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Journal of the European Ceramic Society 26 (2006) 1781–1785

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Effect of Ni substitution on the dielectric properties and lattice vibration of $Ba(Mg_{1/3}Ta_{2/3})O_3$

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Abstract

Far infrared reflectivity spectra for $Ba(Mg_{1/3},Ta_{2/3})O_3$ and $Ba([Mg_{1-x}Ni_x]_{1/3},Ta_{2/3})O_3$ ceramics were measured and eigenfrequencies and damping constants of transverse optical modes were estimated in order to investigate the variations in the dielectric properties with Ni substitution. These ceramics were prepared by the conventional solid phase reaction method using high purity chemicals. The observed reflectivity spectra were fitted as a function of the vibration frequencies and the damping constants. The permittivity and Qf value decreased with Ni substitution. The decrease in permittivity is due to the decrease in the damping constant of 4th vibration mode of the oxygen layer vibration. The decrease in Qf value is due to the increase in the damping constant of 5th vibration mode of the oxygen layer vibration. It was inferred that the increase in the Qf value might be due to the substitution of the Ni ion for the Ta ion in the Ta layer in the BMT.

Keywords: Dielectric properties; Powder-solid state reaction; Lattice vibration

1. Introduction

Recent studies of materials for high frequency wireless communication are focused dielectric loss. Many high *Q* dielectric materials are used for application as substrate, filter and oscillators in several wireless devices. Dielectric resonator is well known as a kind of device used for miniaturization of the components for wireless communication. The wireless communication, especially for base station, requires low loss dielectrics as for RF components for high frequency and quality communication. $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) is a suitable candidate material which satisfies such a requirement for applications as RF components in the base station. A lot of researches were carried out by many worker who improved the dielectric loss on the BMT.[1–4] Recently, we reported the effect of Zn substitution on the lattice vibration and far infrared spectra of the BMT and $Ba([MgZn]_{1/3}Ta_{2/3})O_3$ (BMZT).[5,6]

In the present study the effect of Ni substitution for Mg in BMT on dielectric properties was experimentally investigated and the far infrared spectra between BMZT and $Ba([MgNi]_{1/3}Ta_{2/3})O_3$ (BMNT) was compared and discussed the observed difference in the spectra.

2. Experimental procedure

$Ba([Mg_{1-x}Ni_x]_{1/3}Ta_{2/3})O_3$ ($x = 0$–0.3) were prepared by a conventional mixed-oxide reaction process. To prepare BMNT so that it was in an appropriate state for the far infrared measurement, extremely high purity reagents of magnesium, zinc and tantalum oxides and barium carbonates were used for the process. These oxides and carbonates, which were weighed by stoichiometric composition, were mixed by ball mill using yttria stabilized zirconia balls in deionized water and then calcined for 4 h at 1573 K in air after drying. The calcined powder was then subjected to ball-milling again until the D_{50} of the particle size distribution of about 1 μm was reached. The ground powders were granulated and pressed to form a pellet 12 mm in diameter under a pressure of about 120 MPa. The pellets were sintered at 1823, 1873 and 1923 K for 10, 25 and 50 h using an electric furnace. The sintered pellets were sliced to a height of about 5 and 10 mm and their dielectric properties evaluated.

X-ray diffraction analysis was performed to confirm that no second phases were formed in the BMNT matrices and to determine lattice parameters. The dielectric properties of the samples were measured by Hakki & Coleman's open resonator method in the microwave range using a network analyzer (HP 8720D). The surfaces of the sintered samples were wet polished using about 0.5 μm diamond slurry until the surface roughness (Ra)

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doi:10.1016/j.jeurceramsoc.2005.09.093

was less than 5×10^{-4} μm. It was then washed with acetone in an ultrasonic bath to avoid the influence of the surface impurities on the IR measurement. Far-infrared reflection spectra of the polished samples were measured at room temperature with a Fourier Transform Infrared Spectroscopy (FT-IR; Bruker IFS 66V/S) 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 $1.0\,\mathrm{cm}^{-1}$. The frequencies of lattice vibration were estimated by spectrum fitting of the obtained data.

