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Influence of Zn and Ni substitutions for Mg on dielectric properties of $(Mg_{4\text{-}x}M_x)(Nb_{2-y}Sb_y)O_9$ ($M = Zn$ and Ni) solid solutions

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Abstract

The effects of M substitution for Mg and Sb substitution for Nb in the $(Mg_{4-x}M_x)(Nb_{2-y}Sb_y)O_9$ ($M = Zn$ and Ni) ($x = 0$–2, $y = 0$–1.5) solid solutions on the microwave dielectric properties were investigated in this study. The limits of both $(Mg_{4-x}M_x)Nb_2O_9$ ($M = Zn$ and Ni) solid solutions were approximately $x = 2$, whereas that of $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions was approximately $y = 1.5$. As for the Ni and Zn substitutions for Mg, the quality factor, $Q{\cdot}f$ values of the $(Mg_{4-x}M_x)Nb_2O_9$ ($M = Zn$ and Ni) solid solutions decreased from 192 268 to 28 400GHz with increasing composition x from 0 to 2. On the other hand, the $Q{\cdot}f$ values of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions were remarkably improved by the Sb substitution for Nb; the highest $Q{\cdot}f$ value of 285 423 GHz was obtained at $y = 1$. It was found that an increase in the $Q{\cdot}f$ values of $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions may related to the grain size decreased which is opposite to general results and this relation is consistent with that of Al_2O_3.

Keywords: Dielectric properties; Grain size; Niobates; Powders–solid state reaction

1. Introduction

With the recent progress in microwave components, the development of high-Q materials with a variety of dielectric constants (ϵ_r) and small temperature coefficient of resonant frequency (τ_f) have been required for application as a dielectric resonator, a high-temperature superconductor (HTSC) filter and as the substrate for integrated circuits. The Al_2O_3 substrate is widely used for the integrated circuits because of its suitable dielectric properties for the applications ($\epsilon_r \doteqdot 10$, $\tan\delta < 10^{-4}$).[1] Thus, the development of new dielectric ceramics with low dielectric loss, which are comparable to that of the Al_2O_3 substrate, is required. The $Mg_4Nb_2O_9$ compound with $\tan\delta$ value lower than 10^{-4} which has a corundum-type crystal structure,[2] have been developed in our previous work.[3] In this study, the effects of M ($M = Zn$ and Ni) substitutions for Mg and the Sb substitution for Nb on the microwave dielectric properties were investigated. Thus, the $(Mg_{4-x}M_x)(Nb_{2-y}Sb_y)O_9$ ($M = Zn$ and Ni) solid solutions were synthesized and the relationships among crystal structure, microstructure and microwave dielectric properties of the solid solutions were discussed.

2. Experimental

The $(Mg_{4-x}M_x)(Nb_{2-y}Sb_y)O_9$ ($M = Zn$ and Ni) solid solutions were synthesized by the conventional solid-state reaction method. High purity (>99.9%) MgO, ZnO, NiO, Nb_2O_5 and Sb_2O_5 powders weighed on the basis of the stoichiometric composition were mixed and calcined at 1000 °C for 20 h in air. These calcined powders were milled and mixed with an organic binder, and then pressed into a pellet with 12 mm in diameter and 7 mm in thickness under the pressure of 100 MPa. Subsequently, these pellets were sintered at the various temperatures ranging from 1200 to 1500 °C for 10 h in air. The phases of the samples synthesized were identified by X-ray powder diffraction (XRPD). The microstructure was investigated by using the scanning electron microscopy

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(SEM) and the energy dispersive X-ray (EDX). The lattice parameters and crystal structure of the samples were evaluated according to the Rietveld analysis[4,5] and the least squares method. The microwave dielectric properties were determined by Hakki and Coleman's method.[6]

