

Dielectric behavior and microstructure of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ – BaTiO_3 lead-free piezoelectric ceramics

X. X. Wang,^{a)} S. H. Choy, X. G. Tang, and H. L. W. Chan

Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hung Hom Kowloon, Hong Kong, China

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$(0.95-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3-0.05\text{BaTiO}_3$ lead-free piezoelectric ceramics (abbreviated as BNT–BKT–BT100 x with x varying from 0 to 20 mol %) are prepared by a solid-state reaction process. Variation of the dielectric properties and microstructure of BNT–BKT–BT100 x ceramics with BKT content is studied. The results indicate that the relative permittivity ϵ_r and loss tangent $\tan \delta$ vary with the BKT amount. Scanning electron microscope observation also indicates that BKT in high amount affects the microstructure. X-ray diffraction analysis shows that the incorporated BKT diffuses into the BNT–BT lattice to form a solid solution during sintering. © 2005 American Institute of Physics. [DOI: 10.1063/1.1890453]

I. INTRODUCTION

As one of the important ecoferroelectric materials, lead-free piezoelectric ceramics have attracted considerable attention from researchers as they have no lead pollutant and are better than the widely used lead zirconate titanate $[\text{Pb}(\text{Zr},\text{Ti})\text{O}_3]$ (PZT) piezoelectric ceramics. $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (abbreviated as BNT) composition has been considered to be a good candidate of lead-free piezoelectric ceramics because of its strong ferroelectricity at room temperature and high Curie temperature T_C of 320 °C.^{1–4} It has a rhombohedral perovskitelike structure and shows an anomaly in dielectric properties at about 230 °C, which can be called the depolarization temperature T_d due to a transition from a ferroelectric to antiferroelectric state.^{2–6}

It is known that BNT single crystal shows high piezoelectric properties.⁷ However, BNT ceramics has high conductivity, causing some difficulty in the poling and their electromechanical properties are much lower than PZT ceramics. Furthermore, BNT ceramics depolarize above T_d . Some studies indicate that modifications of BNT ceramics can improve the poling process and the electrical properties. For examples, BNT-based compositions have been modified with BaTiO_3 (BT),⁵ $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BKT),⁶ NaNbO_3 ,⁸ $\text{Bi}_2\text{O}_3\cdot\text{Sc}_2\text{O}_3$,⁹ $\text{Ba}(\text{Cu}_{1/2}\text{W}_{1/2})\text{O}_3$,¹⁰ $\text{BaTiO}_3+\text{CeO}_2$,¹¹ and La_2O_3 .¹² All of them show improved piezoelectric properties and easier treatment in the poling process compared with pure BNT ceramics. But, the electromechanical properties are still too low for practical use or T_d is reduced significantly. The high piezoelectric properties are only obtained on some BNT-based single crystal.¹³ In order to improve the piezoelectric properties of BNT-based ceramics further without influencing T_d , we have proposed to employ a multicomponent system based on comparison of composition and structure between PZT and BNT ceramics. Our preliminary work has revealed that $(0.95-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3-0.05\text{BaTiO}_3$ ceramics are easy to pole

and have good electromechanical properties and relatively high depolarization temperature.¹⁴ Nagata *et al.* also reported their work on BNT–BKT–BT system even though the report was limited to piezoelectric constant and Curie temperature T_C .¹⁵ Until now, however, there is no report on the dielectric properties and microstructure of the system. In this paper, we present the dielectric behavior and microstructural feature of $(0.95-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3-0.05\text{BaTiO}_3$ ceramics (abbreviated as BNT–BKT–BT100 x , with x value ranging from 0 to 20 mol %).