3. Results and discussion

The effect of Ni substitution on the dielectric properties of BMT is shown in Figs. 1 and 2. As shown in Fig. 1, permittivity remains nearly a constant or decreased slightly with an increase in the substitution amount of Ni for Mg in BMT and the amount of its scatter decreased with increasing sintering temperatures. It has been reported earlier[6] that Zn substitution for Mg in BMT increased the permittivity. In the present case, I found that Ni substitution decreased permittivity. The Qf value decreased gradually with the amount of Ni substitution as indicated in Fig. 2. The degradation behavior of Qf value with Ni substitution was similar to that of Zn substitution in BMT.[5]

In order to find the variation of these dielectric properties with Ni substitution, the lattice vibrations of BMNT were investigated by far infrared reflectivity method. Fig. 3 shows the far infrared reflectivity and its fitting curve of BMT and BMNT ($x = 0.3$). The spectrum fitting was carried out using the product rule Eqs. (1) and (2) derived for the vertical incidence of the infrared radiation.

$$\varepsilon = \varepsilon_{\infty} \prod_{j=1}^{16} \frac{\Omega_{j\mathrm{LO}}^{2} - \omega^{2} + i\omega\gamma_{j\mathrm{LO}}}{\Omega_{j\mathrm{TO}}^{2} - \omega^{2} + i\omega\gamma_{j\mathrm{TO}}} \tag{1}$$

$$R = \frac{|\varepsilon^{1/2} - 1|^{2}}{|\varepsilon^{1/2} + 1|^{2}} \tag{2}$$

A slight difference of the reflectivity appeared between BMT and BMNT as shown in Fig. 3. The degradation of the reflectivity was observed in the frequency range of $220–250\,\mathrm{cm}^{-1}$ and the difference is relatively clear in the spectra in Fig. 3(a) and (b). The vibration parameters: the vibration frequencies and damping constants were calculated by the spectrum fitting method and it was found that the degradation of reflectivity in that range was caused by the damping constant of the lattice vibration. Fig. 4 shows the variation of damping constants of the 4th and 5th lowest vibration modes, which are corresponding to oxygen layer vibration.[7,8] The damping constant of the 4th lowest vibration

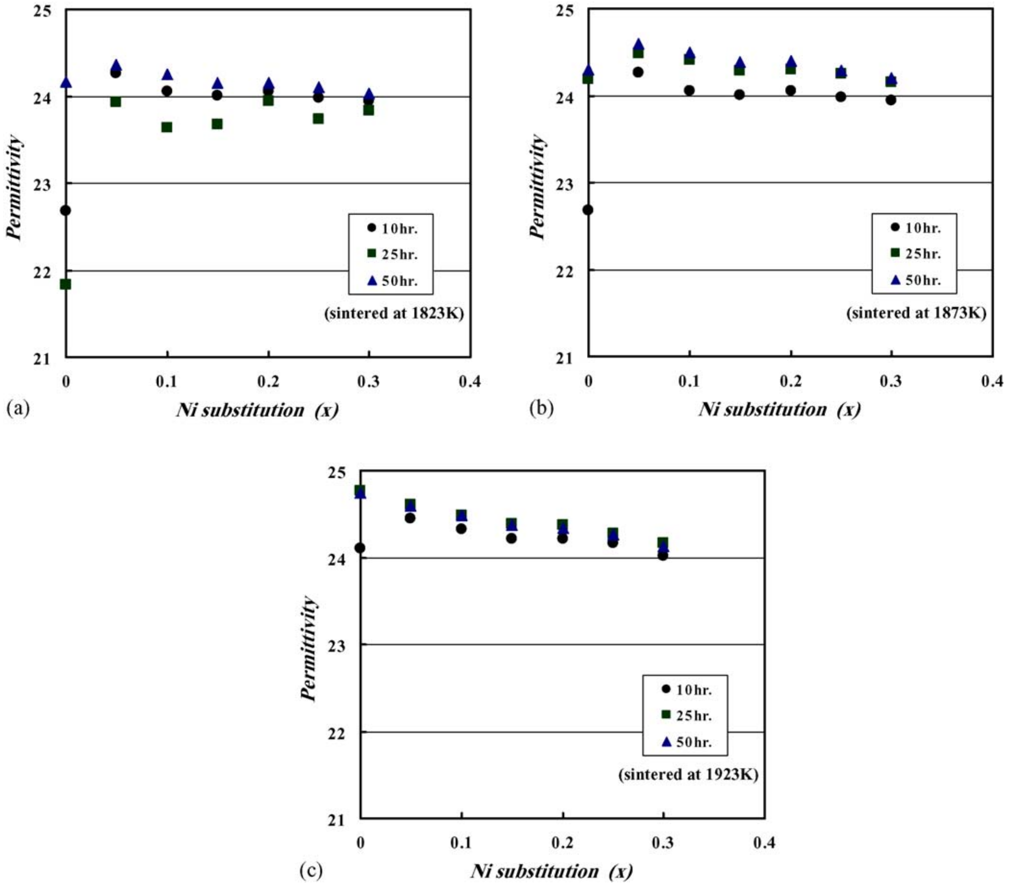

Fig. 1. Variation in permittivity of BMNT with Ni substitution.

