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Crystal structural refinement of corundum-structured $A_4M_2O_9$ (A = Co and Mg, M = Nb and Ta) microwave dielectric ceramics by high-temperature X-ray powder diffraction

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Abstract

The microwave dielectric properties and crystal structure of corundum-structured $Mg_4Nb_2O_9$ (MN), $Co_4Nb_2O_9$ (CN) and $Mg_4Ta_2O_9$ (MT) compounds were investigated in this study. The crystalline phases of the ceramics were characterized by using the high-temperature X-ray powder diffraction and the crystal structures of the compounds were refined in terms of Rietveld analysis. The temperature coefficient of resonant frequency (τ_f) varied from −70 to −10 ppm/°C with increasing the composition x when Mg was substituted by Co. From the calculation of covalency of cation–oxygen bonds, it is found that the covalency of Co—O bond is lower than that of Mg—O bond and the difference in the covalency of these cation–oxygen bonds influences on the temperature dependence of dielectric constant on the compounds. As for the dielectric constant (ε_r) and the quality factor ($Q{\cdot}f$) of the ceramics, these values ranged from 10 to 16 and from 210,000 to 5000 GHz, depending on the composition x.

Keywords: Dielectric property; Crystal structure

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1. Introduction

A variety of microwave dielectric ceramics have been utilized for the microwave dielectric applications including the filters and resonators in the wireless communication system. When evaluating the microwave dielectric ceramics, there are three physical properties, i.e., dielectric constant (ε_r), quality factor (Q) and temperature coefficient of resonant frequency (τ_f). Firstly, in order to miniaturize the size of microwave dielectric resonator, a high dielectric constant is desirable because the size of resonator is known to be proportional to $1/\sqrt{\varepsilon_r}$, though a low dielectric constant is suitable for the application at high frequency. Secondly, the temperature coefficient of resonant frequency which ideally has near zero value is necessary because the resonant frequency must be stable at the various operating temperatures. Thirdly, the low dielectric loss ($\tan\delta = 1/Q$) is required for the commercial applications. In most of microwave dielectric applications, a microwave dielectric ceramic with high $Q{\cdot}f$ value is required; the $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramic which has a 1:2 ordering of B site cation in perovskite-type structure is known to be one of the high-Q materials. Therefore, most of recent work has been focused on the perovskite-structured microwave dielectric ceramics with the B site ordering such as BMT[1] and $Ba(Zn_{1/3}Ta_{2/3})O_3$[2] ceramics.

In the corundum-structured ceramic, i.e., $Mg_4Nb_2O_9$ (MN) compound, it is also reported that the $Q{\cdot}f$ values of MN and their solid solutions are comparable to those of Al_2O_3,[3] though the temperature coefficients of resonant frequency of these compounds have a negative value as well as that of Al_2O_3. However, the temperature dependence of dielectric property and the crystal structure on these compounds has not been certified to date and such the analyses in these compounds are considered to be important in order to obtain a microwave dielectric ceramic which has a high $Q{\cdot}f$ and a near-zero τ_f values. Thus, the corundum-structured MN, $Co_4Nb_2O_9$ (CN), and $Mg_4Ta_2O_9$ (MT) compounds were synthesized and the relationship between the crystal structure and microwave dielectric properties of the compounds was investigated in terms of the combination of crystal structure refinement and the high-temperature X-ray powder diffraction.

2. Experimental method

The samples with nominal composition of $A_4M_2O_9$ compounds (A = Mg and Co, M = Nb and Ta) were prepared via

