Preparation of BaTi₂O₅ Single Crystal 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 single crystal was transparent having a (001) cleavage plane. The space group was C2, and the lattice parameters were $a = 1.6909(9)$ nm, $b = 0.3937(1)$ nm, $c = 0.9419(4)$ nm and $\beta = 103.12(6)^\circ$. The permittivity perpendicular to a (010) plane showed the maximum value of 20500 at 748 K. The permittivity perpendicular to (100) and (001) planes were about 140 and 70, respectively, independent of temperature.

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1. Introduction

BaO–TiO₂ system compounds, in particular BaTiO₃,^{1,2)} have been widely used for many dielectric applications due to excellent ferroelectricity and positive temperature coefficient (PTC). TiO₂ rich BaO–TiO₂ system compounds such as BaTi₄O₉^{3,4)} and Ba₂Ti₉O₂₀^{3,5,6)} are also expected as dielectric materials to be used at microwave frequencies. However, no report has been published on the compound having higher permittivity than those compounds in the BaO–TiO₂ system.

Many researchers have investigated on the BaO–TiO₂ phase diagram,^{4,7–11)} because the BaO–TiO₂ system includes several useful dielectric and ferroelectric materials. In those papers, the thermal stability of BaTi₂O₅ has been discussed. Figure 1 shows a part of phase diagram for the BaO–TiO₂ system by Rase *et al.*⁸⁾ They indicated the BaTi₂O₅ phase between BaTiO₃ and BaTi₃O₇ in the phase diagram. However, Negas *et al.*,⁹⁾ O'Bryan, Jr. *et al.*⁴⁾ and Ritter *et al.*¹⁰⁾ reported that the BaTi₂O₅ phase would decompose to

Fig. 2 A phase diagram of the BaO–TiO₂ system.¹⁰⁾

Fig. 1 A phase diagram of the BaO–TiO₂ system.⁹⁾

BaTiO₃ and Ba₆Ti₁₇O₄₀ in the temperature range between 1423 and 1585 K, and proposed a phase diagram as shown in Fig. 2. It has been believed that the BaTi₂O₅ phase could be stable under 1420 K, and therefore no one has synthesized BaTi₂O₅ from a melt solidification process such as a floating zone (FZ) method.

The crystal structure and phase transformation of BaTi₂O₅ have been discussed by using polycrystalline specimens in literatures;^{4,8–12)} however, no electrical property of single crystalline BaTi₂O₅ has been reported. In this study, single crystalline BaTi₂O₅ specimens were first synthesized by a FZ method, and the relationship between crystal orientation and dielectric property was investigated.

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

*Graduate Student, Tohoku University.

rods were melted and directionally solidified by a FZ method at a rate of $5.6 \times 10^{-6} \text{ ms}^{-1}$ in flowing Ar-21%O₂ gas. The phase was identified by powder X-ray diffraction (CuK α). The crystal orientation was determined by pole figure X-ray diffraction.

The single crystalline specimens were cut perpendicular to (100), (010) and (001) planes. Permittivity was measured perpendicular to each plane using an AC impedance analyzer (Solartron 1260, 1296) at frequencies from 10^2 to 10^7 Hz in air and temperature range between 293 and 1073 K.

3. Results and Discussion

Figure 3 shows an as-grown directionally solidified BaTi₂O₅ specimen. The specimen was about 5 mm in diameter. Many cracks were observed and cleaved parallel to the growth direction. Transparent single crystals were cut from the as-grown specimens.

Figure 4 shows the X-ray diffraction patterns of the powdered single crystalline BaTi₂O₅ specimen. Every peak was indexed using the space group of C2 and lattice parameters of $a = 1.6908(9) \text{ nm}$, $b = 0.3937(1) \text{ nm}$, $c =$

Fig. 3 As grown BaTi₂O₅ specimen by a FZ method.

Fig. 5 X-ray pole figure from the cleavage plane of single crystalline BaTi₂O₅.

