

Dielectric and resonance frequency investigations of phase transitions in Nb-doped PZT95/5 and 75/25 ceramics

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 L171

(<http://iopscience.iop.org/0953-8984/9/11/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 23:06

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Dielectric and resonance frequency investigations of phase transitions in Nb-doped PZT95/5 and 75/25 ceramicsX L Dong[†] and S Kojima

Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki, 305, Japan

Received 20 December 1996

Abstract. The low-temperature–high-temperature rhombohedral-ferroelectric phase transition ($F_R(LT)$ – $F_R(HT)$) and the rhombohedral-ferroelectric–cubic-paraelectric ($F_R(HT)$ –PE) phase transition in Nb-doped $Pb(Zr_{1-x}Ti_x)O_3$ ceramics ($x = 0.05$ and 0.25) were investigated using dielectric and resonance frequency measurements. The dielectric behaviour in PZT(Nb)95/5 is found to obey the Curie–Weiss law above T_c , while that of PZT(Nb)75/25 deviates from the linear Curie–Weiss law in a temperature range of ~ 50 K above T_c , and can be described by the relation $1/\varepsilon \sim (T - T_c)^\gamma$ with the exponent γ in the range $1 < \gamma < 2$. Dielectric dispersions are observed in the rhombohedral-ferroelectric region for both compositions. Dielectric anomalies and thermal hysteresis are observed in PZT(Nb)95/5; in contrast, no anomaly appears in PZT(Nb)75/25. Around the $F_R(LT)$ – $F_R(HT)$ phase boundary region, the temperature dependences of the resonance frequencies for both compositions show remarkable anomalies. The piezoelectric constant d_{31} of PZT(Nb)95/5 rapidly decreases, but that of PZT(Nb)75/25 gradually increases. These results are discussed on the basis of the coupling of M-type and R-type oxygen octahedra tilts to the polarization and strain.

In the Zr-rich compositional region ($0.05 < x < 0.35$) of the solid solutions of lead zirconate titanate, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) [1], there exist two phase transitions, namely the low-temperature–high-temperature rhombohedral-ferroelectric transition ($F_R(LT)$ – $F_R(HT)$) and the rhombohedral-ferroelectric–cubic-paraelectric transition ($F_R(HT)$ –PE). Both types of phase transition have attracted much attention owing to the considerable interest in the applications and theory. The $F_R(HT)$ –PE phase transition of the end member $PbZrO_3$ has a well defined first-order character [2, 3]. The degree of first-order character has been shown to decrease in going from $PbZrO_3$ to PZT94/6, whereupon a tricritical point occurs and the transition changes to a second-order one [4, 5]. The second-order behaviour was found to exist from PZT94/6 to at least PZT88/12. The compositions with Zr/Ti ratios of 65/35 or close to it show a strongly diffuse phase transition [6, 7], and a glassy polarization model was recently proposed [8, 9]. However, in the composition range from Zr/Ti ratio 65/35 to 90/10, the experimental data have not been sufficient to clarify the character of the $F_R(HT)$ –PE phase transition.

The $F_R(HT)$ – $F_R(LT)$ phase transition of the PZT system has been characterized by different experimental methods. Barnett [10] first reported an anomaly in the dielectric loss, a pyroelectric charge release, and a thermal expansion strain at the phase transition point in 1 wt% Nb_2O_5 -doped PZT96/4 ceramics. Clarke *et al* [11, 12] observed a discontinuity in the spontaneous polarization (P_s), the oxygen octahedron tilt angle (θ), and the strain (ζ)

[†] On leave from: Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China.

for PZT90/10 near the $F_R(\text{HT})$ – $F_R(\text{LT})$ phase boundary via temperature-dependent neutron powder diffraction. Considering the coupling between the spontaneous polarization and the oxygen octahedron tilt angle, Halemane *et al* [13] developed a phenomenological theory to describe the $F_R(\text{HT})$ – $F_R(\text{LT})$ phase transition. On the other hand, pyroelectric devices such as infrared detectors and Vidicons have been made of doped PZT ceramics with high Zr content ($z < 0.05$), for which the pyroelectric coefficient of the $F_R(\text{HT})$ – $F_R(\text{LT})$ phase transition is very large and the dielectric constant is low. However, most papers have been on the compositions with $Zr/Ti > 90/10$. In the case where $Zr/Ti < 90/10$, no anomaly in the dielectric, pyroelectric, and thermal properties was detected within experimental accuracy. Only pronounced anomalies in the resonance frequency and longitudinal sound velocity were observed through the $F_R(\text{HT})$ – $F_R(\text{LT})$ phase transition in PZSnT [14] and PLZT $_x/65/35$ ceramics [15], which suggested that the $F_R(\text{HT})$ – $F_R(\text{LT})$ phase transition characteristics are significantly changed over the rhombohedral phase region.