II. EXPERIMENT

The conventional mixed oxide method was used to prepare the $(0.95-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3-0.05\text{BaTiO}_3$ (BNT–BKT–BT100 x with x varying from 0 to 20 mol %) ceramics. The commercially available Bi_2O_3 (99.9%, Acros Organics), Na_2CO_3 (99.5%, Wako Chem. Co. Ltd), BaCO_3 (99.9%, Wako Chem. Co. Ltd), KCO_3 (99.0%, Panreac Quimica SA), and TiO_2 (99.9%, Aldrich Chem. Co.) were used as raw materials. BNT, BKT, and BT were prepared separately. BNT and BKT were calcined at 800 °C for 1 h and BT was calcined at 1150 °C for 2 h. Then, they were weighted according to the above formula and were milled in alcohol using Y_2O_3 -stabilized zirconia balls for 10 h. The mixtures were dried and mixed with Polyvinyl alcohol (PVA) as a binder for granulation. The granulated powders were uniaxially pressed to form 22-mm-diameter and 2-mm-thickness disks. The compacted disks were sintered at 1170 °C for 2 h in air. Silver paste was applied on both surfaces of the disks and fired at 650 °C as electrodes. The samples for measurement of dielectric properties were poled in silicone oil at 80 °C under 4.5 kV/mm for 5 min.

Dielectric properties of the samples were determined as a function of frequency using the HP4294A impedance analyzer. The temperature dependence of relative permittivity and loss tangent of the poled samples was examined using a programmable furnace with an impedance analyzer (HP 4192A Impedance Analyzer) at 10 kHz. The crystalline phase of the sample was examined using an x-ray diffracto-

^{a)}FAX: +852-23337629; electronic mail: xx.wang@polyu.edu.hk

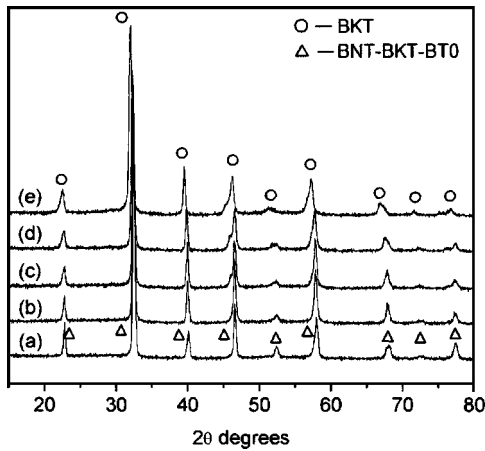


FIG. 1. X-ray diffraction patterns of (a) BNT-BKT-BT0, (b) BNT-BKT-BT5, (c) BNT-BKT-BT10, (d) BNT-BKT-BT20, and (e) BKT ceramics.

meter (XRD-Philips Expert System). The microstructures of the sintered samples were observed using a scanning electron microscope (SEM-Leica Stereoscan 440).

III. RESULTS AND DISCUSSION

The XRD patterns of the BNT-BKT-BT0, BNT-BKT-BT5, BNT-BKT-BT10, BNT-BKT-BT20, and BKT ceramics in Fig. 1 show that all the samples have pure perovskite structure. BKT appears to have diffused into the lattice to form a solid solution. The microstructures of the sintered BNT-BKT-BT100 x ceramics containing 0, 5, 10, and 20 mol % BKT were observed using SEM, and the micrographs of these samples are shown in Fig. 2. The incorporation of 5 mol % BKT caused no evident change in the microstructure except for a slight increase in the grain size [Figs. 2(a) and 2(b)]. However, further increase in the amount of BKT to 10 mol % leads to an obvious change in the feature of grain shape [Fig. 2(c)]. When the amount of BKT is increased to 20 mol %, the grain growth is suppressed and the grains grow into clear and neat rectangular shapes [Fig. 2(d)].

Figure 3 reveals relative permittivity ϵ_r and loss tangent $\tan \delta$ of poled and unpoled BNT-BKT-BT100 x ceramics as a function of BKT content. It can be seen that the unpoled

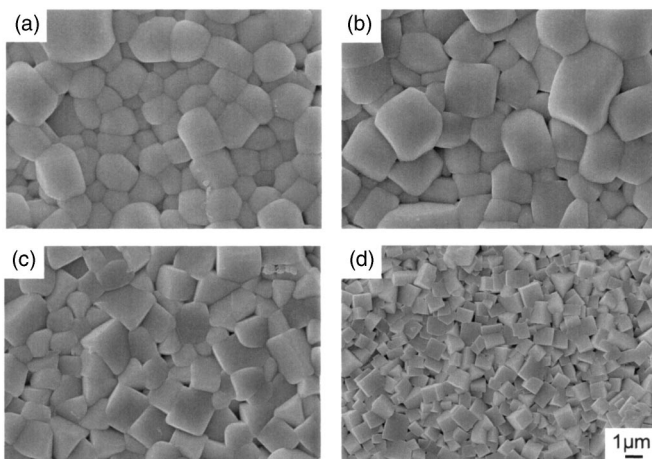


FIG. 2. SEM micrographs of (a) BNT-BKT-BT0, (b) BNT-BKT-BT5, (c) BNT-BKT-BT10, and (d) BNT-BKT-BT20 ceramics.

