Wideband dielectric spectroscopy of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics and its microscopic mechanism of polarization

Motoharu SAKURAI, Kazuki KANEHARA, Hiroaki TAKEDA, Takaaki TSURUMI and Takuya HOSHINA[†]

Nano-Phononics Lab., Graduate School of Science and Engineering, Tokyo Institute of Technology,
2-12-1 Meguro, Tokyo 152-8552, Japan

$(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics were fabricated by a solid state reaction, and a wideband dielectric spectrum was measured for understanding the microscopic polarization mechanism of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics. It was revealed that the dielectric permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics at 25°C was determined by dipole polarization as well as ionic polarization, whereas the permittivity of SrTiO_3 is mainly determined only by ionic polarization. The temperature dependence of permittivity suggested that $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics belongs to ferroelectric relaxor, in which off-center Bi^{3+} ions contribute to the formation of polar nanoregions (PNRs). The origin of the dipole polarization is considered the dipole fluctuations of PNRs. On the other hand, the ionic polarization of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was suppressed by an influence of Sr-site vacancy, compared to that of SrTiO_3 . High permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics is mainly due to the dipole polarization associated with dipole fluctuation of PNRs.

©2016 The Ceramic Society of Japan. All rights reserved.

Key-words : Strontium titanate, Dielectric material, Ferroelectric relaxor, Polarization mechanism, High frequency measurement, THz ellipsometry

[Received January 25, 2016; Accepted April 5, 2016]

1. Introduction

Ferroelectric perovskite oxides exemplified by BaTiO_3 have a high permittivity and have been widely used for dielectric devices such as ceramic capacitors. Permittivity of ferroelectric perovskite oxide is mainly determined by two kinds of polarization mechanisms, i.e., dipole polarization derived from domain-wall vibration^{1)–4)} or dipole fluctuations of polar nanoregions (PNRs)^{1),5)–8)} etc., and ionic polarization derived from lattice vibration (in particular, the soft phonon mode contributes most to the ionic polarization).^{1),9)–13)} These polarizations can be controlled by changing the constitutive elements, e.g., $(\text{Ba},\text{Sr})\text{-TiO}_3$ ceramics have higher ionic polarizability than pure BaTiO_3 ceramics,^{1),14),15)} and, in contrast, $\text{Ba}(\text{Zr},\text{Ti})\text{O}_3$ ceramics have higher dipole polarizability than pure BaTiO_3 ceramics.^{1),7)} Therefore, it is important to understand the polarization mechanism to improve the dielectric properties of ferroelectric perovskite oxides.

Pure SrTiO_3 are the most well-known quantum paraelectric material.¹⁶⁾ The temperature dependence of permittivity (ε') at higher temperatures than 50 K obeys the Curie–Weiss law $\varepsilon' = C/(T - T_C)$ with $T_C \approx 35$ K, which indicates a possible ferroelectric transition at around 35 K. At lower temperatures, the permittivity increases with decreasing temperature, but deviates from the Curie–Weiss relation. In particular at below 4 K, the permittivity is almost independent of temperature and keeps high value of $\varepsilon' \approx 2 \times 10^4$, which is the influence of the paraelectric state stabilized by the quantum fluctuation at low temperatures. However, ferroelectric order can be introduced by doping substitutional elements in SrTiO_3 . The most common examples are Ca- or Ba-doped SrTiO_3 : small amount of Ca- or Ba-doping is

effective for inducing a quantum ferroelectric transition which is characterized by a dielectric maximum at a certain temperature.^{17),18)} The transition behavior is interpreted as originating from the coupling of the soft mode of the host lattice SrTiO_3 and the dipole moment of an off-center Ca^{2+} ion for Ca-doped SrTiO_3 ,¹⁹⁾ and the elastic strains induced by the mismatch of ionic radius for Ba-doped SrTiO_3 .²⁰⁾ For large amount of Ba-doping, sharp ferroelectric transition behavior appears and the ferroelectric transition temperature increases with doping amount. Similar ferroelectric order can be introduced also by Bi doping. G. I. Skanavi^{21),22)} and C. Ang et al.^{23)–28)} reported a dielectric maximum of Bi-doped SrTiO_3 [$(\text{Sr}_{1-1.5x}\text{Bi}_x)\text{TiO}_3$], in which a part of Sr^{2+} ions were substituted with Bi^{3+} ions and Sr-site vacancies were generated because of the valence difference between Sr^{2+} and Bi^{3+} ions. Moreover, C. Ang and co-workers reported that Bi-doped SrTiO_3 indicated typical ferroelectric relaxor behavior and pointed out that the relaxor state was derived from Bi^{3+} ion off-centering and Sr-site vacancies. In addition, one of the characteristics on the dielectric property is that Bi-doped SrTiO_3 indicates a very broad dielectric maximum and a small temperature dependence of permittivity. The dielectric property of Bi-doped SrTiO_3 ceramics may be derived from the relaxor behavior, however, the detail in the microscopic polarization mechanism of the permittivity remains unclear. In this study, we measured a wideband dielectric spectrum of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics for understanding the microscopic polarization mechanism, and discussed the influence of Bi-doping and Sr-vacancy on the polarization of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics.

