

Development of dielectric measurement technique for micrometer-ordered pure BaTiO₃ and Ba(Zr_{0.1}Ti_{0.9})O₃ single crystals

Satoshi Wada, Shingo Uraki, Hirofumi Kakemoto and Takaaki Tsurumi

Department of Metallurgy & Ceramics Science, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, JAPAN
Fax: 81-3-5734-2514, e-mail: swada@ceram.titech.ac.jp

Dielectric properties of micrometer-ordered barium zirconium titanate (Ba(Zr_xTi_{1-x})O₃) single crystals with a size of 50-75 μm were investigated using a new developed dielectric measurement system. The micrometer-ordered Ba(Zr_xTi_{1-x})O₃ single crystals with various x values were grown by a conventional flux method using a BaCl₂ flux. The sizes of the grown Ba(Zr_xTi_{1-x})O₃ single crystals were decreased with increasing x. The size of the pure BaTiO₃ single crystals was about 1-2 mm while that of Ba(Zr_{0.1}Ti_{0.9})O₃ single crystals was about 50 μm. Therefore, these pure BaTiO₃ and Ba(Zr_{0.1}Ti_{0.9})O₃ single crystals were chosen for the dielectric measurement. The pure BaTiO₃ crystals were sized into about 75 μm while for Ba(Zr_{0.1}Ti_{0.9})O₃ crystals, as-grown 50 μm cube crystals were used. For the dielectric measurements, the capacitance of these crystals was almost a couple hundred fF, and it was very difficult to measure a small capacitance below a pF precisely. For this purpose, a new dielectric measurement system was developed. Using this system, the dielectric properties of the pure BaTiO₃ crystals were measured from 20 to 170 °C, and this result almost consisted with the reported one. Moreover, the dielectric properties of Ba(Zr_{0.1}Ti_{0.9})O₃ crystals were also measured from 20 to 170 °C, and exhibited the typical diffuse phase transition behavior.

Key word: micrometer-ordered single crystals, dielectric property, barium zirconium titanate, flux method, diffuse phase transition

1. INTRODUCTION

Today, the oxide materials are used as very important electric materials in the various application fields. However, in the most of these oxide electric materials used for the practical application, there were a lot of unknown intrinsic physical properties and the unknown relationships between the properties and the crystal structures. In general, these oxide electric materials were used as a form of ceramics, and these physical property measurements were also performed using these ceramics. The ceramics is composed of many single crystals, *i.e.*, grains, with different crystallographic orientations. If the physical properties are measured using the ceramics, only the average physical properties can be obtained. This means that using the ceramics, it is very difficult to clear the precise relationship between the intrinsic physical properties and the crystal structures. Therefore, to reveal this accurate relation, the study using the single crystals must be required. However, it is very difficult to grow the large oxide single crystals with an enough size over a couple mm for the physical property measurements. On the other hand, it is not difficult to grow the small single crystals such as the powders with a micrometer size. If we can handle the micrometer-ordered oxide single crystals and measure the some intrinsic electric properties, it is possible to clear the relations between the intrinsic electric properties and the crystal structures.

In this manuscript, we focus on the dielectric properties of the micrometer-ordered Ba(Zr_xTi_{1-x})O₃ single crystals with various x. This is because Ba(Zr_xTi_{1-x})O₃ ceramics has been used for the multi-layer ceramics capacitors (MLCCs) with the EIA Y5V specification^{1,6} while in these dielectric properties, there are still a lot of unknown things. Some researchers focus on the piezoelectric application using Ba(Zr_xTi_{1-x})O₃ ceramics⁷ and single crystals^{8, 9}. However, it is known that the ferroelectric-related properties of Ba(Zr_xTi_{1-x})O₃ were significantly

