

Dielectric Property of Single Crystalline BaTi₂O₅ Prepared by a Floating Zone Method

Takaya Akashi, Hiroaki Iwata* and Takashi Goto

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Single crystalline BaTi₂O₅ was prepared by a floating zone method. The permittivity of single crystalline BaTi₂O₅ perpendicular to a (010) plane showed the maximum value of 20500 at 748 K obeying the Curie-Weiss law at higher temperatures. The permittivity perpendicular to (100) and (001) planes were 140 and 70, respectively almost independent of temperature. A transition temperature measured by a dilatometer was in agreement with a Curie temperature. The relationship between polarization and electrical field perpendicular to the (010) plane showed ferroelectric hysteresis. No hysteresis was observed in the direction perpendicular to (100) and (001) planes. The electrical conductivity perpendicular to the (010) was larger than those of (100) and (001) planes. The activation energy of electrical conductivity was 147 to 180 kJ mol⁻¹ independent of directions.

(Received April 23, 2003; Accepted June 30, 2003)

Keywords: BaTi₂O₅ single crystal, anisotropy, permittivity, hysteresis, electrical conductivity, thermal expansion

1. Introduction

BaO–TiO₂ system compounds are intriguing materials for many dielectric applications. BaTiO₃ in particular has been widely applied to capacitors and actuators due to excellent ferroelectricity and positive temperature coefficient (PTC). TiO₂ rich BaO–TiO₂ system compounds such as BaTi₄O₉^{1,2)} and Ba₂Ti₉O₂₀²⁻⁴⁾ are also exhibited attractive dielectric properties such as low dielectric loss and high dielectric constant at microwave frequencies. However, BaTi₂O₅ has not been investigated in detail as a dielectric material.

The crystal structure and thermal stability of BaTi₂O₅ were studied in the past.^{2,5-9)} Rase *et al.*⁶⁾ showed BaTi₂O₅ in a phase diagram as a stable phase. Then, Negas *et al.*⁷⁾ and O'Bryan, Jr. *et al.*²⁾ reported that the BaTi₂O₅ phase was metastable at temperatures below a solidus line, because it decomposed to BaTiO₃ and Ba₆Ti₁₇O₄₀ phase. Therefore, BaTi₂O₅ phase was not indicated in phase diagrams by Negas *et al.*⁷⁾ and O'Bryan, Jr. *et al.*²⁾ and Kelvin *et al.*⁹⁾ On the other hand, Ritter *et al.*⁸⁾ reported that BaTi₂O₅ was stable at low temperatures below 1420 K.

Pfaff¹⁰⁾ reported that the BaTi₂O₅ phase synthesized by a sol-gel method had a permittivity around 40 at room temperature. However, no paper has mentioned the temperature dependence of permittivity and electrical conductivity of BaTi₂O₅. We reported that single crystalline BaTi₂O₅ prepared by a floating zone method had a high permittivity perpendicular to a (010) plane.¹¹⁾ In this paper, we report ferroelectricity, phase transition and electrical conductivity of single crystalline BaTi₂O₅. The ferroelectricity was evaluated by a polarization (*P*)-electric field (*E*) hysteresis loop. The phase transition temperature was measured by a dilatometer.

2. Experimental Procedures

Dried powders of BaCO₃ and TiO₂ (99.9% purity) were mixed with a small amount of ethanol in an agate mortar in a

molar ratio of BaCO₃/TiO₂ = 1/2. The mixed powders were isostatically pressed at 10 MPa in a latex tube with 10 mm in diameter, and sintered at 1503 K for 43 ks in air. The sintered rods were melted and directionally solidified by a FZ method at a rate of 5.6 × 10⁻⁶ ms⁻¹ in flowing Ar–21%O₂ gas. The crystal structure and the crystal orientation were reported elsewhere.¹¹⁾ The composition of single crystal was confirmed by a electron probe microanalyzer (EMPA).

The single crystalline specimens were cut perpendicular to (100), (010) and (001) planes. Permittivity and electrical conductivity were measured perpendicular to each plane using an AC impedance analyzer (Solartron 1260, 1296) at frequencies from 10² to 10⁷ Hz in air and at temperatures from 293 to 1073 K. The ferroelectricity of single crystalline specimens was evaluated by measuring polarization (*P*)-electric field (*E*) hysteresis loops (Radiant RT6000S). The thermal expansion was measured by a dilatometer (Mac science, Dilatometer 5000).

3. Results and Discussion

Single crystals cut from the as grown specimens were transparent without cracks. A molar ratio of Ba/Ti measured by an EPMA was 1/2. BaTi₂O₅ single crystals were dark blue due to slightly oxygen deficient composition, because they became transparent after a heat treatment at 1073 K in air for 3.6 ks. The BaTi₂O₅ single crystals were stable even after a heat treatment at 1523 K for 173 ks, although BaTi₂O₅ powder was decomposed to BaTiO₃ and Ba₆Ti₁₇O₄₀ at 1503 K.

