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Dielectric loss and damping constants of lattice vibrations in $Ba(Mg_{1/3},Ta_{2/3})O_3$ ceramics

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Abstract

Far-infrared reflectivity spectra for $Ba(Mg_{1/3},Ta_{2/3})O_3$ ceramics (prepared from high quality oxide reagents) sintered at 1600 °C for 4 and 50 h were measured at room temperature, to determine eigen frequencies and damping constants of lattice vibration in order to understand why the $Q{\cdot}f$ value at microwave frequency was improved by sintering time. The observed reflectivity spectra were fitted to 16 IR active modes predicted by factor group analysis in order to estimate the fitting parameters. Differences in reflectivity and damping constants were confirmed between the two samples by observation of the measurement spectra and their spectrum fitting. The fitting parameters were used to simulate dielectric loss at low frequency. Results of the simulation suggested a contribution of 3rd, 4th and 5th vibration modes to dielectric loss at low frequency.
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Keywords: Compositions; Dielectric properties; Functional applications; Perovskites; $Ba(Mg,Ta)O_3$

1. Introduction

$Ba(Mg_{1/3},Ta_{2/3})O_3$ (BMT) ceramic shows very good microwave dielectric properties which are relatively high permittivity, extremely low loss tangent and zero temperature coefficient of frequency. Much research has been carried out in order to improve the properties of BMT and some modifications of its preparation processes have been examined by some materials addition into BMT formulations. One of the primary studies for BMT was carried out by Nomura et al.[1] who achieved excellent dielectric properties of BMT. However, the $Q{\cdot}f$ value they obtained was relatively low compared to that reported in a recent study.[2] The study of Liang et al[2] implied that the properties of BMT are very sensitive to processing conditions, particularly with a view to obtaining a $Q{\cdot}f$ value above 300,000 GHz. Investigations of the preparation process were also carried out by many researchers[3–7] in which some crystallographic technologies were used to analyze the material properties, but they did not come to elucidate a problem why $Q{\cdot}f$ value changed by the preparation process. This implies that it is difficult to solve the problem only by crystallographic consideration. One of the clues to elucidate the process dependence of $Q{\cdot}f$ value may be found by research of lattice dynamics such as infrared measurement study. Sagala et al. reported the earliest investigation for the lattice vibration of BMT. They measured infrared reflection and made clear the vibration parameters of BMT using the dispersion relation.[8] However, their study was a fundamental one, and there were no details about the preparation process. they did not mention about the difference in $Q{\cdot}f$ values by the preparation process.

In the present study, two kinds of samples sintered at 1600 °C for 4 and 50 h were prepared and their dielectric properties were measured in order to investigate the difference in their properties. In addition, X-ray diffraction and far infrared reflection were examined to analyze the process dependence of the measured dielectric properties.

2. Experimental procedure

Tow kinds of BMT were prepared by the conventional mixed-oxide reaction method. High purity reagents of magnesium and tantalum oxides and barium carbonates were used to prepare BMT ceramics. These oxides and carbonates, which were weighted by stoichiometric composition, were mixed by ball mill with zirconia ball in deionized water and calcined for 4 h at 1300 °C after drying. And then the calcined powder was ball-milling again and the powders were pressed into a

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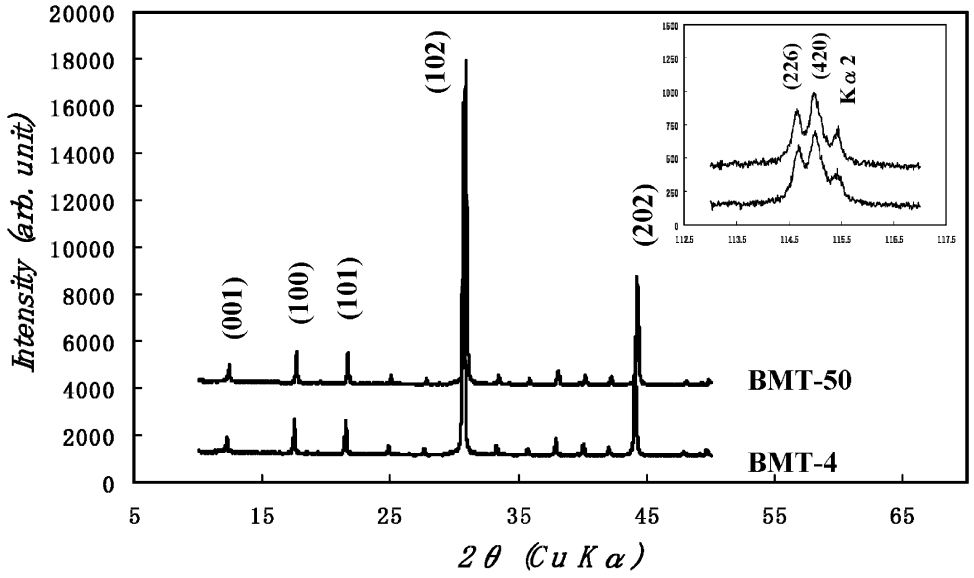

