

Dielectric behavior and phase transition in perovskite oxide $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}\text{Ti}_x\text{O}_3$ single crystal

Yanmin Jia,^{1,2,a)} Haosu Luo,² Siu Wing Or,³ Yu Wang,⁴ and Helen Lai Wa Chan⁴

¹Novel Aerospace Materials Group, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands

²State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Chengbei Road 215, Jiading, Shanghai 201800, China

³Department of Electrical Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong

⁴Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong

(Received 2 February 2009; accepted 24 May 2009; published online 26 June 2009)

Perovskite oxide $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ crystals, which were grown using a modified Bridgman method, show a high low-frequency dielectric constant response at room temperature. The Curie phase transition occurs at 523 K. The characteristic frequency of the dielectric dispersion versus the inverse of temperature obeys an Arrhenius relation, which shows a thermally activated behavior. The thermal activation energy for relaxation was found to be ~ 0.14 eV. The high dielectric permittivity was attributed to oxygen vacancies and conduction via hopping carriers. © 2009 American Institute of Physics. [DOI: 10.1063/1.3156655]

I. INTRODUCTION

Materials with a high dielectric constant are of great importance for microelectronic applications such as memory devices based on capacitive components. So far, many materials with high dielectric constant have been reported,¹⁻³ however their dielectric constant shows strong temperature and frequency dependence, which is undesirable for the application in microelectronics.⁴ Recently, complex perovskite oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) crystals have attracted much attention^{1,2} because of their colossal dielectric constant ($\sim 10^5$) around room temperature and a flat temperature dependence of the dielectric constant over a broad temperature range. Such temperature independent behavior can occur either at low or high temperatures depending on the physical mechanism and the characteristic thermal activation energy.³

Jha *et al.*⁴ reported that the presence of a partially filled *d*-band, as present in metallic copper, gives rise to conducting (often superconducting) properties in copper-based materials, which may also apply to the Cu containing perovskite oxide. To develop dielectric materials with even better properties, we have chosen to replace the copper in the complex perovskite oxide with iron atoms.

Perovskite-type oxide $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) has recently generated considerable interest because of its unusual properties, including low sintering temperatures,^{5,6} mutiferrous,⁷ diffuse phase transition,⁸ and positive temperature coefficient of resistivity effect.⁹ However, the Curie temperature of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ is low (~ 387 K), which limits its application in microelectronics. Just like its counterparts, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ or $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ materials,^{10,11} its Curie temperature can be enhanced by adding PbTiO_3 to fabricate binary solid solutions. In this paper we report a kind of PFN-based oxide material, $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}\text{Ti}_x\text{O}_3$ (PFNT), whose dielectric properties

appear promising. We analyzed its structural characteristics by x-ray diffraction (XRD) and studied the temperature and frequency dependence of its dielectric relaxation.

PFN is structured in rhombohedral symmetry (space group = $R3m$) at room temperature with Curie temperature of ~ 387 K. Also PbTiO_3 (PT) is a perovskite compound with the structure of tetragonal symmetry (space group $P4/mmm$) at room temperature. Its Curie temperature is ~ 763 K. PFNT system is regarded as relaxor ferroelectric with a morphotropic phase boundary (MPB).^{12,13} The nature of phase transition in PFNT changed from diffuse ferroelectric to relaxor ferroelectric to normal ferroelectric on increasing the PT content. MPB compositions have anomalously high dielectric and ferroelectric properties as a result of enhanced polarizability arising from the coupling between two equivalent energy states, i.e., the tetragonal and rhombohedral phases, allowing optimum domain reorientation during the poling process. In PFNT ceramics, the location of the MPB is controversial. According to reports,¹⁴ the MPB is located around $x=0.05 < X < 0.06$, $x=0.08$,¹⁵ $x=0.06-0.08$,¹² $x=0.1-0.2$,¹⁶ or $x=0-0.1$.¹³ This structure is rhombohedral up to MPB and tetragonal for higher content of PT.

