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# Dielectric Property of Single Crystalline BaTi<sub>2</sub>O<sub>5</sub> Prepared by a Floating Zone Method

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Single crystalline BaTi<sub>2</sub>O<sub>5</sub> was prepared by a floating zone method. The permittivity of single crystalline BaTi<sub>2</sub>O<sub>5</sub> 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<sup>-1</sup> independent of directions.

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## 1. Introduction

BaO–TiO<sub>2</sub> system compounds are intriguing materials for many dielectric applications. BaTiO<sub>3</sub> in particular has been widely applied to capacitors and actuators due to excellent ferroelectricity and positive temperature coefficient (PTC). TiO<sub>2</sub> rich BaO–TiO<sub>2</sub> system compounds such as BaTi<sub>4</sub>O<sub>9</sub><sup>1,2)</sup> and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub><sup>2-4)</sup> are also exhibited attractive dielectric properties such as low dielectric loss and high dielectric constant at microwave frequencies. However, BaTi<sub>2</sub>O<sub>5</sub> has not been investigated in detail as a dielectric material.

The crystal structure and thermal stability of BaTi<sub>2</sub>O<sub>5</sub> were studied in the past.<sup>2,5-9)</sup> Rase *et al.*<sup>6)</sup> showed BaTi<sub>2</sub>O<sub>5</sub> in a phase diagram as a stable phase. Then, Negas *et al.*<sup>7)</sup> and O'Bryan, Jr. *et al.*<sup>2)</sup> reported that the BaTi<sub>2</sub>O<sub>5</sub> phase was metastable at temperatures below a solidus line, because it decomposed to BaTiO<sub>3</sub> and Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub> phase. Therefore, BaTi<sub>2</sub>O<sub>5</sub> phase was not indicated in phase diagrams by Negas *et al.*<sup>7)</sup> and O'Bryan, Jr. *et al.*<sup>2)</sup> and Kelvin *et al.*<sup>9)</sup> On the other hand, Ritter *et al.*<sup>8)</sup> reported that BaTi<sub>2</sub>O<sub>5</sub> was stable at low temperatures below 1420 K.

Pfaff<sup>10)</sup> reported that the BaTi<sub>2</sub>O<sub>5</sub> 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 BaTi<sub>2</sub>O<sub>5</sub>. We reported that single crystalline BaTi<sub>2</sub>O<sub>5</sub> prepared by a floating zone method had a high permittivity perpendicular to a (010) plane.<sup>11)</sup> In this paper, we report ferroelectricity, phase transition and electrical conductivity of single crystalline BaTi<sub>2</sub>O<sub>5</sub>. 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 BaCO<sub>3</sub> and TiO<sub>2</sub> (99.9% purity) were mixed with a small amount of ethanol in an agate mortar in a

molar ratio of BaCO<sub>3</sub>/TiO<sub>2</sub> = 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<sup>-6</sup> ms<sup>-1</sup> in flowing Ar–21%O<sub>2</sub> gas. The crystal structure and the crystal orientation were reported elsewhere.<sup>11)</sup> 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 10<sup>2</sup> to 10<sup>7</sup> 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. BaTi<sub>2</sub>O<sub>5</sub> 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 BaTi<sub>2</sub>O<sub>5</sub> single crystals were stable even after a heat treatment at 1523 K for 173 ks, although BaTi<sub>2</sub>O<sub>5</sub> powder was decomposed to BaTiO<sub>3</sub> and Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub> at 1503 K.

Figure 1 shows the frequency dependence of permittivity for single crystalline BaTi<sub>2</sub>O<sub>5</sub> 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 BaTiO<sub>3</sub> ( $\epsilon = 7600$  at 400 K)<sup>12)</sup> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> ( $\epsilon = 600$  at 940 K).<sup>13)</sup> The permit-

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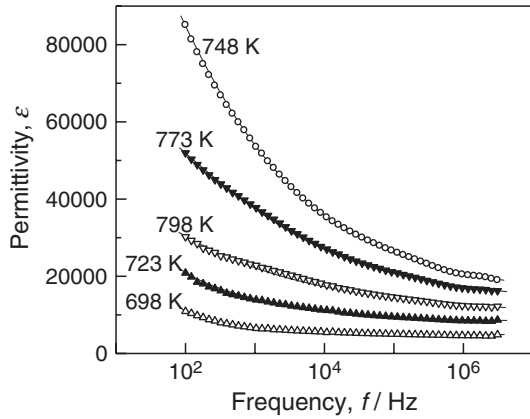


Fig. 1 Frequency dependence of permittivity for single crystalline BaTi<sub>2</sub>O<sub>5</sub> perpendicular to a (010) plane.