Fig. 1. X-ray diffraction patterns of BMT-4 and BMT-50.

pellet of 12 mm in diameter. The pellets were sintered at 1600 °C for 4 and 50 h in an oxygen atmosphere. In this paper BMT-4 and BMT-50 are put as symbols against 4 and 50 h sintered samples respectively. After sintering, the pellet samples were sliced 4.5 and 9 mm thick to use for determination of dielectric properties.

X-ray diffraction analysis was examined to observe degree of ordering for B sites ions; Mg and Ta, to determine the crystal parameters and to confirm that no second phases were formed in BMT matrices. Dielectric properties of the samples were measured by Hakki and Coleman's open resonator method at about 8 GHz.

The surfaces of the pellet samples (4.5 mm thick) were wet polished using about 1 μm diamond slurry by which the surface roughness (Ra) was less than 2.0×10^{-3} μm, and then washed with acetone in an ultra sonic bath to remove the influence of the surface impurities into the IR measurement. Far-infrared reflectivity spectra of the polished samples were measured at 25 °C with a Fourier Transform Infrared Spectroscopy (FT-IR; Bruker 113V) having a SiC glow bar lamp and Au reflector as the measurement reference. The incident angle of radiation was 11° and the spectra resolution was 1.0 cm^{-1}. The frequencies of lattice vibration were estimated by spectrum fitting of the measured data.

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of BMT-4 and BMT-50. As shown in these profiles, both samples revealed hexagonal perovskite structure and there were no differences between BMT-4 and BMT-50 in the observation of XRD patterns. Especially, it was a significant point that (420) lines obviously split as shown in both profiles, i.e. ordering of B site ions was of same degree between both samples. And dielectric properties and density of the samples are listed in Table 1. Obviously only $Q{\cdot}f$ values indicate a definite difference in comparison with BMT-4 and BMT-50. However, XRD analysis did not indicate such an apparent difference, i.e. it was suggested that the sintering time dependence of $Q{\cdot}f$ values might not be explained only by ordering of B site ions.

A difference in $Q{\cdot}f$ values by sintering temperature in BMT were investigated using TEM technique by Lin et al.[2] They showed the appearance of the various defects introduced by the dislocation and stacking fault near the grain boundary. The difference of $Q{\cdot}f$ values in our investigation might be also due to such defects. However observation of the crystallographic defects does not explain the intrinsic dielectric loss at low frequencies in full. Then, in order to investigate a lattice vibration microscopically and elucidate the sintering time dependence of $Q{\cdot}f$ value, we tried to observe far infrared reflectivity and tried to analyze its measurement spectrum. Figs. 2 and 3 show the far infrared reflectivity of the samples. The solid lines express fitting spectra for the measurement ones. The XRD pattern gives a space

Table 1
Dielectric properties and density of BMT-4 and BMT-50

Materials	Permittivity	$Q{\cdot}f$ value (GHz)	τ_f (ppm/K)	Density (g/cm^3)
BMT-4	24.82	109,067	1.69	7.61
BMT-50	24.69	312,818	1.86	7.61

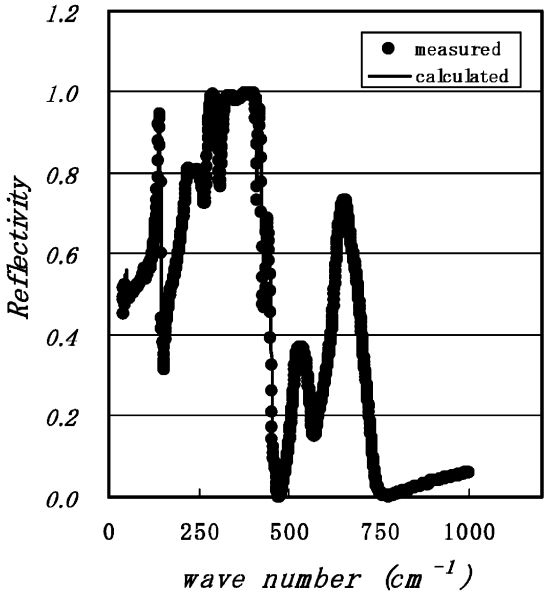

Fig. 2. Far infrared reflectivity and fit of BMT-4.