dependent on the Zr contents.¹⁰⁻²² In general, Ba(Zr_xTi_{1-x})O₃ ceramics can be classified into three types of ferroelectrics on the basis of their dielectric property (ε_r) vs temperature (T) behaviors.^{18, 19} At first, in the Ba(Zr_xTi_{1-x})O₃ ceramics below x=0.10, there are three phase transitions in the temperatures from -90°C to 130°C, and these three phase transitions approaches to one phase transition with increasing Zr contents. This dielectric behavior is called as the "normal" phase transition. Secondly, in the Ba(Zr_xTi_{1-x})O₃ ceramics above x=0.25, the ε_r vs T curve exhibits the frequency dependence, which indicates that these ceramics are the relaxor materials. This dielectric behavior is called as the "relaxor" phase transition. Thirdly, in the Ba(Zr_xTi_{1-x})O₃ ceramics with x from 0.10 to 0.25, their ε_r vs T curves shows a large broad peak without the frequency dependence, and this dielectric behavior is called as the "diffuse" phase transition. In special, the Ba(Zr_xTi_{1-x})O₃ ceramics with x from 0.10 to 0.25 are useful for MLCCs application,^{4,6} but there are few informations about their diffuse phase transition behaviors and their origin. There are still a lot of unknown things about phase transition behaviors and properties in Ba(Zr_xTi_{1-x})O₃, *i.e.*, the dependence of the dielectric behaviors on the Zr contents in Ba(Zr_xTi_{1-x})O₃, and the role of Zr ions in Ba(Zr_xTi_{1-x})O₃. Thus, it is important to clarify a role of Zr ions for the above three phase transition behaviors.

Our final objective is to reveal the relations between the intrinsic dielectric properties and the crystal structures of Ba(Zr_xTi_{1-x})O₃, using the micrometer-ordered Ba(Zr_xTi_{1-x})O₃ single crystals. As the 1st step, Ba(Zr_xTi_{1-x})O₃ single crystals with various x were grown using a flux method. Moreover, to handle the micrometer-ordered crystals and measure their small capacitances below a pF precisely, a new dielectric measurement system was developed. Moreover, to confirm the validity of the results obtained using this measurement system, the pure BaTiO₃ single crystals was used as the standard

materials, and the temperature dependence of the dielectric properties was measured. Finally, the dielectric properties of $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ single crystals were measured at various temperatures and its phase transition behavior was discussed.

2. EXPERIMENTAL

2.1 $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ single crystal growth

$\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ single crystals were grown by a conventional flux method with the BaCl_2 flux. ZrO_2 , BaCO_3 , and TiO_2 high-purity (> 99.9%) powders were used as the raw materials. These powders were weighed at a Ba/Ti/ Zr ratio of 1/0.9/0.1, ball-milled for 24 hours, dried and then calcined at 1350 °C for 3 hours. The calcined $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ powders were ball-

milled for 24 hours again. Next, these powders were dry-mixed with the BaCl_2 flux powders at $\text{BaCl}_2/\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ratio of 1/1. The mixed powders were loaded into a platinum crucible, which was placed in an alumina crucible sealed with an alumina lid and an alumina cement to minimize the BaCl_2 volatilization. The double-layered crucible was placed in a furnace, and held at 1400 °C for 20 hours, followed by slow cooling (2 °C/h above 900 °C). Acetic acid and distilled water were used to separate the crystals out of the rest of the melt. The crystal structure of the grown crystals was measured by a powder XRD measurement. The chemical composition of the crystals was investigated by an EDX analysis. Moreover, the crystal size and domain structure were observed by a polarizing microscope.

2.2 Development of a new dielectric measurement system

In this study, 50-75 μm cube crystals were handled and their dielectric properties were measured. It should be noted that even if the dielectric constant is about 1,000, the capacitance of the 50 μm cube crystal is only about 400 fF. This value is very small, and comparable to an electric noise and the floating capacitance of the measurement attachment. Thus, the noise and floating capacitance must be reduced below 1 fF. For this purpose, we developed a new dielectric measurement system, as shown in Fig. 1. This system included the microscope, the digital camera and its monitor, and the crystal was always observed on the monitor. The measurement cell was located in the electric heater, and the temperature was changed from 20 °C to 200 °C. The temperature was measured using a thermocouple located near the crystals. Figure 2 shows the typical crystal holding state. As a probe, Ag wires with a diameter of 50 μm were used. The 50-75 μm cube crystals were chosen as the samples. As an electrode, Pt paste was used, painted on two faces of the crystals, and dried at 250 °C for 30 min. After that, the crystal with Pt electrodes was contacted by two Ag wire probes, as shown in Fig. 2, and located in the center of the measurement cell, as shown in Fig. 3. To reduce the electric noise and the floating capacitance of this system, this measurement cell had three features, *i.e.*, (1) four probing lines from an impedance analyzer (HP-4294A) were combined just front of the crystal, (2) four probing lines were always shielded by Ag paste, and (3) Pt ring was located near the crystal to shield the line of electric force of the surrounding crystal as shown in Fig. 4. Using this special measurement cell, the electric noise and the floating capacitance were reduced below 1 fF. Using the new developed dielectric measurement system, the dielectric properties of $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ single crystals were measured.

