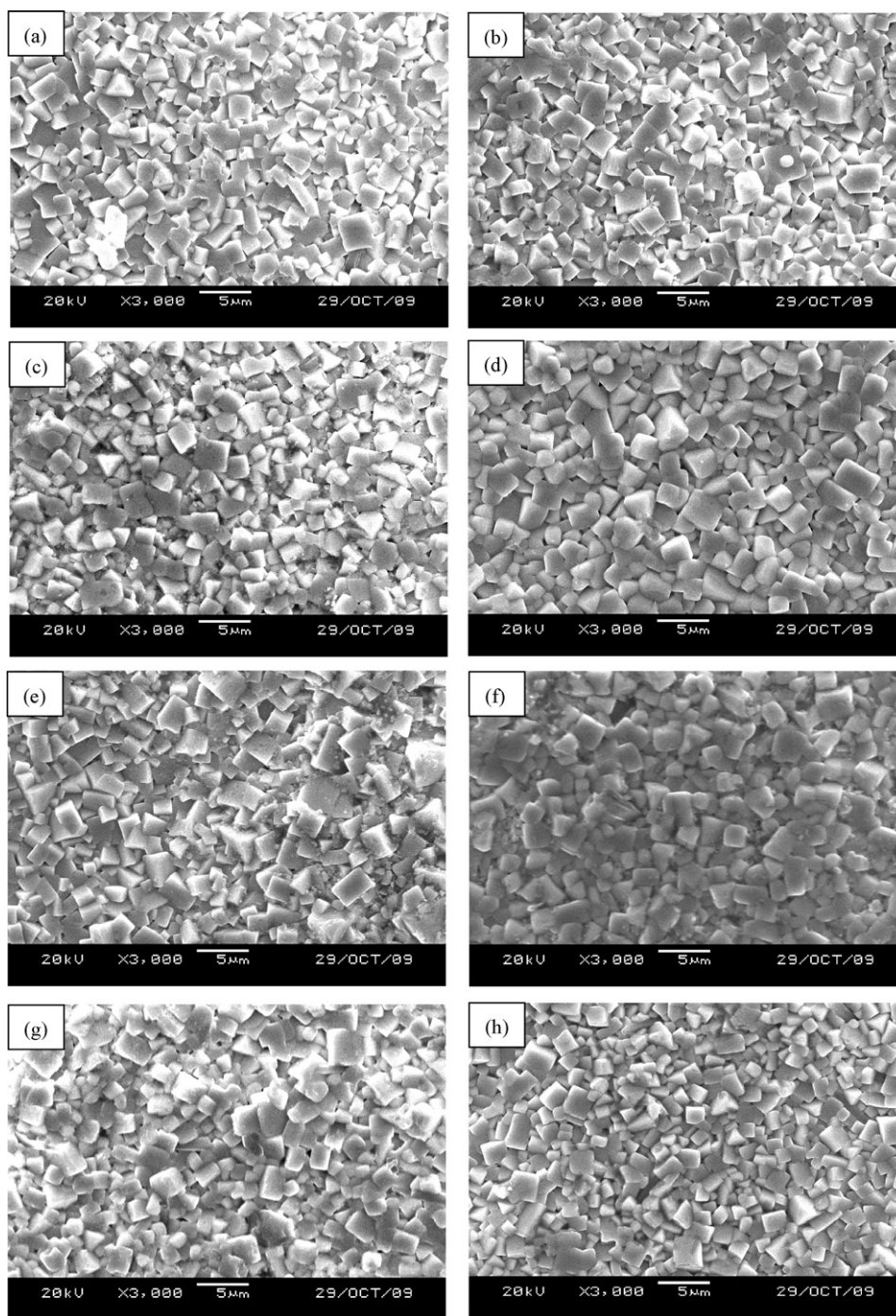


Fig. 3. SEM images of the 0.82BNT–0.18BKT ceramics with (a)  $x=0.0$ , (b)  $x=0.1$ , (c)  $x=0.2$ , (d)  $x=0.3$ , (e)  $x=0.4$ , (f)  $x=0.5$ , (g)  $x=0.6$ , (h)  $x=0.7$ .

decrease of  $Q_m$  can also be attributed to the domains movement [26–28].

