JOURNAL OF MATERIALS SCIENCE 31 (1996) 4951–4955

Mechanical loss and Young's modulus associated with phase transitions in barium titanate based ceramics

B.L. CHENG, M. GABBAY*, W. DUFFY, Jr.‡, G. FANTOZZI*
Department of Physics, South China University of Technology, Guangzhou 510641, Peoples Republic of China
*and *GEMPPM, CNRS UMR 5510, INSA Lyon, 69621 Villeurbanne Cedex, France*
and ‡Department of Physics, Santa Clara University, Santa Clara, CA 95053, USA

The mechanical loss (Q^{-1}) and Young's modulus (E) were measured as a function of temperature in the range $100\ \text{K} < T < 450\ \text{K}$ on rectangular plate specimens of $BaTiO_3$ driven electrostatically in flexural vibration mode at resonance frequencies between 2–4 kHz. $Q^{-1}(T)$ and $E(T)$ curves show the following three phase transitions in $BaTiO_3$: rhombohedral to orthorhombic ($T_{\text{R-O}}$), orthorhombic to tetragonal ($T_{\text{O-T}}$), and tetragonal to cubic (T_{Curie}). Each phase transition induces a very narrow mechanical loss peak of Q^{-1} and a very sharp anomaly in the elastic modulus. Moreover, three other mechanical loss peaks are located below the phase transition temperatures in coarse grained specimens and these peaks seem to be associated with the motion of domain walls. These secondary peaks are not observed in fine grained undoped ceramics. The use of dopants such as Co or Nb produces an attenuation of the mechanical loss, a smoothing of elastic modulus anomalies, and a shifting of the phase transition temperatures.

1. Introduction

Barium titanate ($BaTiO_3$) is a ferroelectric ceramic material which is widely used in the electronics industry for various applications (capacitors, non-linear positive-temperature-coefficient resistors and piezoelectric transducers). The material can exist in four crystal structures (rhombohedral, orthorhombic, tetragonal, and cubic) between 173–412 K. Associated with the structural phase transitions in the pure material are large variations of permittivity and dielectric loss. In order to avoid such disadvantages, only doped materials are used for electronic devices. For example, for a capacitor with an X7R-specification, which means that the variations in the dielectric constant ε_r should be controlled to be within ± 15% at the ε_r value at 298 K in the temperature range 218–398 K. Commonly, Nb and Co are added to $BaTiO_3$ in order to stabilize the permittivity and also to reduce the dielectric loss [1, 2]. In the literature, there are numerous studies of the $BaTiO_3$ phase transitions using dielectric loss and permittivity measurements [3–10]. However, there are very few published studies on the measurement of the mechanical loss and the elastic modulus of the material [11–14]. The aim of the present paper is to report experimental results of mechanical loss and elastic modulus measurements on $BaTiO_3$ ceramics, to discuss the respective influence that dopants such as Nb and Co have on the phase transitions and to analyse the effects of Nb and Co on a ceramic with an X7R-specification.

2. Experimental procedures

Four kinds of $BaTiO_3$ ceramics were prepared: (1) undoped material, (2) material doped with 2.0 or 4.0 at % Nb, (3) material doped with 0.6 or 1.0 at % Co and a material doped with 0.5 at % Co and 2.0 at % Nb with an X7R specification.

The barium titanate powder (Elmic BT 100: 0.7–1.0 μm particle size, Ba: Ti = 0.996 ± 0.004) was supplied by Rhone-Poulenc. Niobium pentoxide and/or cobalt carbonate powders were added to the barium titanate powder in an alcoholic suspension. The suspension was mixed by vibration milling with agate balls for 2 h. The mixture was then dried and suitable organic binders were added. After drying and deagglomeration, the powders were pressed uniaxially at 30 MPa to make prismatic bars (8 × 8 × 50 mm) and then pressed isostatically at 300 MPa. The compacts were sintered in air for 2 h at 1513 K or 1573 K at a heating and cooling rate of 300 K per h. The compacts were then sliced into rectangular plates (1 × 5 × 40 mm).

