

# Dynamics of the phase transitions in Bi-layered ferroelectrics with Aurivillius structure: Dielectric response in the terahertz spectral range

D. Nuzhnyy, S. Kamba,\* P. Kužel, S. Veljko, V. Bovtun, M. Savinov, and J. Petzelt

*Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic*

H. Amorín, M. E. V. Costa, and A. L. Kholkin

*Department of Ceramics and Glass Engineering, University of Aveiro, 3810-193 Aveiro, Portugal*

Ph. Boullay

*Laboratoire de Sciences des Procédés Céramiques et Traitements de Surface, Université de Limoges, 123 Avenue Albert Thomas, F-87060 Limoges Cedex, France*

M. Adamczyk

*Institute of Physics, University of Silesia, 40-007 Katowice, ulica Uniwersytecka 4, Poland*

(Received 11 May 2006; published 5 October 2006; corrected 10 October 2006)

We have investigated the dielectric response in the terahertz (THz) spectral range of a series of Bi-layered ferroelectrics with Aurivillius structure involving ferroelectric compounds ( $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ,  $\text{SrBi}_2\text{Nb}_2\text{O}_9$ ), a relaxor ferroelectric ( $\text{BaBi}_2\text{Nb}_2\text{O}_9$ ), and intermediate-type compound ( $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Ta}_2\text{O}_9$ ). The lowest-frequency polar phonons were studied by means of the time-domain THz transmission spectroscopy in the frequency range 0.1–2 THz at temperatures 10–950 K. Although previous structural studies suggested a displacive character of the structural phase transitions, no soft-mode anomalies were observed in our THz spectra near  $T_c$  in any of the investigated compounds. A gradual and only partial softening of the lowest frequency polar phonon was revealed during heating. Dielectric anomalies near  $T_c$  in all the compounds should be caused by slowing down of relaxations, directly observed in some cases below the polar phonon range. The ferroelectric transitions are therefore not classically displacive. In analogy to other relaxor ferroelectrics, existence of dynamic polar clusters is suggested to be in origin of such relaxations. Ferroelectric transitions in such cases are connected with an abrupt freezing and rise of these clusters into domains and the classical division of phase transitions into displacive and order-disorder is no more sufficient.

DOI: [10.1103/PhysRevB.74.134105](https://doi.org/10.1103/PhysRevB.74.134105)

PACS number(s): 78.30.-j, 63.20.-e, 77.22.-d, 64.70.Kb

## I. INTRODUCTION

Bi-layered ferroelectrics with Aurivillius structure have the general chemical formula  $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$  ( $n=1-4$ ) and the crystal structure consists of perovskitelike blocks  $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$  interleaved with fluoridelike  $(\text{Bi}_2\text{O}_2)^{2+}$  layers perpendicular to pseudotetragonal  $c$  axis. Here  $B$  is a diamagnetic transition metal such as  $\text{Ti}^{4+}$  or  $\text{Nb}^{5+}$  and  $A$  is an alkali or alkaline earth cation.<sup>1</sup> Although the ferroelectric properties of these oxides have been known for more than 50 years,<sup>2,3</sup> most extensive studies have been carried out only during the last 10 years. The increased interest is owing to the high spontaneous polarization, fatigue-free behavior and low leakage currents of these compounds, which makes them promising for applications in nonvolatile ferroelectric memories.<sup>4-6</sup> The most intensively studied are  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) ( $n=2$ ) thin films, which are already utilized in FERAMs, but  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) ( $n=3$ ) thin films seem to be even more promising, as they show a higher polarization and can be deposited at lower temperatures.<sup>6,7</sup>

Much effort has been devoted to the specification of crystal structures and phase diagrams of Bi-layered Aurivillius compounds. Recent papers revealed that the results of the earlier structural determinations must be revised. New intermediate phases (between ferroelectric and paraelectric ones) with a doubled unit cell have been observed in some com-

pounds with two or three perovskite layers,<sup>8-11</sup> and significantly more advanced characterization of ferroelectric phases is now available.<sup>12-16</sup>

It is worth noting that no structural study has revealed any dynamical disorder; in addition, a temperature-dependent lowest-frequency optic mode observed by means of the Raman scattering experiments<sup>17-20</sup> has been identified with the ferroelectric soft mode. Based on these findings it has been generally accepted that the phase transitions in Bi-layered Aurivillius compounds are of displacive type. However, the intensity of the soft Raman mode, in agreement with the Raman selection rules, rapidly decreases upon heating and finally vanishes when the transition temperature  $T_c$  is approached. In this respect, the infrared (IR) spectroscopy has an advantage, because in the case of proper ferroelectric transitions the soft mode is IR active in both ferroelectric and paraelectric phases.

Up to now only  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) has been investigated by means of the IR and THz spectroscopy.<sup>10,21-23</sup> Surprisingly, the soft mode with frequency near  $28\text{ cm}^{-1}$  has shown no anomaly around  $T_c$ . Only a weak gradual softening of this mode was observed in the THz spectra during heating up to 950 K and, consequently, its contribution to the low frequency permittivity is much smaller than that needed to account for the reported dielectric anomaly near  $T_c=600\text{ K}$ . An additional relaxation was identified in the THz spectra and it

TABLE I. List of crystal structures and phase-transition temperatures in investigated compounds. Paraelectric phase has one formula unit per primitive unit cell ( $Z=1$ ), while other phases (except for BBN) have  $Z=2$ .  $T$  denotes temperature.

Material	Low $T$ str.	$T_{c1}$ (K)	Intermediate str.	$T_{c2}$ (K)	High $T$ str.
SBT	$A2_1am$ (Refs. 9 and 11)	$\sim 600$	$Amam$ (Refs. 9 and 11)	$\sim 770$	$I4/mmm$
SBN	$A2_1am$ (Refs. 13 and 16)	$\sim 710$			$I4/mmm$
BBN	$I4mm$ (Ref. 14)	$\sim 300$			$I4/mmm$
SBBT	$A2_1am$ (Ref. 31)	$\sim 430$			$I4/mmm$
BiT	$B1a1$ (Ref. 12), $B2cb$ (Ref. 15)	$\sim 940$	$Cmca$ (Ref. 15)	$\sim 970$	$I4/mmm$

was shown that its dielectric contribution is presumably responsible for the dielectric anomaly near  $T_c$ . Therefore it was proposed that the phase transition in SBT is prevalingly of order-disorder type.<sup>23</sup> Since no other Bi-layered Aurivillius compound was investigated in a similar way, we have performed such kind of studies on several materials, which are summarized, together with the list of their phase transition temperatures and space groups, in Table I.

