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Far-infrared reflection and microwave properties of $Ba([Mg_{1-x}Zn_x]_{1/3},Ta_{2/3})O_3$ ceramics

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Abstract

Far-infrared reflectivity spectra for $Ba(Mg_{1/3},Ta_{2/3})O_3$ and $Ba([Mg_{1-x}Zn_x]_{1/3},Ta_{2/3})O_3$ ceramics were measured and eigen frequencies and damping constants of lattice vibration were calculated. In this paper, decrease of Qf value by Zn substitution was analyzed using the vibration parameters. These ceramics were prepared by conventional solid phase reaction using high purity reagents. The observed reflectivity spectra were fitted by 16 IR active modes predicted by factor group analysis in order to estimate the vibration eigen frequencies and damping constants. A slight change of reflectivity appeared in the low frequency region, and it was found that there was certain correlation between the changes of dielectric loss and damping constants in lattice vibration in 4th and 5th modes. The decrease of Qf value might be caused by the correlation in this system.

Keywords: Dielectric properties; Functional applications; Perovskites

1. Introduction

Development of microwave technology using dielectric material is very important for the advanced wireless communication systems. $Ba(Mg_{1/3},Ta_{2/3})O_3$; BMT ceramic is well known as a dielectric material showing great dielectric properties which are relatively high permittivity, extremely low loss tangent and zero temperature coefficient of frequency in the range of microwave frequency. These excellent properties are also important for the component at quasi-millimeter wave frequency. $Ba(Zn_{1/3},Ta_{2/3})O_3$; BZT has also excellent dielectric properties, which are important for microwave filter using at 4–10 GHz. The chemical formulas of BMT and BMZT suggest the possibility of solid solution of these materials, and it is expected that the solid solution shows dielectric properties of the middle of both. In order to control dielectric property of BMT–BZT solid solution $Ba([Mg_{1-x}Zn_x]_{1/3},Ta_{2/3})O_3$; BMZT, the dielectric properties of each material were investigated by many researchers.[1–3] Most of the investigations were researches on Qf value by analysis of crystal structure including B site ions ordering. Also theoretical and experimental investigation on lattice vibration of these materials were carried out by Wakino,[4] Tamura,[5,6] and Sagala.[7,8] Their studies proved that microwave dielectric properties of BMT and BZT were deeply influenced by the lattice vibrations at low frequency. Although the theoretical or experimental results in their studies on lattice vibration are significant and useful to elucidate the origin of dielectric loss in dielectric materials, there are little investigation for the solid solution of BMT–BZT system. In the present study, dielectric properties of BMT and BMZT were surveyed at microwave frequency and far-infrared reflectivity spectra were measured in order to determine lattice vibration parameter. And then the variation of the dielectric properties with increase of Zn substitution to Mg site was analyzed using the vibration parameters.

2. Experimental procedure

BMT and BMZT ($x=0.1$–0.3) were prepared by the conventional mixed-oxide reaction method. High purity reagents of magnesium, zinc and tantalum oxides and barium carbonates were used to prepare their samples. These oxides and carbonates, which were weighted by

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stoichiometric composition, were mixed by ball mill with zirconia ball in deionized water and calcined for 4 h at 1573 K after drying. And then the calcined powder was ball-milled again and the powders were pressed into pellet 12 mm in diameter. The pellets were sintered at 1873 K for 50 h with a electric furnace. The sintered pellets were sliced to evaluate their dielectric properties.

X-ray diffraction analysis was examined to confirm that no second phases were formed in BMT and BMZT matrices and to determine crystal parameter. Dielectric properties of the samples were measured by using Hakki & Coleman's open resonator method at microwave range.

The surfaces of the sliced samples were wet polished using about 1 μm diamond slurry by which the surface roughness (Ra) was less than 3×10^{-4} μm, and then washed with acetone in an ultra sonic bath to remove the influence of impurities into the IR measurement. Far-infrared reflection spectra of the polished samples were measured at 300 K with a Fourier Transform Infrared Spectroscopy (FT-IR) having a SiC glow bar lamp and Au reflector as the measurement reference. The incident angle of radiation was 11° and the spectra resolution was 1.0 cm^{-1}. The frequencies of lattice vibration were estimated by spectrum fitting of the obtained data.