For the mechanical loss and the Young's modulus measurements, the sample was printed by air-dry silver and was horizontally supported at its nodal lines by two pairs of fine nickel wires. The plate was driven electrostatically in its fundamental flexural mode of vibration. The vibration amplitude was recorded as a function of frequency. The mechanical loss (Q^{-1}) was calculated from the resonance curve according

0022–2461

to [15]

$$Q^{-1} = \Delta f/(f_r(3)^{1/2})$$

where Δf is the width of the resonance curve at half-maximum value of amplitude and f_r is the resonance frequency. The Young's modulus E was calculated according to [16]

$$E = 0.9464\rho L^4 f_r^2/d^2,$$

where ρ is the density, L is the length, and d is the thickness. The $Q^{-1}(T)$ and $E(T)$ were measured from 100–450 K at a heating rate of 1 K per min in vacuum. The frequency of vibration was about 3 kHz and the maximum strain amplitude was 1×10^{-6}.

Scanning electron microscopy (SEM) observations were made on samples mechanically polished and lapped from 6 to 1 μm roughness using diamond paste and finally etched in acid (5% HCl, 0.5 vol% HF, 94.5% H_2O).

3. Experimental results

Fig. 1 (a and b) are SEM micrographs of a ceramic sintered at 1573 K for 2 h, which has a large grain size (about 40 μm) and contains numerous 90° domains. For a ceramic sintered at a lower temperature (1513 K for 2 h) the SEM micrograph shows a more homogeneous structure of fine grains with simple 90° domain walls as is shown in Fig. 2.

Fig. 3 (a and b) shows the variations in the elastic modulus E and the mechanical loss Q^{-1} as a function of temperature T of an undoped $BaTiO_3$ ceramic sintered in air at 1573 K for 2 h. The $E(T)$ curve shows three very sharp anomalies A3 (190 K), A2 (278 K) and A1 (405 K), which correspond to the following three phase transitions:

A3: rhombohedral to orthorhombic symmetry,
A2: orthorhombic to tetragonal symmetry,
A1: tetragonal to cubic symmetry.

These anomalies are respectively associated with three narrow peaks P3, P2 and P1 on the $Q^{-1}(T)$ curve. Moreover, the $Q^{-1}(T)$ curve shows a large peak designated R2 (250 K) and two small peaks R3 (178 K) and R1 (395 K).

The results for an undoped $BaTiO_3$ sample sintered at a lower temperature (1513 K) in air for 2 h are shown in Fig. 4 (a and b). The three phase transitions show similar elastic modulus anomalies (A3: 185 K, A2: 280 K and A1: 399 K) and also similar mechanical loss peaks (P3, P2 and P1). However, the R peaks are not observed.

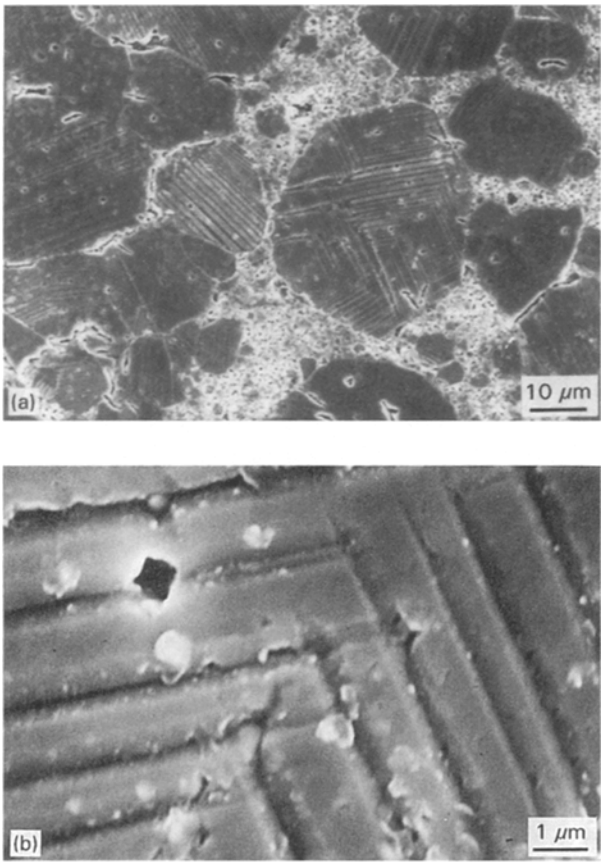

Figure 1 The microstructure of undoped barium titanate sintered at 1573 K for 2 h.

