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Crystal structure of corundum type $Mg_4(Nb_{2-x}Ta_x)O_9$ microwave dielectric ceramics with low dielectric loss

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Abstract

New microwave dielectric ceramics, i.e. $Mg_4(Nb_{2-x}Ta_x)O_9$ (MNT) solid solutions, were synthesized and their microwave dielectric properties and crystal structure were investigated in this study. From the discrete variational Xα (DV-Xα) method, it was found that the Ta–O bonds in the TaO_6 octahedron become more covalent than Nb–O bonds in the NbO_6 octahedron; this result leads to the decrease of the ionicity in the Ta^{5+} ion. The dielectric constants of MNT were slightly decreased from 12.4 to 11.5; this result might be due to the covalent interaction of Ta–O bonding. The quality factors of the samples were found to exhibit high value ($Q{\cdot}f \fallingdotseq 350\,000$ GHz for $x = 2$) which is comparable to those of Al_2O_3.

Keywords: Dielectric properties; Niobates; Tantalates; X-ray methods; $Mg_4(Nb,Ta)_2O_9$; Microwave ceramics

1. Introduction

Much attention has been paid to the microwave dielectric properties of the materials such as Al_2O_3, $SrTiO_3$, $LaAlO_3$, $Sr(Al_{1/2}Ta_{1/2})O_3$ (SAT) and $Sr(Al_{1/2}Nb_{1/2})O_3$ (SAN) in order to develop high-temperature superconductor (HTS) microwave devices.[1–4] Although Al_2O_3 is widely used for integrated circuits because of its low dielectric loss (tanδ),[5] the chemical reaction at the interface between the Al_2O_3 substrate and the $YBa_2Cu_3O_{7-x}$ (YBCO) film has a detrimental effect on the dielectric properties. The $SrTiO_3$ substrate has the appropriate lattice parameters which are close to those of YBCO, whereas the tanδ of $SrTiO_3$ is too high for HTS devices. The dielectric properties of $LaAlO_3$, with a good lattice match to the YBCO film, are suitable for the application to HTS devices, but it is known that the $LaAlO_3$ substrate is twinned at a temperature of 435 °C. Although SAN and SAT substrates have low tanδ and no chemical reaction at the interfaces between the YBCO film and the substrate, the sintering temperature of these materials (>1600 °C) are too high to utilize in commercial applications.[4] Thus, the appropriate substrate materials which satisfy all the requirements for the HTS devises such as filters have not been developed. In addition, the substrate materials should have low dielectric loss because the conduction loss of the YBCO film is negligible small. Therefore, the development of materials with high-Q, even higher than that of Al_2O_3, is important to the production of HTS filters with low loss. In recent work, the $Q{\cdot}f$ values of $Mg_4Nb_2O_9$ (MN) ceramics, the crystal structure[6] of which is similar to that of Al_2O_3, were found to be high (>200,000 GHz). However, the relationship between the microwave dielectric properties of $Mg_4(Nb_{2-x}Ta_x)O_9$ (MNT) solid solutions and the electronic state, such as bond strength and the ionicity of cations, has not been elucidated. Thus, in this paper, the microwave dielectric properties of MNT were investigated and the bond strength and ionicity of cations in MNT were calculated by using the discrete variational Xα (DV-Xα) method[7] in order to discuss the effect of the Ta substitution for Nb on the microwave dielectric properties.

2. Experimental

The $Mg_4(Nb_{2-x}Ta_x)O_9$ solid solutions were prepared by solid state reaction of MgO, Nb_2O_5 and Ta_2O_5

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powders with 99.9% purity. These powders were mixed with acetone and then calcined at 1200 °C for 20 h in air. The powders were ground with an organic binder (polyvinyl alcohol) and pressed into pellets with 12mm in diameter and 7 mm in thickness under a pressure of 100 MPa. Subsequently, the sintering of the pellets obtained was performed in the temperature range of 1350–1400 °C for 10 h in air and annealed at 850 °C in order to remove the strain on the surface of the pellets. X-ray powder diffraction (XRPD) was used to identify the synthesized materials. The microwave dielectric properties of the samples were evaluated according to the Hakki and Coleman method.[8] Variations in the bond strength of *M*–O (*M* = Nb and Ta) bonds and the net charges of the cations caused by the Ta substitution for Nb in MNT were simulated by using the DV-Xα method. Further details on the calculation method have been reported by Adachi et al.[9,10]

3. Results and discussion

Fig. 1 shows the XRPD patterns of MNT with $x = 0$, 0.5, 1, 1.5 and 2. The formation of impurity phase was not detected in these profiles over the whole composition range. The lattice parameters of MNT almost constant values over the whole composition range because the ionic radii of Nb^{5+} and Ta^{5+} ions were the same values (0.64 Å) under the same coordination number.[11]

The cluster model of $(Mg_{18}M_2O_{60})^{-74}$ (M = Nb and Ta), which was constructed on the basis of the refined lattice parameters and crystal structure parameters in this study, is shown in Fig. 2. In this crystal structure, the Ta^{5+}, Nb^{5+} and Mg^{2+} ions are surrounded by the six (O1 and O2) oxygen ions and these ions comprise the TaO_6, NbO_6, $Mg(1)O_6$ and $Mg(2)O_6$ octahedra. Cations are located in the centers of the octahedra.