Our experimental results, along with recent first-principle studies,<sup>24–28</sup> enable us to discuss the microscopic origin of the ferroelectric transitions in these compounds.

## II. EXPERIMENT

SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> (SBN) single crystal was grown using a modified high-temperature self-flux solution method described elsewhere.<sup>29</sup> A colorless, transparent, and defect-free sample with irregular shape and size  $\approx 4 \times 6 \times 0.1$  mm<sup>3</sup> was polished down to a 14- $\mu$ m-thick plate for the THz measurements.

Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BiT) single crystal was grown by the flux method in Bi<sub>2</sub>O<sub>3</sub> excess in a two-step process. First, BiT powder was synthesized at 850 °C from Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, using NaCl/KCl as a melting agent, and then washed in hot water. Single crystals were grown from the BiT powder in a Bi<sub>2</sub>O<sub>3</sub> excess (BiT:Bi<sub>2</sub>O<sub>3</sub> in a 1:8 molar ratio). About 6 g of powder was placed in a covered platinum crucible and subjected to the following thermal treatment: heating up to 1100 °C at 300 °C/h, dwelling 10 h, cooling down to 940 °C at 5 °C/h with intermediate dwelling (2 h) every 40 °C and final natural cooling down to room temperature. Single crystals were extracted from the melt using hydrochloric acid. Our investigated crystal  $\approx 6 \times 8 \times 0.1$  mm<sup>3</sup> was polished down to a plane-parallel plate of 50  $\mu$ m thickness for THz transmission studies. In both cases the plates of SBN and BiT were (001) oriented because the crystals grow slowly in the  $c$  direction. The crystals were polydomain, therefore the  $a$  and  $b$  axes could not be distinguished.

BaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> (BBN) ceramics were prepared using the conventional mixed-oxide processing technique and the details are described elsewhere.<sup>30</sup> A similar method has also been used for preparation of ceramic Sr<sub>0.5</sub>Ba<sub>0.5</sub>Bi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> (SBBT).<sup>31</sup> 50- $\mu$ m-thick ceramic plates with a diameter of 8 mm were used for the THz experiments, a needle-shaped BBN ceramic with a diameter of 0.9 mm and a length of 7 mm was used for the dielectric measurements between 1 MHz and 8.8 GHz.

The lowest polar mode appeared at a frequency of less than 30 cm<sup>-1</sup> in all investigated compounds. Therefore we used time-domain THz transmission spectroscopy, which is more accurate than Fourier transform IR spectroscopy in this frequency range. Our THz spectrometer is based on an amplified femtosecond laser system. Two ZnTe crystal plates were used to generate (by optic rectification) and to detect (by electro-optic sampling) the THz pulses. Both the transmitted field amplitude and phase shift were simultaneously measured; this allowed us to determine directly the complex dielectric response  $\varepsilon^*(\omega)$  in the range of 4–80 cm<sup>-1</sup>. An Optistat CF cryostat with thin mylar windows was used for measurements down to 10 K. For sample heating, we used an adapted commercial high-temperature cell (SPECAC P/N 5850) with 1-mm-thick sapphire windows.<sup>23</sup>

The dielectric response of the BBN ceramics was investigated from 10 to 700 K using low-frequency impedance analyzer HP 4192A (100 Hz–1 MHz) and high-frequency impedance analyzer Agilent 4291B (1 MHz–1.8 GHz, 100–500 K) with a coaxial measuring cell. The composite dielectric resonator method and network analyzer Agilent E8364B was used at 8.8 GHz and temperatures 100–380 K.<sup>32</sup>

## III. RESULTS AND EVALUATIONS

Figures 1–4 show experimental complex dielectric spectra of all investigated samples at different temperatures. In the case of (001) oriented single crystals (SBN and BiT), the spectra were taken in the  $ab$  plane. The complex dielectric spectra were fitted with a sum of  $n$  damped Lorentz oscillators describing the polar phonons

$$\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \sum_{j=1}^n \frac{\Delta\varepsilon_j \omega_j^2}{\omega_j^2 - \omega^2 + i\omega\gamma_j} + \varepsilon_\infty, \quad (1)$$

where  $\omega_j$ ,  $\gamma_j$ , and  $\Delta\varepsilon_j$  denote the eigenfrequencies, damping, and dielectric contribution of the  $j$ th polar phonon mode, respectively, and  $\varepsilon_\infty$  describes the high-frequency permittivity originating from the electronic polarization and from the polar phonons above 80 cm<sup>-1</sup>. A single oscillator model was used for the fit of BiT spectra, while two oscillators were needed to account for the BBN and SBBT spectra and, finally, a sum of three oscillators was used in the case of SBN. Temperature dependences of the fit parameters are summarized in Fig. 5.

