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Sintering mechanism and microwave dielectric properties of $BaTi_4O_9$ ceramics fabricated by plasma active sintering method.

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ABSTRACT

$BaTi_4O_9$ was sintered by spark plasma sintering method. The dielectric constant and temperature dependence of a Q value and a resonance frequency were measured by two infinite parallel perfectly conducting resonance cavity method. The dielectric constant ε_r and Q value taken at 3.5 GHz were 32 and 2500, respectively. The temperature coefficient of the resonance frequency was 30 ppm/°C between -40 and 120°C. Qf of the sample showed temperature hysteresis. This is due to the moisture of atmosphere or the roughness of the sample surface.

1. INTRODUCTION

Recently, high quality microwave dielectric ceramics, which can miniaturize of resonators, have attracted much attention in microwave telecommunication [1, 2]. There are three requisite problems for the microwave ceramics. The first one is high dielectric constant. The next one is high dielectric factor Q. The temperature coefficient of the resonance frequencies is required to be as close to 0 ppm/°C as possible, finally.

It has been reported that $BaTi_4O_9$ have superior dielectric properties for microwave resonator applications as follows [3-6]: ε_r=38, Q=8000 and τ_f=-6.0 ppm/°C. However, there are some problems to prepare the stoichiometric $BaTi_4O_9$ sample. The $BaTi_4O_9$ compound is sintered at rather high temperature about 1400°C, and decomposed at 1430°C peritectically [7, 8].

The spark plasma sintering apparatus is the combined machine consisting of a hot-press and a plasma generator. This method can offer high dense samples at lower sintering temperatures for short time compared with hot-pressing and pressureless sintering.

We have studied the sintering mechanisms of $BaTi_4O_9$ prepared by the spark plasma sintering and the dielectric measurement at microwave frequencies (3-5GHz).

2. EXPERIMENTAL PROCEDURES

2.1 Sample preparation and characterization

The starting materials were $BaCO_3$ (Shin Nihon Chemical Ind. Co., Ltd. : 99.8%) and TiO_2 (Toho Titanium Co., Ltd. : 99.8%). These powders of Ba : Ti = 1 : 4 was mixed for 24 h using ball milling with aluminum balls (10 mmϕ) and methanol. The mixed powder was calcined at 850°C for 10 h. After calcining, the ground and ball-milled powders were charged in the graphite die (20 mmϕ). This graph-

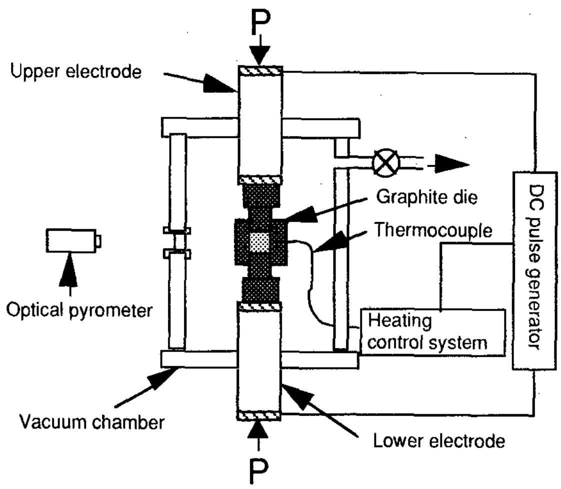

Figure 1. Schematic diagram of spark plasma sintering apparatus.

ite die was set in the spark plasma sintering apparatus (Sumitomo Coal Mining Co., Ltd., SPS-1050) shown in Fig. 1 and under the stress about 200 kg/cm^2. The die was heated by direct pulse current. Sintering was done in a vacuum.

As sintered specimen was dark in color. As the specimen has high electrical conductivity, the ceramics was finally annealed at 1000°C for 20 h in 0.2 MPa oxygen atmosphere. The color changed pale light brown after oxidation.

Specimens were cut in a column shape (20 mm in diameter and 10 mm in height) and polished in order to use microwave band (3-5 GHz). Surface roughness of samples were measured by a roughness tester (Taylar Hobson Model : 112/2564-319). The crystalline structure was determined by X-ray diffraction using CuKα radiation (Rigaku RAD-C system).