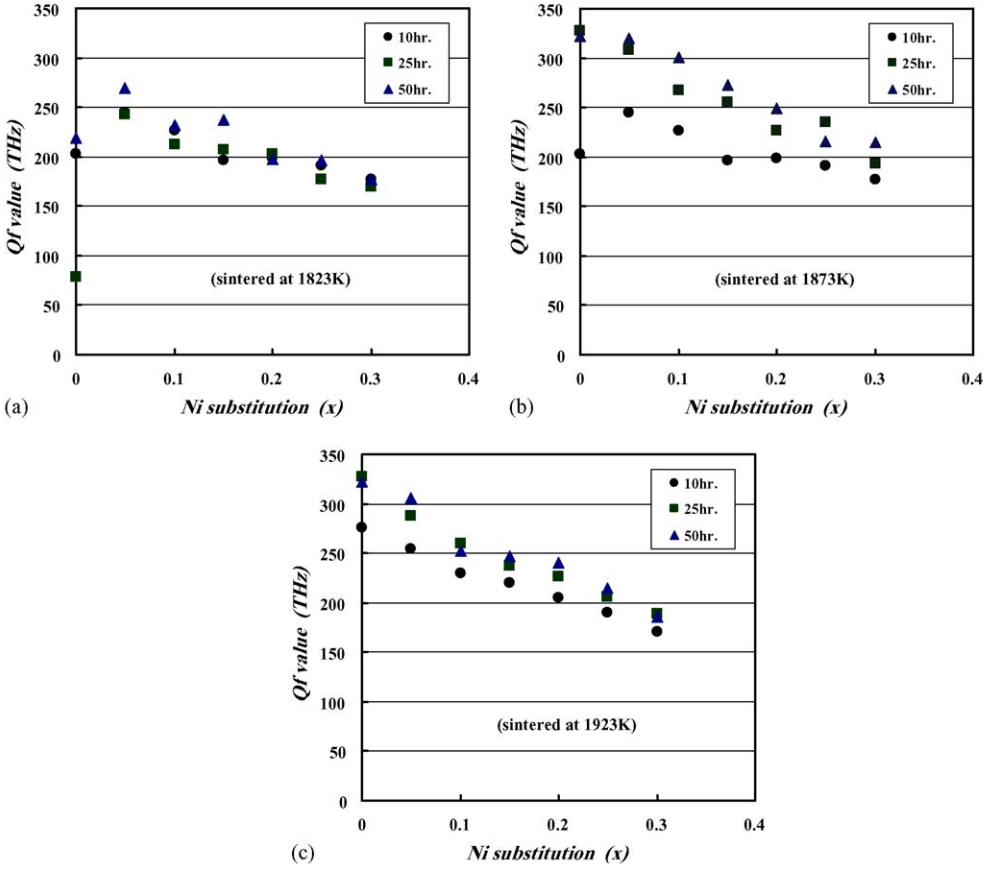

Fig. 2. Variation in Qf value of BMNT with Ni substitution.