2. Experimental procedure

$(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics were fabricated by a solid-state reaction. SrCO_3 (Kojundo Chemical Laboratory, purity 3N), Bi_2O_3 (Kojundo Chemical Laboratory, purity 5N), and TiO_2 (Toho Titanium, purity 3N) powders were weighed according to the chemical composition of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$, and mixed with a ball

[†] Corresponding author: T. Hoshina; E-mail: hoshina.t.aa@m.titech.ac.jp

[‡] Preface for this article: DOI <http://dx.doi.org/10.2109/jcersj2.124.P6-1>

mill in ethanol for 24 h using $\phi 3$ mm zirconia balls. The mixed powder was dried and calcined at 950°C for 2 h in air atmosphere. The calcined powder was ground again and isostatically pressed into a disks at 200 MPa. The resulting green compacts were sintered at 1350°C for 4 h in a closed alumina crucible to prevent evaporation of Bi. The sample sintered in the closed crucible had a high dielectric loss derived from oxygen vacancies. Therefore, the samples were annealed at 1000°C for 6 h in oxygen atmosphere to reduce the oxygen vacancies. The obtained $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was characterized using the following methods. Powder X-ray diffraction (XRD; Rigaku RINT-2000) was performed to determine crystal structure. The density was measured by the Archimedes' method. Microstructure of fractured surface was observed using a scanning electron microscopy (SEM; JEOL JCM-6000).

The dielectric properties of the ceramics in a wide frequency range from kHz to THz were evaluated using three measurement methods. In the frequency range from 40 Hz to 1 MHz, the complex permittivity of the ceramics was measured by a conventional capacitance measurement method. Au electrodes were formed on the two facing surfaces of ceramic plates by DC sputtering. Capacitance and loss tangent ($\tan \delta$) were measured using an impedance analyzer (Agilent Technology 4294A). In the frequency range up to 3 GHz, the micro-sized planer electrode method²⁹⁾ was employed. Micro-sized planer Au electrodes were formed on the sample surface through a lift-off method. The complex admittance between a pair of planer electrodes was measured using an impedance analyzer (Agilent Technology E4991A). The complex permittivity of the ceramics was determined with the help of electromagnetic field simulation (Sonet Software). In the frequency region from 1.3 to 7.5 THz, the complex permittivity was determined by far-infrared spectroscopic ellipsometry,^{30–32)} which enable us to measure the complex permittivity of an opaque substance in THz region without any assumptions or preliminary knowledge. We used a far-infrared spectroscopic ellipsometer system uniquely developed using a Fourier transform far-infrared (FTFIR) spectrometer (JASCO FARIS-1). The system was constituted mainly of Michelson interferometer of Fourier-transform spectrometer, a rotating analyzer-type ellipsometer, and a detector using Si bolometer unit. The detail is described elsewhere.^{30),31)} The ellipsometry determines $\rho = r_p/r_s = \tan \Psi \exp(i\Delta)$, where r_p and r_s are complex reflection coefficients for p- and s-polarized waves, respectively, and the amplitude ratio of p- and s-polarized waves Ψ and phase difference Δ are ellipsometric parameters. The complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ is calculated using ellipsometric parameters Ψ and Δ as following equations:

$$\varepsilon' = n^2 - \kappa^2 = \sin^2 \theta_0 \left[1 + \frac{\tan^2 \theta_0 (\cos^2 2\Psi - \sin^2 2\Psi \sin^2 \Delta)}{(1 + \sin 2\Psi \cos \Delta)^2} \right], \quad (1)$$

$$\varepsilon'' = 2n\kappa = \sin^2 \theta_0 \frac{\tan^2 \theta_0 \sin 4\Psi \sin \Delta}{(1 + \sin 2\Psi \cos \Delta)^2}, \quad (2)$$

where n and κ are the refraction and extinction coefficient, respectively, and θ_0 indicates the incident angle of the light. From the wideband dielectric spectrum of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics, we discuss the microscopic polarization mechanisms which contribute to the dielectric permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics.