2.2 Microwave dielectric measurement

The complex dielectric constant at microwave frequencies was measured by a two infinite parallel perfectly conducting resonance cavity method, introduced by Hakki and Coleman [9] using a vector network analyzer (Hewlett Packerd Model HP8720C).

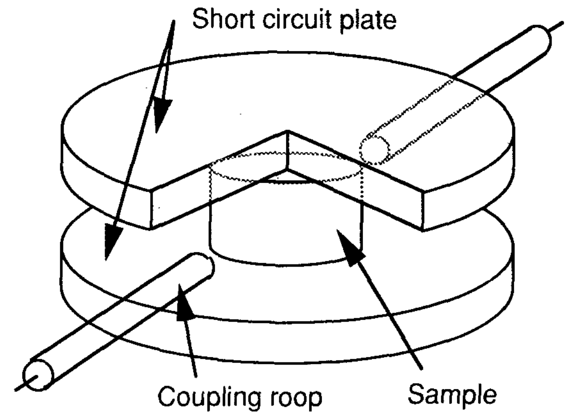

Figure 2. Electrode structure of two infinite parallel perfectly conducting resonance cavity method.

A sample holder of the dielectric measurement is shown in Fig. 2. The surface roughness of electrodes was ± 0.5 μm.

The equations for the calculation of dielectric constant (ε_r) and Q factor were as follows.

$$\lambda = C/F \quad (1)$$

$$\beta = 2\pi a/\lambda[(l\lambda/2L) - 1]^{1/2} \quad (2)$$

$$\varepsilon_r = (\alpha\lambda/2\pi L)^2 + (l\lambda/2L)^2 \quad (3)$$

$$Q = f_r/(f_2 - f_1) \quad (4)$$

(a : diameter of sample, L : height of sample, l : TE mode (l=1), f : frequency of TE_{011} mode)

β was obtained by equation (2). ε_r was obtained by substituting α from α-β chart proposed by R. W. Hakki, P. D. Coleman [10] into equation (3).

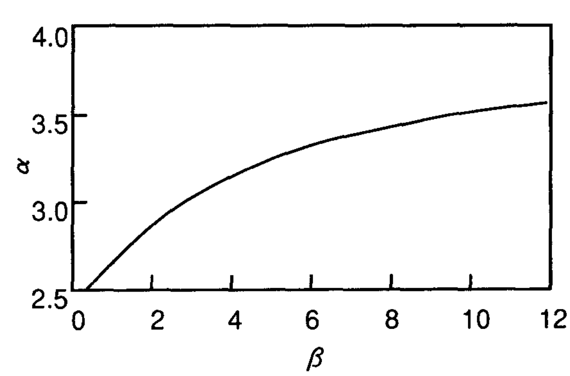

Figure 3. Solution of characteristic equation for TE_{0n1} modes for n=1 to 3[10].

3. RESULTS AND DISCUSSION

The bulk density of the sample was 4.325 g/cm^3 and the relative density was about 97.5%. Surface roughness of the sample was about $\pm$ 5 μm.

A X-ray diffraction pattern of the sample is shown in Fig. 4. Sample was the single phase of $BaTi_4O_9$. Lattice constants of this sample were estimated to be a=6.377, b=14.595 and c=3.806.

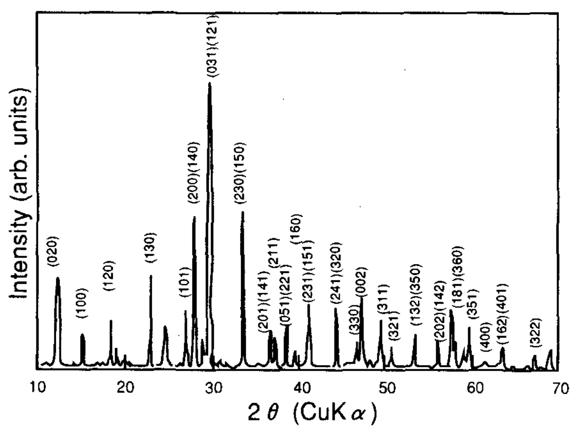

Figure 4. X-ray diffraction pattern of $BaTi_4O_9$ prepared by spark plasma sintering.