The total density of states (DOS) and the energy level diagrams of MNT ($x = 0$ and 2) are shown in Fig. 3. In the energy level diagrams, the solid and dotted lines indicate the occupied and unoccupied molecular orbitals, respectively. The highest occupied molecular orbital (HOMO) levels lie on the top of the O-2*p* valence

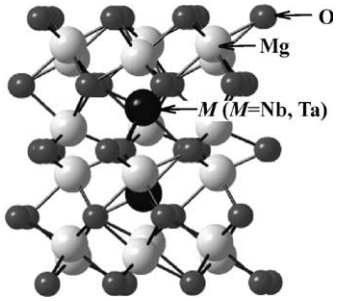

Fig. 2. Cluster model used in the calculation: $(Mg_4M_2O_{22})^{-26}$ (M = Nb and Ta).

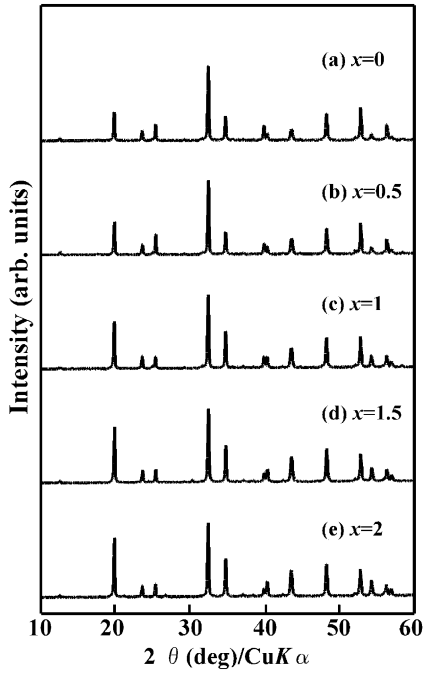

Fig. 1. XRPD patterns of $Mg_4(Nb_{2-x}Ta_x)O_9$ solid solutions with $x = 0$, 0.5,1, 1.5 and 2.

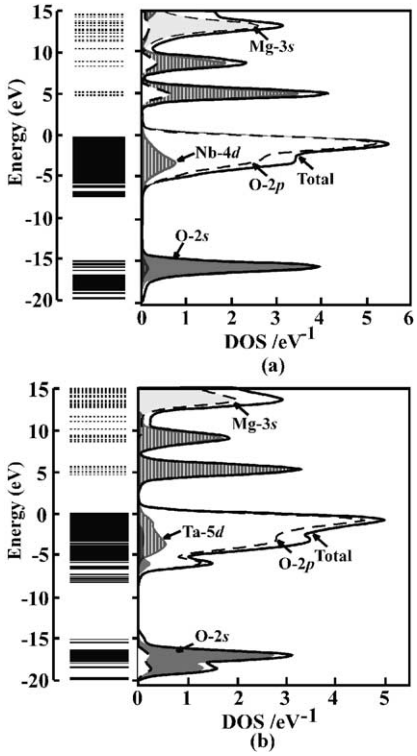

Fig. 3. Energy level diagrams and total and partial density states of (a) $Mg_4Nb_2O_9$, (b) $Mg_4Ta_2O_9$ by $(Mg_{18}M_2O_{60})^{-74}$ (M = Nb, Ta) cluster.

band; the occupied bands located from −7 to 0 eV and from −20 to −15 eV are mainly composed of O-2*p* and O-2*s* orbitals, respectively. The unoccupied orbitals located above 5 eV of MNT ($x=0$ and 2) are made up of Mg-3*s*, Nb-4*d* and Ta-5*d* orbitals as shown in Fig. 3. Significant amounts of Nb-4*d* and Ta-5*d* states are found in the O-2*p* band are found, suggesting that the Nb–O and Ta–O bonds are covalent. The net charges, which define the ionicity of atoms, for the Nb and Mg ions at $x=0$ were 2.55 and 1.81, respectively, and those of the Ta and Mg ions at $x=2$ were 2.55 and 1.82, respectively. Thus, the covalent interactions of the Nb–O and Ta–O bonds are considered to be strong and the Mg–O bond at $x=0$ and 2 may be an ionic interaction. From these results, it is considered that the Ta substitution for Nb in the $Mg_4(Nb_{2-x}Ta_x)O_9$ solid solutions exerts an influence on the average bond strength of the Nb–O and Ta–O bonds in the NbO_6 and TaO_6 octahedra. The bond order, which represents the strength of covalent Nb–O and Ta–O bonding in NbO_6 and TaO_6 octahedra, were determined in order to discuss the covalent interactions in more detail. The bond order of Ta–O bonds (0.180) is larger than that of the Nb–O bonds (0.133), whereas those of the Mg–O bonds in $Mg1O_6$ and $Mg2O_6$ did not change with Ta substitution for Nb. From these results, it was clarified that the Ta–O bond became more covalent than that of the Nb–O bond.