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conventional solid-state reaction method. The initial powder reactants MgO (99.99%), CoO (99.9%), Nb_2O_5 (99.9%) and Ta_2O_5 (99.9%) were weighed in the stoichiometric proportions and mixed with acetone. These powders were calcined at a temperature of 1100 °C for 10 h in air. After calcining, the obtained powders were ground, mixed with polyvinyl alcohol and uniaxially pressed at 100 MPa into the pellets with 12 mm in diameter and 7 mm thickness. These pellets were sintered at the optimum temperatures for 10 h in air in order to obtain the highest bulk density. The sintering temperatures of $Mg_4Nb_2O_9$, $Co_4Nb_2O_9$ and $Mg_4Ta_2O_9$ compounds were 1350, 1200 and 1450 °C, respectively. Subsequently, the sintered pellets were polished, and then the typical dimensions of samples for the temperature dependence of dielectric constant measurement were 10 mm in diameter with 1 mm thickness. Each sample was electroded using Pt paste for the temperature dependence of dielectric property measurement on compounds and was fired at 850 °C for 1 h in air. The temperature dependence of dielectric constant on compounds at 1 MHz was evaluated by using Agilent 4284A precision LCR meter in the temperature range of 30–400 °C. The microwave dielectric properties at microwave frequency were also measured in terms of Hakki and Coleman method,[4] using Agilent 8720ES *s*-parameter vector network analyzer. The temperature coefficient of resonant frequency was determined from the resonant frequencies at the temperatures of 20 and 80 °C. The polycrystalline phase of the sintered samples was identified by using X-ray powder diffraction (XRPD, Rigaku RINT-2200) with Cu Kα radiation at 20 °C. In order to clarify the relationship between the temperature dependence of dielectric property and crystal structure, the XRPD profiles of these compounds at the various temperatures were also obtained in this study. The crystal structural refinements were performed in terms of the Rietveld analysis[5] program, i.e., RIETAN 2000.[6] The initial structural model for MN, CN and MT compounds was taken from the work by Kumada et al.[7] who characterized the crystal structure of MN compound, using neutron powder diffraction at room temperature.

3. Results and discussion

Fig. 1 shows a typical final result of the crystal structural refinement for the MN compound at 20 °C where Δ represents the difference between the calculated and measured intensities of XRPD patterns. The crystal structural refinements of MN, CN and MT performed in this study fitted to a trigonal structure with space group of $P\text{-}3c1$ and the phase transition of these compounds was not recognized in the temperature range of 20–400 °C. The reliability factor for the weighted pattern (R_{wp}) and the goodness of fit indicator (s) of the Rietveld analysis were ranged from 4.37 to 6.72% and from 1.33 to 1.67, respectively.

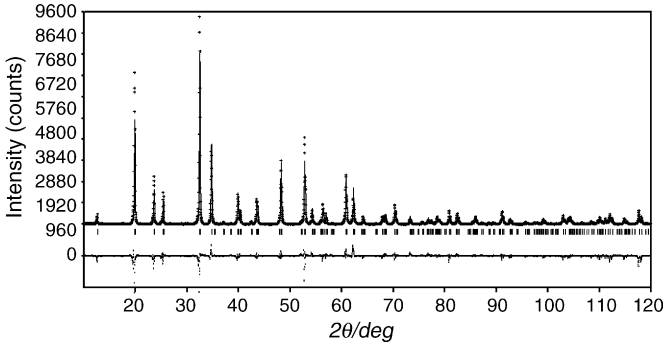

Fig. 1. Refined XRPD patterns of $Mg_4Nb_2O_9$ (MN) compounds at 20 °C.

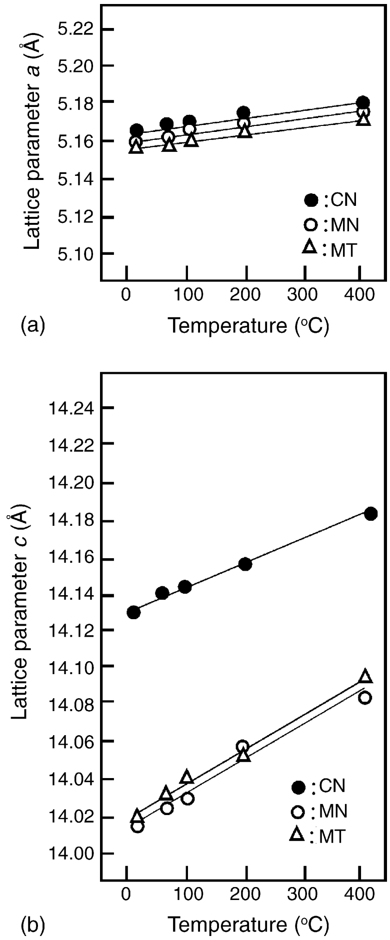

Fig. 2. Variations in lattice parameters of $Mg_4Nb_2O_9$ (MN), $Co_4Nb_2O_9$ (CN) and $Mg_4Ta_2O_9$ (MT) compounds as a function of temperature.