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of BMT and BMZT in the range of 10–60°in 2θ. Profiles of (420) reflections in XRD are also shown in Fig. 1. According to the XRD patterns, all of the samples revealed fundamental BMT perovskite structure. As shown in (420) and (226) reflections, these profiles obviously split in all samples and it suggests the considerable ordering of B site ions in the material. Fig. 2 shows dielectric properties at microwave frequency. Permittivity plotted against Zn substitution for Mg indicated a linear increase relation. Conversely, Qf value gradually decreased with increase of Zn substitution. It is apparent from the XRD patterns of BMT and BMZT that only B site-ordering situation does not decide the dielectric properties of these materials. Therefore, crystallographic analysis by XRD does not give a sufficient evidence for the variations of the dielectric properties in this system. Lattice vibrations are really sensitive for material substitution and IR spectroscopy gives much information for the lattice vibrations. Fig. 3 shows IR reflectivities and fitting spectra of BMT and BMZT ($x=0.2$). X-ray diffraction patterns of BMT and BMZT give the space group $P\bar{3}m(D^3_{3d})$ and the following irreducible representation is derived by the factor group analysis for the Brillouin-zone-center vibration modes.[8]

$$\Gamma = 2A_{1u} + 8A_{2u} + 4A_{1g} + A_{2g} + 10E_u + 5E_g \quad (1)$$

Sixteen polarized vibration modes are observed in IR spectra since the irreducible representations predict infrared active ($7A_{2u}+9E_u$), Raman active ($4A_{1g}+5E_g$), silent ($A_{2g}+2A_{1u}$) and acoustic ($A_{2u}+E_u$) modes.[8] The result from the factor group analysis was applied to a dispersion relation written by Eq. (2), which is basically derived from FPSQ model.[9]

$$\varepsilon = \varepsilon_\infty \prod_{j=1}^{16} \frac{\Omega^2_{j\mathrm{LO}} - \omega^2 + i\omega\gamma_{j\mathrm{LO}}}{\Omega^2_{j\mathrm{TO}} - \omega^2 + i\omega\gamma_{j\mathrm{TO}}} \quad (2)$$

the permittivity were transformed into reflection by a following relation.[3]

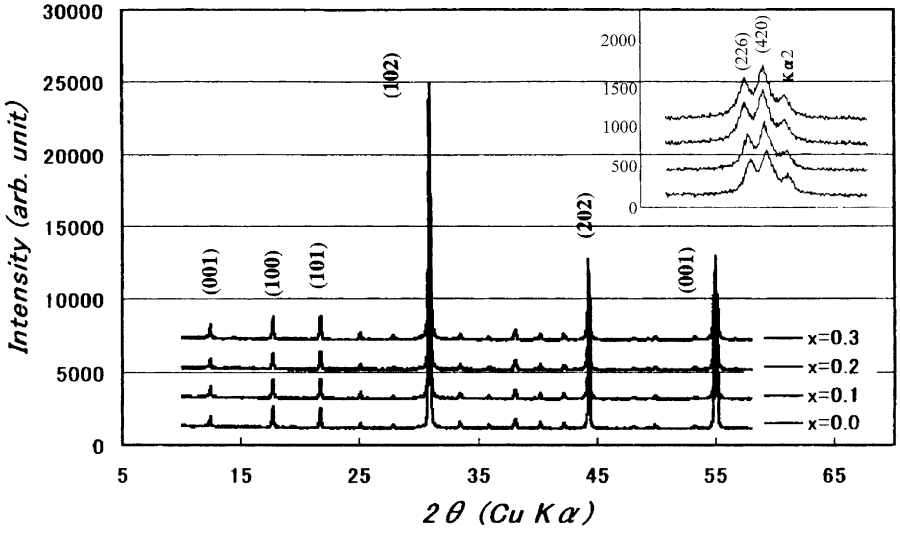

Fig. 1. X-ray diffraction patterns of BMT and BMZT.