Figure 1 shows the frequency dependence of permittivity for single crystalline BaTi₂O₅ perpendicular to a (010) plane. The permittivity decreased with increasing frequency, and became almost constant over 1 MHz. Figure 2 shows the temperature dependence of permittivities perpendicular to (100), (010) and (001) planes at 1 MHz. The permittivity perpendicular to the (010) plane showed the sharp maximum at 748 K. The maximum value ($\epsilon = 20500$ at 748 K) was several times greater than those of BaTiO₃ ($\epsilon = 7600$ at 400 K)¹²⁾ and Bi₄Ti₃O₁₂ ($\epsilon = 600$ at 940 K).¹³⁾ The permit-

*Graduate Student, Tohoku University.

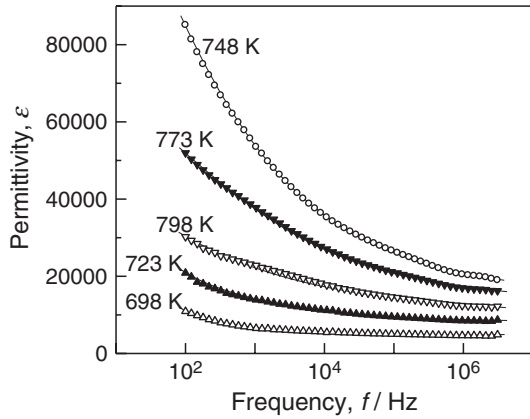


Fig. 1 Frequency dependence of permittivity for single crystalline BaTi₂O₅ perpendicular to a (010) plane.

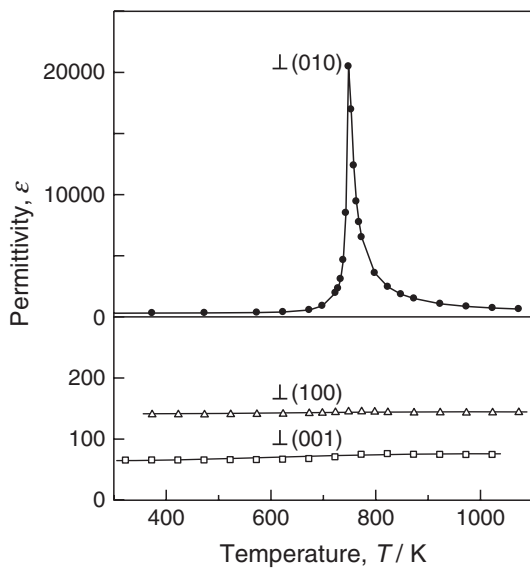


Fig. 2 Temperature dependence of permittivity for single crystalline BaTi₂O₅ perpendicular to (100), (010) and (001) planes ($f = 1$ MHz).

ivities perpendicular to the (100) and (001) planes were about 140 and 70, respectively, almost independent of temperature. Figure 3 shows the relationship between reciprocal permittivity and temperature perpendicular to the (010) plane. The temperature dependence of permittivity obeyed the Curie Weiss law at higher temperatures. The Curie-Weiss temperature was calculated to be 747 K.

Figure 4 shows the polarization (P) vs. electric field (E) plots perpendicular to (100), (010) and (001) planes at room temperature. The P - E plot perpendicular to the (010) plane showed hysteresis indicating ferroelectricity. No hysteresis was observed in the directions perpendicular to (100) and (001) planes. The remanent polarization and coercive electric field perpendicular to the (010) plane at room temperature was $1.92 \times 10^{-2} \text{ Cm}^{-2}$ and $2.44 \times 10^5 \text{ Vm}^{-1}$, respectively. The space group of BaTi₂O₅ has been reported to be $C2/m$,^{6,14} which has a mirror plane parallel to a (010) plane. The space group of $C2/m$, however, disagrees with the ferroelectricity perpendicular to a (010) plane. Therefore, we conclude that the space group is $C2^{11}$ and the ferroelectricity results from the shift of Ba²⁺ and Ti⁴⁺ ions to $\langle 010 \rangle$

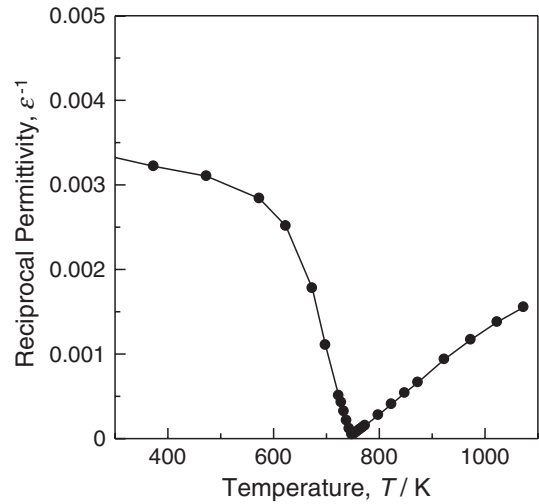


Fig. 3 Relationship between temperature and reciprocal permittivity for single crystalline BaTi₂O₅ perpendicular to a (010) plane ($f = 1$ MHz).