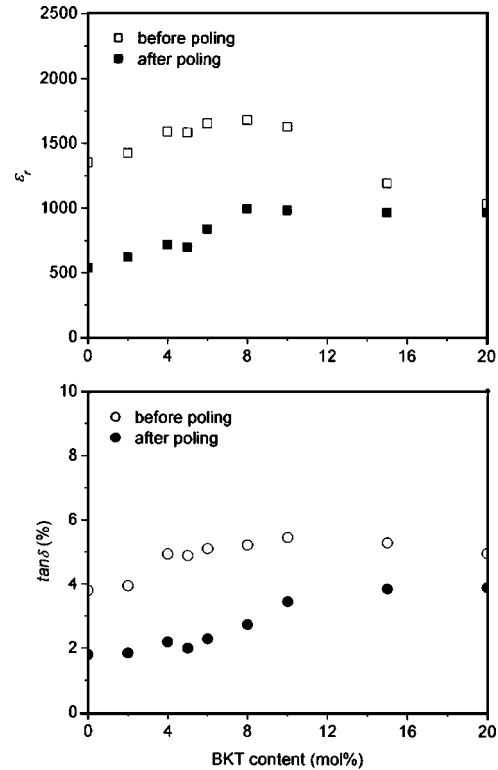


FIG. 3. Relative permittivity and loss tangent of the BNT-BKT-BT100 x ceramics as a function of the amount of BKT.

samples have ϵ_r and $\tan \delta$ higher than those of poled samples. This shows that under a poling field, the movement of domains results in a decrease in ϵ_r and $\tan \delta$. The difference in ϵ_r and $\tan \delta$ between unpoled and poled samples depends on BKT content, which is ascribed to the influence of the BKT content on the structure. When BKT content increases, tetragonal feature in the BNT-BKT-BT100 x ceramics increases, which reduces the differences between unpoled and poled samples.¹⁴ For both unpoled and poled samples, the relative permittivity increases with increasing BKT amount initially, reaches a maximum at 8 mol % of BKT, and then shows a slight decrease with further increase in BKT. Incorporation of BKT into BNT-BKT-BT0 composition reveals a tendency to increase the loss tangent.

Figure 4 shows the frequency dependence of ϵ_r and $\tan \delta$ for the samples with different amounts of BKT at room temperature, respectively. It is seen that ϵ_r decreases with increasing frequency up to 1000 kHz. But, at relatively low frequency, ϵ_r depends on frequency strongly, showing a dielectric dispersion evidently. Such a strong dispersion seems to be a common feature in ferroelectric materials concerned with ionic conductivity, which is referred as low-frequency dielectric dispersion.¹⁶ When the frequency increases, the relative effect of ionic conductivity becomes small and as a result, the frequency dependence of ϵ_r becomes weak. In contrast, $\tan \delta$ reveals a different variation with frequency and increases when frequency rises, which can be ascribed to ionic conductivity. With an increase in frequency, retardation in polarization caused from ionic conductivity is enhanced, leading to an increase in $\tan \delta$.