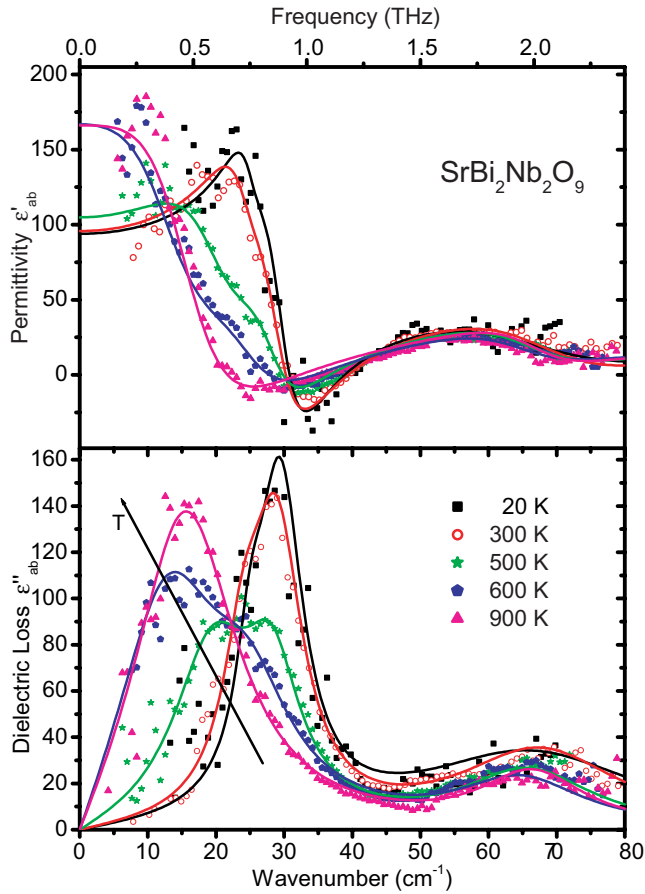


FIG. 1. (Color online) Complex dielectric spectra  $\varepsilon_{ab}^*(\omega)$  of SBN single crystal at selected temperatures. Solid lines are results of the quasiharmonic oscillator fits [Eq. (1)]. Direction of rise of temperature is marked by an arrow. Splitting of the  $E_u$  mode is most remarkably seen at 600 and 500 K.

#### IV. DISCUSSION

Let us discuss first the SBN THz spectra (see Figs. 1 and 5). At 900 K two polar phonon modes are clearly seen. The weak higher frequency mode near  $65 \text{ cm}^{-1}$  shows only small temperature dependence and will be not discussed here, while the lower frequency mode near  $17 \text{ cm}^{-1}$  exhibits a remarkable temperature dependence, which is best seen in dielectric loss spectra  $\varepsilon''(\omega)$ . The mode splits into two parts below  $T_c=700 \text{ K}$  and both components harden and reduce their damping on cooling. Finally, below 300 K both modes have very similar frequencies so that they are almost not resolved in the spectra. This temperature dependence will be explained below together with other samples. Let us stress another feature: The phonon contribution to the permittivity  $\varepsilon'$  in the  $ab$  plane does not exceed 200, while  $\varepsilon'_{ab}$  (1 MHz) reaches  $\sim 2500$  at  $T_c$ .<sup>29</sup> Clearly, the dielectric strength of polar phonons cannot explain the dielectric anomaly near  $T_c$  in SBN crystal: similarly as in SBT<sup>23</sup> an additional lower frequency excitation (probably with a relaxational character) is required.

Even smaller phonon contribution to the static  $\varepsilon'$  is found in BBN ceramics (Fig. 2),  $\varepsilon'$  at  $5 \text{ cm}^{-1}$  is smaller than 110 at all temperatures. In contrast to SBN, BBN exhibits a diffuse

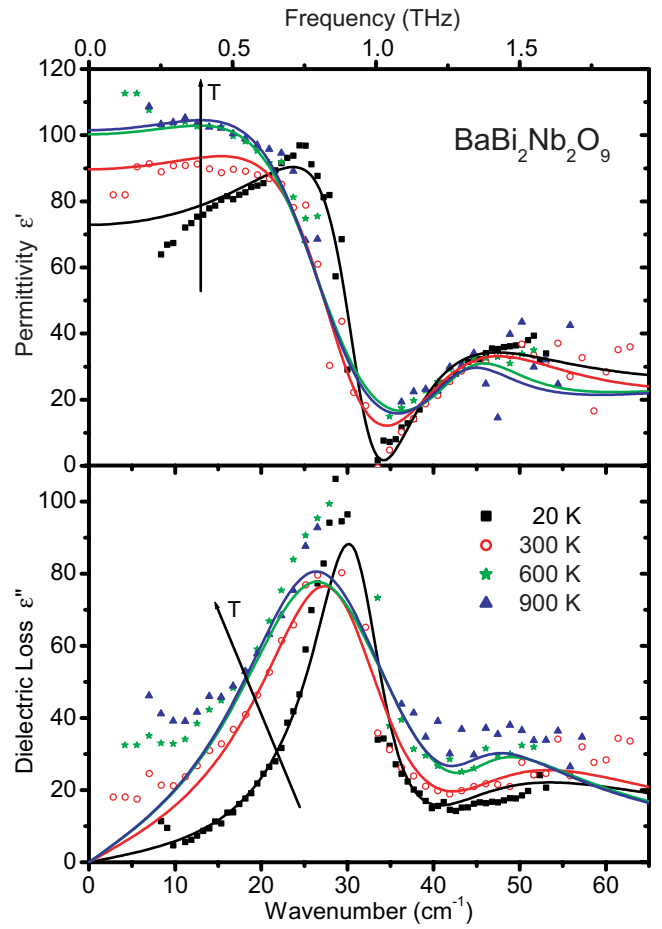


FIG. 2. (Color online) Experimental complex dielectric spectra of BBN ceramic (points) together with their fits (solid lines).

(relaxor) ferroelectric transition near 300 K with  $\varepsilon'_{max} \leq 700$ , see Refs. 33 and 34 where the dielectric spectra were obtained at low frequencies up to 1 MHz. We have extended this study to the 100 Hz–8.8 GHz frequency range (see Figs. 6 and 7). A broad dielectric relaxation is observed in the temperature dependence of the dielectric permittivity and losses (Fig. 6). The relaxational process slows down and broadens on cooling: it is seen in Fig. 7 that the mean relaxation frequency  $\omega_R$  [corresponding to the maximum of  $\varepsilon''(\omega)$ ] lies in the range of  $10^7$ – $10^8$  Hz at 500 K and slows down on cooling so that it appears below 100 Hz at 300 K. Frequency independent but nonvanishing  $\varepsilon''(\omega)$  is observed below 150 K which is a typical feature for all relaxor ferroelectrics at low temperatures. This behavior is connected to a small but measurable dispersion of  $\varepsilon'(\omega)$  observed at low frequencies for these temperatures. Such a dispersion is observed even below the freezing temperature  $T_f \approx 90 \text{ K}$  [obtained from a Vogel-Fulcher fit of  $\varepsilon''_{max}(T, \omega)$ ]. Note also that at 20 K the permittivity in the kHz range ( $\varepsilon' \geq 90$ ) is still larger than the permittivity extrapolated from the THz spectra ( $\varepsilon' \approx 70$ ). The low temperature behavior of BBN can be described by a broad distribution of activation energies for hopping of dynamically disordered ions.<sup>35</sup> The origin of the relaxation in BBN will be discussed below.