3. RESULTS AND DISCUSSION

3.1 Characterization of the grown $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ single crystals

Figure 5 shows an optical microscope image of the as-grown crystals. There were many single crystals with various shapes and sizes. At first, all of the as-grown crystals were crashed, and their crystal structures were measured using a powder XRD. Figure 6 exhibits a XRD pattern of these crystals. This pattern can be assigned to a typical perovskite-type crystal structure. However, each peak was

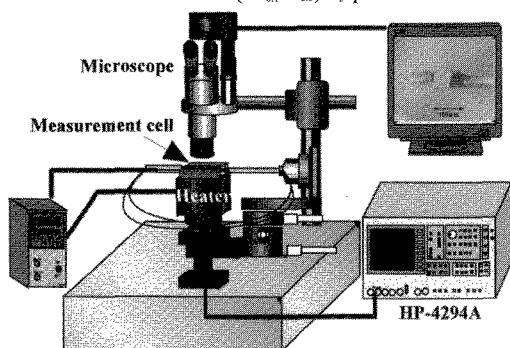


Fig. 1 A schematic diagram of a new developed dielectric measurement system.

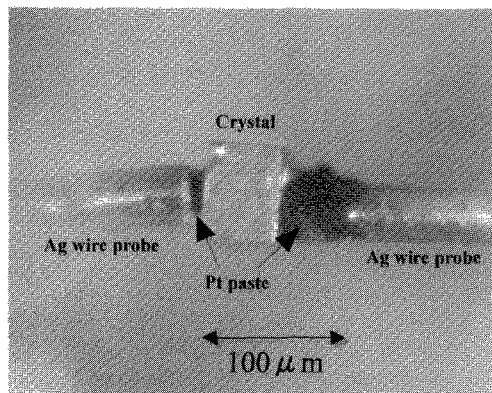


Fig. 2 A typical crystal holding state.

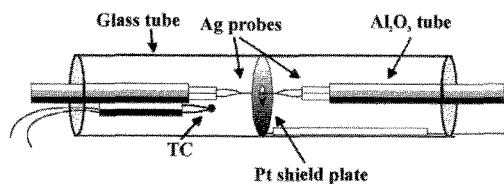


Fig. 3 A schematic diagram of a special measurement cell.

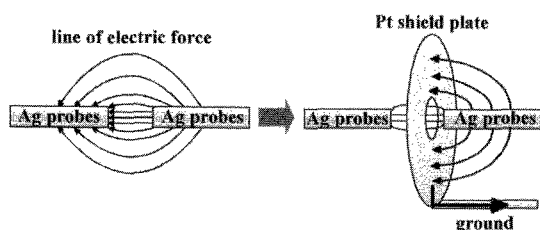


Fig. 4 A schematic role of Pt shield plate to remove the excess line of electric force.

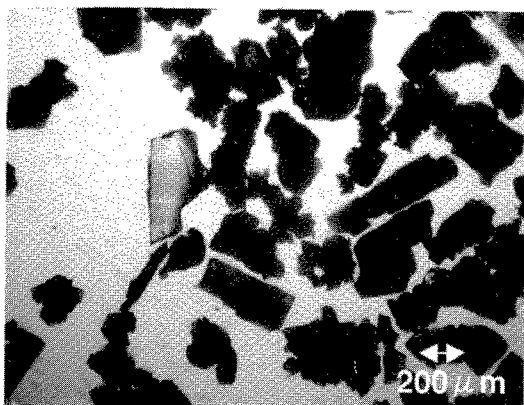


Fig. 5 A optical photograph of the as-grown $\text{Ba}(\text{Zr,Ti})\text{O}_3$ single crystals.

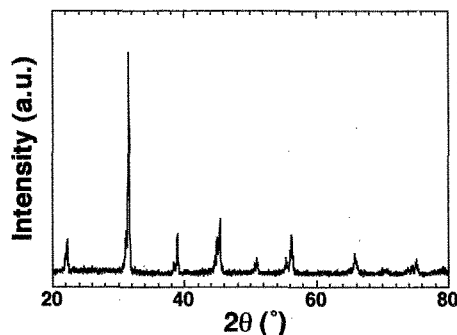


Fig. 6 A XRD pattern of the as-grown $\text{Ba}(\text{Zr,Ti})\text{O}_3$ single crystals.