II. EXPERIMENTAL

High quality $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ single crystals were grown in a modified Bridgman method.¹⁷ No grain boundaries were found in the crystal by naked eyes. Segregation coefficient is up to $>95\%$.¹⁷ The x-ray powder diffraction on the crystals confirmed the pure perovskite structure without impurities.¹⁷ No pyrochlore phase was found. The crystalline quality of the crystal was evaluated by x-ray rocking curve analysis.¹⁷⁻¹⁹ Powder XRD data were obtained with a Bruker D8 advance diffractometer with Cu $K\alpha$ radiation. A step size of 0.05° with a step time of 1 s was used for the 2θ range of $10^\circ-70^\circ$. As-grown crystals were oriented along the $\langle 001 \rangle_{\text{cub}}$ direction on basis of the XRD results and

^{a)}Electronic addresses: y.jia@tudelft.nl and yanmin_jia@yahoo.com.cn.

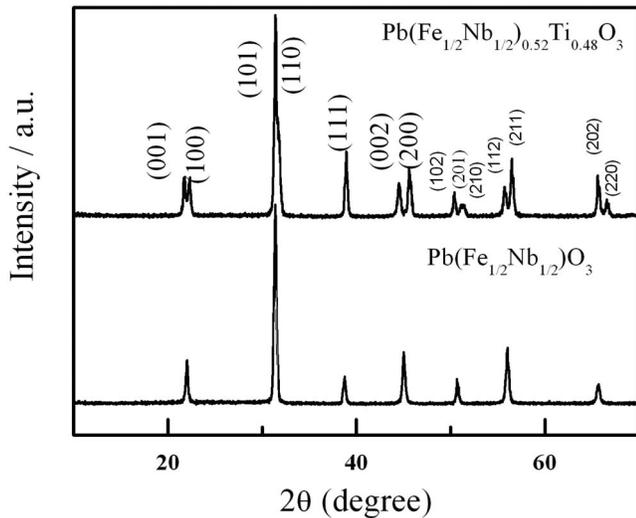


FIG. 1. XRD pattern of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ and pure $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ samples.

were cut into the dimensions of $5 \times 5 \times 1 \text{ mm}^3$. The as-prepared samples were sputtered with gold to create two electrodes on either side of the sample. The complex dielectric permittivity, ac electrical conductivity, and dielectric loss over a broad temperature range (80–580 K) and frequency range ($5\text{--}1.3 \times 10^7 \text{ Hz}$) were measured in vacuum with a HP 4192A impedance analyzer. The low temperature data were obtained starting from liquid nitrogen temperature. The rate of temperature increase was computer controlled and set at 1 K/min.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ and pure PFN samples. XRD analysis confirmed that no additional pyrochlore phases were formed. The crystal structure varied with PT content. For pure PFN, the structure is rhombohedral. For $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$, the structure is tetragonal.

The dielectric permittivity versus temperature curve for the $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ sample at a frequency of 10 MHz was plotted in Fig. 2. The dielectric permittivity peak is found at 523 K. $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ crystal is known to possess the tetragonal structure at room temperature and shows a normal ferroelectric behavior. The sharp change in dielectric permittivity corresponds to a phase transition from the tetragonal ferroelectric phase (FE_T) to the cubic paraelectric phase (PE_C). The dielectric constants exhibit a very little frequency dispersion over this temperature range.

The frequency dependence of the dielectric permittivity of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ single crystals and their dissipation factor is shown in Figs. 3(a) and 3(b). $\epsilon'(f)$ curve generally shows two plateaus at low-frequency and high frequency ranges, respectively. The drop from the high plateau value to the low one drops with increasing of frequency showing a large frequency dispersion region. At fixed temperatures, $\epsilon''(f)$ curve shows overdamped, inhomogeneously broadened peaks at characteristic frequencies $\omega(T) = 2\pi f(T)$

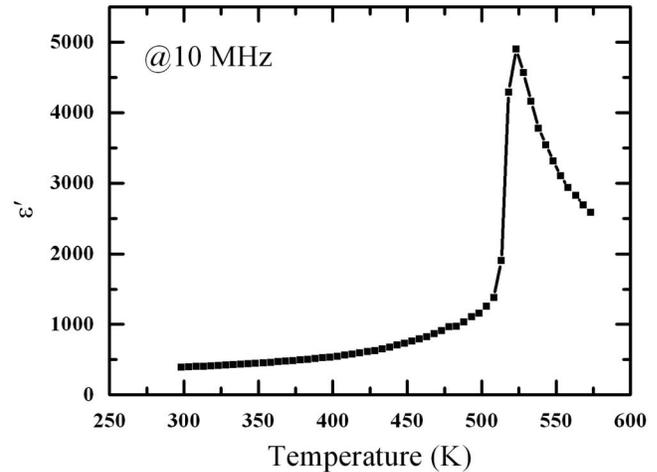


FIG. 2. Temperature dependence of dielectric permittivity at 10 MHz frequency of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ single crystals.

