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Dielectric properties of $BaTi_4O_9$ single crystals

ISAO TANAKA, HIRONAO KOJIMA
Institute of Inorganic Synthesis, Faculty of Engineering, Yamanashi University, Miyamae 7, Kofu 400, Japan

The barium tetratitanate ($BaTi_4O_9$) single crystals grown in a nitrogen gas by the floating zone method was characterized by dielectric property in the frequency range 1 kHz to 1 MHz. The as-grown crystals had an electric behaviour such as shown by a semiconductor. When the crystals were annealed at 1300° C for 5 h in air, the dielectric constant was independent of the frequencies and was anisotropic, and the Q-value became higher than that of the grown crystals. Further, from electron spin resonance measurements it was found that the as-grown crystals contained the Ti^{3+} ion. This seems to suggest that the electrical conductivity of the as-grown crystals is due to the Ti^{3+}–Ti^{4+} hopping mechanism.

1. Introduction

In the $BaTiO_3$–TiO_2 system, four compounds of $Ba_6Ti_{17}O_{40}$, $Ba_4Ti_{13}O_{30}$, $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ other than $BaTiO_3$ exist [1–4]. Of these $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ exhibit superior dielectric properties in the microwave region and are used as microwave resonators [5–7]. The dielectric properties of $BaTi_4O_9$ ceramics have been investigated, but they depend on sintering conditions, grain size and the grain boundary [8–11]. Thus, dielectric measurement using single crystals is suitable for investigating the dielectric properties of the bulk. Because $BaTi_4O_9$ has orthorhombic symmetry ($a = 0.3795$ nm, $b = 1.4530$ nm, $c = 0.6292$ nm), it is estimated that the various properties are anisotropic. $BaTi_4O_9$ single crystals were grown by the floating zone method [12]. In this study, the $BaTi_4O_9$ single crystals were characterized by their dielectric properties in the range 1 kHz to 1 MHz. The effects of heat treatment and the dependence on crystallographic axes and frequencies of the dielectric properties were investigated. The cause of the difference between the dielectric property of the as-grown crystals and the annealed crystals was investigated by electron spin resonance (ESR).

2. Experimental procedure

The $BaTi_4O_9$ single crystals were grown by the floating zone method using an infrared heating furnace. The growth conditions were a nitrogen gas atmosphere and a growth rate of 2.0 mm h^{-1}, and the details were discussed previously [12]. Some of the as-grown crystals were annealed at 1300° C for 5 h in air.

The as-grown and annealed $BaTi_4O_9$ crystals were cut to about $4 \times 4 \times 1\,mm^3$, each flat plane being perpendicular to the crystallographic axis. The plates were metallized on the surfaces using an In–Ga alloy. A multi-frequency LCR-meter (Hewlett Packard, model 4275A) for the as-grown crystals and a mutual inductance bridge (Ando electric, model TR-10C) for the annealed crystals were used to measure dielectric properties where the electrical resistance of the as-grown crystals was much lower than that of the annealed crystals; and where it was not possible to measure the dielectric properties of both crystals using the same apparatus. The measurement conditions were in the frequency range 1 kHz to 1 MHz at room temperature.

The spectrometer used in ESR measurement was a Jeol model JES-FE1XG which was operated at X-band with 100 kHz field modulation. The $BaTi_4O_9$ single crystals, about $2 \times 2 \times 2\,mm^3$ in size, were etched in phosphoric acid at 150° C for 10 min to remove the surface layer of the crystals, and were then used as samples for the ESR measurement. Each of the crystallographic axes was set parallel to the external magnetic field and the ESR measurement was carried out at room temperature. The magnetic field was calibrated with Mn^{2+} in MgO ($g = 1.987$).