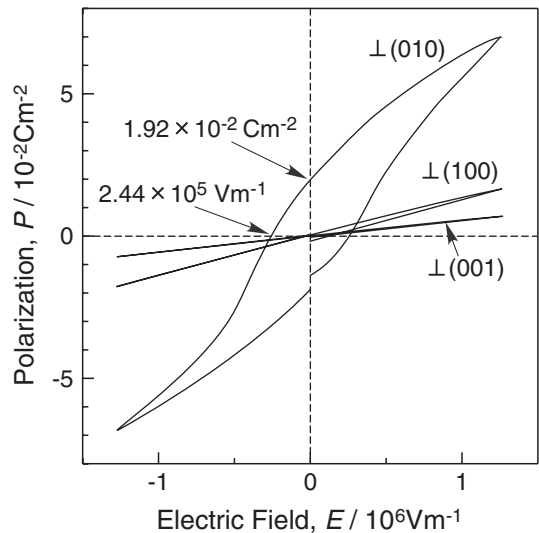


Fig. 4 P - E loops for single crystalline BaTi₂O₅ perpendicular to (100), (010) and (001) planes at room temperature.

direction. Ferroelectricity did not observed perpendicular to (100) and (001) planes because of two-fold symmetry in a ac plane. Figure 5 shows the P - E plots perpendicular to the (010) plane at high temperatures. The hysteresis loops became larger with increasing temperature, and the polarization was almost saturated at 523 K. The remanent polarization and coercive electric field at 523 K were $10.4 \times 10^{-2} \text{ Cm}^{-2}$ and $2.69 \times 10^5 \text{ Vm}^{-1}$, respectively.

Figure 6 shows the thermal expansion of single crystalline BaTi₂O₅ perpendicular to a (010) plane. With increasing temperature, the thermal expansion coefficient was changed around 750 K. No hysteresis of thermal expansion was observed with increasing and decreasing temperature. The temperature where the thermal expansion coefficient changed was in good agreement with that of highest permittivity, indicating a ferroelectric phase transition.

Figure 7 shows the electrical conductivities perpendicular to (100), (010) and (001) planes. The electrical conductivities in these directions were smaller than that of polycrystalline

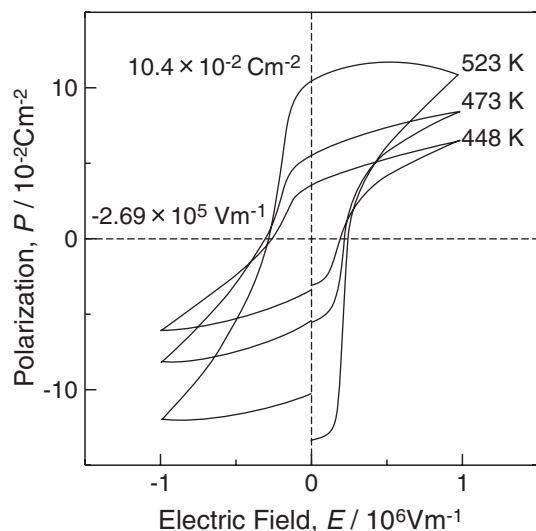


Fig. 5 P - E hysteresis loops for single crystalline BaTi_2O_5 perpendicular to a (010) plane.

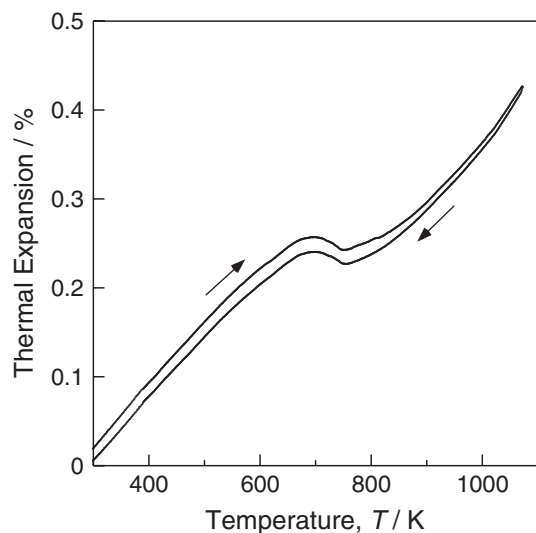


Fig. 6 Thermal expansion of single crystalline BaTi_2O_5 perpendicular to a (001) plane.