The ϵ_r and $\tan \delta$ of BNT-BKT-BT100 x ceramics were

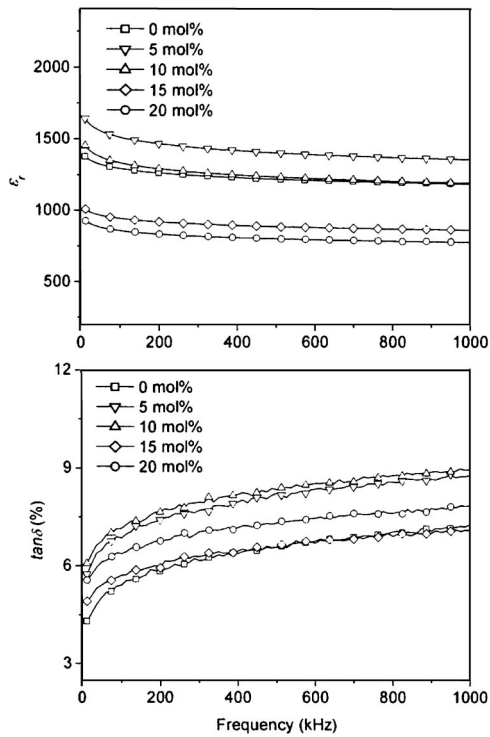


FIG. 4. Relative permittivity and loss tangent of the BNT–BKT–BT100 x ceramics at different amounts of BKT as a function of frequency.

measured as a function of temperature, as shown in Fig. 5. It can be seen that all ϵ_r versus temperature curves are similar. The relative permittivity of the samples increases with temperature with a sharp jump at T_d and reaches a maximum at a temperature T_m . Then they decrease gradually with further increase in temperature. It is seen that the peaks corresponding to T_m are broad, implying that the phase transition is of a diffuse type. Furthermore, they can be divided into three different regions by T_d and T_m , which may be similar to those reported in the previous study.⁵ But, ϵ_r increases as the BKT content increases. In contrast, $\tan\delta$ versus temperature curves of the samples show different changes except that they increase abruptly at T_d . BNT–BKT–BT0 ceramics show a relatively low loss tangent at room temperature, but the value increases greatly when the temperature is above 200 °C. Addition of BKT increases $\tan\delta$ of the samples at room temperature, but decreases them significantly at temperature even over T_m , implying a reduction of conduction. If $\tan\delta$ of BNT–BKT–BT0 ceramics above T_m is mainly related to the movement of Na^+ , addition of BKT in BNT–BKT–BT0 composition suppresses such movement and reduces $\tan\delta$ at relatively high temperature. In addition, T_d and T_m of BNT–BKT–BT100 x ceramics also depend on the BKT content. At a higher level of BKT, both of them increase. That is to say, the transition from a cubic phase to a