mode decreases and that of 5th increases with increasing Ni substitution. Fig. 5(a) and (b) show the complex permittivity spectra of some vibration modes at relatively lower frequencies, calculated using the vibration parameters obtained by spectra fitting. Obviously both 4th and 5th modes strongly influence low frequency range. In other word, the most influenced mode to the permittivity is the 4th mode and to the dielectric loss is the both 4th and 5th modes. From Figs. 4 and 5, it was found that the slight permittivity decrease with Ni substitution was due to decrease in the damping constant of the 4th vibration mode, that is, the decrease in the permittivity by the decrease in the damping constant is due to a slight drop of the skirt curve in the permittivity spectrum at low frequency. This is the significant difference between Ni and Zn substitution in BMT. As reported in previous study,[5] the substitution of Zn for Mg increases the damping constant of the 4th vibration mode so that the permittivity of the BMT increases by Zn substitution. This phenomenon is completely opposite effect to that of Ni substitution in spite of the same B site substitution. From the reflectivity spectra, since the strength of the lattice vibration did not vary with Ni substitution, it was found that the damping constant contributed greatly to the variation in the permittivity of BMZT and BMNT. In addition it may also be noted that the dielectric polarizability of Ni is slightly lower as compared to that of Mg.[9] The polarizability of Zn is slightly higher than Mg and hence Zn substitution increases the permittivity. Therefore, it may be possible from these data to show the relation between the polarizability of these ions and the lattice vibration, especially its damping constant, of the predominant vibration mode. The decrease in the Qf value was due to increase in the damping constant of the 5th vibration mode. This means that an increase in damping constant lead to a rise of the skirt curve in the dielectric loss spectrum. For these samples it was confirmed by XRD and EPMA observation that there were no impurity phases and the loss did not come from grain size effect of the material.

The crystal structure of ordered BMT and oxygen layer corresponding to the 4th and 5th lowest vibrations is shown in Fig. 6. The increase in the damping constant of the oxygen layer vibration (5th vibration mode) may be due to the substitution of Ni ions at the Ta site in the material. Since the 2nd lowest mode slightly shifted to higher frequency as shown in Table 1, it was inferred that the Ta ion in Ta layer was predominantly substituted by a part of Ni ion. However, there are more possibilities in substitution form of the Ni ion, so it is necessary that the substitution form is confirmed by other experimental techniques.

Table 1
Vibration frequency of the second lowest (Ta layer) mode

	Vibration frequency (cm^{-1})			
	$x = 0.0$	$x = 0.1$	$x = 0.2$	$x = 0.3$
Ni substitution	138.5	139.9	140.0	140.3
Zn substitution	138.5	138.1	138.0	137.9

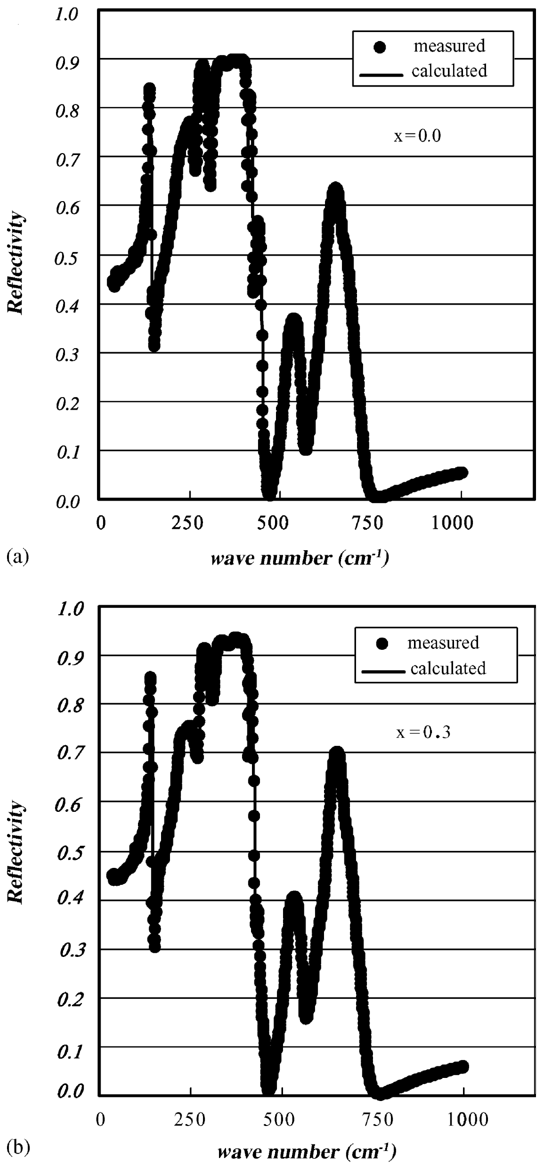

Fig. 3. (a) Far IR reflectivity of BMT. (b) Far IR reflectivity of BMNT ($x = 0.3$).