The solid solution of SBT and  $\text{BaBi}_2\text{Ta}_2\text{O}_9$  (BBT) for a 1:1 ratio ( $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Ta}_2\text{O}_9$  abbreviated as SBBT) exhibits

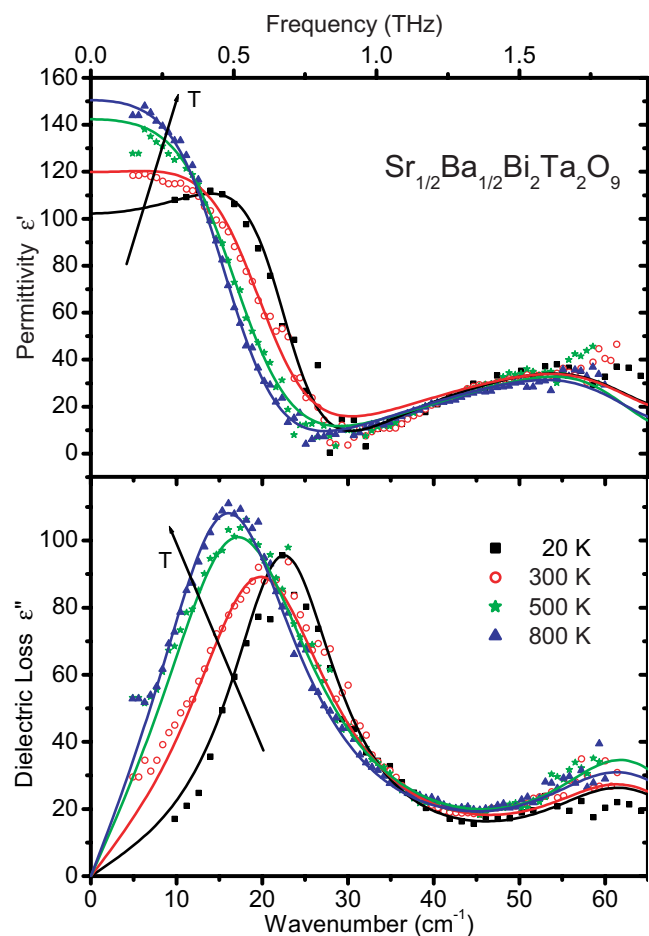


FIG. 3. (Color online) Experimental complex dielectric spectra of SBBT ceramic (points) together with their oscillator fits (solid lines).

similar THz dielectric spectra like BBN (see Fig. 3) with a slightly higher permittivity value. While SBT is a ferroelectric, BBT is a relaxor.<sup>34</sup> SBBT exhibits relaxor properties with a maximum  $\epsilon'(T) \approx 500$  near  $T_{max} = 430$  K.<sup>31</sup> Again, like in the previously discussed compounds, a small continuous softening of the phonon frequency is observed upon heating and no anomaly appears near  $T_c$  in the THz spectra (see Fig. 5). The phonon contributions to the permittivity do not exceed 150 which means that in analogy with BBN an additional dielectric relaxation below phonon frequencies should be expected with a dielectric strength of about 400 near 430 K.

The highest phonon contribution to the static  $\epsilon'_{ab}$  is seen in the THz spectra of BiT single crystal (Fig. 4). The phonon strongly absorbs in the range of  $\epsilon''_{ab}$  maximum, therefore the sample is not transparent in the vicinity of the phonon resonance at temperatures below 300 K. Above room temperature, the sample is opaque above the phonon frequency, therefore only low frequency data are presented in Fig. 4. The spectra were taken at temperatures up to 950 K (limit of our furnace), which is approximately equal to  $T_{c1} = 943$  K<sup>15</sup> so that we cannot study the dielectric anomaly above  $T_{c1}$  and in the vicinity of  $T_{c2}$ . Fouskova and Cross<sup>36</sup> published  $\epsilon'_{ab}(T)$  at 5 MHz, which corresponds to our THz data in the whole

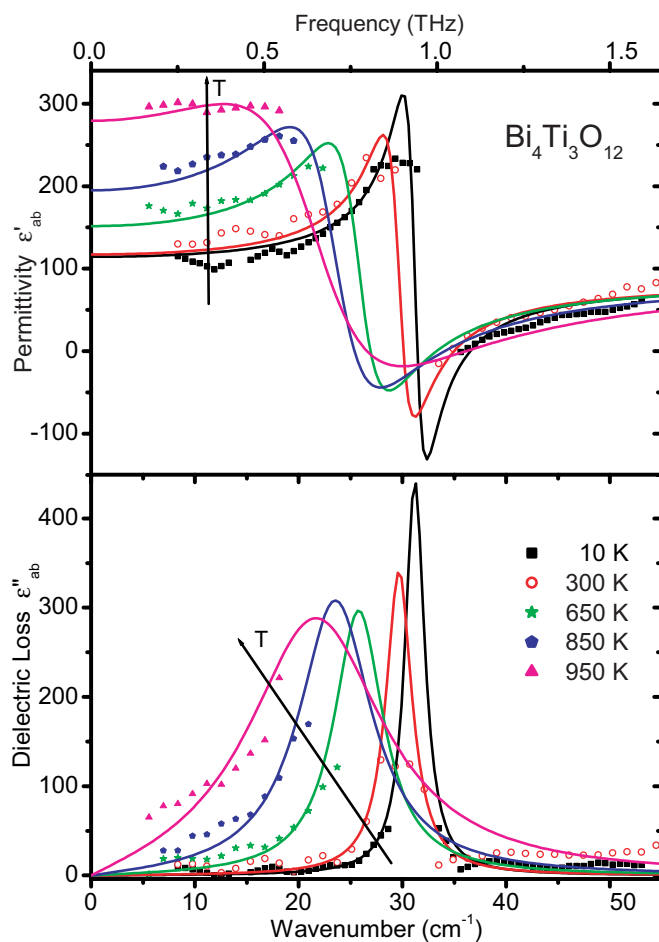


FIG. 4. (Color online) Experimental complex dielectric spectra  $\epsilon_{ab}^*(\omega)$  of BiT single crystal (points) together with their oscillator fits (solid lines).

temperature range. This means that, in contrast with all the materials discussed above, no additional dispersion below phonon frequencies is required in the ferroelectric phase. The ferroelectric phase transition is of the first order and a large stepwise decrease of  $\epsilon'_{ab}$  was observed at  $T_{c1}$  on cooling.<sup>36</sup> From the paraelectric side  $\epsilon'_{ab}(T_{c1}) \approx 1700$  at 5 MHz: it is then likely that a dielectric relaxation appears in the paraelectric phase, however, higher temperature THz experiments are missing to confirm or disprove this hypothesis.