Fig. 2 shows the temperature dependence of lattice parameters on MN, CN and MT in the temperature range of 20–400 °C. The lattice parameters of MN, CN and MT linearly increased with increasing the temperatures. When comparing the lattice parameters of MN with those of MT, the remarkable differences in the lattice parameters between MN and MT were not observed because of the same ionic radii of Nb^{5+} and Ta^{5+} (0.64 Å) cations.[8] The increase in the lattice parameters of CN in comparison with those of MN and MT is due to the ionic radii of Co^{2+} (0.745 Å) and Mg^{2+} (0.72 Å) cations.[8] In order to clarify the temperature dependence of crystal structure on MN, CN and MT, the cation–oxygen bond lengths in each octahedron were also determined in this study. The relationship between the cation–oxygen bond length and temperature of MN, CN and MT is shown in Fig. 3 and the crystal structure of MN, which corresponds to the corundum structure, is also shown in Fig. 4. In the crystal structure of MN, the $Mg(1)O_6$ octahedron is composed

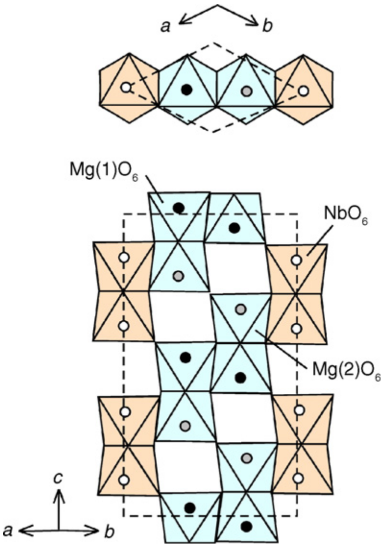

Fig. 3. Schematic diagram on crystal structure of $Mg_4Nb_2O_9$ (MN).

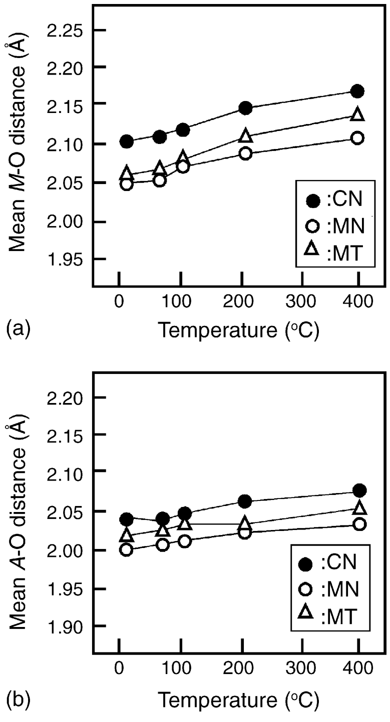

Fig. 4. Plots of cation–oxygen bonds in octahedra vs. temperature of $Mg_4Nb_2O_9$ (MN), $Co_4Nb_2O_9$ (CN) and $Mg_4Ta_2O_9$ (MT) compounds.

