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Temperature and frequency dependence of dielectric loss of $Ba(Mg_{1/3}Ta_{2/3})O_3$ microwave ceramics

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Abstract

$Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramic possessing extremely high $Q \times f$ value of more than 300 THz at microwave frequency was developed in our previous study. It is of great interest to understand the mechanism of microwave absorption in such a practical material. In the present study we report on the temperature dependence of the dielectric loss in the $Ba(Mg_{1/3}Ta_{2/3})O_3$. The mechanism of the microwave absorption is discussed using two phonons difference process. The samples were prepared by conventional solid state reaction and sintered at 1893 K in oxygen atmosphere. Dielectric properties in the microwave range were measured by Hakki & Colemann and resonant cavity methods in the temperature range of 20–300 K. Whispering gallery mode technique was used for the measurement of the dielectric properties at the millimeter wave frequency. Dielectric loss of the $Ba(Mg_{1/3}Ta_{2/3})O_3$ at the microwave frequency increases with temperature between 200 and 300 K in general agreement with the theory of intrinsic dielectric loss derived from the two phonon difference process. However below 200 K, the dielectric loss has shown a distinctive behavior with a loss peak at 40 K. It was inferred that the loss peak of the $Ba(Mg_{1/3}Ta_{2/3})O_3$ was caused by the local orientation polarization having dispersion at the microwave frequency.

Keywords: Dielectric properties; Spectroscopy; Phonon; Perovskite

1. Introduction

It is well-known that $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramics is a dielectric material possessing a low dielectric loss which makes it suitable for applications as a dielectric resonator in a band pass filters for wireless communication at microwave frequency. In general the dielectric loss of the ceramics includes intrinsic and extrinsic components loss as written by Eq. (1).

$$\tan\delta_t = \tan\delta_{in} + \tan\delta_{ex} \quad (1)$$

where $\tan\delta_t$ is the total dielectric loss and $\tan\delta_{in}$ and $\tan\delta_{ex}$ are the intrinsic and extrinsic dielectric loss of materials. In most cases of practical dielectric ceramics extrinsic dielectric loss due to impurities, grain boundaries, stress or electrical conductivity is higher than the intrinsic dielectric loss. Measurements of dielectric properties in a broad frequency and temperature range can assist in distinguishing between intrinsic and extrinsic dielectric loss. There have been several reports on the temperature dependence of dielectric loss of the BMT. Room temperature measurements on BMT in the microwave and millimeter range have revealed deviation from the purely intrinsic behavior of $\tan\delta$[1] below 50 GHz. Analysis of the whispering gallery modes (WGM) of BMT above 50 GHz indicates that the least upper bound of the $Q \times f$ value of BMT is about 430 THz, which corresponds to 2×10^{-5} in $\tan\delta$ at 9 GHz.[1] Ichinose and Shimada[2] obtained BMT ceramics having dielectric loss close to the value given in Ref. 1. It is important to analyze lattice vibration spectrum of the crystals because the intrinsic dielectric loss is directly related to the lattice vibration of the materials. In our previous study, the far infrared reflectivity of the BMT was measured and the lattice vibration parameters were calculated by spectrum fitting method.[3,4] The lattice vibration can directly absorb the far infrared photons in the process that creates one phonon from one photon. The photon energy in this process is too high in comparison with the microwave energy and the phonon cannot be created by absorption of the

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microwave in the one phonon process. Sparks et al. showed a possibility of the microwave absorption by two phonon process at the Brillouin zone (BZ) boundary.[5] Aupi et al. investigated the temperature dependence of the dielectric loss of Al_2O_3 and MgO single crystals.[6] They were successful in analysis of the temperature dependence of dielectric loss and suggested the contribution of acoustic phonons at the BZ boundary.

In the present study the temperature and frequency dependence of dielectric loss of BMT were analyzed in a similar way as that proposed by Aupi et al. The variation of dielectric loss with the temperature is discussed in terms of frequency dependence of the dielectric loss.