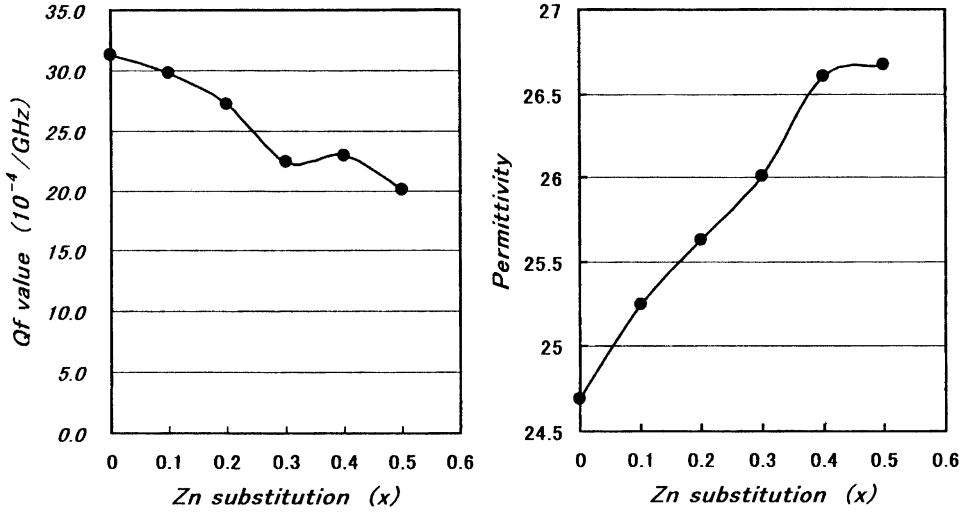

Fig. 2. Dielectric properties of BMT and BMZT.

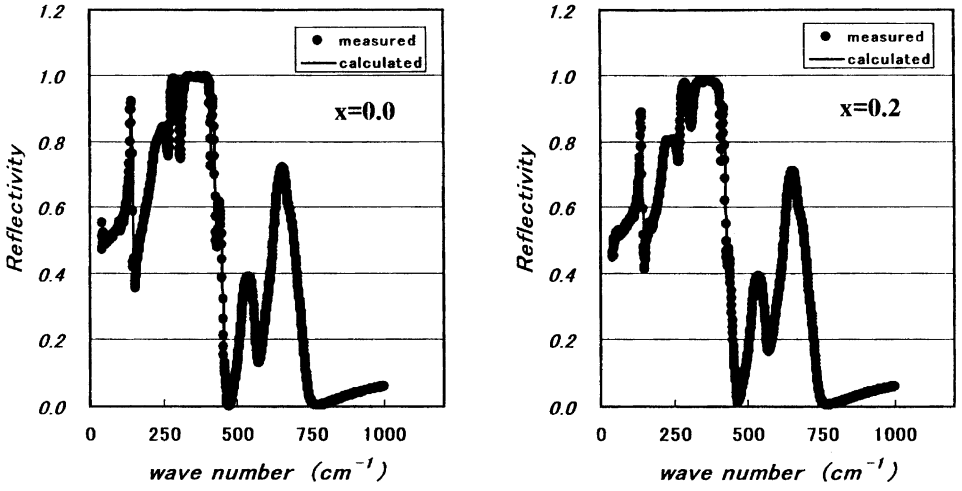

Fig. 3. Far IR reflectivity of BMT and BMZT.

$$R = \left|\varepsilon^{1/2} - 1\right|^2 / \left|\varepsilon^{1/2} + 1\right|^2 \quad (3)$$

where ϵ, ϵ_∞, ω, and R are the permittivity, the permittivity at high frequency, the frequency and the reflectivity respectively. Ω_{jLO} and Ω_{jTO} are the eigen frequencies of LO and TO modes, and γ_{jLO} and γ_{jTO} are the damping constants of LO and TO modes respectively. The calculated reflection spectra of BMT and BMZT($x=0.2$) shown in Fig. 3 were obtained by spectra fitting using Eqs. (2) and (3). The calculated spectra are in good agreement with the measured ones. As listed in Table 1, Ω_{jTO} and Ω_{jLO} of BMT and BMZT at low frequency converged same values within fitting accuracy. Fig. 4 shows the fitting spectra for imaginary part of permittivity of BMT and BMZT in far infrared region. As shown in Fig. 4, the dielectric losses increased with Zn substitution and this tendency was in agreement with the variation of Qf value shown in Fig. 2. However, as listed in Table 2, low frequency limit of dielectric loss are higher than the value for another report[10] because of intrinsic accuracy for extrapolation from IR fit and error of the spectra at low frequency. A little problem is in the accuracy in each measurement but the agreement of the increase tendency of the dielectric loss between microwave and IR data is evident in their measurement. More significant problem is why the dielectric loss