$= 1/\tau$ [where $\tau(T)$ is the relaxation time]. Strong relaxation peaks lead to a colossal dielectric constant below $\omega(T)$, observed up to 410 K and even above.

The peak position in Fig. 3(b) shifts toward higher frequency with increasing the temperature. The frequency of the peak maximum is an indication of a transition from a short range to a long range hopping at decreasing frequency.²⁰ On the low-frequency side of the peak, the electrons can hop over long distances, i.e., electrons can perform successful hopping from one site to the neighboring site. On the high frequency side of the peak, the electrons are spatially confined to their potential energy wells and can make localized motion. The broadening of the peak indicates the

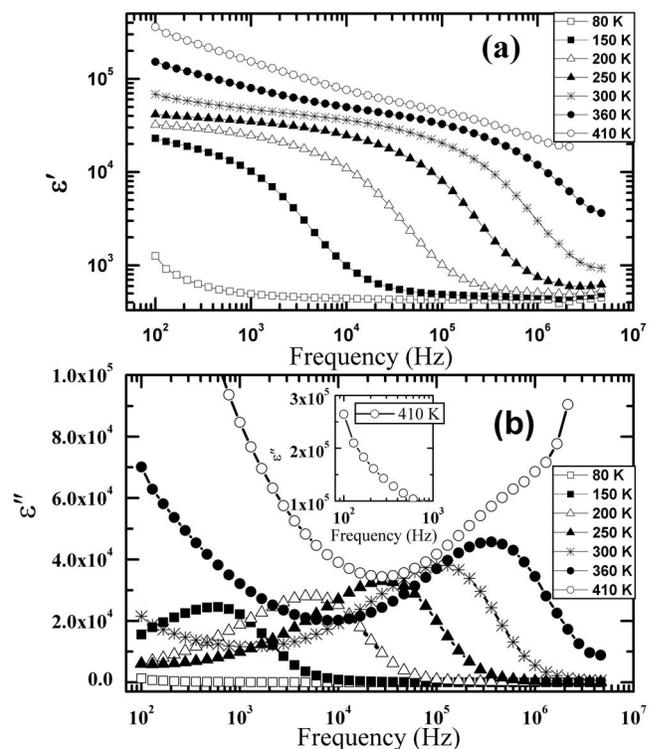


FIG. 3. Frequency dependence of dielectric permittivity at several temperatures.

spread of relaxation with different time constants. The electron (polaron) hopping in ionic crystals is usually evidenced by optical absorption¹ and conductivity. It is well known that charge carriers can produce direct current conduction and make a contribution to the dielectric behavior. At low frequency, dielectric responses are to be expected from any localized charge carriers. Under the action of an ac electric field, the charge can hop between the equivalent lattice sites available. The conductivity mechanism of hopping is equivalent to the reorientation of an electric dipole, which gives a frequency dependent complex dielectric permittivity.

It is well known that in dielectric materials several polarization mechanisms may be responsible for the relaxation phenomena, namely, space charge, interfacial, and dipolar polarizations. Generally speaking the dielectric relaxation due to space charge or interfacial polarization occurs at low frequency (<1 MHz) while dipolar relaxation appears usually in the radio frequency or microwave frequency ranges. Oxygen vacancies and the heterovalent impurities of Fe³⁺ are the source of free charges that provides the elastic energy, which is necessary for a polaronic state to occur.¹⁹ At low temperature, the oxygen vacancy density is low and the hopping distance is lower (electric dipoles frozen),¹ so the height of peak in Fig. 3(b) is low.

According to Kang and Yoon,²¹ the semiconductive behavior is due to the hole conductivity caused by the partial reduction from Fe³⁺ to Fe²⁺. The hole conductivity contributes to the colossal dielectric permittivity and anomaly dielectric behavior. Ikeda *et al.*²² reported that the elementary process of dispersion is related to electron hopping between Fe²⁺ and Fe³⁺ ions in polycrystalline ErFe₂O_{4- δ} , which behaves a similar frequency and temperature dependence of dielectric permittivity.