Fig. 6 shows the temperature dependence of  $\epsilon_r$  and  $\tan \delta$  of  $\text{Sm}_2\text{O}_3$ -doped 0.82BNT–0.18BKT ceramics with 0, 0.2, 0.4 and 0.7 wt.%  $\text{Sm}_2\text{O}_3$  addition at 1 kHz, 10 kHz and 100 kHz. Similar to the BNT ceramic [8,10], the 0.82BNT–0.18BKT ceramics exhibited two abnormal dielectric peaks at  $T_d$  and  $T_m$ .  $T_d$  is the depolarization temperature at which phase transition between ferroelectric and antiferroelectric happens, while  $T_m$  is the maximum temperature corresponding to the maximum value of dielectric constant.  $T_d$  can also be derived from the peak in the temperature plot of  $\tan \delta$  [29]. In Fig. 6,  $\epsilon_r$  for all ceramics increases almost linearly up

to  $T_d$  and reaches the maximum at  $T_m$  as the temperature increases. Besides, both  $\epsilon_r$ ,  $T_d$  and  $T_m$  are strongly frequency dependence, suggesting that the  $\text{Sm}_2\text{O}_3$ -doped 0.82BNT–0.18BKT ceramics still have relaxation. According to the compositional fluctuation or random local electric fields [30] and stress-induced phase transition theory [31], the relaxor ferroelectric behavior should be attributed to  $\text{Sm}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions distributed randomly in the A-site [32], which was also shown by Said and Mercurio [33]. The variation in the values of  $T_d$  and  $T_m$  with different amount of  $\text{Sm}_2\text{O}_3$  additive for the 0.82BNT–0.18BKT ceramics (at 100 kHz) is presented in Fig. 7. It is found that both  $T_d$  and  $T_m$  exhibit an obvious dependency on  $x$ . For the pure 0.82BNT–0.18BKT ceramics, the  $T_d$  and

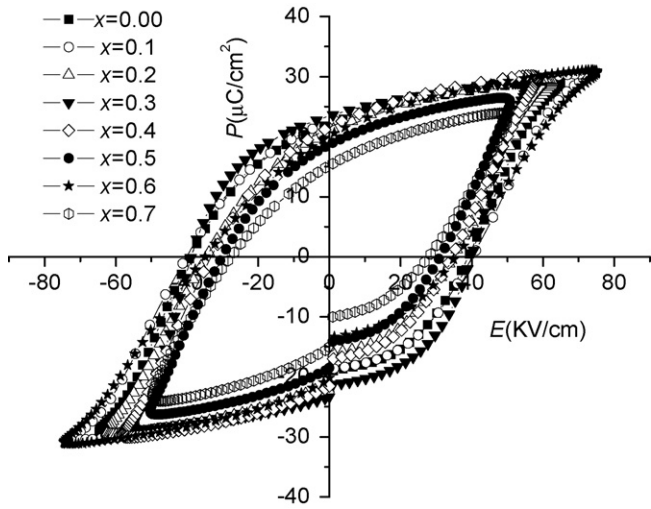


Fig. 4. P-E hysteresis loops of 0.82BNT-0.18BKT ceramics with different amount of  $\text{Sm}_2\text{O}_3$  additive.

$T_m$  were  $69^\circ\text{C}$  and  $321^\circ\text{C}$ , respectively. After adding proper  $\text{Sm}_2\text{O}_3$  (when  $x = 0.3$  wt.%), both  $T_d$  and  $T_m$  shifted to higher temperatures as shown in Fig. 7 ( $T_d = 73^\circ\text{C}$ ,  $T_m = 325.5^\circ\text{C}$ ). However, both  $T_d$  and  $T_m$  slightly decreased with further increasing  $\text{Sm}_2\text{O}_3$  concentration. These results indicate that  $\text{Sm}_2\text{O}_3$  can effectively prompt the applications of the 0.82BNT-0.18BKT ceramics.