In the present study, special attention was paid to the characteristics of the $F_R(\text{HT})$ –PE and $F_R(\text{HT})$ – $F_R(\text{LT})$ phase transitions of PZT ceramics with $Zr/Ti < 90/10$. To make a comparison, investigations for the case where $Zr/Ti > 90/10$ were also performed.

The two typical 1 wt% Nb_2O_5 -doped $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ compositions with $x = 0.05$ and $x = 0.25$ were chosen for study; these are denoted as PZT(Nb)95/5 and PZT(Nb)75/25, respectively. The ceramic samples were prepared by a conventional mixed-oxide method using high-purity oxide powders. The mixtures were calcined at 850 °C for 2 h; the green bodies were then sintered at 1290–1330 °C for 1 h in a controlled PbO atmosphere. Disc-like specimens were cut and polished to dimensions of $\text{Ø}15 \times 1$ mm. Silver electrodes were painted onto the parallel surfaces. The samples were poled under a DC electric field of 2 kV mm^{-1} at 120 °C in silicon oil for ten minutes.

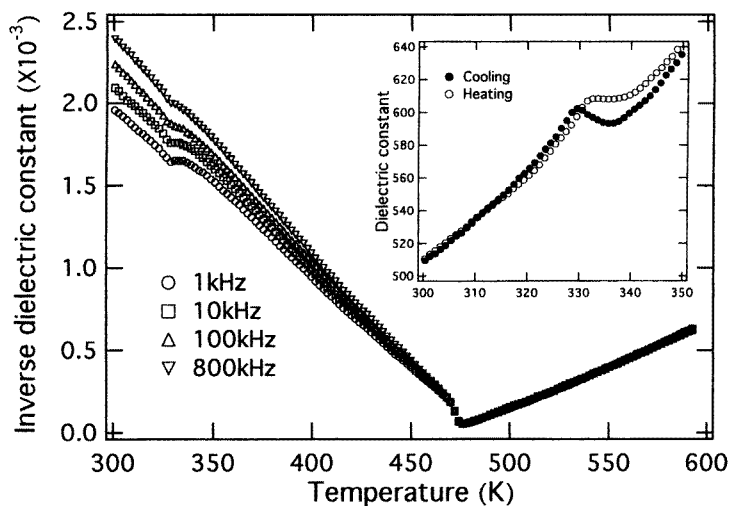


Figure 1. The inverse dielectric constant as a function of temperature for PZT(Nb)95/5 ceramics at frequencies of 1, 10, 100 and 800 kHz from bottom to top. The inset shows the thermal hysteresis at low temperature.

The complex dielectric constant was measured in the frequency range from 1 kHz to 1 MHz using HIOKI 3530 LCR HiTester; the data were automatically acquired using a computer at heating and cooling rates of 1 °C min^{-1} . The resonance frequencies were

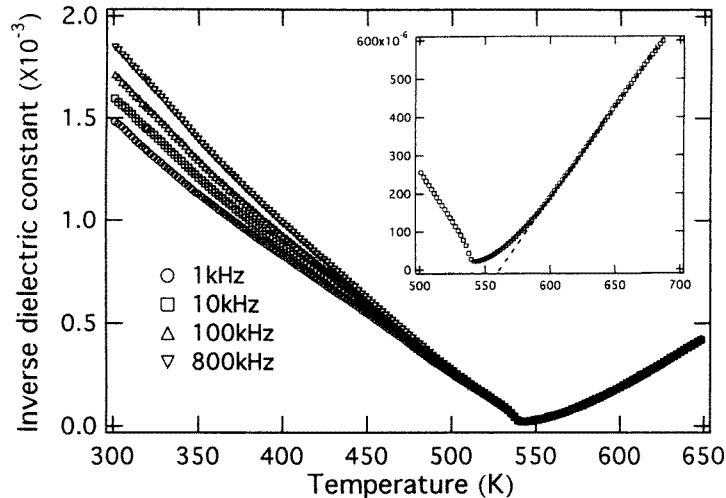


Figure 2. The inverse dielectric constant as a function of temperature for PZT(Nb)75/25 ceramics at frequencies of 1, 10, 100 and 800 kHz from bottom to top. The inset shows the deviation from Curie-Weiss behaviour above T_c ; the solid line is the result of a fitting to equation (1), and the dashed line shows the Curie-Weiss behaviour determined in the higher-temperature region.