3. Results and discussion

When Bi-doped SrTiO_3 ceramics were sintered at a high temperature in air atmosphere, a part of Bi evaporated from the sample during the sintering. Therefore, it is necessary to suppress

Fig. 1. $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics sintered in closed crucible (a), and subsequently annealed in oxygen atmosphere (b).

Fig. 2. Powder XRD pattern of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics.

the evaporation of Bi in order to obtain dense ceramic samples having a target composition. In this study, a closed crucible was used to sinter the $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ sample to prevent the evaporation of Bi. The mass of the sample did not change before and after sintering in the closed crucible and the density was considerably higher than that of the ceramics simply sintered in air atmosphere. However, the ceramics sintered in the closed crucible was gray colored sample with a high dielectric loss tangent of 14% at 100 Hz [Fig. 1(a)], which suggested that the obtained sample had semiconducting property. Since oxygen gas was poorly supplied in the closed crucible, oxygen vacancies were introduced in $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics, resulting the generation of semiconductor carrier. To obtain insulating ceramics with less oxygen vacancies, the samples were annealed at 1000°C for 4 h in oxygen atmosphere. The sample annealed in oxygen atmosphere was light yellow colored, and the mass of the sample did not change before and after annealing. The relative permittivity and loss tangent were respectively 916 and 0.1% at 100 Hz [Fig. 1(b)], which meant the dielectric ceramics were successfully obtained. **Figure 2** shows a powder XRD profile of the obtained ceramics. The $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics had a cubic perovskite-type structure with a lattice parameter of $a = 3.908 \text{ \AA}$ which is little longer than that of pure SrTiO_3 . The ion radius of Bi^{3+} is smaller than that of Sr^{2+} in 12 coordination. Therefore, the lattice expansion of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ is not explained by the substitution of Bi^{3+} ion to Sr site. It seems to be reasonable to think that the Sr-site vacancy causes the lattice expansion of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ so as to minimize the repulsive force between the Sr-site vacancy and O^{2-} ion in the vicinity of the vacancy. **Figure 3** shows a fractured surface of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics. From the observation with SEM, it was found that the ceramics was dense and the average grain size was $5.6 \mu\text{m}$. The relative density of the ceramics was estimated to 93.3% using Archimedes' method. From these characterizations, it was concluded that we could obtain a suitable sample for measuring dielectric properties of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$.

Fig. 3. Microstructure of fractured surface of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics.

Fig. 4. Temperature dependences of complex permittivities of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ and SrTiO_3 ceramics¹⁷⁾ at various frequencies.

Figure 4 shows temperature dependences of dielectric property of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics at various frequencies. Dielectric maximum was observed at around -100°C , and the peak of the dielectric maximum shifted toward higher temperatures with increasing frequency. Such frequency dispersion of dielectric maximum is often observed in ferroelectric relaxors,^{5)-8),33)} and therefore it is considered that $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ belongs to a ferroelectric relaxor. C. Ang and co-workers²³⁾⁻²⁷⁾ reported that the Bi^{3+} ion in SrTiO_3 occupy at an off-center position at Sr site in $(\text{Sr,Bi})\text{TiO}_3$ system, and the off-center Bi^{3+} ions form dipoles. With increasing Bi concentration, the dipoles may form polar cluster in $(\text{Sr,Bi})\text{TiO}_3$ system, which contribute to the ferroelectric behavior. In contrast, the heterovalence substitution of Bi and Sr-site vacancies may cause high local random fields, which block the long-range ordering of dipoles. Therefore, $(\text{Sr,Bi})\text{TiO}_3$ system exhibits relaxor behavior instead of normal ferroelectric behavior, which is associated with ferroelectric macro-domains. At a higher temperature than the dielectric maximum temperature, the permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was almost three times higher than that of SrTiO_3 ceramics. To understand the microscopic polarization mechanisms of the permittivity, we measured a wideband dielectric spectrum of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics.