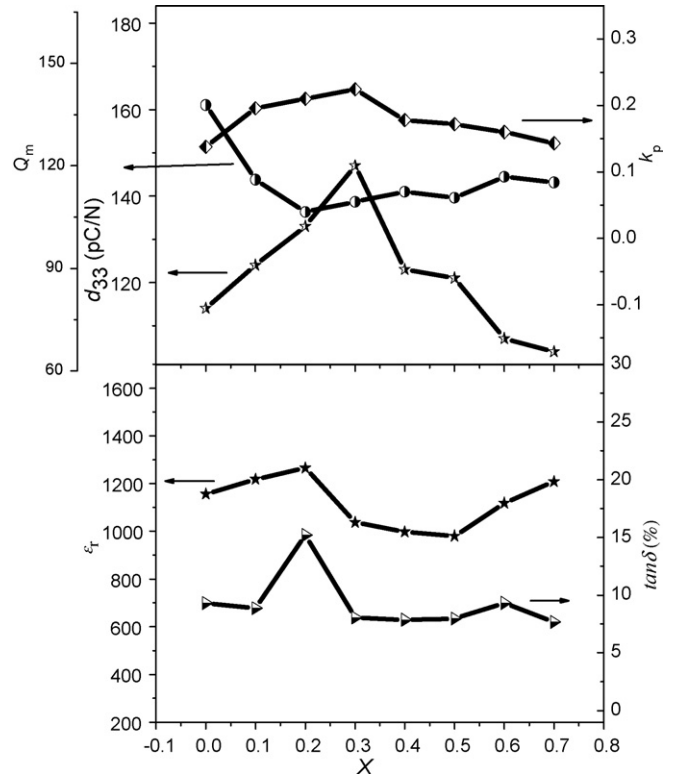


Fig. 5. Variations of  $d_{33}$ ,  $k_p$ ,  $Q_m$ ,  $\epsilon_r$ , and  $\tan \delta$  with different amount of  $\text{Sm}_2\text{O}_3$  additive for the 0.82BNT-0.18BKT ceramics.