3. Results and discussion

3.1. $(Mg_{4-x}M_x)Nb_2O_9$ (M = Zn and Ni) solid solutions

Figs. 1 and 2 show the XRPD patterns of $(Mg_{4-x}Zn_x)Nb_2O_9$ and $(Mg_{4-x}Ni_x)Nb_2O_9$ solid solutions, respectively. The XRPD results show that the $(Mg_{4-x}Zn_x)Nb_2O_9$ ceramics were single phase at the compositions x ranging from 0 to 2, whereas three phases, i.e., ZnO, $ZnNb_2O_6$ and $Zn_3Nb_2O_8$, coexisted at $x = 4$ as shown in Fig. 1(c). The XRPD results of $(Mg_{4-x}Ni_x)Nb_2O_9$ ceramics showed the presence of NiO and $NiNb_2O_6$ at $x = 4$ instead of $Ni_4Nb_2O_9$ compound. These results suggest that both the limits of $(Mg_{4-x}Zn_x)Nb_2O_9$ and the $(Mg_{4-x}Ni_x)Nb_2O_9$ solid solutions may be the compositions between $x = 2$ and $x = 4$. The influence of the differences in ionic radii of Mg^{2+}, Zn^{2+} and Ni^{2+} ions on the crystal structure, the lattice parameters of the $(Mg_{4\text{-}x}M_x)Nb_2O_9$ solid solutions are determined as shown in Fig. 3. Further details on the crystal structure of the ceramics at $x = 0$, i.e., that of the $Mg_4Nb_2O_9$ compound were reported by Kumada et al.[2] It has a trigonal structure (S.G. $P\bar{3}c1$) with the lattice parameters, $a = 5.1612$Å and $c = 14.028$Å. The lattice parameters of the ceramics at $x = 0$ obtained in this study coincided with those values. The lattice parameters, a and c, of the $(Mg_{4-x}Zn_x)Nb_2O_9$ solid solutions were increased linearly with increasing the compositions x ranging from 0 to 2 and then these values substantially saturated at the composition $x = 2$. Moreover, in the case of Ni substitution for Mg, the lattice parameter a was decreased with increasing the compositions x while that of c was increased as shown in Fig. 3. The variations in the lattice parameters of each sample depend on the differences in the ionic radii of Mg^{2+}(0.72Å), Zn^{2+}(0.74Å) and Ni^{2+}(0.68Å) ions under the same coordination number (C.N. = 6 for the MgO_6 and MO_6 octahedra). The microwave dielectric properties of $(Mg_{4-x}M_x)Nb_2O_9$ (M = Zn and Ni) (x = 0–2) solid solutions are listed in Table 1. The $Q{\cdot}f$ values of the $(Mg_{4-x}M_x)Nb_2O_9$ (M = Zn and Ni) ceramics deteriorated with the M substitutions for Mg. The τ_f values of the $(Mg_{4-x}Zn_x)Nb_2O_9$ solid solutions were decreased from −70.5 to −95.8 ppm/°C, and those of $(Mg_{4-x}Ni_x)$-Nb_2O_9 solid solutions were slightly increased from −70.5 to −66.5ppm/°C.

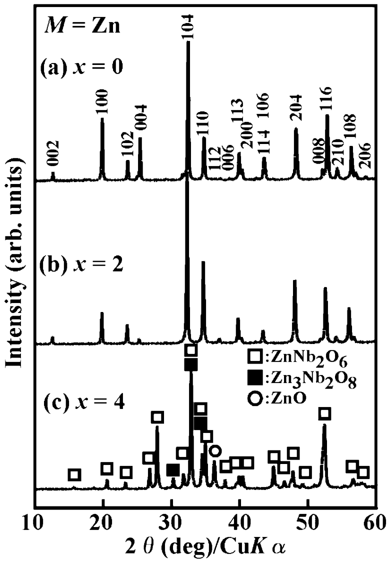


Fig. 1. XRPD patterns of the $(Mg_{4-x}Zn_x)Nb_2O_9$ solid solutions.

3.2. $Mg_4(Nb_{2-y}Sb_y)O_9$ (y = 0–1.5) solid solutions

From the XRPD results of the Sb-substituted $Mg_4(Nb_{2-y}Sb_y)O_9$ (y = 0–1.5) solid solutions, no secondary phase was detected in the compositions ranging from 0 to 1.5. The lattice parameters and unit cell volumes of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions were decreased lineally because the ionic radius of Sb^{5+} is smaller than that of Nb^{5+} and the lattice parameters in the compositions y ranging from 0 to 1.5 were shown in Table 2. The microwave dielectric properties of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions are shown in Table 3. The ϵ_r values of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions varied from 12.4 to 10.0. The $Q{\cdot}f$ values of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions were extremely increased from 192 268 to 285 423 GHz, depending on the compositions y. The highest value, i.e., $Q{\cdot}f = 285\,423$ GHz, was obtained at $y = 1$. Thus, it was found that the Sb substitution for Nb is effective in increasing the $Q{\cdot}f$ values of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions.