$0.9418(4) \text{ nm}$ and $\beta = 103.12(5)^\circ$. No second phase was included in the specimen. These lattice parameters were in good agreement with the reported values of $a = 1.6914 \text{ nm}$, $b = 0.3935 \text{ nm}$, $c = 0.9412 \text{ nm}$ and $\beta = 103.11^\circ$.⁸⁾ The pole figure X-ray diffraction pattern from the cleavage plan is shown in Fig. 5. A (002) diffraction spot appeared at the center, suggesting that the cleavage plane could be parallel to the (001) plane. Figure 6 illustrates a schematic crystal structure of BaTi₂O₅. Distorted TiO₆ octahedrons are connected at corners and/or edges, and layered parallel to the (001) plane. Ba atoms are located between the layers of TiO₆ octahedrons. The cleavage nature of BaTi₂O₅ could be caused of the layered structure.

Figure 7 shows the permittivity of single crystalline BaTi₂O₅ perpendicular to a (010) plane as a function of

Fig. 4 X-ray diffraction pattern of powdered single crystalline BaTi₂O₅.

Fig. 6 A schematic crystal structure of BaTi_2O_5 . Black sphere: Ba atom, octahedron: TiO_6 .

frequency. The permittivity of single crystalline BaTi_2O_5 perpendicular to the (010) plane decreased with increasing frequency, and almost constant around 1 MHz. The intrinsic permittivity values would be obtained at a frequency of 1 MHz.

Figure 8 shows the permittivities of single crystalline BaTi_2O_5 perpendicular to (100), (010) and (001) planes as a function of temperature at 1 MHz. The permittivity perpendicular to the (010) plane showed the sharp maximum of 20500 at 748 K. This value was several times greater than those of BaTiO_3 ($\epsilon = 7600$ at 400 K) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($\epsilon = 600$ at 940 K). The permittivities perpendicular to the (100) and (001) planes were about 140 and 70 respectively, independent of temperature.

Fig. 8 Permittivity of single crystalline BaTi_2O_5 perpendicular to (100), (010) and (001) planes as a function of temperature ($f = 1$ MHz).

Fig. 7 Permittivity of single crystalline BaTi_2O_5 perpendicular to a (010) plane as a function of frequency.

4. Conclusion

Single crystalline BaTi_2O_5 was prepared by a FZ method. The specimens were transparent and cleaved parallel to the (001) plane. The lattice parameters were $a = 1.6908(9)$ nm, $b = 0.3937(1)$ nm, $c = 0.9418(4)$ nm and $\beta = 103.12(5)^\circ$. The permittivity of single crystalline BaTi_2O_5 perpendicular to the (010) plane showed the maximum of 20500 at 748 K. This value is several times greater than that of single crystalline BaTiO_3 . The permittivities perpendicular to (100) and (001) planes were 140 and 70, respectively, independent of temperature.

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REFERENCES

- 1) W. J. Merz: Phys. Rev. **76** (1949) 1221–1225.
- 2) T. Akashi, K. Morita, T. Hirai, H. Yamane and T. Goto: Mater. Trans. **42** (2001) 1823–1826.
- 3) H. M. O'Bryan, Jr., J. Thomson, Jr. and J. K. Plourde: J. Am. Ceram. Soc. **57** (1974) 450–453.
- 4) H. M. O'Bryan, Jr. and J. Thomson, Jr.: J. Am. Ceram. Soc. **57** (1974) 522–526.
- 5) H. M. O'Bryan and J. Thomson: J. Am. Ceram. Soc. **66** (1983) 66–68.
- 6) S. Nomura, K. Tomaya and K. Kaneta: Japan. J. Appl. Phys. **22** (1983) 1125–1128.
- 7) W. O. Statton: J. Chem. Phys. **19** (1951) 33–40.
- 8) D. E. Rase and R. Roy: J. Am. Ceram. Soc. **38** (1955) 102–113.
- 9) T. Negas, R. S. Roth, H. S. Parker and D. Minor: J. Solid State Chem. **9** (1974) 297–307.
- 10) J. J. Ritter, R. S. Roth and J. E. Blendell: J. Am. Ceram. Soc. **69** (1986) 155–162.
- 11) K. W. Kirby and B. A. Wechsler: J. Am. Ceram. Soc. **74** (1991) 1841–1847.
- 12) F. W. Harrison: Acta Cryst. **9** (1956) 495–500.