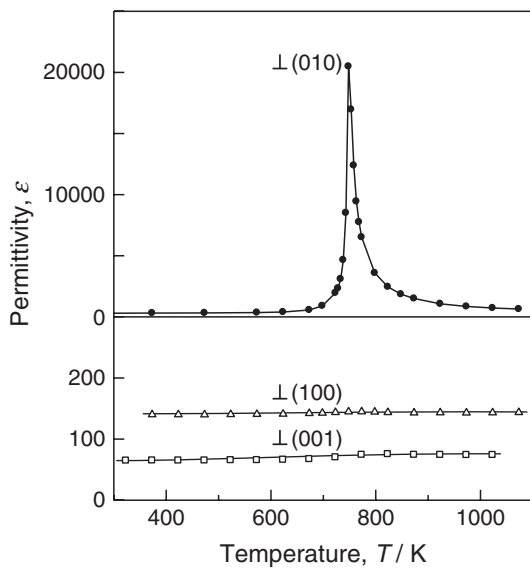


Fig. 2 Temperature dependence of permittivity for single crystalline BaTi<sub>2</sub>O<sub>5</sub> perpendicular to (100), (010) and (001) planes ( $f = 1$  MHz).

permittivities 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 BaTi<sub>2</sub>O<sub>5</sub> has been reported to be  $C2/m$ ,<sup>6,14</sup> 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 Ba<sup>2+</sup> and Ti<sup>4+</sup> ions to  $\langle 010 \rangle$

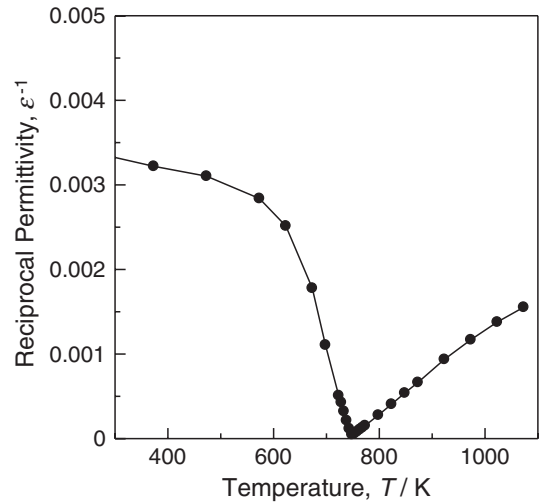


Fig. 3 Relationship between temperature and reciprocal permittivity for single crystalline BaTi<sub>2</sub>O<sub>5</sub> perpendicular to a (010) plane ( $f = 1$  MHz).

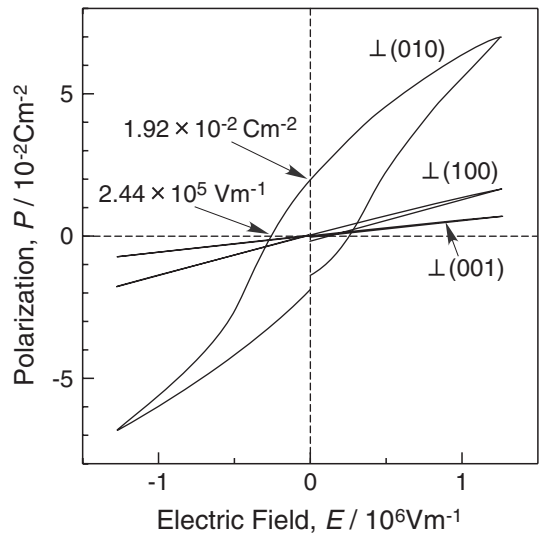


Fig. 4  $P$ - $E$  loops for single crystalline BaTi<sub>2</sub>O<sub>5</sub> perpendicular to (100), (010) and (001) planes at room temperature.