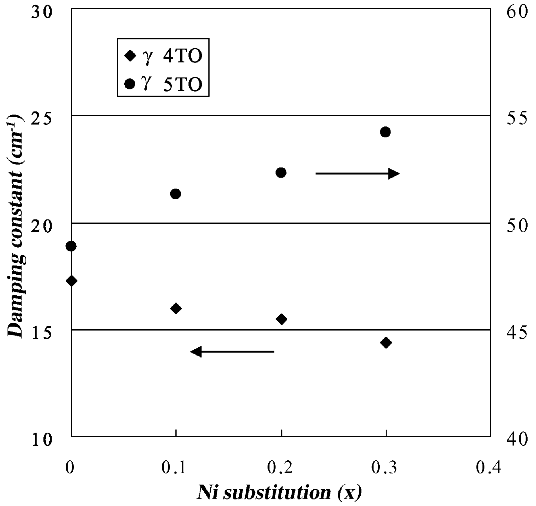

Fig. 4. Variation in damping constants of the 4th and 5th TO modes with Ni substitution.

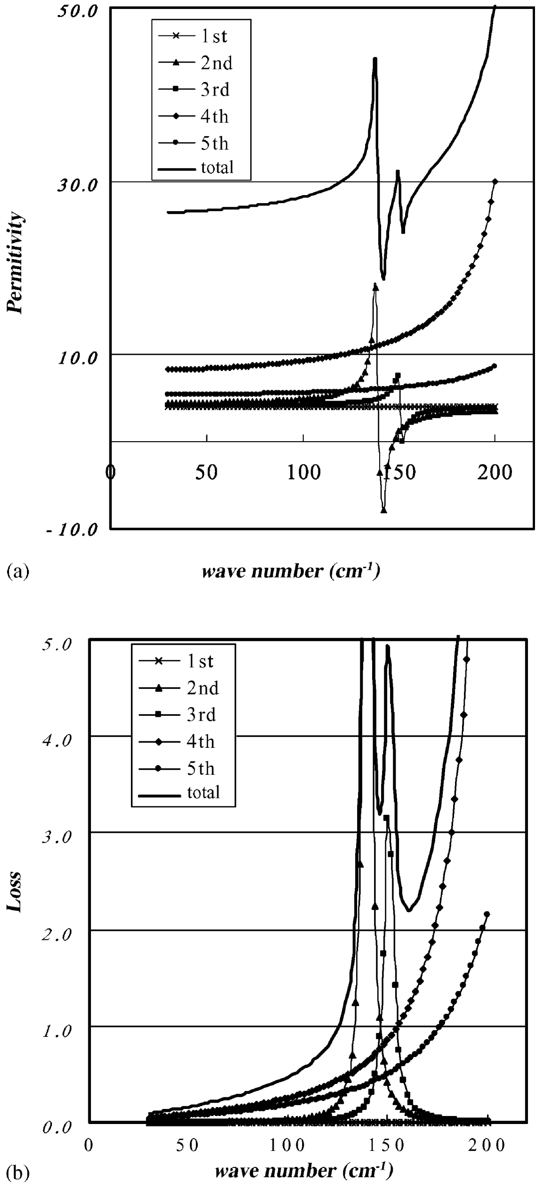

Fig. 5. (a) Permittivity spectra calculated from fitting parameters. (b) Loss spectra calculated from fitting parameters.

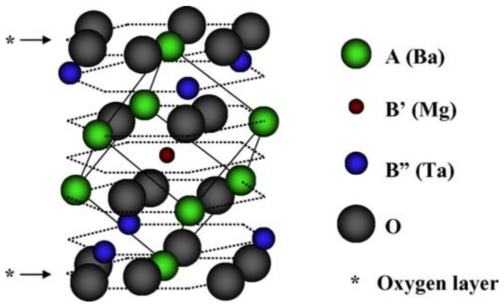

Fig. 6. Crystal structure of BMT.

4. Conclusions

In the present study, the variation in the dielectric properties of BMNT with Ni substitution is investigated. The permittivity decreases with Ni substitution for Mg and is attributed to the decrease in the damping constant of oxygen layer vibration (4th vibration mode). Dielectric loss increases with Ni substitution and is due to the increase in the damping constant of oxygen layer vibration (5th vibration mode). The increase in damping constant may be due to the substitution of small amount of Ni ion for the Ta ion.

Acknowledgements

The author would like to appreciate Dr. Sebastian for his suggestion on polarizability of the ions in the BMT. The author believes that the discussion with him will lead to elucidate the relation between the polarizability and lattice vibration in the BMT material.

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