The Pb(Fe_{1/2}Nb_{1/2})_{0.52}Ti_{0.48}O₃ system, in which the Fe ions are in 3+ valence states, should behave as an insulator with very low dielectric losses. However, during the crystal growth processes, oxygen vacancies and charge carriers (electrons and holes) are generated contributing to a complex system of conduction mechanisms. Using the Kroger-Vink notation of defects, the occurrence of oxygen vacancies can be represented by the thermally activated reaction



where the two liberated electrons can be captured by the Fe³⁺ ions,



Thus, oxygen vacancies act as donor centers promoting extrinsic *n*-type conduction. Moreover, their existence leads to the hopping mechanism of conductivity which is believed to be dominant in PFN and other PFN-like oxides.^{23,24} The electric conduction mechanism for Pb(Fe_{1/2}Nb_{1/2})_{0.52}Ti_{0.48}O₃ system proposed is that the electric conduction in the solid solution system arises from the hopping of electrons from Fe²⁺ to Fe³⁺ through oxygen vacancies.^{25,26}

The relaxation process had the characteristics of a simple Debye-type relaxation process.^{1,3} On basis of the data in Fig.

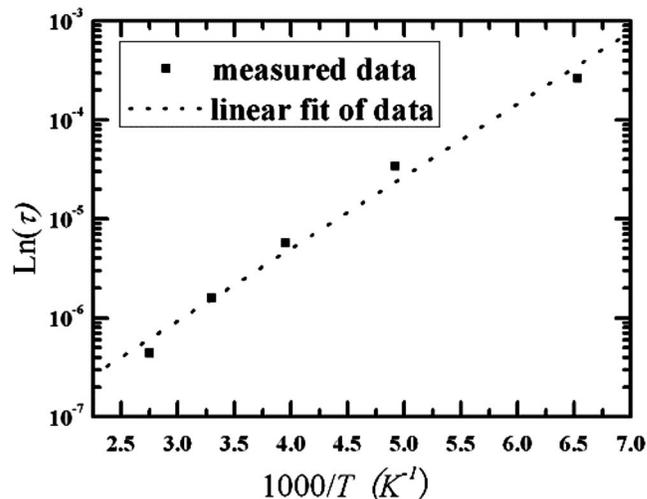


FIG. 4. The logarithm of the relaxation time τ vs $1/T$ for Pb(Fe_{1/2}Nb_{1/2})_{0.52}Ti_{0.48}O₃ single crystals which shows the activated behavior $\tau = \tau_0 \exp(U/k_B T)$; a linear regression of the data (dotted lines) yields the values $U = 0.145$ eV and $\tau_0 \sim 6.01$ ns.

3, we can plot the curve of the logarithm of the relaxation time τ versus $1/T$, as shown in Fig. 4, to reveal a regular thermally activated behavior described by

$$\tau = \tau_0 \exp(U/k_B T), \quad (2)$$

where τ_0 is a prefactor and U is the activation energy. A linear regression of the data (dotted lines) yields the following values for U , $U = 0.145$ eV and τ_0 , $\tau_0 \sim 6.01$ ns. This value for the activation energy is consistent with the one reported for PFN crystals (0.14 eV).²³ As the temperature increases, the relaxational time shortens and the dielectric permittivity increases dramatically.

The activation energy of the conductivity is rather small (0.145 eV). It is believed to be mainly connected with charge carrier mobility. It shows on a hopping mechanism of the conductivity associated with the occurrence of oxygen vacancies and valence change in the transition elements Fe³⁺ and Fe²⁺. In an oxide ion conductor, current flows by the movement of oxide ions through the crystal lattice. This is a thermally activated process, where the ions hop from one lattice site to the other (from one potential valley to the other) in a random way. Ionic hopping conduction depends on the mobility of the ions and therefore on temperature. With the increasing of temperature, the conductivity becomes higher. The crystal has to contain unoccupied sites that are equivalent to the occupied sites by lattice oxygen ions. The energy barrier for migration from an occupied site to an unoccupied site must be small (≤ 1 eV). The relative size of the oxygen ions is bigger than metal ions (which seem more easily migrate in an electric field). So there are only a few special structures that make oxygen ion migration possible: fluorite structured oxides, perovskites, one-dimensional semiconductor (NbSe₄)₃I,²⁷ and so on.