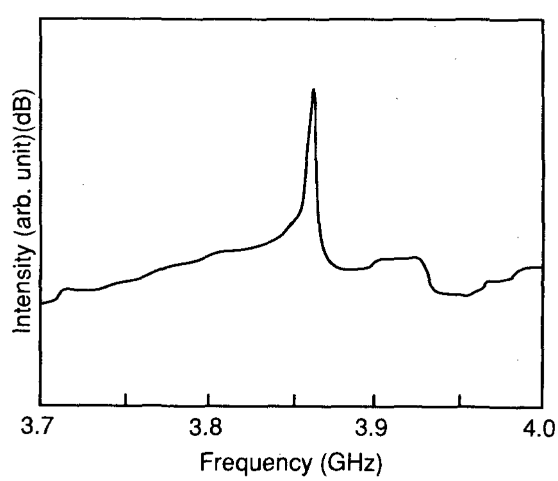

Figure 5. Resonant frequency spectra for microwave dielectric $BaTi_4O_9$.

Figures 5 and 6 show the spectra and the temperature dependence of resonance frequency for the microwave dielectric $BaTi_4O_9$. The value of dielectric constant and Q value of the sample measured at f=3.5 GHz were 32 and 2500 respectively. These values were smaller than that of single crystal (ε=40, Q=9000) . This is due to the moisture of atmosphere and the roughness of the sample surface. The temperature coefficient of resonance frequency was 30 ppm/°C.

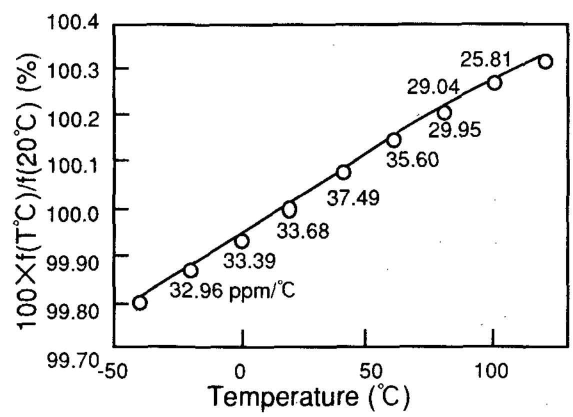

Figure 6. Temperature dependence of resonance frequencies for microwave dielectric $BaTi_4O_9$.

Figure 7 shows the temperature dependence of Qf products measured from -40 to 120° C. Qf took low value about 5000 GHz near the room temperature. Qf value was increased with increasing temperature. After measurement, Qf became a high value about 15000 GHz. This is due to the dehumidification of the moisture adsorbed on sample before the measurement.

4. CONCLUSION

$BaTi_4O_9$ was sintered by the spark plasma sinter-

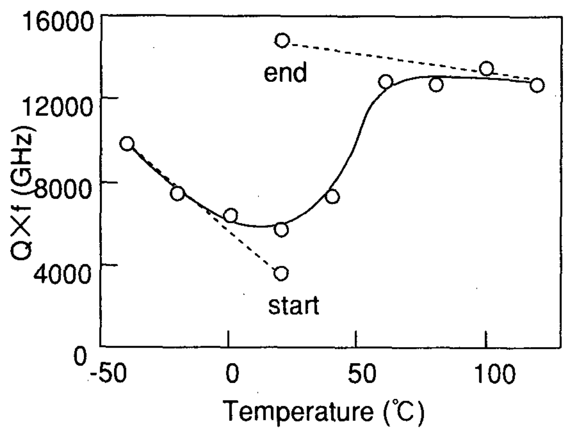

Figure 7. Temperature dependence of Qf products for microwave dielectric $BaTi_4O_9$.

ing method. The dielectric constant and temperature dependence of Q value and the resonance frequency were measured by the two infinite parallel perfectly conducting resonance cavity method. Results are summarized as follows :

(1) The bulk density of the $BaTi_4O_9$ sample was 4.325 g/cm^3 and relative density was about 97.5%.

(2) The dielectric constant ε_r and Q value measured at 3.5 GHz are 32 and 2500, respectively.

(3) The temperature coefficient of resonance frequency taken from -40 to 120°C was 30 ppm/°C.

(4) Qf of sample showed the temperature hysteresis. This is due to the moisture of atmosphere or the roughness of the sample surface.

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