Let us now discuss the temperature dependence of the lowest frequency phonons in samples with two perovskite layers (SBN, BBN, SBT,<sup>23</sup> and SBBT). In all cases only partial phonon softening was observed with no phonon frequency anomaly near  $T_c$  (or  $T_{max}$  in relaxors) and the phonon contribution to static  $\epsilon'$  cannot explain the dielectric anomaly near  $T_c$  or  $T_{max}$ . Perez-Mato *et al.* analyzed the dynamics of phase transitions in SBT using the *ab initio* calculations and revealed a rather complex scenario:<sup>27,28</sup> The ferroelectric phase is the result of superposition of four frozen phonon modes. One mode of  $E_u$  symmetry is polar (IR active) and it is responsible for the spontaneous polarization. This mode describes an antiphase displacement of the Bi atoms and the perovskite layers along the (110) direction of the tetragonal unit cell, plus a much smaller shift of the Sr

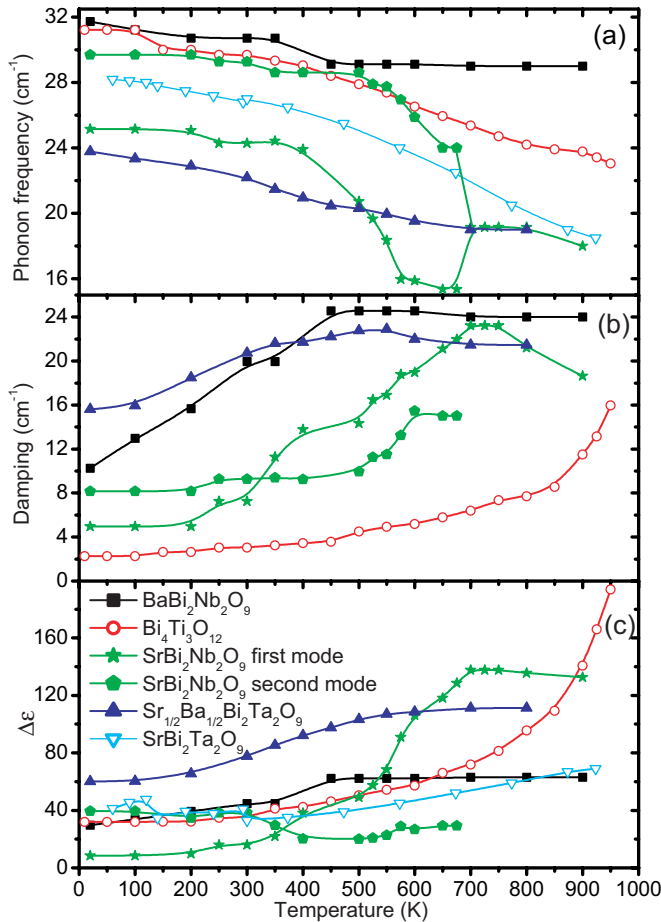


FIG. 5. (Color online) Temperature dependencies of (a) the low-est phonon frequency  $\omega_1$ , (b) phonon damping  $\gamma_1$  and (c) dielectric strength  $\Delta\epsilon_1$ . The parameters of two lowest frequency phonons are shown for SBN crystal. Parameters of SBT are taken from Ref. 23. The lines are guides for the eyes.

and Ta cations with respect to the oxygen in the perovskite blocks. The other three modes of  $X_2^+$  and  $X_3^-$  symmetry stem from the Brillouin zone boundary. The strongest instability of the tetragonal prototype structure corresponds to an octahedral tilting mode of  $X_3^-$  symmetry. The freezing of this single mode at higher temperatures results in intermediate improper ferroelastic phase with the  $Amam$  space group. Since such an intermediate phase was not observed in SBN or BBN, the  $X_3^-$  mode has to freeze simultaneously with the  $E_u$  mode in these materials. The  $E_u$  and  $X_3^-$  modes exhibit a very strong positive biquadratic coupling. The freezing of the third weakly unstable  $X_2^+$  mode associated with rotation of the octahedra around the  $c$  axis does not change the fundamental competition of the two main unstable modes. The additional freezing of the fourth mode, a hard mode of  $X_2^+$  symmetry, which involves only the oxygen atoms within the  $\text{Bi}_2\text{O}_2$  layers, is then essential for the final stabilization of the ferroelectric phase.<sup>27,28</sup>

How does such a theoretical prediction correspond to our experimental results?  $X_3^-$  and  $X_2^+$  modes are not IR active in the paraelectric phase, but they become IR active in the ferroelectric phase due to the folding of the Brillouin zone and lowering of the crystal symmetry. The lowest frequency