BaTiO_3 .¹²⁾ The electrical conductivity perpendicular to the (010) was larger than those of (100) and (001) planes. The activation energy of electrical conductivity of BaTi_2O_5 was 147 to 180 kJ mol^{-1} independent of directions and higher than that of BaTiO_3 . The crystal structure of BaTi_2O_5 is more complicated than that of BaTiO_3 . This may cause the higher activation energy than that of BaTiO_3 .

4. Conclusion

The single crystalline BaTi_2O_5 has a maximum permittivity of 20500 at 748 K perpendicular to a (010) plane. The temperature dependence of permittivity perpendicular to a (010) plane obeyed the Curie-Weiss law at higher temperatures. The P - E hysteresis loops indicated a ferroelectricity perpendicular to a (010) plane at lower temperatures, but no hysteresis was observed perpendicular to (100) and (001)

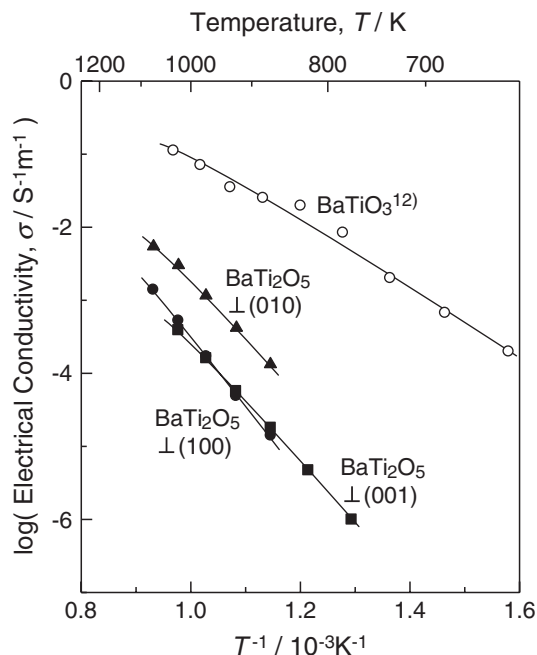


Fig. 7 Temperature dependence of electrical conductivity for BaTi_2O_5 perpendicular to (100), (010) and (001) planes.

planes. The ferroelectric phase transition temperature by AC impedance measurements was in good agreement with that by a dilatometer. The electrical conductivity perpendicular to the (010) was larger than those of (100) and (001) planes. The activation energy of electrical conductivity was almost independent of directions.

Acknowledgment

The specimens were prepared by using the facility at Laboratory for Advanced Materials, Institute for Materials Research, Tohoku University.

REFERENCES

- 1) H. M. O'Bryan, Jr., J. Thomson, Jr. and J. K. Plourde: *J. Am. Ceram. Soc.* **57** (1974) 450-453.
- 2) H. M. O'Bryan, Jr. and J. Thomson, Jr.: *J. Am. Ceram. Soc.* **57** (1974) 522-526.
- 3) H. M. O'Bryan and J. Thomson: *J. Am. Ceram. Soc.* **66** (1983) 66-68.
- 4) S. Nomura, K. Tomaya and K. Kaneta: *Jpn. J. Appl. Phys.* **22** (1983) 1125-1128.
- 5) W. O. Statton: *J. Chem. Phys.* **19** (1951) 33-40.
- 6) D. E. Rase and R. Roy: *J. Am. Ceram. Soc.* **38** (1955) 102-113.
- 7) T. Negas, R. S. Roth, H. S. Parker and D. Minor: *J. Solid State Chem.* **9** (1974) 297-307.
- 8) J. J. Ritter, R. S. Roth and J. E. Blendell: *J. Am. Ceram. Soc.* **69** (1986) 155-162.
- 9) K. W. Kirby and B. A. Wechsler: *J. Am. Ceram. Soc.* **74** (1991) 1841-1847.
- 10) G. Pfaff: *J. Mater. Sci. Lett.* **9** (1990) 1145-1147.
- 11) T. Akashi, H. Iwata and T. Goto: *Mater. Trans.* **44** (2003) 802-804.
- 12) T. Akashi, K. Morita, T. Hirai, H. Yamane and T. Goto: *Mater. Trans.* **42** (2001) 1823-1826.
- 13) E. C. Subbarao: *Phys. Rev.* **122** (1961) 804-807.
- 14) F. W. Harrison: *Acta Crystallogra.* **9** (1956) 495-500.