Table 1
Vibration frequency of TO and LO modes in far infrared region

Mode	Zn substitution ($x=0.0$, 0.1, 0.2, 0.3)							
	1st	2nd	3rd	4th	5th	6th	7th	8th
Ω_{jTO} (cm^{-1})	50.3	138.6	150.6	219.5	235.8	275.1	311.3	372.1
Ω_{jLO} (cm^{-1})	50.3	147.4	153.1	226.6	271.8	307.3	381.7	372.1

increased with Zn substitution. Petzelt et al. explained that dielectric loss is in proportion to $\gamma_{jTO}/\Omega_{jTO}^4$ at microwave frequency using single effective oscillator model.[11] As listed in Table 1, relatively low vibration frequencies until 8th mode, which strongly influenced dielectric loss at microwave frequency, did not change by Zn substitution. Therefore, it seems that the polar phonon eigen frequencies have little influence to the dielectric loss. Fig. 5(a–d) show the reflectivity of the four samples in the frequency range of 200–280 cm^{-1}. Slight changes of the spectra could be distinguished and it was found that the changes were due to increase of damping constants. Fig. 6 shows variation of the damping constant of TO modes with Zn substitution. The damping constants of 4th, 5th and 8th modes indicate obvious increase with amount of Zn substitution. Generally speaking, it is assumed that the vibration parameters in higher frequencies are hardly effective for the dielectric loss at low frequency including microwave region. In the present study, however, it was found that the damping constants of 4th and 5th modes, which are vibration modes in relatively high frequency region, influenced strongly the dielectric loss at low frequency. The simulation spectra of dielectric loss calculated by

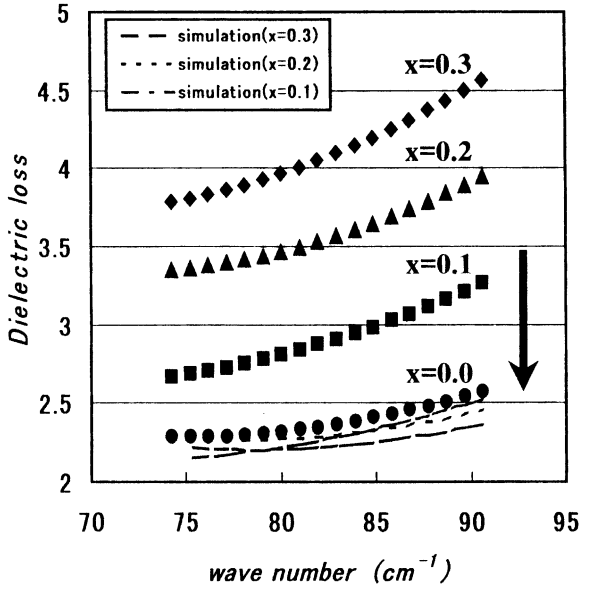

Fig. 4. Imaginary part of permittivity of BMT and BMZT.

Table 2
Vibration frequency of TO and LO modes in far infrared region

Zn substitution (x)	0.0	0.1	0.2	0.3
Extrapolation of ϵ'' to MW range ($/10^{-2}$)	2.88	3.53	4.34	4.98