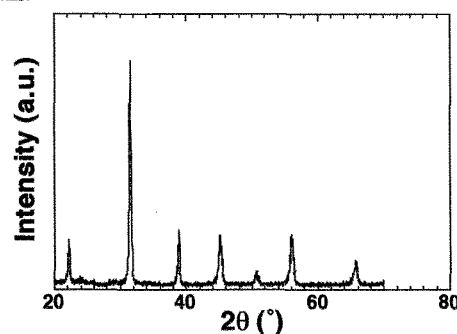


Fig. 7 A XRD pattern of the calcined $\text{Ba}(\text{Zr,Ti})\text{O}_3$ powders.

composed of two peaks, *i.e.*, (1) a small lower-angle peak and (2) a large higher-angle peak. Figure 7 shows a XRD pattern of the calcined powders with the chemical composition of $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$. This crystal structure was assigned to a cubic phase of the perovskite-type structure. The *a*-axis calculated from some peaks was almost consistent with the reported value of $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics. The comparison of Fig. 6 with Fig. 7 revealed that in the XRD pattern in Fig. 6, there were $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ single crystals. Thus, we tried to classify these crystals on the basis of the shape and the size.

As the result, the crystals were classified into two types of the crystals, *i.e.*, (1) the crystals with sizes of a couple hundred μm cube and (2) the crystals with sizes of a few ten μm cube. These two kinds of the crystals were crashed into the powders, and their XRD patterns were measured, respectively. Figure 8 exhibits a XRD pattern of the as-grown crystals with sizes of a couple hundred μm . These all peaks were completely assigned to a tetragonal BaTiO_3 with the

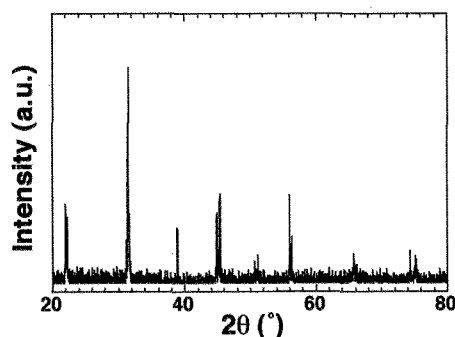


Fig. 8 A XRD pattern of the as-grown $\text{Ba}(\text{Zr,Ti})\text{O}_3$ single crystals with sizes of a couple hundred μm .

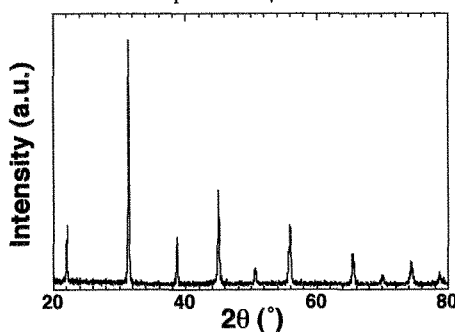


Fig. 9 A XRD pattern of the as-grown $\text{Ba}(\text{Zr,Ti})\text{O}_3$ single crystals with sizes of about 50 μm .

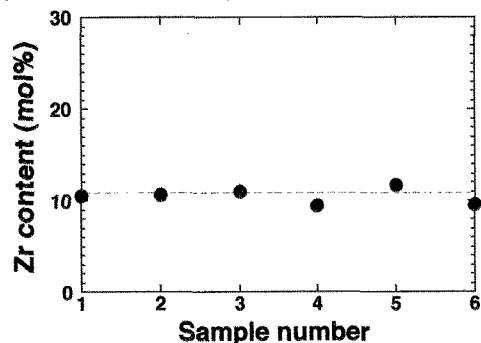


Fig. 10 A Zr contents of the as-grown $\text{Ba}(\text{Zr,Ti})\text{O}_3$ single crystals with sizes of about 50 μm .

c/a ratio of 1.011. Figure 9 indicates a XRD pattern of the as-grown crystals with sizes of about 50 μm . These all peak positions were perfectly consistent with those in Fig. 7, which revealed that these crystals were $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ single crystals. Moreover, to confirm the growth of $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ single crystals, 6 crystals with sizes around 50 μm were randomly picked up, and their chemical compositions were investigated using the EDX analysis. Figure 10 shows the Zr contents in the 6 crystals with sizes around 50 μm . This result revealed that these crystals included $10 \pm 1 \text{ mol}\%$ Zr.