measured using the resonance–antiresonance method with a Solartron 1260 Impedance Gain-Phase Analyzer with a maximum frequency 32 MHz. To ensure thermal equilibrium, the samples were kept for at least 20 min at each measuring temperature.

Figures 1 and 2 show the temperature dependences of the inverse dielectric constants of PZT(Nb)95/5 and PZT(Nb)75/25 at frequencies of 1, 10, 100 and 800 kHz. The inverse dielectric constants show minima at 476 K for PZT(Nb)95/5 and 543 K for PZT(Nb)75/25, corresponding to the $F_R(\text{HT})$ –PE phase transition. The dielectric response of PZT(Nb)95/5 exhibits Curie-Weiss behaviour above T_c , and no frequency dispersion occurs in the vicinity of T_c or in the paraelectric phase (PE). The ratio of the slope $d(\epsilon^{-1})/dT$ just below T_c to that just above T_c is about -2.5 , which is a value intermediate between -4 (that for the first-order phase transition) and -2 (that for the second-order phase transition). Thus it is difficult to identify the order of the $F_R(\text{HT})$ –PE phase transition. On the other hand, on the basis of the discontinuity of the inverse dielectric constant immediately below T_c and a small thermal hysteresis (data not shown), the $F_R(\text{HT})$ –PE phase transition can be considered to be a weakly first-order feature. The difference between the experimental and theoretical ratios of the slopes of the inverse dielectric constant may be due to the imperfect nature of the ceramic samples.

In PZT(Nb)75/25, the deviation from linear Curie-Weiss behaviour ($1/\epsilon \sim T - T_c$) is clearly observed in a temperature interval of ~ 50 K above T_c , as seen in the inset of figure 2. At higher temperature, Curie-Weiss behaviour is observed. Compared with that for classical ferroelectric materials, the extrapolated Curie temperature (T_0) is higher than the temperature at which the dielectric constant is at its maximum. These results are taken to suggest the existence of relaxation in the temperature region.

From figure 3, which shows the frequency dependence of the dielectric constant of PZT(Nb)75/25 near T_c , the relaxation character is further evident. Although sharp peaks of the dielectric constant appear and the Curie temperature T_c does not obviously shift

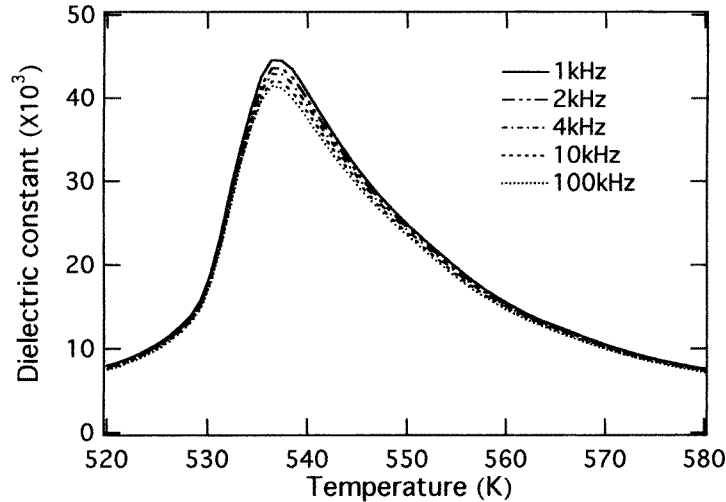


Figure 3. The dielectric constant as a function of temperature for PZT(Nb)75/25 near T_c at frequencies of 1, 2, 4, 10 and 100 kHz from top to bottom.

with frequency within the measuring frequency range, a slight frequency dispersion occurs near to and above T_c , and the peak of the dielectric constant shows a broadening with increasing frequency. This behaviour is very similar to that observed in low-La-content doped PZT65/35 ceramic [16, 17], which is a well known relaxor material. Though at present there is not sufficient evidence to suggest that PZT(Nb)75/25 is itself a relaxor, recently high-frequency dielectric relaxation was observed in the PE phase of Zr-rich PZT single crystals and ceramics, even with Zr/Ti ratios up to 97/3 [18, 19]; this means that some kinds of relaxation do occur in Zr-rich PZT materials.