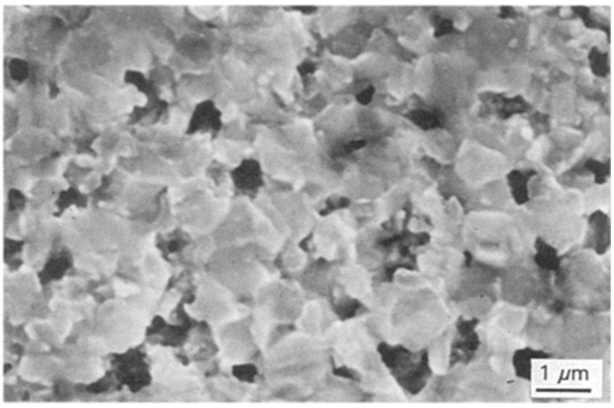

Figure 2 An SEM image of undoped $BaTiO_3$ sintered at 1513 K for 2 h.

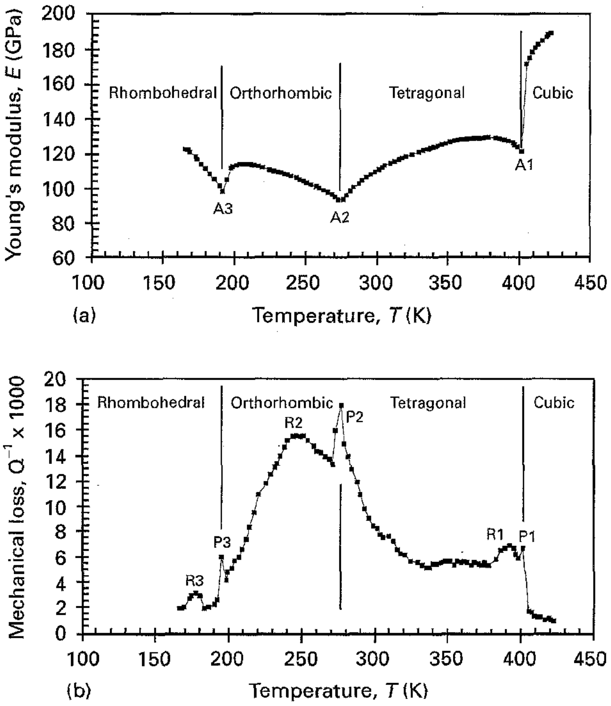

Figure 3 Variations of (a) the Young's modulus E and (b) the mechanical loss Q^{-1} as a function of temperature for undoped coarse grained $BaTiO_3$.

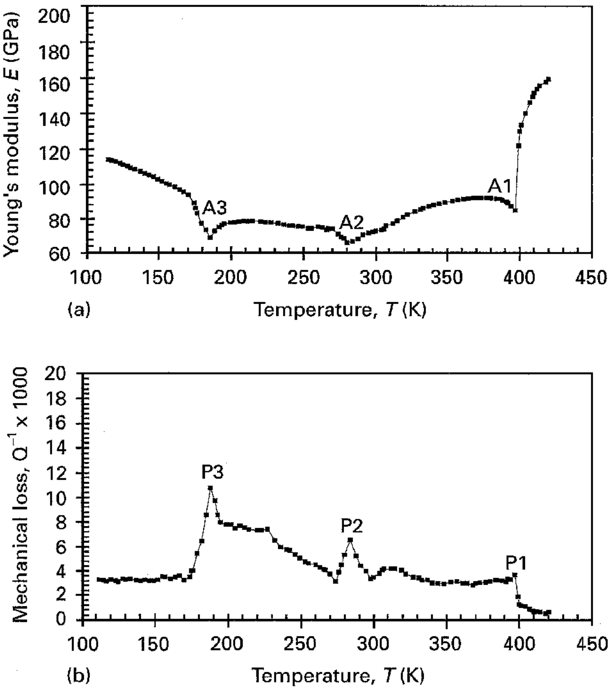

Figure 4 Variations of (a) the Young's modulus E and (b) the mechanical loss Q^{-1} grained as a function of temperature for undoped fine grained $BaTiO_3$.