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 BaTi<sub>2</sub>O<sub>5</sub> 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

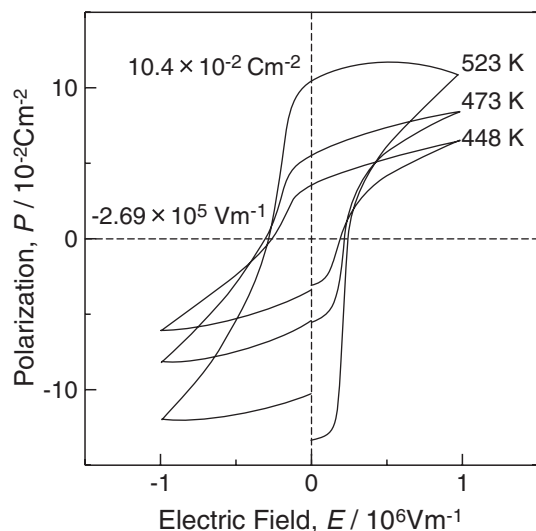


Fig. 5  $P$ - $E$  hysteresis loops for single crystalline  $\text{BaTi}_2\text{O}_5$  perpendicular to a (010) plane.

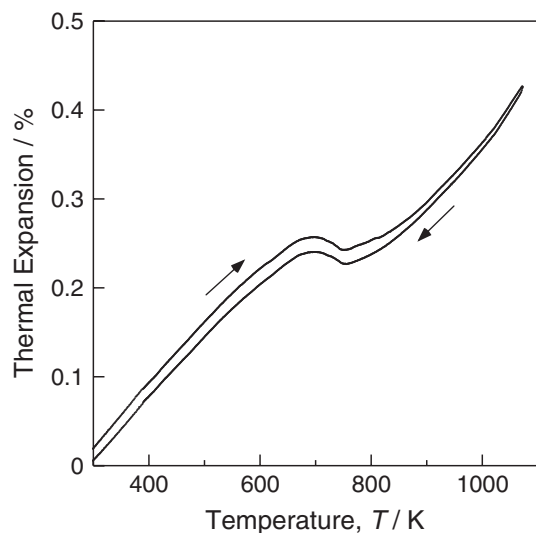


Fig. 6 Thermal expansion of single crystalline  $\text{BaTi}_2\text{O}_5$  perpendicular to a (001) plane.

$\text{BaTiO}_3$ .<sup>12)</sup> The electrical conductivity perpendicular to the (010) was larger than those of (100) and (001) planes. The activation energy of electrical conductivity of  $\text{BaTi}_2\text{O}_5$  was 147 to 180  $\text{kJ mol}^{-1}$  independent of directions and higher than that of  $\text{BaTiO}_3$ . The crystal structure of  $\text{BaTi}_2\text{O}_5$  is more complicated than that of  $\text{BaTiO}_3$ . This may cause the higher activation energy than that of  $\text{BaTiO}_3$ .

#### 4. Conclusion

The single crystalline  $\text{BaTi}_2\text{O}_5$  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)

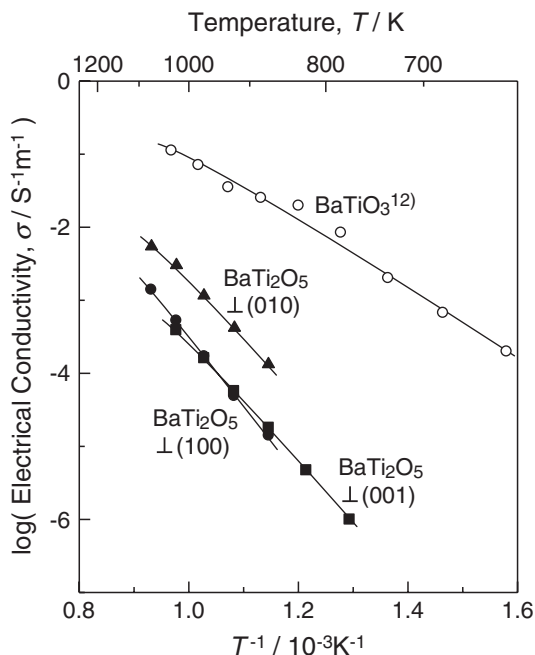


Fig. 7 Temperature dependence of electrical conductivity for  $\text{BaTi}_2\text{O}_5$  perpendicular to (100), (010) and (001) planes.

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.

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#### 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.