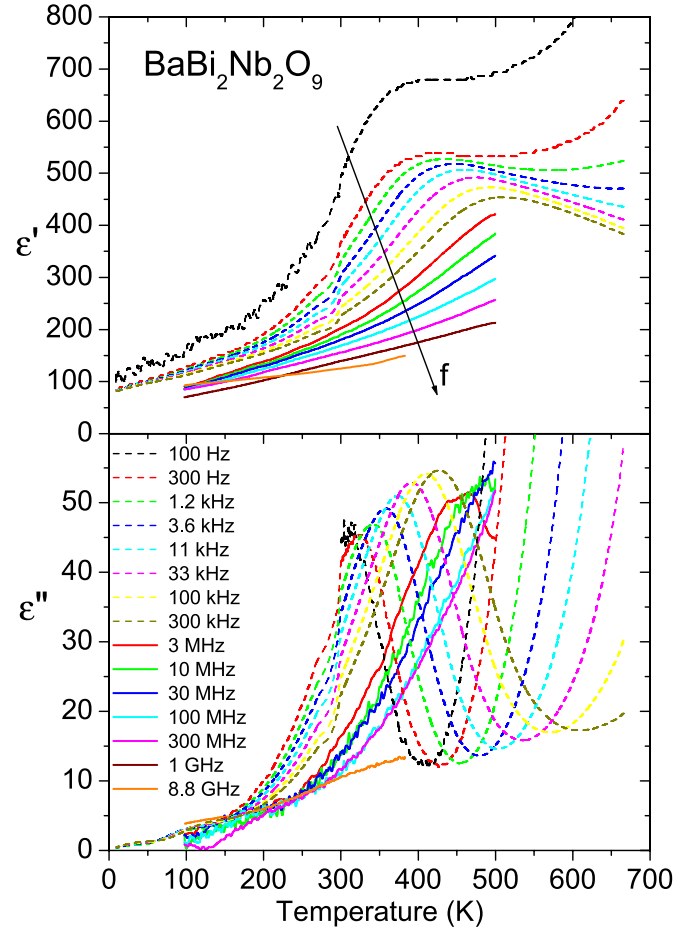


FIG. 6. (Color online) Temperature dependencies of the real and imaginary part of complex permittivity of BBN ceramics at frequencies from 100 Hz up to 8.8 GHz.

phonon seen in our THz spectra at all temperatures is the “soft”  $E_u$  phonon. In SBN crystal it splits clearly into two components below  $T_c$ . It is possible that the second component could belong to the unstable  $X_3^-$  mode, but seems more probable that it represents just the split  $E_u$  mode, which is doubly degenerate in the paraelectric phase and splits in the ferroelectric phase into  $A_1$  and  $B_2$  components (factor group analysis of the phonon modes was published in Ref. 23). In other investigated samples no splitting of the  $E_u$  mode was observed, probably due to smaller orthorhombic distortion. Our high temperature THz spectra of SBT revealed an overdamped (relaxational) mode below the lowest  $E_u$  phonon,<sup>23</sup> which is expected to be responsible for the dielectric anomaly near  $T_{c1}$ , exists also in the paraelectric phase and therefore cannot be related to the  $X_3^-$  mode. This excitation is of strongly anharmonic, not one-phonon nature, maybe originating from a static chemical disorder in the structure. Namely, structural studies on  $\text{ABi}_2\text{Ta}_2\text{O}_9$  (Refs. 37 and 38) and  $\text{ABi}_2\text{Nb}_2\text{O}_9$  ( $A=\text{Ba}, \text{Sr}, \text{Ca}$ )<sup>39</sup> revealed antisite defects of  $\text{Bi}^{3+}$  and  $\text{A}^{2+}$  cations, whose concentration increases with the increasing  $A$  cation size. Simultaneously, the orthorhombic distortion decreases. This can explain why the lattice distortion is smaller in Ba compounds than in Sr compounds. The broad dielectric relaxation in Ba compounds may appear due

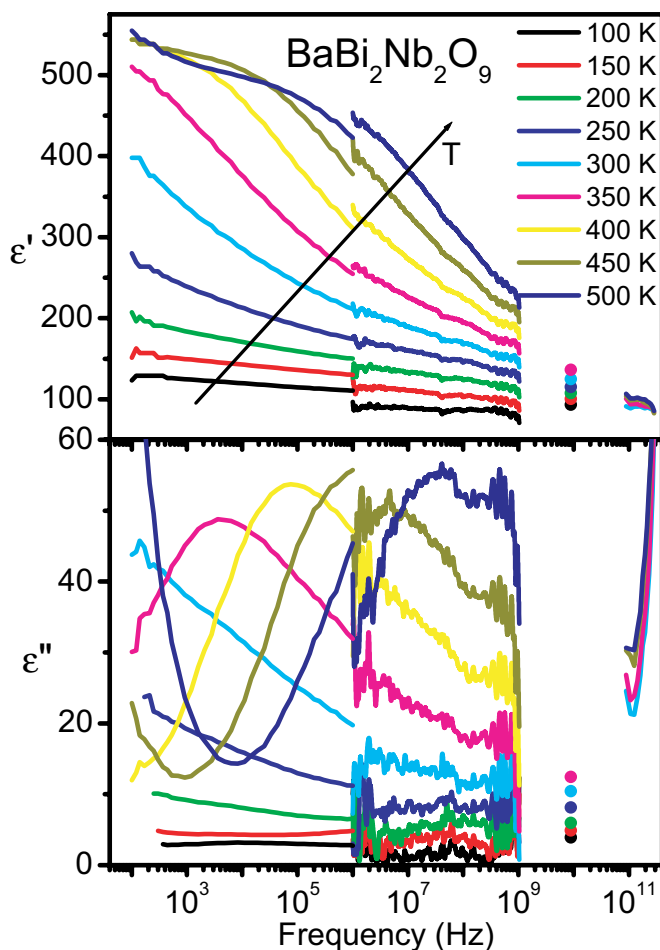


FIG. 7. (Color online) Frequency dependences of the real and imaginary part of complex permittivity of BBN ceramics plotted at selected temperatures. Small discontinuities at 1 MHz are due to the different experimental techniques used.

to a higher chemical disorder (and corresponding higher random fields), and this might be responsible for the relaxor behavior in BBN, BBT, as well as SBBT. In other words, the positional static disorder of Bi and Ba cations is responsible for the ferroelectric relaxor behavior through the formation of nanoregions with different structural distortion levels.