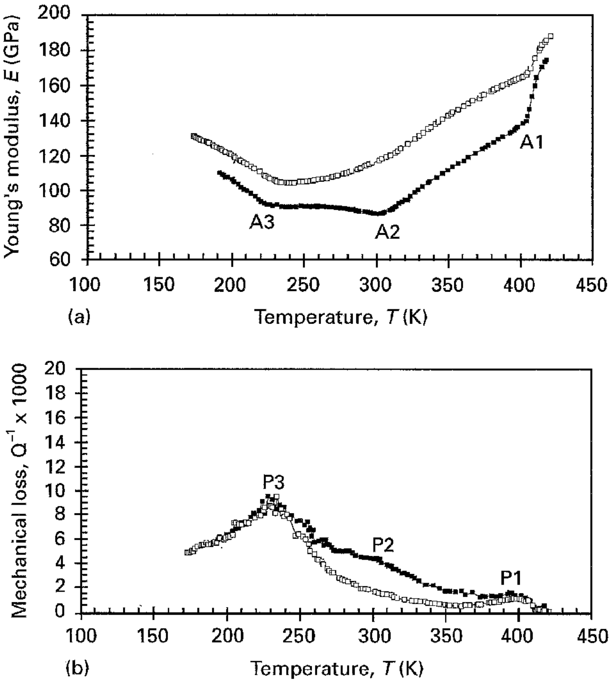

Figure 5 Variations of (a) the Young's modulus E and (b) the mechanical loss, Q^{-1} as a function of temperature for $BaTiO_3$ doped with; (■) 2.0 and (□) 4 at % Nb.

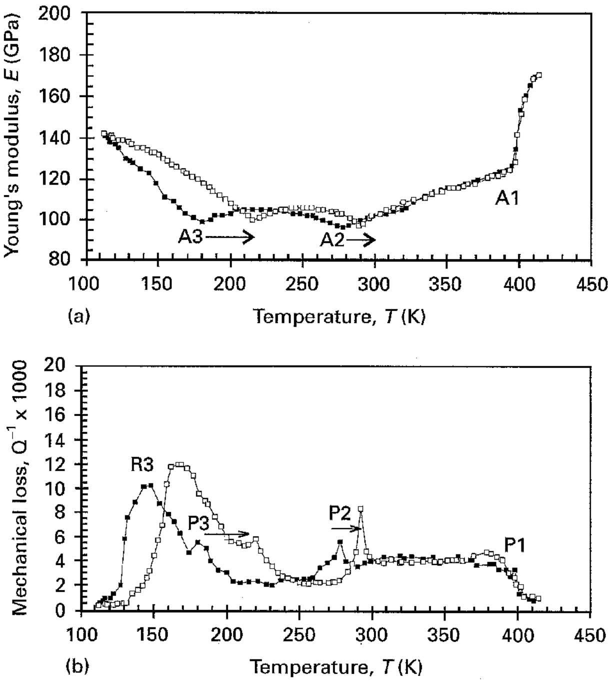

Figure 6 Variations of (a) the Young's modulus E and (b) the mechanical loss, Q^{-1}, as a function of temperature for $BaTiO_3$ doped with (■) 0.6 at % and (□) 1.0 at % Co.

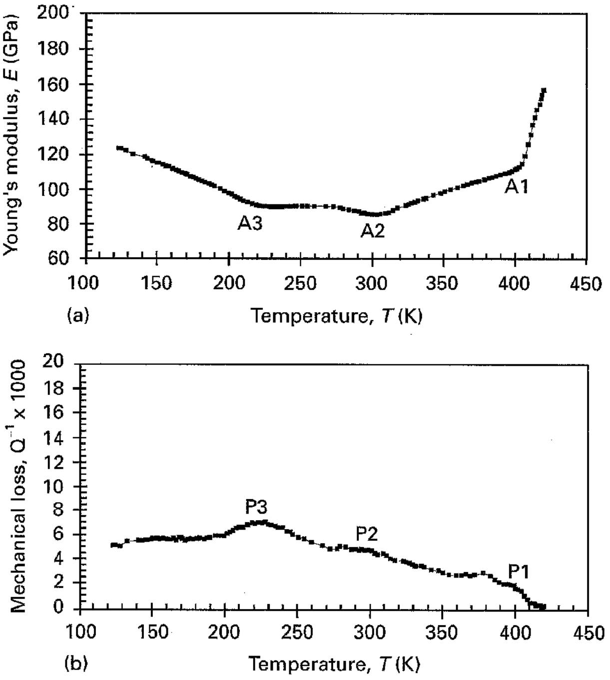

Figure 7 Variations of (a) the Young's modulus E and (b) the mechanical loss Q^{-1} as a function of temperature on X7R-specification $BaTiO_3$ doped with 0.5 at % Co and 2.0 at % Nb.