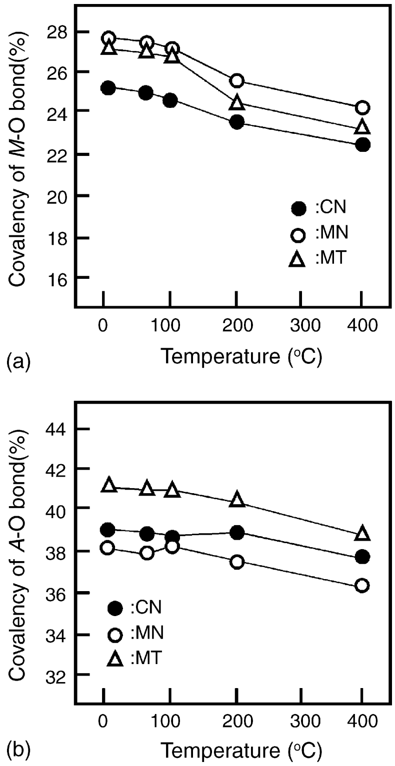

Fig. 5. Relationship between covalency of cation–oxygen bonds and temperature of $Mg_4Nb_2O_9$ (MN), $Co_4Nb_2O_9$ (CN) and $Mg_4Ta_2O_9$ (MT) compounds.

of Mg(1)–O(2) and Mg(1)–O′(2) bonds, while the $Mg(2)O_6$ octahedron consists of Mg(2)–O(1) and Mg(2)–O(2) bonds. In addition, in the case of NbO_6 octahedron, there are two types of Nb–O bonds which are Nb–O(1) and Nb–O(2) bonds, respectively. In all the compounds, the length of Nb–O and Ta–O bonds are shorter than those of Mg–O and Co–O bonds and such the shorter length of Nb–O and Ta–O bonds imply that the covalency of (Nb/Ta)–O bond is high in comparison with that of (Mg/Co)–bond. With increasing the temperature from 20 to 400 °C, the increase in the Mg–O bonds in MN and MT were recognized, while the length of Nb–O and Ta–O bonds in MN and MT were almost constant. The influence of temperature on the covalency of the cation–oxygen bonds was also investigated to clarify the variations in the bond lengths caused by the increase in the temperature. The relationship between the covalency of cation–oxygen bond and the bond length is given by the following two equations[9,10]:

$$s = \left(\frac{R}{R_1}\right)^{-N} \tag{1}$$

and

$$f_c = as^M \tag{2}$$

where s, R, R_1 and N are the bond strength of cation–oxygen bond, refined bond length, empirical constant which depends on the cation site, and the constant which is different for each cation–anion pair, respectively. Moreover, f_c, a and M in Eq. (2) indicate the covalency of the cation–oxygen bond and the empirical constants which depend on the number of electrons.

Fig. 5 shows the variations in the covalency of cation–oxygen bonds for MN, CN and MT as a function of temperature. The covalencies of Nb–O and Ta–O bonds in MN and MT are on the order of approximately 42%, whereas those of Mg–O bonds of MN and MT ranged from 25 to 28%. The covalency of Co(1)–O and Co(2)–O bonds in CoO_6 octahedra of CN are lower than those of Mg(1)–O and Mg(2)–O bonds in MgO_6 octahedra of MN, though the covalency of Nb–O bond in MN and CN was similar value. In all the compounds, the covalency of (Nb/Ta)–O bond is stronger than that of (Mg/Co)–O bond and this result is due to the (Nb/Ta)–O(2) bond length. As for the temperature

Table 1
Microwave dielectric properties of $Mg_4Nb_2O_9$, $Mg_4Ta_2O_9$ and $Co_4Nb_2O_9$ compounds

Compound	Sintering temperature (°C)	ε_r	$Q{\cdot}f$ (GHz)	τ_f (ppm/°C)
$Mg_4Nb_2O_9$	1300	11	210,000	−70
$Mg_4Ta_2O_9$	1450	10	345,000	−70
$Co_4Nb_2O_9$	1200	16	5,000	−10

dependence of covalency on cation–oxygen bonds, the covalencies of Nb–O and Ta–O bonds in MN, CN and MT are almost constant in the temperature range of 20–400 °C. The covalency of Co–O bond in CN remained approximately constant, while the slight decrease in the covalency of Mg–O bonds in MN and MT was observed with increasing the temperature. Thus, it is considered that the variations in the covalency, which depends on the temperature, may influence the temperature dependence of microwave dielectric properties of these compounds.

The microwave dielectric properties of MN, CN and MT at microwave frequency are listed in Table 1. The slight increase in the dielectric constant of CN is caused by the Co substitution for Mg, though the Ta substitution for Nb does not have a significant influence on the dielectric constant of MT. The dielectric constants of MN, CN and MT were approximately 11, 16 and 10, respectively.