Several models have been proposed for interpreting the relaxation phenomenon [20–23]. Smolensky [24] modelled the deviation from Curie–Weiss behaviour using the compositional heterogeneity model predicting a $T - T_c$ relationship:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T - T_c)^\gamma}{C} \quad (1)$$

where T_c is the temperature at which ε is at its maximum value, ε_m ; also C is a constant, and γ ($1 < \gamma < 2$) is a composition-dependent parameter. The inset in figure 2 also shows the result obtained by fitting the experimental data above T_c to equation (1) (as a solid line). It is clear that equation (1) is valid over a temperature range of at least 80–100 K above T_c . In general, γ and C are dependent on the temperature range modelled and the measurement frequency. In the case of a temperature interval of 100 K and a measuring frequency of 10 kHz, $C = 2.65 \times 10^6$, and $\gamma = 1.5$; this latter is a value intermediate between $\gamma = 1$ (that for normal Curie–Weiss behaviour) and $\gamma = 2$ (that for a classical diffuse phase transition). Although ceramic materials are homogeneous on a macroscale, the occurrence of compositional fluctuations on a microscopic scale is beyond any doubt for solid solutions like PZT. Therefore it is reasonable to suppose that the relaxation behaviour is related to microscopic compositional inhomogeneity. This heterogeneity is believed to arise due to a positional disorder of the A- and/or B-site cations, and/or disorder of the tilts of the oxygen octahedra.

At low temperature, an anomaly in the dielectric response is observed for PZT(Nb)95/5

at 333 K, as seen in the inset of figure 1, which corresponds to the $F_R(\text{LT})$ – $F_R(\text{HT})$ phase transition; and a significant thermal hysteresis indicates a first-order phase transition. However, no dielectric anomaly occurs in PZT(Nb)75/25. Recently Dai *et al* [25] characterized the presence of R-type and M-type oxygen octahedra tilts in the Zr-rich PZT system by selected-area electron diffraction (SEAD) investigations. Various oxygen octahedra tilts related to PZT(Nb)95/5 and 75/25 are shown in table 1.

Table 1. Oxygen octahedra tilts in different phase regions of PZT(Nb)95/5 and PZT(Nb)75/25.

Phases	PZT(Nb)95/5	PZT(Nb)75/25
PE	Disordered R-type Disordered M-type	Disordered R-type
$F_R(\text{HT})$	Disordered R-type Ordered M-type	Disordered R-type
$F_R(\text{LT})$	Ordered R-type	Ordered R-type

Obviously, the $F_R(\text{LT})$ – $F_R(\text{HT})$ phase transition in PZT(Nb)95/5 is associated with two kinds of transition, i.e. the transitions from ordered R-type to disordered R-type tilts and from ordered R-type to ordered M-type tilts, while that in PZT(Nb)75/25 is only related to the former transition. Because the dielectric anomaly in the ferroelectric phase transition cannot be driven by pure nonpolar R mode and/or M modes, M-type tilts coupling to the polarization probably play a dominant role in the dielectric response; consequently there is a dielectric anomaly in PZT(Nb)95/5 and no change in PZT(Nb)75/25.

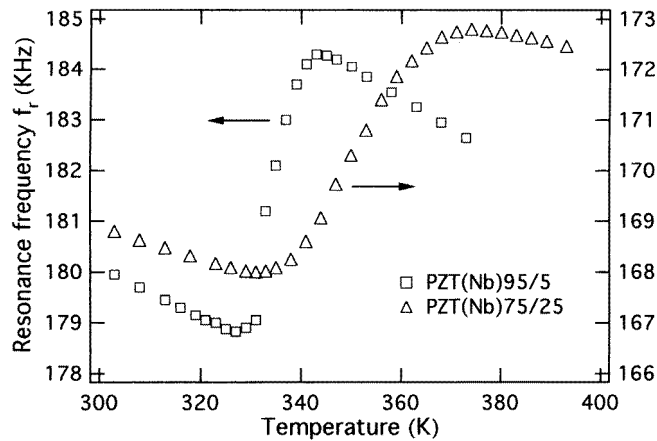


Figure 4. The temperature dependence of the resonance frequency f_r of PZT(Nb)95/5 and PZT(Nb)75/25.