Table 1
Dielectric properties of $(Mg_{4-x}M_x)Nb_2O_9$ solid solutions

M	x	D_r%	ε_r	$Q{\cdot}f$ (GHz)	τ_f (ppm/°C)
	0	92.8	12.4	192 268	−70.5
Zn	0.5	95.0	13.7	105 383	−76.9
	1.0	93.8	14.2	76 273	−84.0
	1.5	94.8	15.3	61 612	−86.7
	2.0	89.8	15.4	52 241	−95.9
Ni	0.5	93.7	12.8	84 270	−68.3
	1.0	92.6	12.6	44 025	−69.1
	1.5	90.3	12.1	33 447	−66.5
	2.0	92.3	11.1	28 440	−69.6

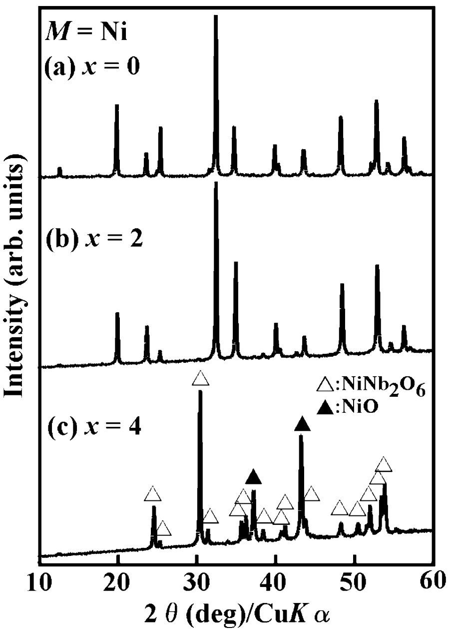


Fig. 2. XRPD patterns of the $(Mg_{4-x}Ni_x)Nb_2O_9$ solid solutions.

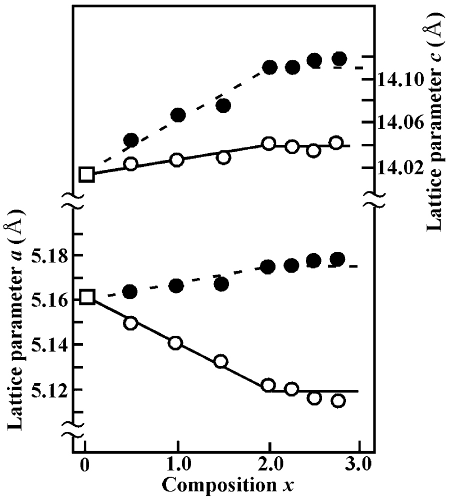


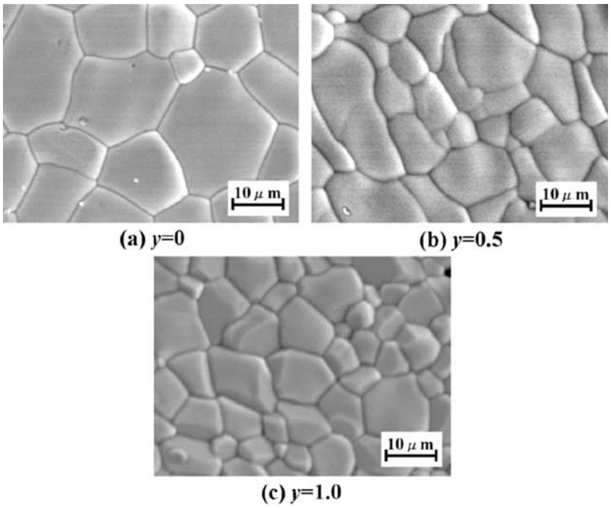
Fig. 3. The lattice parameters of the $(Mg_{4-x}M_x)Nb_2O_9$ solid solutions.

Table 2
Lattice parameters and unit cell volumes of $Mg_4(Nb_{2-y}Sb_y)O_9$(y = 0–1.5) solid solutions

y	Lattice parameter (Å)		Unit cell volume
	a	c	(Å^3)
0	5.1636(3)	14.0273(6)	323.90
0.25	5.1644(2)	14.0200(4)	323.71
0.5	5.1638(2)	14.0114(4)	323.56
0.75	5.1635(1)	14.0018(3)	323.34
1.0	5.1642(1)	13.9952(3)	323.30
1.5	5.1653(1)	13.9860(2)	322.83