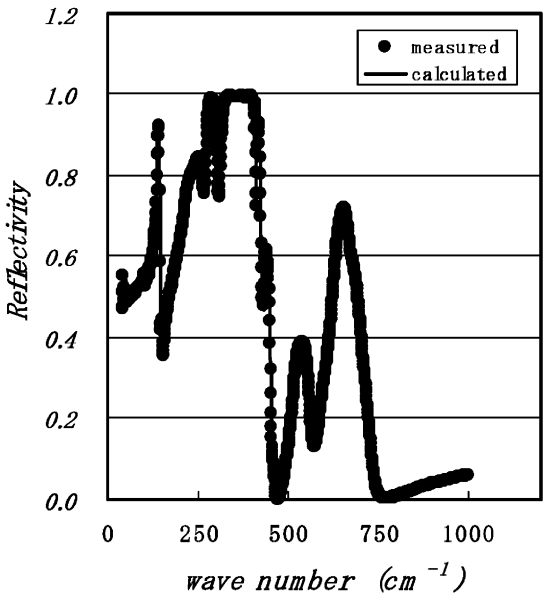

Fig. 3. Far infrared reflectivity and fit of BMT-50.

group P_3m(D_{3d}^3) and the following irreducible representation is derived by the factor group analysis for the Brillouin-zone-center vibration modes.[8]

$$\Gamma = 2A_{1u} + 8A_{2u} + 4\ A_{1g} + \ A_{2g} + 10E_u + 5E_g \quad (1)$$

Sixteen polarized vibration modes are observed in IR spectra since irreducible representations predict infrared active ($7A_{2u}+9E_u$).[8] The result from the factor group analysis is applied to a dispersion relation written by Eq.(2), which is basically derived from FPSQ model.[9]

$$\varepsilon = \varepsilon_\infty \prod_{j=1}^{16} \frac{\Omega_{jLO}^2 - \omega^2 + i\omega\gamma_{jLO}}{\Omega_{jTO}^2 - \omega^2 + i\omega\gamma_{jTO}} \quad (2)$$

the permittivity were transformed into reflectivity by a following relation.

$$R = \left|\varepsilon^{1/2} - 1\right|^2 / \left|\varepsilon^{1/2} + 1\right|^2 \quad (3)$$

where ε, ε_∞, ω and R are the permittivity, the permittivity at high frequency, the frequency and the reflectivity respectively. Ω_{jLO} and Ω_{jTO} are the eigen frequencies of LO and TO modes, and γ_{jLO} and γ_{jTO} are the damping constants of LO and TO modes respectively. The measured spectra were fitted by a least square method using Eqs. (2) and (3), and the eigen frequencies and the damping constants were calculated as fitting parameters. As shown in Figs. 2 and 3, the fitting spectra are

Table 2
Fitting parameter of lattice vibration for BMT ceramics

	BMT-4 (cm^{-1})				$\Delta\varepsilon$	BMT-50 (cm^{-1})				$\Delta\varepsilon$
	Ω_{jTO}	Ω_{jLO}	γ_{jTO}	γ_{jLO}		Ω_{jTO}	Ω_{jLO}	γ_{jTO}	γ_{jLO}	
1	47.6	47.6	3.8	4.4	2.1E-10	48.0	48.0	3.6	4.6	8.6E-12
2	138.5	146.7	2.6	3.3	6.2	138.8	147.3	2.6	3.1	5.8
3	150.3	153.8	10.9	6.2	0.63	150.5	153.1	5.5	5.7	0.41
4	217.5	223.6	15.6	40.5	6.5	221.3	227.2	23.5	38.7	7.8
5	235.5	269.4	54.9	19.6	10.6	235.1	270.3	38.2	18.4	8.9
6	274.3	307.6	9.5	10.6	1.4	274.3	307.3	9.9	11.0	1.1
7	311.4	395.7	12.3	115.8	0.57	311.7	376.3	11.9	113.1	0.59
8	375.8	375.8	115.6	63.6	4.7E-11	365.4	365.4	115.8	63.8	1.1E-11
9	385.9	411.2	67.9	3.9	0.26	370.6	411.8	66.6	3.9	0.22
10	410.7	427.9	3.5	10.1	3.7E-3	411.1	427.7	3.7	10.1	7.5E-3
11	432.4	451.9	12.2	8.6	0.022	431.4	452.0	13.3	9.3	0.022
12	466.0	466.0	16.2	8.6	4.2E-13	463.0	465.3	15.5	8.7	7.2E-3
13	519.0	519.0	21.8	65.4	2.4E-11	521.5	521.5	22.5	67.8	9.3E-13
14	552.8	562.1	58.0	23.6	0.28	549.5	564.9	55.8	23.3	0.33
15	603.2	646.7	121.7	81.0	1.3	620.6	646.0	113.8	85.3	4.1
16	630.4	722.9	32.8	33.1	0.43	624.8	723.2	33.7	32.7	3.3