3. Results and discussion

3.1. Dielectric properties

Fig. 1 shows the dielectric constant–frequency plots of the as-grown single crystals and the annealed single crystals. In the case of the as-grown single crystals (Fig. 1a), the dielectric constant decreased remarkably as the frequency increased. The dielectric constant parallel to the a-axis varied from 82 at 10 kHz to 4.8 at 1 MHz, that parallel to the b-axis varied from 354 to 1.6 and that parallel to the c-axis varied from 26 to 0.8. Thus the dielectric constants were anisotropic. In the case of the annealed crystals (Fig. 1b), the dielectric constant was independent of frequency. The average dielectric constant in the range 10 kHz to 1 MHz parallel to the a-axis was 43, that parallel to the b-axis was 76 and that parallel to the c-axis was 38, so that the dielectric constants were anisotropic. Fig. 2 shows the Q-value–frequency plots of the as-grown and annealed crystals. The Q-values, defined by the reciprocal of dielectric loss (tan δ), differed with crystallographic axis and frequency; those of the as-grown crystals were lower than 1.2, and those of annealed crystals were from 200 to 1000 and became higher

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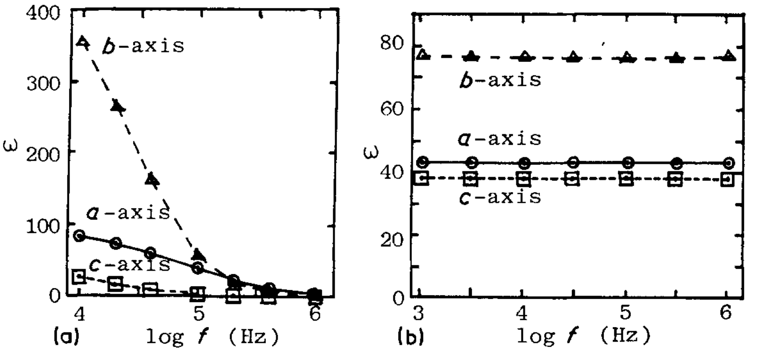

Figure 1 Frequency dependence of dielectric constant of $BaTi_4O_9$ single crystal: (a) before annealing; (b) after annealing in air at 1300° C for 5 h.

than the values of the as-grown crystals. From the results described above, the dielectric properties of the annealed crystals were superior to those of the as-grown crystals for application to dielectrics. Because the $BaTi_4O_9$ single crystals were grown in nitrogen gas, the as-grown crystals were oxygen deficient and/or contained the Ti^{3+} ion, and thus have an electric behaviour such as is shown by semiconductors. For example, the d.c. resistance parallel to the *a*-, *b*- and *c*-axes were 1.67×10^3, 2.29×10^4 and $3.65 \times 10^3\,\Omega$cm at 20° C, respectively.

It was reported that the $BaTi_4O_9$ ceramics had a dielectric constant of 34 to 43 and a *Q*-value of 1000 to 7700 at 1 or 1.5 MHz [8-11]. O'Bryan *et al.* [6] studied the dielectric properties of the composition from 79 to 85 mol % TiO_2 in the BaO–TiO_2 system. They reported that the $BaTi_4O_9$ composition had a dielectric constant of about 38 and a *Q*-value of about 300 at 1 MHz and indicated the presence of a dispersion near 1 MHz in the frequency range 1 kHz to 1 MHz. Their data agreed with those along the *c*-axis of the $BaTi_4O_9$ single crystals, where the dielectric constant was 38, the *Q*-value was 255 at 1 MHz, and a dispersion was present near 1 MHz. This agreement comes about because $BaTi_4O_9$ crystals have a cleavage and a facet perpendicular to the *c*-axis, and thus are easily oriented perpendicular to the *c*-axis even in sintering processes. O'Bryan *et al.* also reported that the dielectric constants of compositions in the range 79 to 85 mol % TiO_2 at 4 GHz agreed with those at 1 MHz and $BaTi_4O_9$ had a high microwave *Q*-value of about 9000 at 4 GHz in the compositions 79 to 85 mol % TiO_2. It is suggested that the $BaTi_4O_9$ single crystals have a higher dielectric constant than $BaTi_4O_9$ ceramics in the microwave region and have a high microwave *Q*-value.