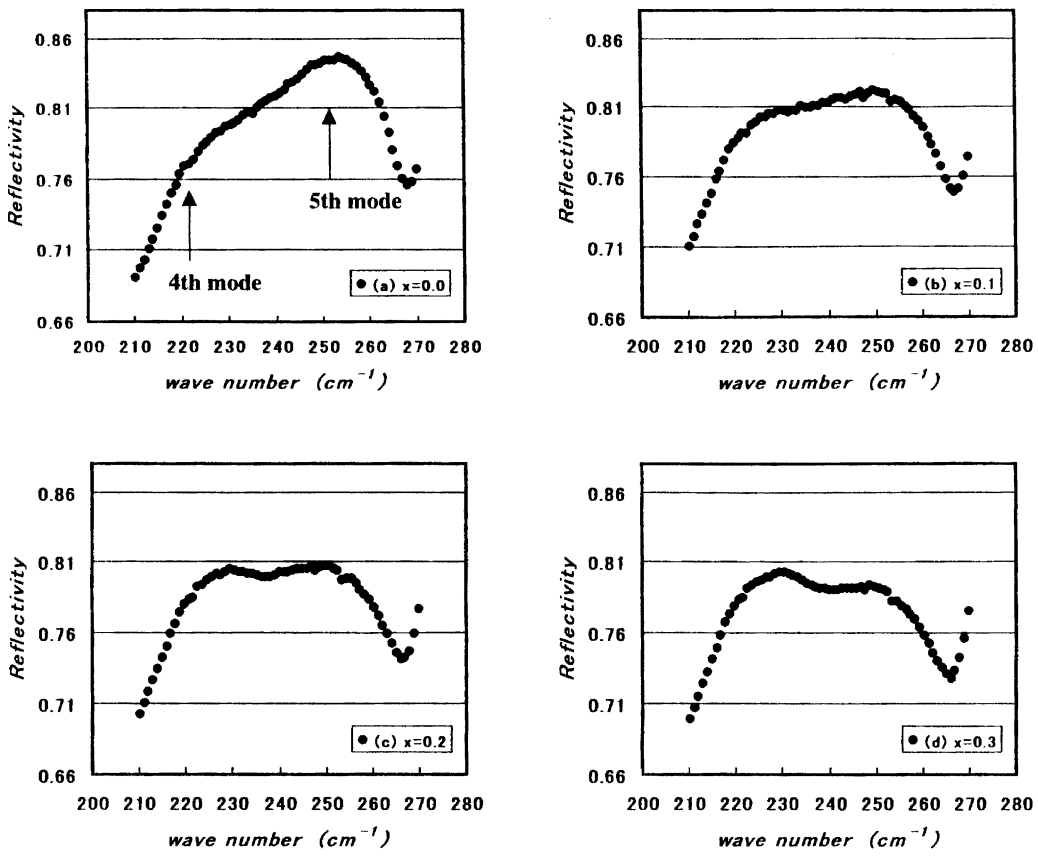

Fig. 5. IR reflectivity of BMT and BMZT in the range of 210–270 cm^{-1}. (a) $x=0.0$, (b) $x=0.1$, (c) $x=0.2$ and (d) $x=0.3$.

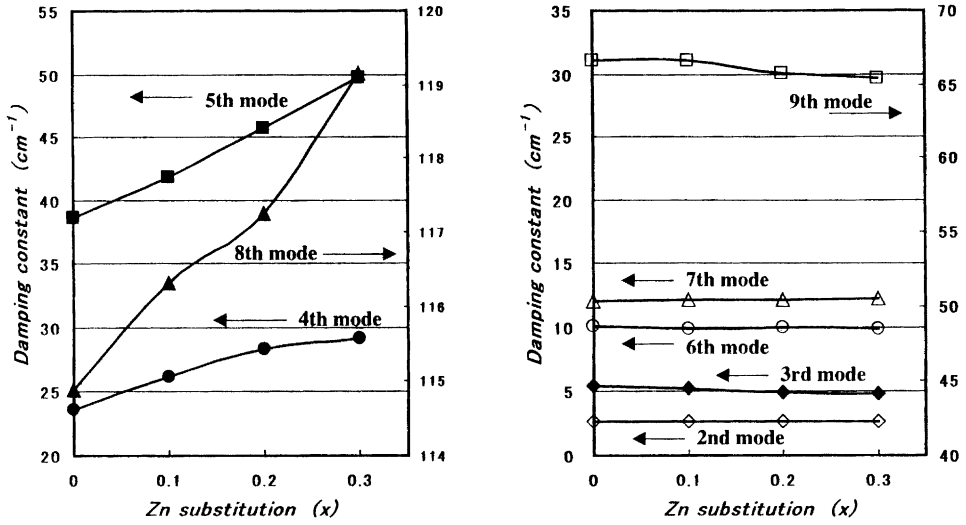

Fig. 6. Damping constants of lattice vibrations.