2. Experimental procedure

BMT ceramics were prepared by a conventional mixed-oxide reaction process and sintered under the condition suggested by Ichinose and Shimada[2] To prepare the BMT possessing extremely low dielectric loss, high purity reagents of magnesium and tantalum oxides and barium carbonates were used. The raw material consisting of oxides and carbonates were weighed to yield stoichiometric composition after they were perfectly dried in the electric furnace. These raw materials were mixed by ball mill using yttria stabilized zirconia balls in deionized water and calcined for 4 h at 1573 K in air after drying. The calcined powder was then subjected to ball-milling again until the particles showed narrow distribution of around 1 μm in average particle size. The ground powders were granulated with PVA and pressed into pellets of 12 mm in diameter under a pressure of 120 MPa using uniaxial pressing. The pellet was sintered at 1893 K for 60 h under $PO_2 = 0.91$ atm. The heating rate during sintering was fixed at 250 °C/h. The sintered pellet was sliced to a height of about 5 mm and their permittivity and $\tan\delta$ were measured by Hakki & Coleman's open resonator method in the microwave range using a network analyzer (HP 8720D). The temperature dependence of dielectric properties was measured using resonant cavity placed in the cryogenic container. For WGM measurements at the millimeter wave range the pellet was cut to a diameter of 5 mm and height of 1 mm. After the measurements of the dielectric properties, the pellets were thinned down to prepare the samples for the TEM observation using JEM 3000F TEM in order to check the crystal lattice properties of the BMT grains.

3. Results and discussion

Obtained BMT ceramics showed extremely low dielectric loss of about 2.5×10^{-5} at 9 GHz. As shown in Fig. 1, it was confirmed by TEM electron beam diffraction that the obtained BMT grains were almost free of twin boundaries and showed ordered hexagonal structure. Fig. 2 shows temperature dependence of dielectric loss of the BMT in the range of 20 K to room temperature at 6.5 GHz. As shown in Fig. 2, it was found that the dielectric loss had a loss peak at 40 K and gradually increased with temperature in the range of 200–300 K. This peculiar frequency dependence of the dielectric loss is well described by dividing it into two contributions as reported by Zuccaro et al.[7]

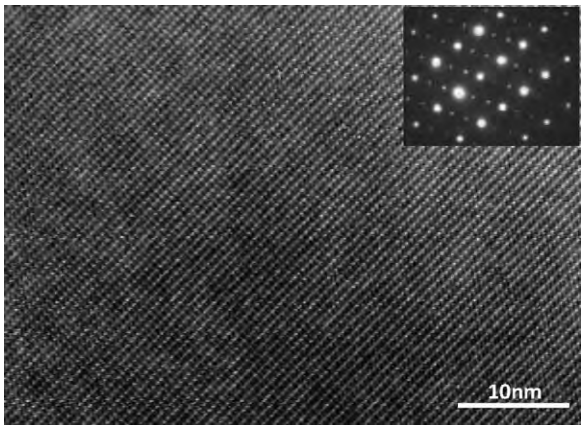

Fig. 1. TEM images of inner grains sintered for 60 h at 1893 K.

One contribution is a microwave absorption by two phonon difference process and another one is an orientation polarization resonance occurring at the microwave frequency. First of all, the contribution to the dielectric loss of the two phonon difference process is discussed according to Aupi et al.[6] The authors of Ref. 6 suggested that the microwave absorption should simply occur at the BZ boundary, and Eq. (2) was derived as a function of temperature using the theory similar to that of Sparks et al.[5] In a more general case, the absorption will occur at the wave vector corresponding to the highest density of states (DOS) of the acoustic phonons; however, it should not affect Eq. (2).

$$\tan\delta \cong \frac{\Gamma_1}{\omega_m(\omega_m+\omega)(\omega_{TO}-\omega_c)}\frac{\hbar\omega}{k_BT}n(\omega_m)[n(\omega_m)+1] \times \left[\tan^{-1}\frac{\omega_{TO}-\omega}{\gamma_p}\tan^{-1}\frac{\omega_c-\omega}{\gamma_p}\right] \quad (2)$$

$$\Gamma_1 = \frac{\varepsilon(0)-\varepsilon_\infty}{\varepsilon(0)}\frac{2h\phi_3^2}{3M_rM_<M_>\omega_{TO}^2} \quad (3)$$

where ω_m is the frequency of the optical phonon at the BZ boundary, ω is the frequency, ω_{TO} is the resonant frequency of the optical phonon at the Γ point, ω_c corresponds to the frequency difference between the optical phonon and acoustic phonon, h ($\hbar = h/2\pi$) is the Plank constant, k_B is the Boltzmann constant, n is the DOS of the acoustic phonon at the BZ boundary, γ_p is

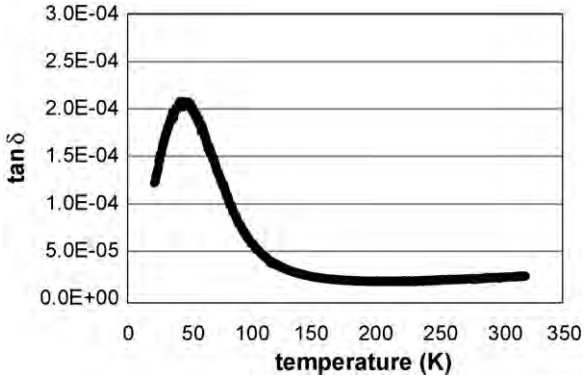

Fig. 2. Temperature dependence of dielectric loss of $Ba(Mg_{1/3}Ta_{2/3})O_3$.