3.2. Electron spin resonance (ESR)

Fig. 3 shows the ESR spectrum of the $BaTi_4O_9$ as-grown crystal when the external magnetic field is parallel to the *b*-axis. Two ESR signals were observed: the A signal with $g = 1.981$ was due to Mn^{2+} as a standard and the B signal was due to $BaTi_4O_9$. The *g*-factors along the *a*-, *b*- and *c*-axes were 1.982, 1.976 and 1.983, respectively, and the *g*-tensor was anisotropic. In the case of the annealed $BaTi_4O_9$ crystals, the B signal was not observed. Angular variations of the *g*-factor of the B signal are shown in Fig. 4. Although each of the angular variations of the *g*-factor had axial symmetry, the *g*-factor in the (0 1 0) plane did not depend on the angular variation as strongly as that in the (1 0 0) and (0 0 1) planes. Because $BaTi_4O_9$ has an orthorhombic symmetry ($a = 0.3795$ nm, $b = 1.4530$ nm and $c = 0.6292$ nm), it is suggested that the *g*-tensor is anisotropic. The Hamiltonian of the electronic Zeeman interaction may be written as

$$\beta \cdot \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) \tag{1}$$

where β is the Bohr magneton and $\boldsymbol{S}$ is the effective-spin operator with value $\boldsymbol{S} = 1/2$. The principal axes (x, y, z) of the $\boldsymbol{g}$-tensor are replaced by the crystallographic axes (a, b, c) and then the *g*-factor is

$$g^2 = g_a^2 \sin^2\theta \cos^2\phi + g_b^2 \sin^2\theta \sin^2\phi + g_c^2 \cos^2\theta \tag{2}$$

where θ is the polar angle between the external magnetic field H and the *c*-axis, and ϕ is the azimuthal angle between H and the *a*-axis. When $g_a = 1.982$, $g_b = 1.976$ and $g_c = 1.983$ were substituted in Equation 2, the calculated *g*-factors agreed with the measured values as shown in Fig. 4.

Because the Ti^{3+} ion and some of the donar centres are paramagnetic, their ESR signals may be observed. Takeda and Watanabe [13] and Tsukioka *et al.* [14] reported that ESR of an F-centre in reduced $BaTiO_3$ single crystals were observed. According to Takeda

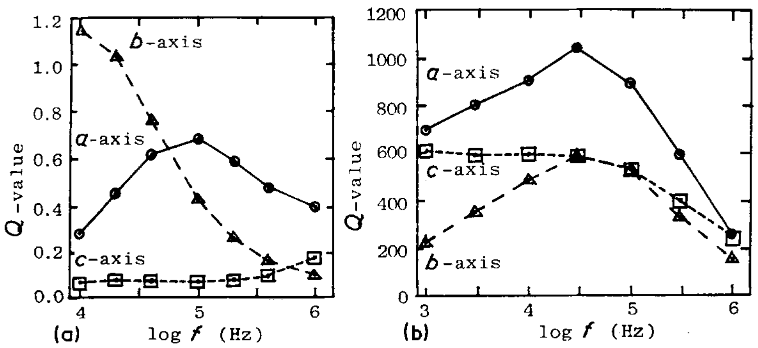

Figure 2 Frequency dependence of *Q*-value of $BaTi_4O_9$ single crystal: (a) before annealing; (b) after annealing in air at 1300° C for 5 h.

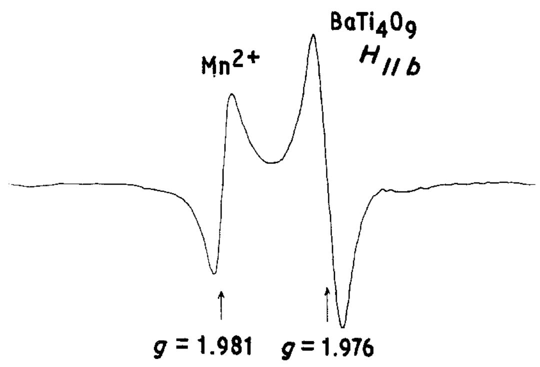

Figure 3 ESR spectrum of as-grown $BaTi_4O_9$ crystal with Mn^{2+} as a standard.