Fig. 5 (a and b) shows the mechanical loss and elastic modulus curves corresponding to 2.0 and 4.0 at % Nb doped $BaTiO_3$. Compared with the results of the undoped ceramic, the anomalies A1, A2 and A3 of the $E(T)$ curves are smoothed off; the higher the Nb content, the more extensive is the smoothing. For 4.0 at % Nb content, the A2 anomaly completely disappears, the mechanical loss peak P1 (400 K) is drastically reduced, and the P2 peak disappears. However, the height of the P3 (233 K) peak remains stable. The temperature of A3 is shifted to higher values (from 225 K to 233 K) with increasing Nb content.

Fig. 6 (a and b) shows the mechanical loss and elastic modulus curves of $BaTiO_3$ doped with 0.6 and 1.0 at % Co. The anomalies A1, A2 and A3 are located at 398, 278 and 180 K for the 0.6 at % Co doped ceramic and at 398, 291 and 215 K for the 1.0 at % Co doped ceramic. The anomalies are also smoothed off by the addition of the Co dopant; the smoothing effect is similar to that observed in the Nb doped material. With regard to the $Q^{-1}(T)$ curves, a comparison with Fig. 3 shows that (1) the heights of the P1, P2 and P3 peaks are reduced (2) the mechanical loss level in the tetragonal phase, between the P1 and P2 peaks, remains unchanged whilst in the orthorhombic phase, between the P2 and P3 peaks it is drastically reduced, and (3) that the R3 peak is strongly enhanced.

Fig. 7 (a and b) shows the temperature variation of the mechanical loss and the elastic modulus curves of the X7R material, doped with 2.0 at % Nb and 0.5 at % Co. Indications of the phase transitions occur on the mechanical loss curves as steps at P1 (403 K) and at P2 (308 K), and a peak at P3 (223 K). There are smoothed modulus anomalies at approximately the same temperatures.

4. Discussion

4.1. The influence of the grain size

The three anomaly-peak pairs (A1, P1), (A2, P2) and (A3, P3) in undoped $BaTiO_3$ ceramics can be obviously attributed to the three structural phase transitions in the material. Concerning the R peaks that are observed only in the coarse grained ceramic sintered at a high temperature (1573 K). The structure observed by SEM shows large grains (about 40 μm in size) with numerous 90° domain walls (Fig. 1). For ceramics sintered at a lower temperature (1513 K), Fig. 2 shows a more homogeneous structure of fine grain size (about 1 μm). The R2 peak may be attributed to the motion of domain walls in the coarse grained ceramics and such a motion could be limited by grain boundaries in fine grained ceramics. It is interesting to point out that such a secondary peak has also been observed in ferroelectric lead zirconate titanate (PZT) [17], in potassium dihydrogen phosphate (KDP) [18], $La_{1-x}Nd_xP_5O_{14}$ (LNPP) [19], triglycine sulphate (TGS) [20] and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) [21], by mechanical and dielectric loss and also permittivity measurements. They have also been studied in alloys with twinned structures such as A15 [22] and Mn–Cu alloys [23]. The analysis of the mechanism of formation such peaks will be discussed in detail in a future paper.

4.2. The influence of the Nb dopants

The mechanical loss decreases with increasing amounts of Nb. The structural transitions from cubic to tetragonal and from tetragonal to orthorhombic structures were smoothed as indicated by the inflections in the modulus data (see Fig. 5). For the $BaTiO_3$ doped with 4 at % Nb. The transitions from cubic to tetragonal and from tetragonal to orthorhombic symmetry cannot be determined at a definite temperature and the T_{R-O} moves to about 230 K. For the mechanical loss there is a very small loss peak for the phase transition from cubic to tetragonal and no loss peak for the phase transition from tetragonal to orthorhombic. This may be due to the shifting of T_{Curie} from 403 K to 313 K [24], at which temperature it overlaps with the T_{T-O}. For reference, the T_{T-O} is about 303 K in the sample doped with 2.0 at % Nb. Thus it is impossible to uniquely determine the T_{Curie} and T_{O-T} when the Nb content is larger than 4.0 at %.