The above results indicated that two kinds of the single crystals were grown using the flux method with the calcined $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ powders, *i.e.*, pure BaTiO_3 and $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ single crystals. Now, we believe that the other Zr-rich materials can become to fine powder, and at the washing process, these Zr-rich materials were removed.

3.2 The dielectric measurement using pure BaTiO_3 and $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ single crystals

In this study, a new dielectric measurement system was developed as the above described. Thus,

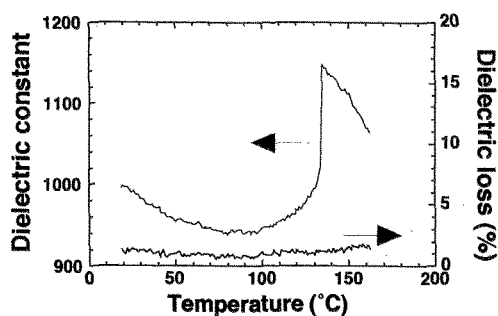


Fig. 11 Temperature dependence of the dielectric properties of pure BaTiO₃ single crystals with a size of 75 μm .

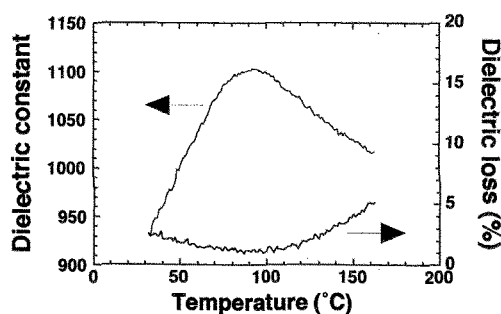


Fig. 12 Temperature dependence of the dielectric properties of Ba(Zr_{0.1}Ti_{0.9})O₃ single crystals with a size of 50 μm .

to confirm the validity of the measurement results using this system, the temperature dependence of the dielectric properties of the pure BaTiO₃ single crystal with a size of 75 μm were measured. Figure 11 shows the results using this BaTiO₃ single crystal. At 20 $^{\circ}\text{C}$, the dielectric constant was almost 1,000. For the single-domain BaTiO₃ single crystal, the dielectric constant along *a*-axis ϵ_a is 4,400 while the dielectric constant along *c*-axis ϵ_c is 140. Therefore, the dielectric constant of 1,000 in this measurement means that the measured BaTiO₃ single crystal had multi-domain structure. Moreover, the dielectric loss at 20 $^{\circ}\text{C}$ was below 2 %, and this suggested that the grown BaTiO₃ single crystal had a good quality as a dielectrics. At 135 $^{\circ}\text{C}$, the maximum dielectric constant of 1,148 was observed, which suggested that the Curie temperature (T_c) was 135 $^{\circ}\text{C}$. This T_c value was almost consistent with the reported T_c . Moreover, it should be noted that from 20 $^{\circ}\text{C}$ to 170 $^{\circ}\text{C}$, the dielectric loss was below 2 %. Therefore, this result revealed that the new developed measurement system exhibited a good work, and the flux grown BaTiO₃ single crystals had the good dielectric properties.

Figure 12 shows the temperature dependence of the dielectric properties of the Ba(Zr_{0.1}Ti_{0.9})O₃ single crystal with a size of 50 μm . This result revealed that there was a large broad dielectric peak with a maximum dielectric constant of 1,103 at 92 $^{\circ}\text{C}$. On the other hand, the dielectric loss under 100 $^{\circ}\text{C}$ was below 2 %, but above 100 $^{\circ}\text{C}$, the dielectric loss increased with increasing temperature ($\tan\delta < 6$ % at 160 $^{\circ}\text{C}$). It should be noted that there was no frequency dependence for the Ba(Zr_{0.1}Ti_{0.9})O₃ single crystal. This suggested that the phase transition behavior of Ba(Zr_{0.1}Ti_{0.9})O₃ was assigned to the diffuse

phase transition. Moreover, this result was almost consistent with those reported for the Ba(Zr_{0.1}Ti_{0.9})O₃ ceramics. The above result revealed that it is very useful to measure the dielectric properties using the micrometer-ordered oxide single crystals. In the future, the relation between the crystal structure and the dielectric properties of the Ba(Zr_{0.1}Ti_{0.9})O₃ single crystals will be cleared. For this objective, the more study should be required.