In the low- and high-temperature rhombohedral phase regions, remarkable dielectric dispersions are observed for both compositions in figures 1 and 2. The degree of dielectric dispersion does not change remarkably with the variation of the Zr/Ti ratio. Hassan *et al* [19] attributed the dielectric dispersion to the influence of the silver electrodes. In the present experiments, the dielectric dispersions also appear after annealing samples at 450 °C for 4 h. A similar phenomenon was reported for pure PZT ceramics with sputtered gold

electrodes. Therefore the influence of the silver electrodes is highly questionable. A possible explanation is that the dielectric dispersion below T_c is due to the R-type tilts coupling to the polarization.

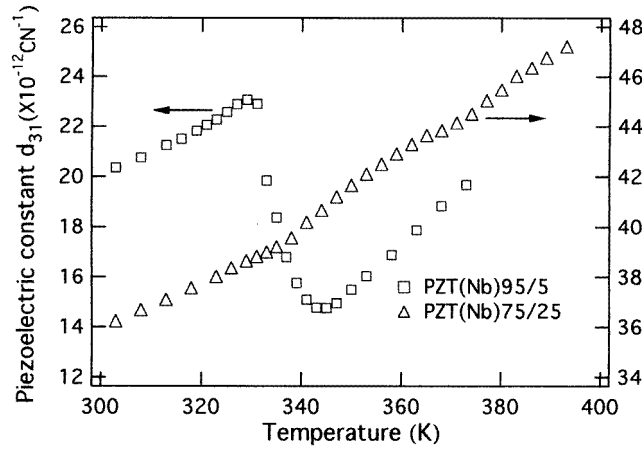


Figure 5. The temperature dependences of the piezoelectric constant d_{31} of PZT(Nb)95/5 and that of PZT(Nb)75/25.

Figure 4 shows the temperature dependence of the resonance frequency f_r of the radial-extension vibration mode of PZT(Nb)95/5 and PZT(Nb)75/25 in the heating process. It is found that the variations of the resonance frequencies with temperature are similar for the two compositions. f_r decreases gradually in the $F_R(LT)$ and $F_R(HT)$ phase regions and increases greatly through the $F_R(LT)$ – $F_R(HT)$ phase transition region. This indicates that for this transition the elastic property is more sensitive to an order–disorder R-type-tilt transition than the dielectric property. PZT(Nb)95/5 exhibits an abrupt increase of f_r at the phase transition point, while the change of f_r for PZT(Nb)75/25 occurs gradually over a relatively wide temperature range of ~ 24 K; thus it is difficult to accurately determine the phase transition temperature. And it is revealed that PZT(Nb)75/25 exhibits a diffuse $F_R(LT)$ – $F_R(HT)$ phase transition, which is probably associated with the transition between ordered R-type and disordered R-type tilts.

Figure 5 shows the temperature dependences of the piezoelectric constant d_{31} of PZT(Nb)95/5 and that of PZT(Nb)75/25. d_{31} is expressed as follows:

$$d_{31} = k_p \sqrt{\varepsilon_{33}^T S_{11}^E} / \sqrt{\frac{2}{1-\sigma}} \quad (2)$$

where ε_{33}^T is the dielectric constant, and the electromechanical coupling factor of the radial mode k_p , the elastic constant S_{11}^E , and Poisson's ratio σ can be derived from the resonance frequency, f_r , f_a , and f_{s1} . Around the $F_R(LT)$ – $F_R(HT)$ phase transition region, PZT(Nb)95/5 exhibits a remarkable decrease ($\sim 40\%$) in d_{31} —whereas no obvious anomaly is observed for PZT(Nb)75/25, and d_{31} increases gradually with the increase of temperature. This indicates that the temperature-induced strain shows an abruptness in PZT(Nb)95/5 and a gradual change in PZT(Nb)75/25 through the phase transition. As the strain is related to the tilt angle and deformation of the oxygen octahedra, our results are consistent with those obtained by neutron powder diffraction for pure PZT90/10 and 75/25 [11, 26], and further reveal that the $F_R(LT)$ – $F_R(HT)$ phase transition is a first-order feature for PZT(Nb)95/5 and

diffuse for PZT(Nb)75/25.