SEM observations show that the Nb dopant inhibits grain growth during sintering. The grain size of Nb doped ceramics is about 1–2 μm. The disappearance of the (A2, P2) pair could be attributed to the shift of the Curie point towards lower temperatures [1]. Such a shift is probably due to the partial intragranular diffusion of Nb which leads to a "core–shell" structure in which the grain core remains pure whilst the dopant concentration increases towards the grain boundary. Such a heterogeneous composition inside the grain gives a distribution of Curie temperatures. The shift of the (A3, P3) pair towards higher temperatures is probably also connected to such a "core–shell" structure.

4.3. The influence of the Co dopants

SEM observations also show that Co inhibits grain growth during sintering. The grain size is about 1–2 μm. Ihrig [25] reported that the effect of a Co dopant was to produce shifts of both T_{Curie} and T_{O-T} towards lower temperatures, and T_{R-O} towards higher temperatures. The results reported here are consistent with these shifts.

It is well known that Nb doped into $BaTiO_3$ will substitute at the Ti lattice sites. (The radius of Nb is 0.067 nm which is near the 0.060 nm radius of Ti). The Nb^{5+} ions have donor properties, the compensation of the surplus charge is affected by vacant sites in the cation lattice [26]. Conversely, Co^{3+} ions, which also substitute at the Ti sites, possess acceptor character, with in this case the charge deficiency being compensated by vacancies in the oxygen lattice [27]. As observed from hysteresis measurements, Härdlt [28] noted that donor dopant ions increase the domain wall mobility and therefore increase the losses connected with that mobility. Conversely acceptor dopant ions fix the domain wall positions and thus reduce the domain wall losses.

In fact, the variations in the mechanical losses as a function of temperature are very different between the materials doped solely with Nb or Co. In the orthorhombic phase the mechanical losses are suppressed by the Co dopant, but not by the Nb dopant. Conversely, in the tetragonal phase the mechanical losses are suppressed by the Nb dopant, but not by the Co dopant. This could due to the acceptor dopant ions Co^{3+} which fix the domain wall positions and thus reduce the domain wall losses in the orthorhombic phase. However this is not the case in the tetragonal phase.

In Co doped ceramics, the large R3 peak, located in the rhombohedral phase, could be due to the motion of domain walls and also the diffusion of oxygen vacancies. The difference between the valence states of the two dopants (Nb^{5+}, Co^{3+}) can be used to explain those different influences on the mechanical loss.

4.4. The influence of combined Nb and Co dopants

Comparing Fig. 7 with Figs 5 and 6, the sample doped with 2.0 at % Nb and 0.5 at % Co (with X7R specification) has two peaks located at 230 K and 310 K, but the sample doped solely with 2.0 at % Nb has only one peak at 220 K. From the variations of the modulus versus temperature, it seems that the influence of the Nb dopants in the orthorhombic phase is dominant for X7R specification materials and the influence of the Co dopants is dominant in the tetragonal phase. In this way the variations of modulus versus temperature from 223–398 K are smoothed. This corresponds to the stable dielectric constant of X7R materials.

5. Conclusion

In coarse grained undoped $BaTiO_3$ ceramics, each phase transition induces a very narrow mechanical loss peak and a very sharp anomaly of the elastic modulus. Moreover, other mechanical loss peaks may be associated with the motion of domain walls. The influence of dopants such as Nb or Co results in the attenuation of mechanical loss and the smoothing of the elastic modulus anomaly. The Nb dopant reduces the mechanical loss in the tetragonal phase and the Co dopant reduces the mechanical loss in the orthorhombic phase. In this way, the combination of Nb and Co dopants gives a smoother variation of mechanical loss and elastic modulus versus temperature. This could be the reason for the X7R-specification ceramic. In order to study the mechanism of formation of the R peaks, low frequency measurements will be carried out and those results will be reported in a future paper.

Acknowledgements

The authors are very grateful to J. Paletto and M. Taha for specimen preparations, to C. Olagnon for SEM observations and to D. Lavielle and G. Orange for valuable discussions.