4. CONCLUSION

Dielectric properties of the micrometer-ordered BaTiO₃ and Ba(Zr_{0.1}Ti_{0.9})O₃ single crystals with sizes of 50-75 μm were investigated using the new developed dielectric measurement system. The micrometer-ordered BaTiO₃ and Ba(Zr_{0.1}Ti_{0.9})O₃ single crystals were grown by the conventional flux method using the BaCl₂ flux. The BaTiO₃ crystals with a 75 μm cube were chosen while for Ba(Zr_{0.1}Ti_{0.9})O₃ crystals, as-grown 50 μm cube crystals were used. For the dielectric measurements, the capacitance of these crystals was almost a couple hundred fF, and it was very difficult to measure small capacitance below a pF precisely. For this purpose, the new dielectric measurement system was developed. Using this system, the dielectric properties of the pure BaTiO₃ crystals were measured from 20 to 170 $^{\circ}\text{C}$, and this result almost consisted with the reported ones. Moreover, the dielectric properties of Ba(Zr_{0.1}Ti_{0.9})O₃ crystals were also measured from 20 to 170 $^{\circ}\text{C}$, and exhibited the typical diffuse phase transition behavior.

5. ACKNOWLEDGMENTS

This study was partially supported by (1) a Grant-in-Aid for Scientific Research (1155164) from the Ministry of Education, Science, Sports and Culture, Japan, (2) Murata Foundation for Science, and (3) TEPCO Research Foundation.

References

- ¹D. Hennings, A. Schnell and G. Simon, *J. Am. Ceram. Soc.* **65**, 539 (1982).
- ²S. M. Neirman: *J. Mater. Sci.* **23** (1988) 3973.
- ³T. R. Armstrong, L. E. Morgens, A. K. Maurice and R. C. Buchanan: *J. Am. Ceram. Soc.* **72** (1989) 605.
- ⁴K. Toyoda, F. Takano, T. Kato and Y. Sakabe: *Ferroelectrics* **93** (1989) 335.
- ⁵S. Sumita, M. Ikeda, Y. Nakano, K. Nishiyama and T. Nomura: *J. Am. Ceram. Soc.* **74** (1991) 2739.
- ⁶H. Shizuno, S. Kusumi, H. Saito and H. Kishi: *Jpn. J. Appl. Phys.* **32** (1993) 4380.
- ⁷K. Toda, *J. Appl. Phys.* **43** (1972) 261.
- ⁸P. W. Rehrig, S.-E. Park, S. Trolrier-McKinstry and G. L. Messing: *J. Appl. Phys.* **86** (1999) 1657.
- ⁹Z. Yu, R. Guo and A. S. Bhalla: *J. Appl. Phys.* **88** (2000) 410.
- ¹⁰McQuarrie: *J. Am. Ceram. Soc.* **37** (1954) 539.
- ¹¹N. S. Novosil'tsev and A. L. Khodakov: *Sov. Phys. -Tech. Phys.* **1** (1956) 306.
- ¹²R. C. Kell and N. J. Helicar: *Acustica* **6** (1956) 235.
- ¹³V. A. Bokov: *Sov. Phys. -Tech. Phys.* **2** (1957) 1639; V. A. Bokov: *Sov. Phys. -Tech. Phys.* **3** (1958) 70.
- ¹⁴T. N. Verbitskaia, G. S. Zhdanov, Iu. N. Venevtsev and S. P. Soloviev: *Sov. Phys. Cryst.* **3** (1958) 182.
- ¹⁵I. N. Polandov: *Sov. Phys. Solid State* **7** (1965) 1508.
- ¹⁶B. Jaffe, W.R. Cook and H. Jaffe: *Piezoelectric Ceramics*, (Academic Press, New York, 1971).
- ¹⁷D. Hennings and H. Schreinemacher: *Mater. Res. Bull.* **12** (1977) 1221.
- ¹⁸J. Ravez and A. Simon: *Eur. J. Solid State Inorg. Chem.* **34** (1997) 1199.
- ¹⁹J. Ravez and A. Simon: *J. Kor. Phys. Soc.* **32** (1998) S955.
- ²⁰R. Farhi, M. El Marssi, A. Simon and J. Ravez: *Eur. Phys. J.* **B9** (1999) 599.
- ²¹T. Tsurumi, Y. Yamamoto, H. Kakemoto, S. Wada, H. Chazono and H. Kishi: *J. Mater. Res.*, (2002) in press.
- ²²S. Wada, H. Adachi, H. Kakemoto, H. Chazono, Y. Mizuno, H. Kishi and T. Tsurumi: *J. Mater. Res.*, (2002) in press.