The slight increase in the dielectric constant of CN caused by the Co substitution for Mg is attributed to the differences in the covalency between Mg–O and Co–O bonds because the covalency of Co–O bond in CN is lower than that of Mg–O bond in MN as described above. The $Q{\cdot}f$ value was increased from 220,000 to 345,000 GHz by the Ta substitution for Nb, whereas the Co substitution for Mg drastically lowered the $Q{\cdot}f$ value of the compound; as a result, the $Q{\cdot}f$ value of approximately 5000 GHz was obtained for the CN compound. As for the τ_f value of the compounds, the τ_f value of MT was similar to that of MN ($\tau_f = -70$ ppm/°C). On the other hand, theτ_f value of CN was approximately −10 ppm/°C and it was found that the Co substitution for Nb exerted an influence on the shift of theτ_f value ranging from −70 to −10 ppm/°C. In general, it is known that the temperature coefficient of resonant frequency of the dielectric ceramics is closely related to the thermal expansion coefficient and temperature coefficient of dielectric constant. It is considered that the variations in the temperature coefficient of dielectric constant are predominant for the τ_f value, since the thermal expansion coefficient of MN, CN and MT which was determined from the lattice parameters at 20 and 80 °C were 9.8, 10.6 and 8.3 ppm/°C, respectively. Thus, the temperature dependence of dielectric constant on MN, CN and MT is investigated and Fig. 6 shows the temperature dependence of dielectric constant of the compounds measured at 1 MHz. The temperature coefficient of dielectric constant of MN, MT and CN determined from at the temperatures of 20 and 80 °C were 176, 188 and 30 ppm/°C, respectively. The dielectric constants of MN and MT increased with an increase in the temperature, resulting the decrease in the covalency of Mg–O bonds as described above. In the case of CN, the variation in dielectric constant of CN was independent of the temperature as well as the relationship between the covalency of Co–O bond and the temperature. From these results, it is suggested that the variations in the covalency of Mg–O and Co–O bonds with an increase in the temperature may relate to the temperature dependence of the dielectric constant.

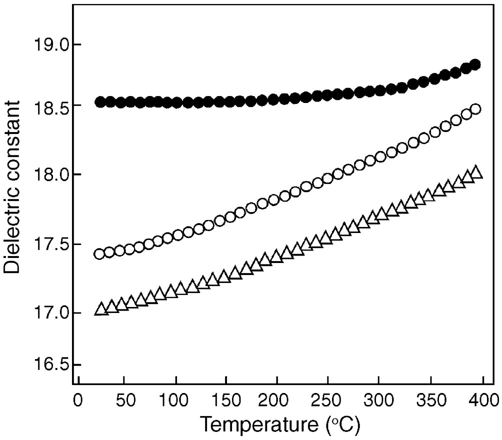

Fig. 6. Temperature dependence of dielectric constant measured at 1 MHz on $Mg_4Nb_2O_9$ (MN), $Co_4Nb_2O_9$ (CN) and $Mg_4Ta_2O_9$ (MT) compounds.

4. Conclusions

The corundum-structured $Mg_4Nb_2O_9$ (MN), $Co_4Nb_2O_9$ (CN) and $Mg_4Ta_2O_9$ (MT) compounds were synthesized, and the temperature dependences of dielectric properties and the covalency on the compounds were investigated in this study. The temperature dependence of the covalency of cation–oxygen bonds showed that the covalencies of Mg–O bond of MN and MT decreased, while covalency of Co–O bond in CN was almost constant. The temperature coefficient of dielectric constant determined from at the temperatures of 20 and 80 °C were 176 ppm/°C for MN, 188 ppm/°C for MT and 30 ppm/°C for CN, respectively. Since the variations in the temperature dependence of dielectric constant showed the similar tendency to those of covalency of Mg–O and Co–O bonds, it is considered that the variations in the covalency of these cation–oxygen bonds influence the temperature dependence of dielectric constant.

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