In conclusion, investigations on the structural phase transitions of Zr-rich PZT ceramics have been performed via dielectric and resonance frequency measurements. Differences between PZT(Nb)95/5 and PZT(Nb)75/25 as regards the nature of the phase transitions were observed. The $F_R(\text{HT})$ –PE phase transition of PZT(Nb)95/5 was confirmed to be a weakly first-order feature, whereas for PZT(Nb)75/25 a weak dielectric relaxation was observed above T_c which obeys the extended Curie–Weiss law. This relaxation is related to microscopic compositional inhomogeneity and/or the disorder of the oxygen octahedra tilts in the PE phase. A dielectric anomaly and thermal hysteresis in the $F_R(\text{LT})$ – $F_R(\text{HT})$ phase transition were detected for PZT(Nb)95/5, but no dielectric anomaly was detected for PZT(Nb)75/25; this may be due to the effect of M-type tilts.

For both compositions, dielectric dispersions were observed for the rhombohedral ferroelectric phases; this is attributed to the R-type and M-type tilts coupling to the polarization. Large anomalies of the resonance frequency were detected through the $F_R(\text{LT})$ – $F_R(\text{HT})$ phase region, but the anomaly of d_{31} appeared for PZT(Nb)95/5 and not for PZT(Nb)75/25.

One of the authors (X L Dong) would like to thank the Japan Society for the Promotion of Science (JSPS) for financial support of his stay at the Institute of Applied Physics, University of Tsukuba. This work was partially supported by the Murata Science Foundation.

References

- [1] Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric Ceramics* (London: Academic) p 136
- [2] Haas C 1965 *Phys. Rev. A* **140** 863
- [3] Samara G A 1970 *Phys. Rev. B* **1** 3777
- [4] Clarke R and Glazer A M 1974 *J. Phys. C: Solid State Phys.* **7** 2147
- [5] Whatmore R W, Clarke R and Glazer A M 1978 *J. Phys. C: Solid State Phys.* **11** 359
- [6] Haerting G H 1987 *Ferroelectrics* **76** 241
- [7] Kapenicks A E, Krumins A W and Dimiza V I 1982 *Ferroelectr. Lett.* **44** 189
- [8] Cross L E 1987 *Ferroelectrics* **76** 241
- [9] Burns G and Dacol F H 1983 *Phys. Rev. B* **28** 2527
- [10] Barnett H J 1962 *J. Appl. Phys.* **33** 1606
- [11] Clarke R and Glazer A M 1976 *Ferroelectrics* **12** 207
- [12] Glazer A M, Mabud S A and Clarke R 1978 *Acta Crystallogr. B* **34** 1060
- [13] Halemane T R, Haun H J, Cross L E and Newnham R E 1985 *Japan. J. Appl. Phys. Suppl.* 24-2 **20** 212
- [14] Berlincourt D, Krueger H H A and Jaffe B 1964 *J. Phys. Chem. Solids* **25** 659
- [15] Krause L T and O'Bryan L M Jr 1972 *J. Am. Ceram. Soc.* **55** 497
- [16] Krumins A, Shiosaki T and Koizumi S 1994 *Japan. J. Appl. Phys.* **33** 4940
- [17] Dai X H, Xu Z and Viehland D 1996 *J. Am. Ceram. Soc.* **79** 1957
- [18] Jankowska-Sumara I, Roleder K, Dec J and Miga S 1995 *J. Phys.: Condens. Matter* **7** 6137
- [19] Hassan H, Maglione M, Fontana M D and Handerek J 1995 *J. Phys.: Condens. Matter* **7** 8647
- [20] Clarke R and Burfoot J C 1974 *Ferroelectrics* **8** 505
- [21] Bell A J 1993 *J. Phys.: Condens. Matter* **5** 8773
- [22] Goodman G 1960 *J. Am. Ceram. Soc.* **43** 105
- [23] Burns G and Dacol F H 1984 *Phys. Rev. B* **30** 4012
- [24] Smolensky G A 1970 *J. Phys. Soc. Japan Suppl.* **28** 26
- [25] Dai X H, Xu Z K and Viehland D 1995 *J. Am. Ceram. Soc.* **78** 2815
- [26] Jirak Z and Kala T 1988 *Ferroelectrics* **82** 79