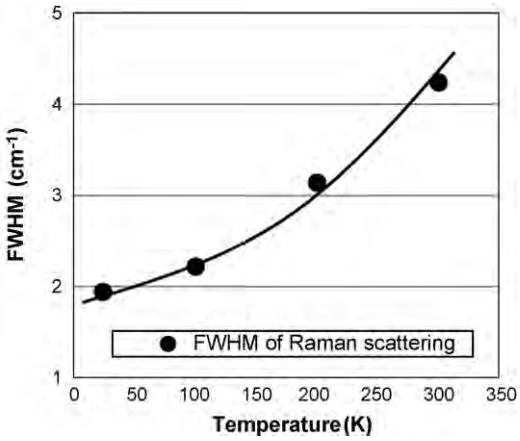

Fig. 3. Temperature dependence of Raman scattering of $A_{1g} + E_g$ mode in $Ba(Mg_{1/3}Ta_{2/3})O_3$.

the FWHM of dispersion curve, $\varepsilon(0)$ is the permittivity at low frequency, ε_∞ is the permittivity at high frequency, ϕ_3 is the third derivation of lattice energy, M_r is the reduced mass and M is the ion mass. Notations > and < imply higher weight ion and lower weight ion, respectively. In order to analyze this process, some assumptions were applied for the calculation; namely, $\omega_m \approx \omega_{TO}$, and ϕ_3 and ω_c were included as the fitting parameters. Temperature dependence of the FWHM in the Raman scattering profile as shown in Fig. 3 was used for theγ_p. The FWHM showed a parabolic variation with the temperature. Aupi et al. [6] suggested that such a variation was often found in single crystals. This means that the BMT prepared in this study shows the close characteristics to those of the single crystal. Fig. 4 shows the contribution of the two phonon difference process to the dielectric loss. The calculated curve takes a close value with the measured data at around room temperature. The deviation from the measured curve at lower temperature becomes larger because of the strong contribution of the dielectric loss peak. As the result of this calculation, the ϕ_3 and ω_c were determined to be −1.15 eV/unit cell and 420 GHz, respectively. The obtained ϕ_3 was in close agreement with the one theoretically calculated by Sagala and Nambu[8] for $Ba(Zn_{1/3}Ta_{2/3})O_3$. It means that the model for the dielectric loss adopted in this study reflects the actual behavior of the microwave absorption in the BMT.

For the curve fitting of the orientation polarization, Eq. (4) for the dielectric loss derived from Debye type dispersion model

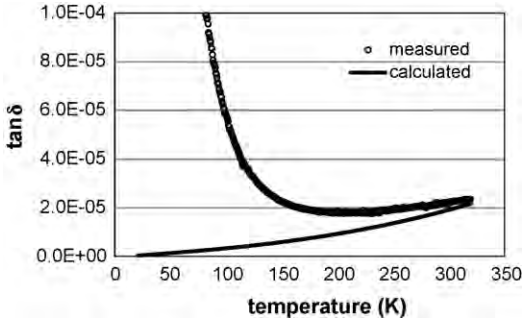

Fig. 4. Temperature dependence of dielectric loss of $Ba(Mg_{1/3}Ta_{2/3})O_3$ calculated using two phonons difference process.