The activation energy and relaxation time values are comparable with those for CCTO ($U = 0.054$ eV and $\tau_0 \sim 84$ ns).¹ On basis of the summary of conduction mechanisms and associated activation energy values for various semiconductive ferroelectric materials reported by Raymond

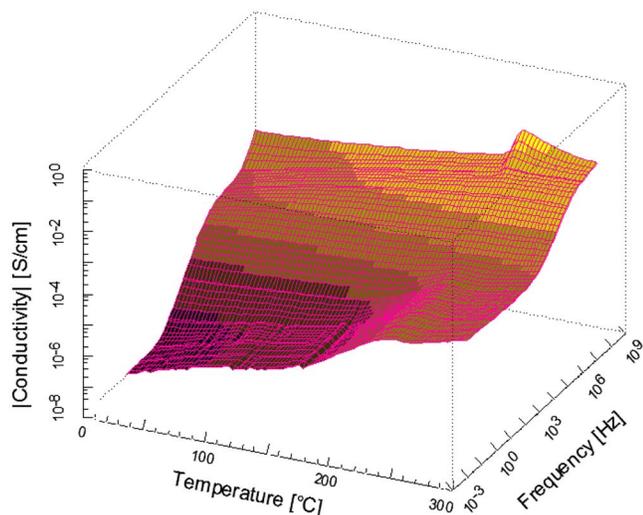


FIG. 5. (Color online) Three dimensional plot of temperature and frequency dependence of ac electrical conductivity for $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ crystals.

et al.,²⁸ the conduction mechanism is charge hopping when the activation energy is <0.4 eV. As the activation energy for our material is well below this value we expect this mechanism to apply here as well.

The temperature and frequency dependence of the ac electrical conductivity for $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ samples are shown in Fig. 5. The activation energy associated with the prevailing conduction mechanism over the analyzed temperature region can be calculated from the slope of the $\ln \sigma$ versus $1/T$ plot.²⁸ At low temperatures, charge hopping (*n*-types) is the main conduction mechanism resulting in a low activation energy.²⁸ At high temperatures (near the Curie temperature), the ionic conductivity is an intrinsic and typical conduction mechanism in ferroelectric materials.^{9,29} Also the activation energy will increase at high temperatures, as is indeed observed. The obvious peak at 250 °C in Fig. 5 is related to the Curie temperature of this $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ system.

IV. CONCLUSIONS

In a summary, a kind of oxide crystal of the formula $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ having a tetragonal perovskite structure has been grown in a modified Bridgman method. This oxide crystal has an unusually high dielectric permittivity compared to most oxides. We have studied high dielectric permittivity and relaxation behavior in this high-dielectric material. The frequency dependence of the dielectric permittivity shows strong dispersion. The Curie phase transition occurs at 523 K. The characteristic frequency of the dielectric dispersion versus the inverse of temperature (kelvin) obeys an Arrhenius relationship, which shows an activated behavior of energy barriers. For $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.52}\text{Ti}_{0.48}\text{O}_3$ crystals, the activated energy is very small (~ 0.14 eV).

Hence, the abnormal dielectric behavior was attributed to oxygen vacancies and the carrier hopping conduction.

ACKNOWLEDGMENTS

This work was supported by the Smartmix program funded by the Dutch government (Grant No. SMVA0607) as part of the program “Smart systems based on integrated piezo,” The Netherlands, 863 High Technology and Development Project of the People’s Republic of China (Grant No. 2006AA03Z107), and the Hong Kong Research Grants Council of the HKSAR Government (Grant No. PolyU 5266/08E). The authors would also like to show their appreciation to Professor Dr. S. van der Zwaag from the Faculty of Aerospace Engineering, Delft University of Technology for helpful discussion and kind embellishment in English language.