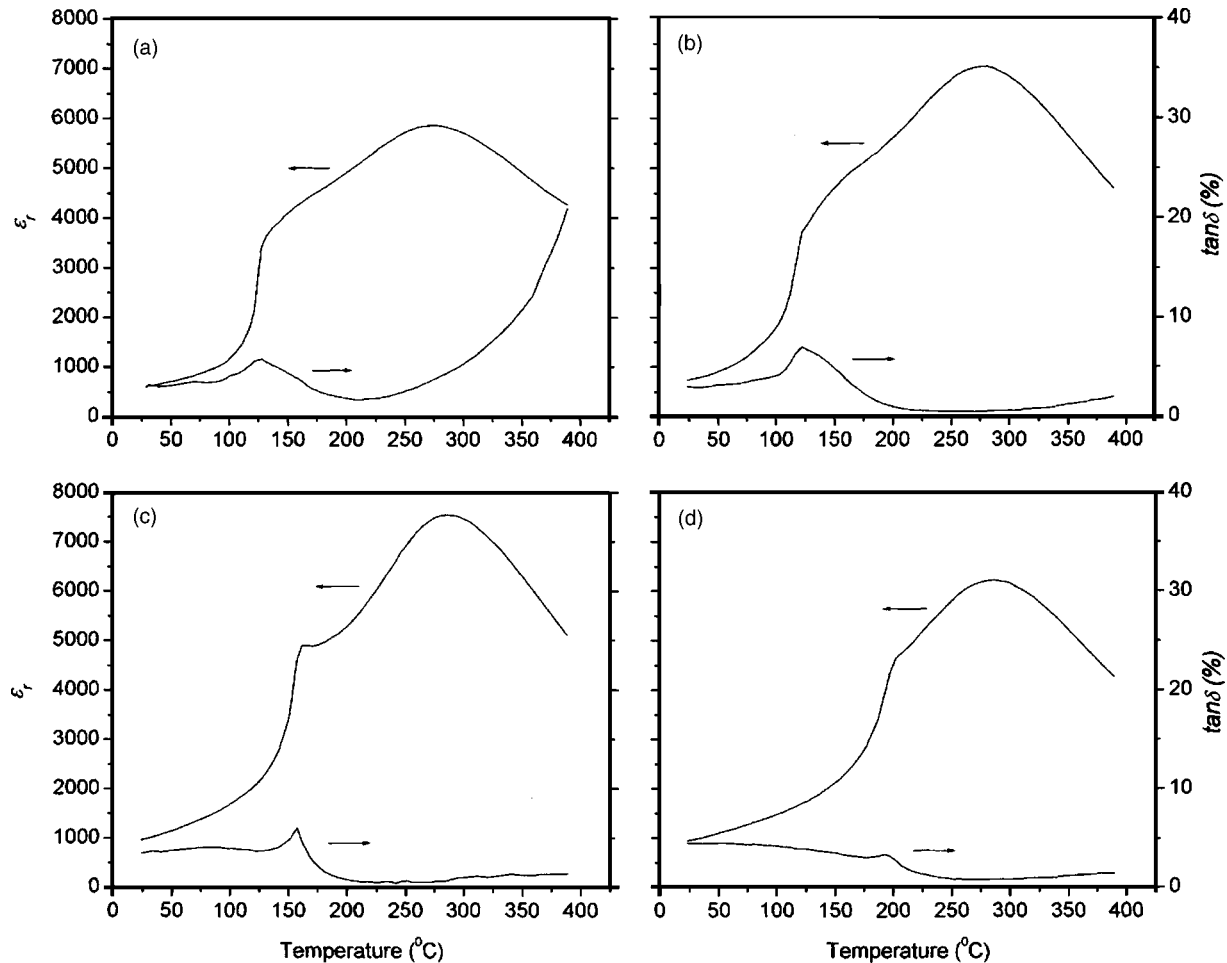


FIG. 5. Relative permittivity and loss tangent of the BNT–BKT–BT100 x ceramics with different amounts of BKT (a) 0, (b) 5, (c) 10, and (d) 20 mol % as a function of temperature at 10 kHz.

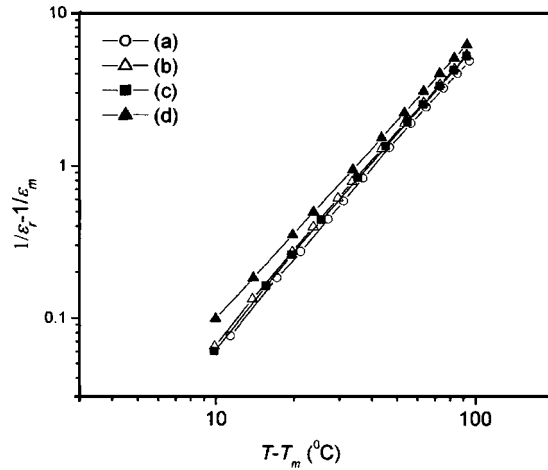


FIG. 6. Logarithm of $(1/\epsilon_r - 1/\epsilon_m)$ against logarithm of $(T - T_m)$ for the BNT-BKT-BT100 x ceramics with different amounts of BKT (a) 0, (b) 5, (c) 10, and (d) 20 mol %.

tetragonal phase and from a tetragonal phase to a rhombohedral phase shift towards higher temperature with increasing content of BKT in the system.

On the basis of the above result, it is obvious that the temperature-dependent permittivity of BNT-BKT-BT100 x ceramics does not follow the classical Curie-Weiss law at temperature higher than T_m . The quantitative assessment of the diffusivity in the paraelectric phase is done using a quadratic relation as follows:

$$(1/\epsilon_r - 1/\epsilon_m) = A(T - T_m)^\gamma, \quad (1)$$

where ϵ_r is the relative permittivity at temperature T , ϵ_m is its maximum value at T_m , and γ is called a diffusion coefficient ranging from 1 to 2 for the materials with a diffuse phase transition.¹⁷ A plot of $\log(1/\epsilon_r - 1/\epsilon_m)$ vs $\log(T - T_m)$ is shown in Fig. 6. The values of γ (1.8–1.9) are calculated from the plots in Fig. 6. These values of γ for BNT-BKT-BT100 x ceramics with difference of BKT give the γ value near 2, which shows that the material is highly disordered. It is known that the broadened peak in ϵ_r versus temperature curve and its deviation from the Curie-Weiss law are the main characteristics of a diffuse phase transition of a material. Both of these phenomena may be ascribed to disordering caused by compositional fluctuation and structural defects.^{18,19} The diffusiveness in ϵ_r versus temperature curve is one of the most important feature of the disordered perovskite structure with diffuse phase transition.²⁰ The diffusiveness in BNT-BKT-BT100 x ceramics seems to occur mainly due to compositional fluctuation and structural disorder in the arrangement of cations in one or more crystallographic sites of the structure.