good agreement with the measurement spectra and the fitting parameters and the dielectric strength ($\Delta\varepsilon$) obtained in these calculations are listed in Table 2. The accuracy of these fitting parameters is greater than that reported by Sawada et al.[10] because of the measurement accuracy and the difference of the number of fitting parameter. Apparently the reflectivity in Figs. 2 and 3 showed mostly similar spectra with each other, but one can find a slight difference in the spectra between the two samples in the frequency ranges of 150–250 cm^{-1}. The difference in measurement spectra are illustrated in Fig. 4(a) and (b), and the spectrum of a sample obtained by still longer sintering (250 h) is shown in Fig. 4(c) for comparison with the spectrum shape of each sample. It was indicated from Table 2 that the difference of spectra shapes of BMT-4 and 50 was due to change of the damping constants of 4th and 5th modes, which varied to 23.5 from 15.6 cm^{-1} and to 38.2 from 54.9 cm^{-1} with increase of sintering time, respectively. Also in 250 h sintering sample, the reflectivity at 250 cm^{-1} increased and the shape of the spectrum varied steeper one. This variation suggests that the damping constant of 5th mode decreased furthermore. In order to confirm the effect that these damping constants give the dielectric loss at low frequency, we carried out a simulation for dielectric loss of BMT-4 in which the damping constants only of 4th and 5th modes in BMT-50 were substituted into those in BMT-4; simulation 1. The simulation showed that the dielectric loss decreased up to the middle level of BMT-4 and BMT-50. However, a result of the simulation was not completely in agreement with BMT-50, so it is found that the simulation 1 does not sufficiently support the contribution of the damping constants of 4th and 5th modes to the dielectric loss. Then, compared to other fitting parameters between BMT-4 and BMT-50 in Table 1, especially at low frequency, one can find a difference in damping constant of 3rd mode. Taking into account the damping constant of 3rd, 4th and 5th modes, a similar simulation was carried out; simulation 2 to confirm the effect of these damping constants. Fig. 5 shows results of the simulation 2 for the dielectric loss. The results showed that the dielectric loss spectra ultimately approached the measurement spectra of BMT-50, that is to say, a