References

1. M. KAHN, *J. Amer Ceram. Soc.* **54** (1971) 455.
2. D. LAVIELLE, J. POUMARAT, Y. MONTARDI, P. BERNARD and O. AGURRE-CHARRIOL, in Proceedings of Second Euro-Ceramics, Augsburg, September 1991, edited by G. Ziegler and H. Hausner, (Deutsche Keramische Gesellschaft e.V., 1991) Vol. 3 p. 1903.
3. R.F. BLUNT and W.F. LOVE, *Phys. Rev.* **76** (1949) 1202
4. H.C. GRAHAM, N.M. TALLAN and K.S. MAZDIYASNI, *J. Amer. Ceram. Soc.* **54** (1971) 548.
5. H.J. HAGEMANN, *J. Phys. C. Solid State* **11** (1978) 3333.
6. G. ARLT, D. HENNINGS and G. DE WITH, *J. Appl. Phys.* **58** (1985) 1619.
7. T.R. ARMSTRONG, K.A. YOUNG and R.C BUCHANAN, *J. Amer Ceram. Soc.* **73** (1990) 700.
8. F. CHU, H.T. SUN, L.Y. ZHANG and X. YAO, *ibid.* **75** (1992) 2939.
9. K. WU and W. A. SCHULZE, *ibid.* **75** (1992) 3385.
10. T.S. FANG, H.L. HSIEH and F.S. SHIAU, *ibid.* **76** (1993) 1205.
11. T. IKEDA, *J. Phys. Soc. Jpn.* **12** (1958) 809.
12. E.J. HUIBREGTSE, W.H. BESSY and M.E. DROUGARD, *J. Appl. Phys.* **30** (1959) 899.
13. A. YU. KUDZIN, L.K. BUNINA and O.A. GRZHEGORZHEVSKII, *Soviet Phys.-Solid State* **11** (1970) 1939.
14. A. YU. KUDZIN, E.P. KASHCHENKO and V.I. KOSTRUB, *ibid.* **12** (1972) 3162.
15. C. ZENER, "Elasticity and Anelasticity of Metals" 2nd Edn (The University of Chicago Press, Chicago, Illinois, 1952) Ch. 6.
16. A.S. NOWICK and B.S. BERRY, "Anelastic Relaxation in Crystalline Solids", (Academic Press, New York, 1972), Appendix F.
17. P.V. POSTNIKOV, V.S. PAVLOV, S.A. GRIDEV and S.K. TURKOV, *Soviet Phys.-Solid State* **10** (1968) 1267.
18. L.N. KAMYSHEVA and S.N. DROZHIN, *Ferroelectrics* **71** (1987) 281.
19. Y.N. WANG, W.Y. SUN, X.H. CHEN, H.M. SHEN, and B. LU, *Phys. Stat. Sol.* (*a*) **102** (1987) 279.
20. X.H. CHEN, Y.N. WANG, H.M. SHEN, Z.M. NIU and P.C.W. FUNG, in Proceedings ICIFUAS-9, Beijing, China, July 1989, edited by T.S. Kê, Pergamon Press, Oxford, 1989) p. 153.
21. D. VIEHLAND, M. WUTTIG and L.E. CROSS, *Ferroelectrics* **120** (1991) 71.
22. C.L. SNEAD JR. and D.O. WELCH, *J. de Physique* **46** [C10] (1985) 589.
23. K. SUGIMOTO and T. MORI, in Proceedings ICIFUAS-5, Aachen, Germany, August 1973, edited by D. Lenz and K. Lucke, (Springer-Verlag, Berlin, 1975) p. 418.
24. D. HENNINGS and G. ROSENSTEIN, *J. Amer Ceram. Soc.* **67** (1984) 249.
25. H. IHRIG, *J. Phys. C: Solid State Phys.* **11** (1978) 819.
26. K.H. HÄRDLT and D. HENNINGS, *J. Amer Ceram. Soc.* **55** (1972) 230.
27. H.J. HAGAMANN and H. IHRIG, *Phys. Rev. B* **20** (1979) 3871.
28. K.H. HÄRDLT, *Ceram. International* **8** (1982) 121.

Received 18 July 1994
and accepted 13 February 1996