The microscopic origin of the ferroelectric instability in BiT was investigated using first principles calculations by Machado *et al.*<sup>26</sup> They predicted two unstable  $E_u$  modes, one involving the motion of  $\text{Bi}_2\text{O}_2$  planes in  $a$  direction relative to the perovskite blocks and the second one involving the motion of the Bi ions in the perovskite  $A$  site with respect to the  $\text{TiO}_6$  perovskite blocks. In fact, the critical excitation should be a linear combination of both the modes. However, Machado *et al.*<sup>26</sup> did not take into account the rotation and deformation of oxygen octahedra and multiplication of the unit cell below  $T_{c1}$ . Symmetry of the ferroelectric phase [two possibilities are in the literature— $B1a1$  (Ref. 12) or  $B2cb$  (Ref. 15) space groups] cannot be derived from the  $I4/mmm$  paraelectric phase by freezing of the  $E_u$  modes from the Brillouin zone center only (this cannot explain multiplication of the unit cell). Freezing of the  $X_3^+$  mode from the Brillouin zone boundary is again needed for symmetry reasons,<sup>15</sup> how-

ever, such mode was not seen in our spectra, presumably due to its weakness. It is worth noting that the oscillator strength  $S_1 = \Delta\epsilon_1\omega_1^2$  of the observed  $E_u$  “soft” mode near  $30\text{ cm}^{-1}$  increases with increasing temperature (almost three times). It may indicate some coupling of this mode with higher frequency modes of the same symmetry and may support indirectly the result of Machado *et al.*<sup>26</sup> about two unstable modes of the  $E_u$  symmetry. The observed small softening of the  $E_u$  mode is very probably not able to explain the large dielectric anomaly above  $T_{c1}$ . No antisite defects can be expected in BiT (in Bi-layers and A perovskite sites are the same Bi-cations). Oxygen vacancies were observed in perovskite layers of BiT,<sup>40</sup> which are responsible for the large dielectric anomalies below  $T_{c1}$  at low frequencies below 1 MHz due to some conductivity effects<sup>36,41</sup> and might be also connected with the high-temperature relaxational mode at higher frequencies.

We can describe the dynamics of the ferroelectric transition in another language, which we in fact prefer. In analogy with other relaxorlike ferroelectrics, we can assume formation of polar clusters in the paraelectric phase. The reason for their formation could be the chemical disorder/defects mentioned above. Then the critical relaxation most probably concerns the dynamics of these mesoscopic clusters, which may change into ferroelectric domains in the ferroelectric phase (partially or completely as in the case of BiT, where no relaxation is needed in the ferroelectric phase). Assuming such a scenario, the structural change at the ferroelectric transition cannot be described using single sublattice displacements or ordering, as required for classical classification into displacive or order-disorder type structural transitions, respectively. In this case the structural change at the transition concerns rather mesoscopic, many-particle objects. In fact, similar behavior without phonon softening near  $T_c$  and clearly revealed dynamical disorder was already observed near ferroelectric transition in several perovskites as ordered  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ ,<sup>42</sup>  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ ,  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ ,<sup>35</sup> and also in tungsten-bronze ferroelectrics  $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$  (Ref. 43) and  $\text{Ba}_2\text{LaTi}_2\text{Nb}_3\text{O}_{15}$ .<sup>44</sup>

## V. CONCLUSION

THz dielectric spectra of five Bi-layered Aurivillius compounds (SBT, SBN, BBN, SBBT, and BiT) obtained at temperatures up to 950 K revealed that the low-frequency dielectric anomalies near and above ferroelectric phase transitions cannot be explained just by softening of polar phonons, as expected for classical displacive ferroelectrics, because the lowest frequency phonon softens on heating only partially with no anomaly near  $T_c$ . Additional dielectric relaxation, directly observed in SBT<sup>23</sup> and BBN, is needed to account for the dielectric anomaly in all the studied compounds, although numerous structural investigations assumed the displacive type of the phase transitions. The required and sometimes also observed dielectric relaxations (analogy to central modes in inelastic scattering experiments) might be caused by cation disorder,<sup>37–39</sup> most remarkable in Ba compounds, where the full relaxor ferroelectric behavior was revealed. Using another language, we suggest an exist-

tence of polar clusters in the paraelectric phase, whose dynamics should be in origin of the (critical) relaxations and which change into ferroelectric domains below the phase transition. For such a scenario, the usual classification into displacive and order-disorder structural transitions is no more appropriate. The microscopic origin of the phase transitions is also discussed in the light of recent first principle calculations. IR reflectivity measurements of Bi-layered Aurivillius ceramics and single crystals are in progress, which

should allow us to assign the polar phonons and compare them with the results of first principle calculations.<sup>26</sup>

#### ACKNOWLEDGMENT

The work was supported by the Grant Agency of the Czech Republic (Project No. 202/06/0403). We would like to thank J. M. Perez-Mato for fruitful discussion.