The influence of Ta substitution for Nb on the dielectric constants and quality factors of MNT as a function of compositions *x* are shown in Fig. 4. The ε_r values of MNT slightly decreased from 12.4 to 11.5 with increasing the compositions *x*; these values for MNT were approximately the same as those for Al_2O_3 or SAT.[4] The dielectric constants of the various microwave dielectric ceramics are known to be affected by ionic polarizability;[12] the ε_r values of MNT decreased by the Ta substitution for Nb as mentioned above. A similar result was reported for SAN and SAT; Guo et al.[4] suggest that the electronic changes which arose from the variations in the Nb–O and Ta–O bond strengths in the crystal structures of SAN and SAT may exert an influence on the decrease in the ε_r value. Thus, it is considered that the variations in the bond strength of Nb–O and Ta–O bonds estimated from the DV-Xα method relate to the dielectric constant of MNT. The observed ionic polarizabilities (α_{obs}) of MNT were estimated in order to clarify the effects of the Ta substitution for Nb on the dielectric constant by using the Clausius-Mosotti equation:

$$\alpha_{obs} = \frac{1}{b}[V_m(\varepsilon - 1)/(\varepsilon + 2)] \quad (1)$$

where ε and V_m represent the measured dielectric constants and molecular volumes which are determined from the unit cell volumes and formula number, *Z*, (in the case of MNT, $Z=2$) respectively, and constant value, *b*, is $4\pi/3$. The obtained α_{obs} values slightly decreased with increasing the compositions *x* as shown in Table 1 and exhibited the similar variations in the dielectric constant as shown in Fig. 4.

With increasing the composition *x*, the $Q{\cdot}f$ values of MNT increased dramatically from 194,000 to 347,000 GHz; these values of MNT at higher compositions that $x=1$ are comparable to those of Al_2O_3. Thus, it is considered that high $Q{\cdot}f$ with low dielectric constant of MNT is one of the suitable materials for the application to the HTS devices.

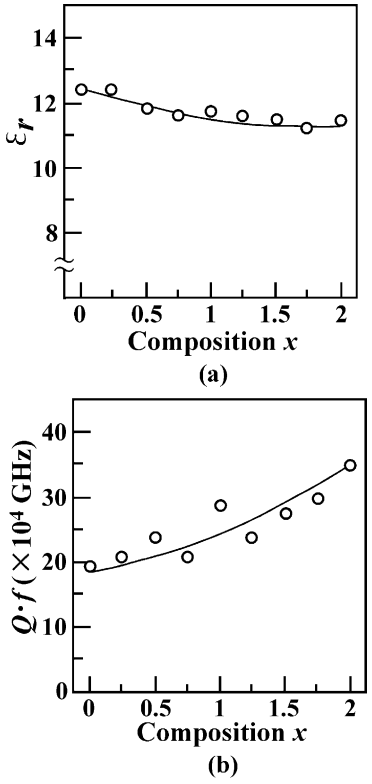

Fig. 4. Variations in the dielectric constant (ε_r) and quality factor ($Q{\cdot}f$) of $Mg_4(Nb_{2-x}Ta_x)O_9$ (MNT) solid solutions as a function of composition *x*.

Table 1
Molecular volumes and observed ionic polarizability of MNT

x	V_m (Å^3)	ε	$\alpha_{obs.}$ (Å^3)
0	161.5	12.4	30.5
0.5	161.8	11.9	30.3
1	161.8	11.8	30.2
1.5	162.0	11.5	30.1
2	162.1	11.5	30.1

x : Composition, V_m : Molecular volume, ε : Dielectric constant, α_{obs}.: Observed ionic polarizability.

The remarkable variations in the τ_f values of MNT were not recognized by the Ta substitution for Nb and these values ranged from −70 to −60 ppm/°C. Thus, it is considered that the additional improvement in the τ_f value is required for the dielectric resonator applications at high frequency.

4. Conclusion

The $Mg_4(Nb_{2-x}Ta_x)O_9$ (MNT) solid solutions were synthesized and the microwave dielectric properties of MNT were investigated. The bond strength of the Nb–O and Ta–O bonds in MNT were investigated by using the discrete variatinal Xα (DV-Xα) method in order to clarify the relationship between the microwave dielectric properties and the crystal structure. The Ta–O and Nb–O bonds exhibited the covalent interaction and the net charges of Ta and Nb ions were approximately same values in MNT. The decrease of the observed ionic polarizabilities of MNT may depend on the bond strength of Ta–O and Nb–O bonds. The dielectric constants of MNT ranged from 12.4 to 11.5 and these values slightly decreased with increasing the composition *x;* this result is considered to relate to the decrease in the observed ionic polarizabilities of MNT. The quality factors of MNT vary from 193 000 to 347 000 GHz; the Ta substitution for Nb is effective in improving the $Q{\cdot}f$ values.

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