- ¹C. C. Homes, T. Vogt, S. Shapiro, S. Wakimoto, and A. P. Ramirez, *Science* **293**, 673 (2001).
- ²S. Y. Chung, I. D. Kim, and S. J. Kang, *Nature Mater.* **3**, 774 (2004).
- ³J. Xu and M. Itoh, *Chem. Mater.* **17**, 1711 (2005).
- ⁴P. Jha, S. Bobev, G. N. Subbanna, and A. K. Ganguli, *Chem. Mater.* **15**, 2229 (2003).
- ⁵B. Fang, Y. Shan, K. Tezuka, and H. Imoto, *Phys. Status Solidi A* **202**, 481 (2005).
- ⁶S. Ananta and N. W. Thomas, *J. Eur. Ceram. Soc.* **19**, 2917 (1999).
- ⁷Y. Yang, J. M. Liu, H. B. Huang, W. Q. Zou, P. Bao, and Z. G. Liu, *Phys. Rev. B* **70**, 132101 (2004).
- ⁸A. A. Bokov, L. A. Shpak, and I. P. Rayevsky, *J. Phys. Chem. Solids* **54**, 495 (1993).
- ⁹S. B. Lee, S. H. Yoon, and H. Kim, *J. Eur. Ceram. Soc.* **24**, 2465 (2004).
- ¹⁰H. S. Luo, G. S. Xu, H. Q. Xu, P. C. Wang, and Z. W. Yin, *Jpn. J. Appl. Phys., Part 1* **39**, 5581 (2000).
- ¹¹B. J. Fang, Y. J. Shan, H. Q. Xu, H. S. Luo, and Z. W. Yin, *Adv. Funct. Mater.* **14**, 169 (2004).
- ¹²V. S. S. S. Sunder and A. M. S. Umarji, *Mater. Res. Bull.* **30**, 427 (1995).
- ¹³S. P. Singh, A. K. Singh, D. Pandey, H. Sharma, and O. Parkash, *J. Mater. Res.* **18**, 2677 (2003).
- ¹⁴S. P. Singh, D. Pandey, S. Yoon, S. Baik, and N. Shin, *Appl. Phys. Lett.* **93**, 182910 (2008).
- ¹⁵S. P. Singh, A. K. Singh, and D. Pandey, *J. Phys.: Condens. Matter* **19**, 036217 (2007).
- ¹⁶T. Hashimoto, K. Ishibashi, and T. Yako, *J. Sol-Gel Sci. Technol.* **9**, 211 (1997).
- ¹⁷Y. Q. Gao, H. Q. Xu, Y. J. Wu, T. H. He, G. S. Xu, and H. S. Luo, *Jpn. J. Appl. Phys., Part 1* **40**, 4998 (2001).
- ¹⁸M. Jin, J. Xu, X. Li, H. Shen, and Q. He, *Cryst. Res. Technol.* **43**, 1074 (2008).
- ¹⁹J. Wang, X. Tang, H. Chan, C. Choy, and H. Luo, *Appl. Phys. Lett.* **86**, 152907 (2005).
- ²⁰M. M. Ahmad, K. Yamada, and T. Okuda, *Solid State Commun.* **123**, 185 (2002).
- ²¹D. H. Kang and K. H. Yoon, *Ferroelectrics* **87**, 255 (1988).
- ²²N. Ikeda, K. Kohn, H. Kito, J. Akimitsu, and K. Siratori, *J. Phys. Soc. Jpn.* **63**, 4556 (1994).
- ²³K. Wójcik, K. Zieleniec, and M. Milata, *Ferroelectrics* **289**, 107 (2003).
- ²⁴X. Qi, J. Dho, R. Tomov, M. G. Blamire, and J. L. MacManus-Driscoll, *Appl. Phys. Lett.* **86**, 062903 (2005).
- ²⁵W. M. Zhu and Z. G. Ye, *Ceram. Int.* **30**, 1435 (2004).
- ²⁶W. M. Zhu and Z. G. Ye, *Appl. Phys. Lett.* **89**, 232904 (2006).
- ²⁷D. Staresinic, P. Lunkenheimer, J. Hemberger, K. Biljakovic, and A. Loidl, *Phys. Rev. Lett.* **96**, 046402 (2006).
- ²⁸O. Raymond, R. Font, N. Suarez-Almodovar, J. Portelles, and J. M. Siqueiros, *J. Appl. Phys.* **97**, 084107 (2005).
- ²⁹S. P. Singh, A. K. Singh, and D. Pander, *Ferroelectrics* **324**, 49 (2005).