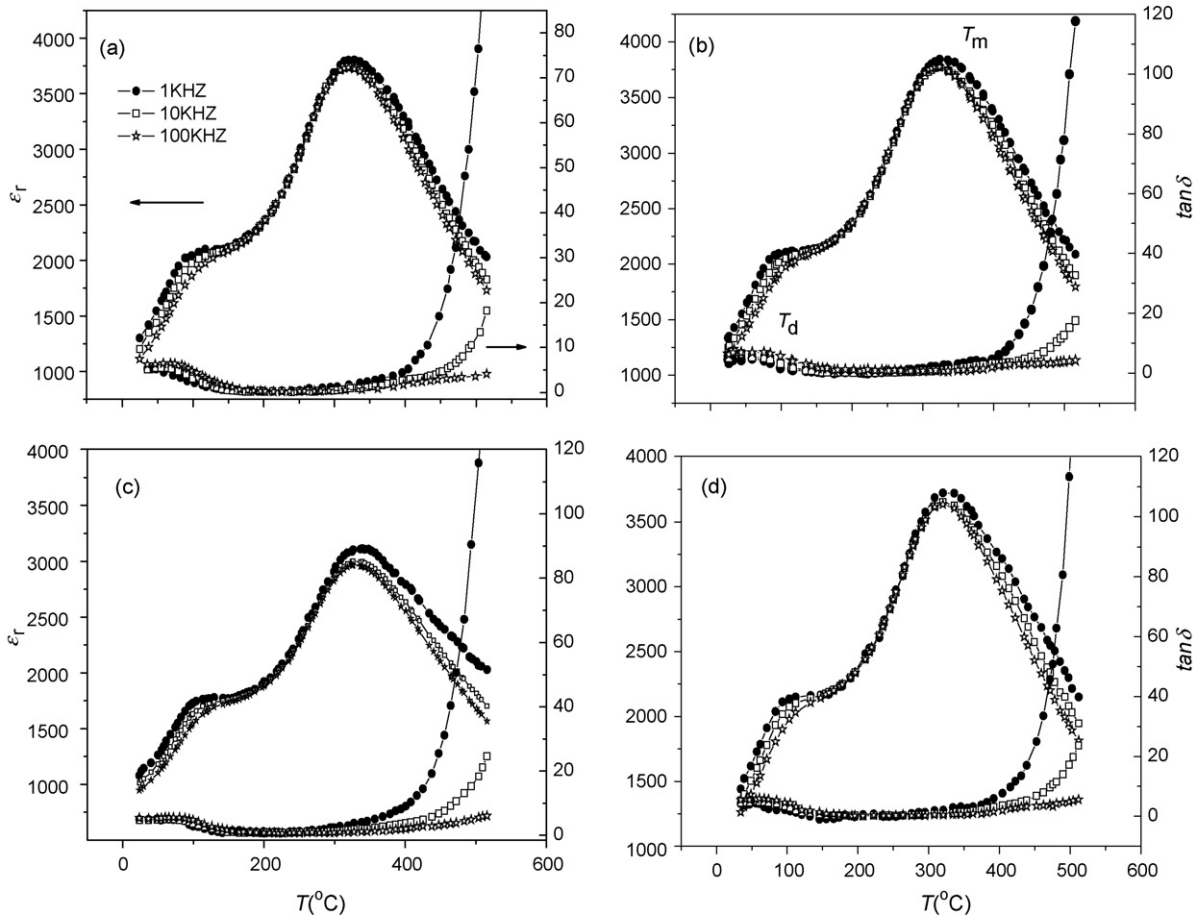


Fig. 6. Temperature dependence of  $\epsilon_r$  and  $\tan \delta$  for  $\text{Sm}_2\text{O}_3$ -doped 0.82BNT-0.18BKT system: (a) 0.00 wt.%; (b) 0.2 wt.%; (c) 0.4 wt.%; (d) 0.7 wt.%.

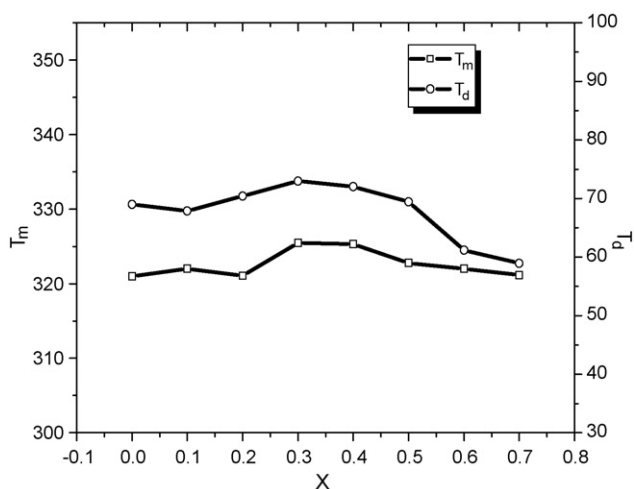


Fig. 7. Variations of  $T_d$  and  $T_m$  with different amount of  $\text{Sm}_2\text{O}_3$  additive for the 0.82BNT–0.18BKT ceramics at 100 kHz.

#### 4. Conclusions

$\text{Sm}_2\text{O}_3$ -doped 0.82BNT–0.18BKT ceramics have been prepared by conventional mixed-oxide method. The XRD patterns indicate that the 0.82BNT–0.18BKT ceramics doped with 0–0.7 wt.%  $\text{Sm}_2\text{O}_3$  still show co-existence of rhombohedral and tetragonal phases. All the ceramics, both doped and undoped, exhibit obvious relaxation characteristics. The piezoelectric properties of 0.82BNT–0.18BKT ceramics have been promoted by  $\text{Sm}_2\text{O}_3$  doping. High magnitude of piezoelectric properties are obtained at 0.03 wt.%  $\text{Sm}_2\text{O}_3$ , i. e.  $d_{33} = 147$  pC/N,  $k_p = 22.4\%$ .

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