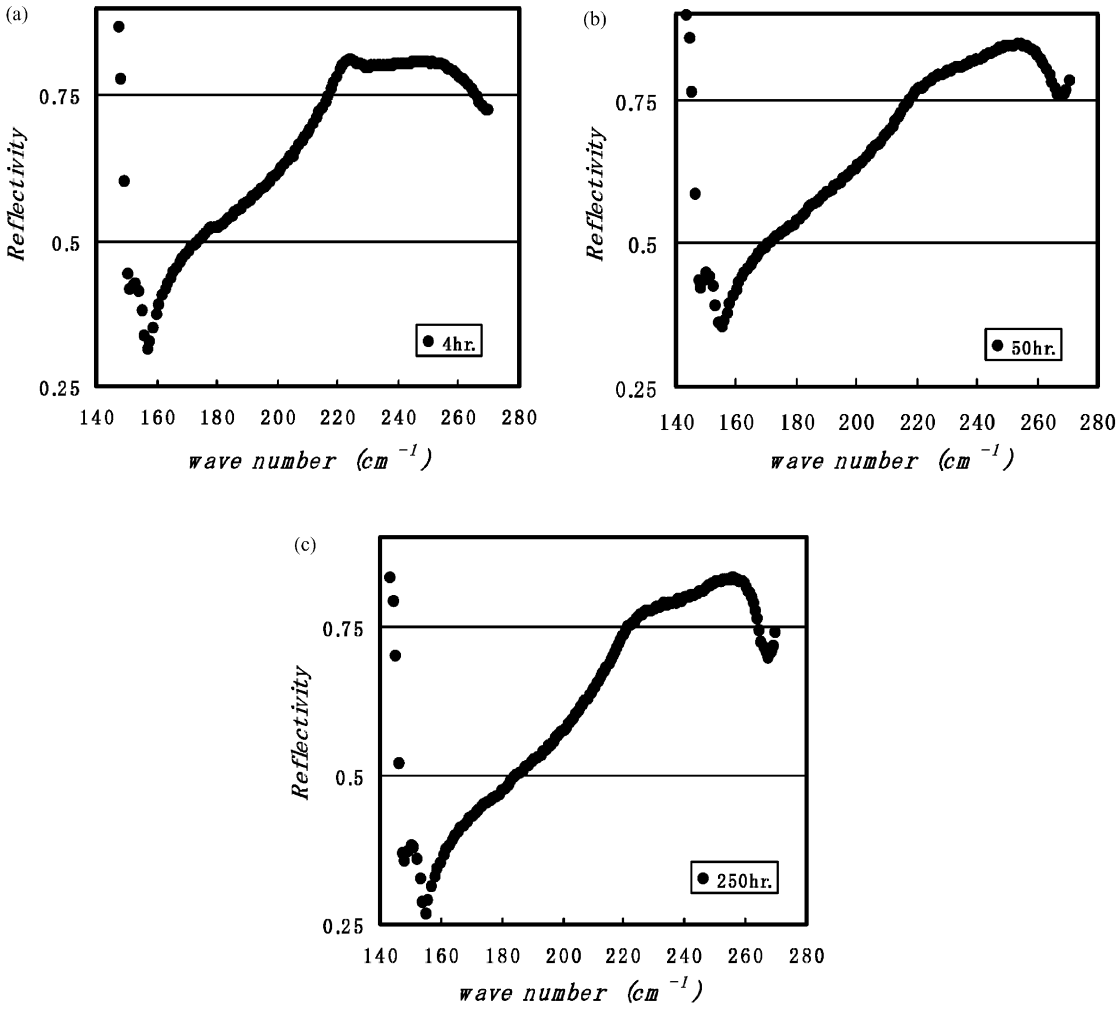

Fig. 4. Difference in reflectivity in the range of 280 from 140. (a) BMT-4, (b) BMT-50, (c) BMT-250.

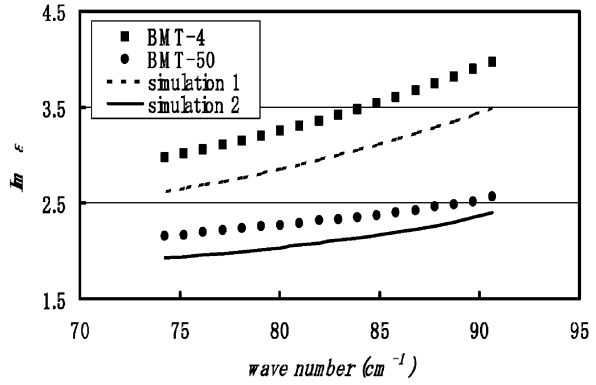

Fig. 5. Results of simulation of dielectric loss at low frequency. Simulation 1: taking into account damping constants of 4th and 5th vibration modes Simulation 2: taking into account damping constants of 3rd, 4th and 5th vibration modes.

contribution of the damping constants of 3rd, 4th and 5th modes for the difference in dielectric loss by the sintering time was made clear by these measurements and simulations. Since the damping constants of 3rd, 4th and 5th modes are relatively higher frequency modes, it is difficult to consider that these modes microscopically contribute to the low frequency dielectric loss containing microwave range. Therefore, it is more reasonable to infer that our result is a secondary effect coming from certain crystal structural variation. However, we could not sufficiently and consistently explain the problem why the three damping constants varied by sintering time. Our measurement and considerations invite further empirical investigation for the variation of the damping constants.

4. Conclusions

Variation of $Q{\cdot}f$ value of BMT ceramics by sintering time has been investigated by measurement of far infrared reflectivity, and it was found that the variation of the damping constants of 3rd, 4th and 5th modes by sintering time appeared in the reflectivity spectra. The spectra simulation suggested that the variation of these modes influenced the $Q{\cdot}f$ value at microwave range of BMT ceramics, and it was inferred that the variation was due to crystal structural effect of BMT ceramics.

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