\*Electronic address: kamba@fzu.cz

- <sup>1</sup>B. Aurivillius, *Ark. Kemi* **1**, 463 (1949).
- <sup>2</sup>G. A. Smolenskii, V. A. Isupov, and A. I. Agranovskaya, *Sov. Phys. Solid State* **3**, 651 (1961).
- <sup>3</sup>E. C. Subbarao, *J. Phys. Chem. Solids* **23**, 665 (1962).
- <sup>4</sup>C. A. Paz de Araujo, J. E. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, *Nature (London)* **374**, 627 (1995).
- <sup>5</sup>J. F. Scott, *Ferroelectr. Rev.* **1**, 1 (1998).
- <sup>6</sup>B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, *Nature (London)* **401**, 682 (1999).
- <sup>7</sup>U. Chon, Hyun M. Jang, M. G. Kim, and C. H. Chang, *Phys. Rev. Lett.* **89**, 087601 (2002).
- <sup>8</sup>I. M. Reaney, M. Roulin, H. S. Shulman, and N. Setter, *Ferroelectrics* **165**, 295 (1995).
- <sup>9</sup>C. H. Hervoches, J. T. S. Irvine, and P. Lightfoot, *Phys. Rev. B* **64**, 100102(R) (2001).
- <sup>10</sup>S. Kamba, J. Pokorný, V. Porokhonsky, J. Petzelt, M. P. Moret, A. Garg, Z. H. Barber, and R. Zallen, *Appl. Phys. Lett.* **81**, 1056 (2002).
- <sup>11</sup>R. Macquart, B. J. Kennedy, B. A. Hunter, Ch. J. Howard, and Y. Shimakawa, *Integr. Ferroelectr.* **44**, 101 (2002).
- <sup>12</sup>A. D. Rae, J. G. Thompson, R. L. Withers, and A. C. Willis, *Acta Crystallogr., Sect. B: Struct. Sci.* **46**, 474 (1990).
- <sup>13</sup>Y. Shimakawa, H. Imai, H. Kimura, S. Kimura, Y. Kubo, E. Nishibori, M. Takata, M. Sakata, K. Kato, and Z. Hiroi, *Phys. Rev. B* **66**, 144110 (2002).
- <sup>14</sup>R. Macquart, B. J. Kennedy, T. Vogt, and Ch. J. Howard, *Phys. Rev. B* **66**, 212102 (2002).
- <sup>15</sup>Q. Zhou, B. J. Kennedy, and Ch. J. Howard, *Chem. Mater.* **15**, 5025 (2003).
- <sup>16</sup>A. Snedden, Ch. H. Hervoches, and P. Lightfoot, *Phys. Rev. B* **67**, 092102 (2003).
- <sup>17</sup>S. Kojima, R. Imaizumi, S. Hamazaki, and M. Takashige, *Jpn. J. Appl. Phys., Part 1* **33**, 5559 (1994).
- <sup>18</sup>P. R. Graves, G. Hua, S. Myhra, and J. G. Thompson, *J. Solid State Chem.* **114**, 112 (1995).
- <sup>19</sup>S. Kojima, *J. Phys.: Condens. Matter* **10**, L327 (1998).
- <sup>20</sup>P. S. Dobal and R. S. Kariyar, *J. Raman Spectrosc.* **33**, 405 (2002), and references therein.
- <sup>21</sup>M. Kempa, P. Kužel, S. Kamba, P. Samoukhina, J. Petzelt, A. Garg, and Z. H. Barber, *J. Phys.: Condens. Matter* **15**, 8095 (2003).
- <sup>22</sup>P. Kužel, A. Pashkin, M. Kempa, F. Kadlec, S. Kamba, and J. Petzelt, *Ferroelectrics* **300**, 125 (2004).
- <sup>23</sup>F. Kadlec, S. Kamba, P. Kužel, C. Kadlec, J. Kroupa, and J. Petzelt, *J. Phys.: Condens. Matter* **16**, 6763 (2004).
- <sup>24</sup>M. G. Stachiotti, C. O. Rodriguez, C. Ambrosch-Draxl, and N. E. Christensen, *Phys. Rev. B* **61**, 14434 (2000).
- <sup>25</sup>K. Miura, *Appl. Phys. Lett.* **80**, 2967 (2002).
- <sup>26</sup>R. Machado, M. G. Stachiotti, R. L. Migoni, and A. H. Tera, *Phys. Rev. B* **70**, 214112 (2004).
- <sup>27</sup>J. M. Perez-Mato, M. Aroyo, A. García, P. Blaha, K. Schwarz, J. Schweifer, and K. Parlinski, *Phys. Rev. B* **70**, 214111 (2004).
- <sup>28</sup>I. Etxebarria, J. M. Perez-Mato, A. García, P. Blaha, K. Schwarz, and J. Rodriguez-Carvajal, *Phys. Rev. B* **72**, 174108 (2005).
- <sup>29</sup>H. Amorín, R. S. Martins, A. L. Kholkin, and M. E. V. Costa, *Ferroelectrics* **320**, 43 (2005).
- <sup>30</sup>M. Adamczyk, Z. Ujma, and M. Pawelczyk, *J. Mater. Sci.* **41**, 5317 (2006).
- <sup>31</sup>A. L. Kholkin, M. Avdeev, M. E. V. Costa, and J. L. Baptista, *Integr. Ferroelectr.* **37**, 635 (2001).
- <sup>32</sup>J. Krupka, T. Zychowicz, V. Bovtun, and S. Veljko, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* (to be published).
- <sup>33</sup>A. L. Kholkin, M. Avdeev, M. E. V. Costa, J. L. Baptista, and S. N. Dorogovtsev, *Appl. Phys. Lett.* **79**, 662 (2001).
- <sup>34</sup>V. V. Shvartsman, M. E. V. Costa, M. Avdeev, and A. L. Kholkin, *Ferroelectrics* **296**, 187 (2003).
- <sup>35</sup>E. Buixaderas, S. Kamba, and J. Petzelt, *Ferroelectrics* **308**, 131 (2004).
- <sup>36</sup>A. Fouskova and L. E. Cross, *J. Appl. Phys.* **41**, 2834 (1970).
- <sup>37</sup>R. Macquart, B. J. Kennedy, Y. Kubota, E. Hishibori, and M. Takata, *Ferroelectrics* **248**, 27 (2000).
- <sup>38</sup>R. Macquart, B. J. Kennedy, and Y. Shimakawa, *J. Solid State Chem.* **160**, 174 (2001).
- <sup>39</sup>S. M. Blake, M. J. Falconer, M. McCreedy, and P. Lightfoot, *J. Mater. Chem.* **7**, 1609 (1997).
- <sup>40</sup>Y. Noguchi, T. Matsumoto, and M. Miyayama, *Jpn. J. Appl. Phys., Part 2* **44**, L570 (2005).
- <sup>41</sup>N. Zhong, S. Okamura, K. Ychiyama, and T. Shiosaki, *Appl. Phys. Lett.* **87**, 252901 (2005).
- <sup>42</sup>S. Kamba, M. Berta, M. Kempa, J. Hlinka, J. Petzelt, K. Brinkman, and N. Setter, *J. Appl. Phys.* **98**, 074103 (2005).
- <sup>43</sup>E. Buixaderas, M. Savinov, M. Kempa, S. Veljko, S. Kamba, J. Petzelt, R. Pankrath, and S. Kapphan, *J. Phys.: Condens. Matter* **17**, 653 (2005).
- <sup>44</sup>S. Kamba, S. Veljko, M. Kempa, M. Savinov, V. Bovtun, P. Vaněk, J. Petzelt, M. C. Stennett, I. M. Reaney, and A. R. West, *J. Eur. Ceram. Soc.* **25**, 3069 (2005).