Figure 5 shows the wideband dielectric spectrum of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics at 25°C . In Fig. 5, Debye-type dielectric relaxation at around 10^9 Hz was attributable to dipole polarization, whereas resonance-type dielectric dispersions at the frequencies above 10^{12} Hz were attributable to ionic polarizations associated with lattice vibrations. It is known that the permittivity of pure SrTiO_3 ceramics is dominantly determined by ionic

Fig. 5. Wideband dielectric spectrum of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics at 25°C .

polarizations, i.e., other polarizations hardly contribute to the permittivity. In contrast, the permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was determined by dipole polarization as well as by ionic polarizations. The relative permittivities derived from dipole and ionic polarizations were estimated to approximately 780 and 135, respectively. This result indicated that the high permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was mainly due to the dipole polarization. As mentioned before, $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics belongs to a ferroelectric relaxor. Generally the microscopic origin of the dipole polarization in the ferroelectric relaxor is associated with thermally fluctuating dipoles in polar nanoregions (PNRs), i.e., the rotations of dipoles and the increase in volume of PNRs by an applied electric field contributes to the dipole polarization.^{1),5)-7)} Therefore, it is considered that the dipole polarization of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics originates from dipole fluctuations in PNRs. It is also to be noticed that the ionic polarizability of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was lower than that of pure SrTiO_3 ceramics. A. Pashkin and co-workers³⁴⁾ have measured dielectric spectra of $(\text{Sr,Bi})\text{TiO}_3$ ceramics in THz region by terahertz time-domain spectroscopy and have pointed out the suppression of the ionic polarizability by Bi doping. The decrease in ionic polarizability was mainly due to the hardening of soft mode (Slater mode). Generally an increase in ferroelectric phase transition temperature of perovskite oxide is caused by a softening of soft mode, however, $(\text{Sr,Bi})\text{TiO}_3$ system did not correspond to it. The Bi^{3+} ion itself contributes to increase the ferroelectricity in the form of PNRs and may be effective to increase the ferroelectric phase transition temperature. In contrast, the Sr-site vacancy probably suppresses the ferroelectricity, and therefore we think that the hardening of soft mode is mainly due to the Sr-site vacancy in $(\text{Sr,Bi})\text{TiO}_3$ system. The $(\text{Sr,Bi})\text{TiO}_3$ is a complicated system in which the Bi^{3+} ion and Sr-site vacancy concern the development mechanism of relaxor state. By measuring the wideband dielectric spectrum of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics, it was revealed that the origin of high dielectric permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was the dipole polarization associated with dipole fluctuation of PNRs rather than the ionic polarization associated with ferroelectric phase transition.

4. Conclusion

By measuring wideband dielectric spectrum of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics, it was confirmed that the permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was determined by not only the ionic polarization but also the dipole polarization. Because $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics indicated a frequency dispersion of dielectric maximum which is typical ferroelectric relaxor behavior, the dipole polarization is derived from dipole fluctuations in PNRs. The origin of high dielectric permittivity of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics was the dipole polarization associated with dipole fluctuation of PNRs rather

than the ionic polarization associated with ferroelectric phase transition.