using fitting parameters are also shown in Fig. 4 by the solid and dotted lines. The dotted lines and solid lines represent the fit and the simulation respectively. The simulations are the result calculated on the assumption that the damping constants of 4th and 5th modes are of same order with BMT. As shown in Fig. 4, the simulations converged the measurement line of BMT. This convergence suggests that the increase of dielectric loss by substituting Zn for Mg ion is due to variation of damping constant of 4th and 5th modes. As to the damping constant of 8th mode, it hardly influences the dielectric loss at low frequency because the eigen frequency of 8th mode is extremely higher. However because the 4th and 5th modes are also not so low compared with the lowest mode, the microscopic theory does not support the contribution of these two modes to low frequency losses. Therefore the variation of the damping constant might be due to macroscopic changing of the BMZT. In our case, the microscopic and the macroscopic effect made certain crystal chemical correlation in the samples, and then it might appear that the damping constants of 4th and 5th modes directly had an influence on the dielectric loss at low frequency. We found the correlation between the dielectric loss and the damping constants of 4th and 5th modes in BMT and BMZT. However, a cause for the decrease of damping constants and the correlation between the microscopic and the macroscopic aspects were not made clear in this study. A full understanding of the cause of the variation in the damp awaits future studies.

References

1. Nomura, S., Toyama, K. and Kaneta, K., $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with temperature stable high dielectric constant and low microwave loss. *Jpn. J. Appl. Phys.*, 1982, **21**(10), L624–L626.
2. Kawashima, S., Nishida, M., Ueda, I. and Ouchi, H., $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with low dielectric loss at microwave frequency. *J. Am. Ceram. Soc.*, 1983, **66**, 421–423.
3. Barber, D. J., Moulding, K. M. and Zhou, J., Structural order in $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ microwave dielectric ceramics. *J. Mater. Sci.*, 1997, **32**, 1531–1544.
4. Wakino, K., Murata, M. and Tamura, H., Far infrared reflection spectra of $Ba(Zn,Ta)O_3$–$BaZrO_3$ dielectric material. *J. Am. Ceram. Soc.*, 1986, **69**, 34–37.
5. Tamura, H., Sagala, D. A. and Wakino, K., Lattice vibrations of $Ba(Zn_{1/3}Ta_{2/3})O_3$ crystal with ordered perovskite structure. *Jpn. J. Appl. Phys.*, 1986, **25**(6), 787–791.
6. Three-dimensional dielectric dispersion equation for Zn-Ta-Ta System in $Ba(Zn_{1/3}Ta_{2/3})O_3$ crystal. *Jpn. J. Appl. Phys.*, 1993, 32 (part 1, No. 6A), 2774-2779.
7. Sagala, D. A. and Nambu, S., Microscopic calculation of dielectric loss at microwave frequencies for complex perovskite $Ba(Zn_{1/3}\ Ta_{2/3})O_3$. *J. Am. Ceram. Soc.*, 1992, **75**(9), 2573–2575.
8. Sagala, D. A. and Koyasu, S., Infrared reflection of $Ba(Mg_{1/3}\ Ta_{2/3})O_3$ ceramics. *J. Am. Ceram. Soc.*, 1993, **76**(10), 2433–2436.
9. Gervais, F. and Piriou, B., Anharmonicity in several-polar-mode crystals: adjusting phonon self-energy of LO and TO modes in Al_2O_3 and TiO_2 to fit infrared reflectivity. *J. Phys. C: Solid State Phys.*, 1974, **7**, 2374–2386.
10. Kamba, S., Petzelt, J., Freer, R., Ferreirn, V. M., Zurmhlen, R. and Koukal, V., Origin of losses in some microwave ceramics investigated by submillimetre spectroscopy. *Proceedings of Electroceramics V*, 1996, **2**, 63–66.
11. Petzelt, J., Kamba, S., Kozlov, G. V. and Volkov, A. A., Dielectric properties of microwave ceramics investigated by infrared and submillimeter spectroscopy. *Ferroelectrics*, 1996, **176**, 145–165.