IV. CONCLUSION

Dielectric properties and microstructure of $(0.95 - x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - x(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3 - 0.05\text{BaTiO}_3$ (BNT-BKT-BT100 x with $x=0-20$ mol%) lead-free piezoelectric ceramics have been investigated. The relative permittivity of the samples at room temperature and temperature T_m increases with the content of BKT up to a certain amount. Incorporation of BKT increases the loss tangent at room temperature, but lowers it at the temperature above T_d . The results show the feature of the disordered perovskite structure with diffuse phase transition. Different BKT contents also affect the microstructure. During sintering, the incorporated BKT diffuses into the lattice of BNT-BKT-BT0 composition to form a solid solution.

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- ¹T. Takanaka, *Ultrasonic Technology* **8**, 2 (2001).
- ²G. A. Smolenskii, V. A. Isupov, A. I. Agranovskaya, and N. N. Krainik, *Sov. Phys. Solid State* **2**, 2651 (1961).
- ³J. Suchanicz, K. Roleder, A. Kania, and J. Handerek, *Ferroelectrics* **77**, 107 (1988).
- ⁴M. S. Hagiyev, I. H. Ismaizade, and A. K. Abiyev, *Ferroelectrics* **56**, 215 (1984).
- ⁵T. Takenaka, K. Maruyama, and K. Sakata, *Jpn. J. Appl. Phys., Part 1* **30**, 2236 (1991).
- ⁶A. Sasaki, T. Chiba, Y. Mamiya, and E. Otsuki, *Jpn. J. Appl. Phys., Part 1* **38**, 5564 (1999).
- ⁷S.-E. Park, S.-J. Chung, and I.-T. Kim, *J. Am. Ceram. Soc.* **79**, 1290 (1996).
- ⁸T. Takenaka, T. Okuda, and K. Takegahara, *Ferroelectrics* **196**, 175 (1997).
- ⁹T. Takenaka and H. Nagata, *Jpn. J. Appl. Phys., Part 1* **36**, 6055 (1997).
- ¹⁰X. X. Wang, H. L. W. Chan, and C. L. Choy, *J. Am. Ceram. Soc.* **86**, 1809 (2003).
- ¹¹X. X. Wang, H. L. W. Chan, and C. L. Choy, *Solid State Commun.* **125**, 395 (2003).
- ¹²A. Herabut and A. Safari, *J. Am. Ceram. Soc.* **80**, 2954 (1997).
- ¹³Y. M. Chiang, G. W. Farrey, and A. N. Soukhovjak, *Appl. Phys. Lett.* **73**, 3683 (1998).
- ¹⁴X. X. Wang, X. G. Tang, and H. L. W. Chan, *Appl. Phys. Lett.* **85**, 91 (2004).
- ¹⁵H. Nagata, M. Yoshida, Y. Makiuchi, and T. Takenaka, *Jpn. J. Appl. Phys., Part 1* **42**, 7401 (2003).
- ¹⁶S. P. Yordanov, I. Ivanov, and C. P. Carapanov, *J. Phys. D* **31**, 800 (1998).
- ¹⁷S. M. Pilgrim, A. E. Sutherland, and S. R. Winzer, *J. Am. Ceram. Soc.* **73**, 3122 (1990).
- ¹⁸C. G. F. Stenger and A. I. Buggraaf, *J. Phys. Chem. Solids* **41**, 25 (1980).
- ¹⁹L. E. Cross, *Ferroelectrics* **76**, 241 (1987).
- ²⁰Y. Yokoizo, T. Takahashi, and S. Nomura, *J. Phys. Soc. Jpn.* **28**, 1278 (1970).

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