References

- 1) T. Tsurumi, J. Li, T. Hoshina, H. Kanemoto, M. Nakada and J. Akedo, *Appl. Phys. Lett.*, **91**, 182905 (2007).
- 2) T. Teranishi, T. Hoshina and T. Tsurumi, *Mater. Sci. Eng., B*, **161**, 55–60 (2009).
- 3) T. Teranishi, N. Horiuchi, T. Hoshina, H. Takeda and T. Tsurumi, *J. Ceram. Soc. Japan*, **118**, 679–682 (2010).
- 4) T. Hoshina, K. Takizawa, J. Li, T. Kasama, H. Kakemoto and T. Tsurumi, *Jpn. J. Appl. Phys.*, **47**, 7607–7611 (2008).
- 5) T. Tsurumi, K. Soejima, T. Kamiya and M. Daimon, *Jpn. J. Appl. Phys.*, **33**, 1959–1964 (1994).
- 6) A. E. Glazounov and A. K. Tagantev, *Phys. Rev. Lett.*, **85**, 2192–2195 (2000).
- 7) T. Teranishi, T. Hoshina, H. Takeda and T. Tsurumi, *J. Appl. Phys.*, **105**, 114102 (2009).
- 8) J. Zhang, J. Zhai and Y. Zhang, *Phys. Status Solidi (a)*, **208**, 2853–2860 (2011).
- 9) W. G. Spitzer, R. C. Miller, D. A. Kieinman and L. E. Howarth, *Phys. Rev.*, **126**, 1710–1721 (1962).
- 10) J. L. Servoin, F. Gervais, A. M. Quittet and Y. Luspín, *Phys. Rev. B*, **21**, 2038–2041 (1980).
- 11) J. A. Sanjurjo, R. S. Katiyar and S. P. S. Porto, *Phys. Rev. B*, **22**, 2396–2403 (1980).
- 12) J. Hlinka, J. Petzelt, S. Kamba, D. Noujni and T. Ostapchuk, *Phase Transit.*, **79**, 41–78 (2006).
- 13) J. Petzelt, *Ferroelectrics*, **375**, 156–164 (2008).
- 14) J.-H. Jeon, *J. Eur. Ceram. Soc.*, **24**, 1045–1048 (2004).
- 15) T. Teranishi, T. Hoshina, H. Takeda and T. Tsurumi, *J. Appl. Phys.*, **105**, 054111 (2009).
- 16) K. A. Müller and H. Burkhard, *Phys. Rev. B*, **19**, 3593–3602 (1979).
- 17) T. Mitsui and W. B. Westphal, *Phys. Rev.*, **124**, 1354–1358 (1961).
- 18) S. Miura, M. Marutake, H. Unoki, H. Uwe and T. Sakudo, *J. Phys. Soc. Jpn.*, **38**, 1056–1060 (1975).
- 19) J. G. Bednorz and K. A. Müller, *Phys. Rev. Lett.*, **52**, 2289–2292 (1984).
- 20) V. V. Lemanov, E. P. Smirnova, P. P. Syrnikov and E. A. Tarakanov, *Phys. Rev. B*, **54**, 3151–3157 (1996).
- 21) G. I. Skanavi and E. N. Matveeva, *Sov. Phys. JETP*, **3**, 905–908 (1957).
- 22) G. I. Skanavi, I. M. Trigubenko, V. A. Trigubenko and V. G. Prokhvatilov, *Sov. Phys. JETP*, **6**, 250–259 (1958).
- 23) C. Ang, Z. Yu, P. M. Vilarinho and J. L. Baptista, *Phys. Rev. B*, **57**, 7403–7406 (1998).
- 24) C. Ang, Z. Yu, P. Lunkenheimer, J. Hemberger and A. Loidl, *Phys. Rev. B*, **59**, 6670–6674 (1999).
- 25) C. Ang, Z. Yu and L. E. Cross, *Phys. Rev. B*, **62**, 228–236 (2000).
- 26) C. Ang and Z. Yu, *Phys. Rev. B*, **61**, 957–961 (2000).
- 27) C. Ang and Z. Yu, *J. Phys. Rev.*, **91**, 1487–1494 (2002).
- 28) C. Ang and Z. Yu, *Appl. Phys. Lett.*, **88**, 162902 (2006).
- 29) J. Li, H. Kakemoto, S. Wada, H. Kawaji and T. Tsurumi, *J. Appl. Phys.*, **100**, 024106 (2006).
- 30) K. Kanehara, T. Hoshina, H. Takeda and T. Tsurumi, *Appl. Phys. Lett.*, **105**, 042901 (2014).
- 31) T. Hoshina, K. Kanehara, H. Takeda and T. Tsurumi, *Jpn. J. Appl. Phys.*, **53**, 09PD03 (2014).
- 32) K. Kanehara, T. Hoshina, H. Takeda and T. Tsurumi, *J. Ceram. Soc. Japan*, **105**, 303–306 (2015).
- 33) E. V. Colla, E. Yu. Koroleva, N. M. Okuneva and S. B. Vakhrushev, *J. Phys.: Condens. Matter*, **4**, 3671–3677 (1992).
- 34) A. Paskin, P. Samoukhina, T. Ostapchuk, P. Kužel, P. Vilarinho and J. Petzelt, *Ferroelectrics*, **294**, 133–139 (2003).