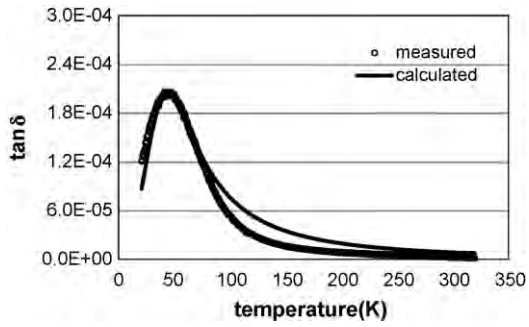

Fig. 5. Comparison in Debye type dielectric loss between measurement and calculated values in $Ba(Mg_{1/3}Ta_{2/3})O_3$.

was applied.[9]

$$\tan\delta(\omega, T) = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_{o\infty})\omega\tau}{\varepsilon_s + \varepsilon_{o\infty}\omega^2\tau^2} \quad (4)$$

where ε' and ε'' are the real and imaginary parts of the permittivity respectively, ε_s is the static permittivity, $\varepsilon_{o\infty}$ is the high frequency permittivity but it almost agrees with $\varepsilon(0)$ introduced in Eq. (3) and τ is the relaxation time of the orientation polarization. Fig. 5 shows the fitting result of the dielectric loss curve under the assumption that the orientation polarization is a dominant contribution to the peak shape of the dielectric loss. In this figure, the contribution from the orientation polarization was extrapolated by subtracting the contribution from the two phonons difference process. As shown in the figure, there is a slight difference between the measured and calculated curves in the temperature range of 100–200 K, but overall agreement with the model is quite good. The fitting parameters obtained in this calculation are listed in Table 1. It is found that the difference between ε_s and $\varepsilon_{o\infty}$, namely the contribution of orientation polarization into the dielectric constant is extremely small, so it is very difficult to discriminate the existence of this contribution from the permittivity spectrum alone obtained from the far infrared measurements.[3] Also the relaxation time for the orientation polarization is very short; this means that the orientation contribution easily follows the microwave frequency. Therefore it is concluded that the contribution of this polarization comes from very small and localized orientation of the impurity ions, it might be due to electron distribution or lattice defects formed in the BMT crystal. Fig. 6 shows the temperature dependence of dielectric loss at millimeter wave frequency which was measured using the WGM technique. As confirmed from this figure, the orientation polarization observed at the microwave frequency has disappeared in the millimeter wave range. This observation indicates that the orientation polarization cannot follow the field change of the millimeter wave. So it is expected that the $Q \times f$ value of the BMT in the millimeter wave range is higher than the

Table 1
Fitting parameter of orientation polarization calculated from temperature dependence of dielectric loss.

	ε_s	$\varepsilon_{o\infty}$	τ (ps)
BMT	24.51	24.50	20.0

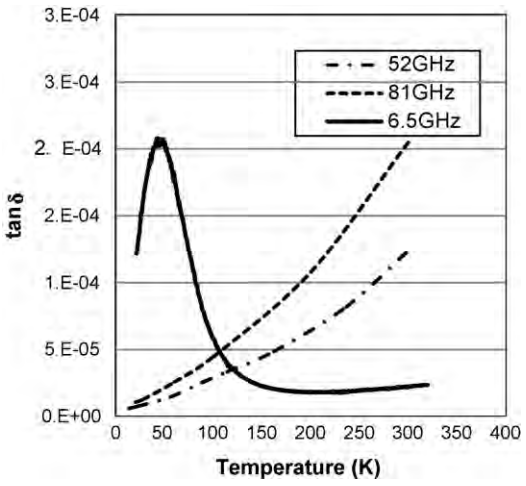

Fig. 6. Temperature dependence of dielectric loss of $Ba(Mg_{1/2}Ta_{2/3})O_3$ at millimeter wave frequencies.

value predicted from the $Q \times f$ measurements at the microwave frequency. In the present study it was clear that the total dielectric loss of BMT at the microwave frequency consisted of two terms: (i) the microwave absorption by the excitation of the acoustic phonons to optical phonons and (ii) the local orientation polarization. The location or the type of the ions responsible for this polarization behavior have not been specified yet in the present study. In order to elucidate the extrinsic dielectric loss in detail, the contribution of ion substitution in the BMT should be investigated in the future.

4. Conclusion

In the present study, temperature and frequency dependence of the dielectric loss of $Ba(Mg_{1/2}Ta_{2/3})O_3$ ceramics were measured and analyzed in order to investigate the mechanism of the intrinsic dielectric loss. It was found that the dielectric loss of the $Ba(Mg_{1/2}Ta_{2/3})O_3$ consisted of two contributions, namely intrinsic one due to the two phonon difference process and extrinsic one due to Debye dispersion. These two contributions well explained the temperature dependence of the dielectric loss of $Ba(Mg_{1/2}Ta_{2/3})O_3$. The energy difference between the optical and acoustic phonon is about 420 GHz at the BZ boundary. It was found that the local orientation polarization existed in the $Ba(Mg_{1/2}Ta_{2/3})O_3$ and it interacted with the microwave at relatively low temperature.

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