and Watanabe [13], the ESR signal was an F-centre for the following reasons: in the $BaTiO_3$ single crystals grown in a platinum crucible from KF flux, a fraction of Pt^{3+} and K^+ ions were introduced into Ti^{4+} and Ba^{2+} sites, respectively, to make an electron trap; the K^+ ion was not contained in $BaTiO_3$ single crystals grown from the melt, and the ESR signal was not observed. In this work, the $BaTi_4O_9$ single crystals were grown from the melt without a platinum crucible, and contained no impurities such as K^+ and Pt^{3+} ions. Therefore, this suggests that the ESR signals of the $BaTi_4O_9$ as-grown crystals result from the existence of the Ti^{3+} ion in the crystals. The g-factors of the Ti^{3+} ion were reported as follows: $g_x = 1.974$, $g_y = 1.977$ and $g_z = 1.941$ in reduced rutile [15]; $g = 1.949$ to 1.963 in the oxides TiO_x ($x = 1.5$ to 2.0) [16]; $g_{\parallel} = 1.067$ and $g_{\perp} \leq 0.1$ in corundum [17]. The g-factors of the Ti^{3+} ion in $BaTi_4O_9$ were higher than those reported values. This fact shows that $BaTi_4O_9$ has a weaker crystal field than those crystals because the spin-orbit interaction of the Ti^{3+} ion in $BaTi_4O_9$ is weaker than in those crystals.

4. Conclusions

The $BaTi_4O_9$ single crystals grown in nitrogen gas were characterized by their dielectric properties in the frequency range 1 kHz to 1 MHz. It was found that the crystals had an electric behaviour such as that shown by semiconductors from the following results: the dielectric constant decreased remarkably as frequency increased, and was anisotropic; the Q-values depended on the crystallographic axes and frequencies, and were less than 1.2. When the as-grown $BaTi_4O_9$ crystals were annealed at 1300° C for 5 h in air, the dielectric properties were superior to those of the as-grown crystals for application to dielectrics. The dielectric constant was independent of frequency and was anisotropic. The average dielectric constants in the range 1 kHz to 1 MHz parallel to the a-, b- and c-axes were 43, 76 and 38. The Q-values, which depended on the crystallographic axes and the frequencies, were 200 to 1000 and became higher than those of as-grown crystals.

As a result of ESR measurement, an ESR signal of the Ti^{3+} ion was observed only from the as-grown crystals and which seem to suggest that the electrical conductivity of the as-grown crystals is due to the Ti^{3+}–Ti^{4+} hopping mechanism.

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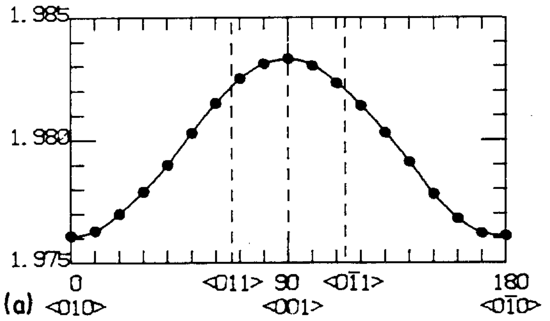

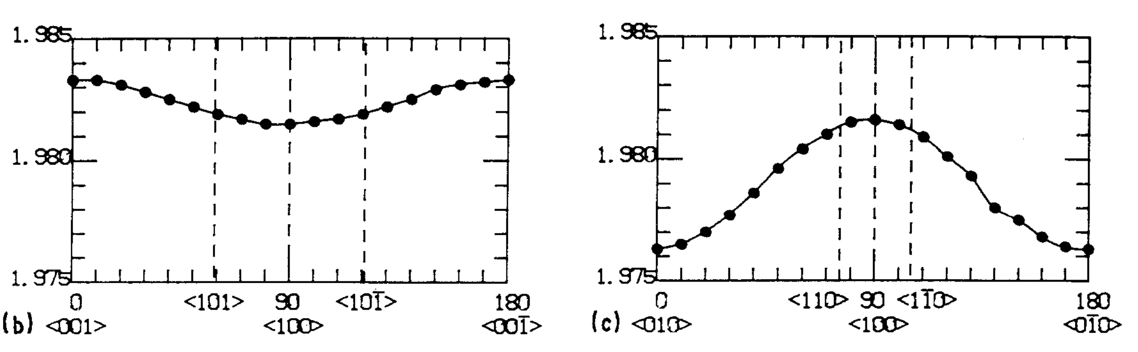

Figure 4 Angular variation of the g-factor: external magnetic field is (a) in the (1 0 0) plane; (b) in the (0 1 0) plane; (c) in the (0 0 1) plane.

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