Table 3
Dielectric properties of $Mg_4(Nb_{2-y}Sb_y)O_9$(y = 0–1.5) solid solutions

y	D_r(%)	ε_r	$Q{\cdot}f$ (GHz)	τ_f(ppm/°C)
0.25	96.2	12.2	164854	−66.5
0.5	97.2	11.9	186496	−69.2
0.75	96.9	11.07	227904	−69.9
1.0	93.0	10.0	285423	−66.2
1.5	85.0	4.5	54686	−49.9



(a) y=0 (b) y=0.5 (c) y=1.0

Fig. 4. FE-SEM micrographs (SEI) of the $Mg_4(Nb_{2-y}Sb_y)O_9$ (y = 0–1) solid solutions at (a) y = 0, (b) y = 0.5 and (c) y = 1.0 sintered at 1400 °C for 10 h.

However, The samples with compositions higher than y = 1, the microwave dielectric properties of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions were decreased because of the Sb vaporization. Thus, in order to clarify the relationship between the microstructure and an increasing in the $Q{\cdot}f$ values caused by the Sb substitution for Nb. The FE–SEM micrographs (SEI) of $Mg_4(Nb_{2-y}Sb_y)O_9$ (y = 0–1) solid solutions sintered at 1400 °C for 10 h in air are shown in Fig. 4. Though the grain sizes of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions were decreased with increasing compositions y, the formation of porosity and impurities were not observed in the compositions y ranging from 0 to 1. In general, it is known that the $Q{\cdot}f$ values of the ceramics strongly depend on the ordering, morphological changes such as porosity, grain size, impurities and grain boundary.[7] As for the grain size of the other materials it has been observed that as grain size increases the loss is reduced, in contrast to the results of Al_2O_3[7] and the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions presented here. Fig. 5 is the plot of the tanδ and average grain size against its compositions y. Both variations in the grain size and the tanδ exhibit the similar tendencies with increasing the compositions y. Thus, it was found that the decrease in the grain size relates with the increasing $Q{\cdot}f$ values.

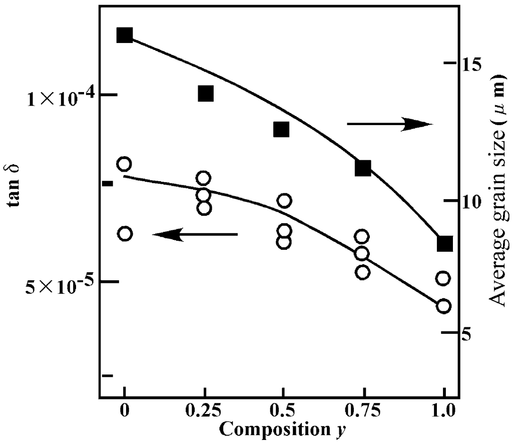


Fig. 5. The tanδ and the average grain sizes of the $Mg_{.4}(Nb_{2-y}Sb_y)O_9$

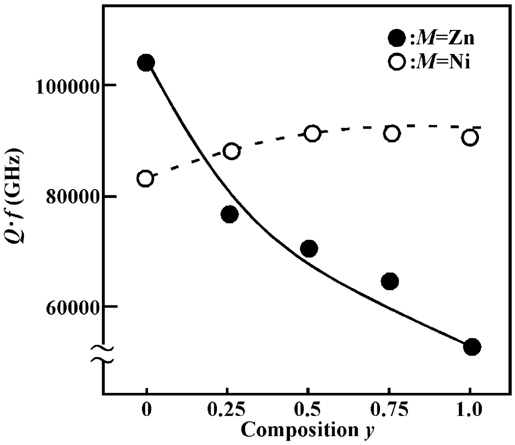


Fig. 6. The $Q{\cdot}f$ values of the $(Mg_{.3.5}M_{0.5})(Nb_{2-y}Sb_y)O_9$ ($y=0$–1) solid solutions as a function of composition y.

3.3. $(Mg_{3.5}M_{0.5})(Nb_{2-y}Sb_y)O_9$ (M = Zn and Ni) ($y=0-1$) solid solutions

In the case of the M substitution for Mg, the $Q{\cdot}f$ value of the $(Mg_{4-x}M_x)Nb_2O_9$ solid solutions were decreased with increasing the composition x as mentioned above. However, the $Q{\cdot}f$ value of the samples at $x=0.5$ are higher than those of the RAlO$_3$ and $R(Mg_{1/2}Ti_{1/2})O_3$ ceramics.[8,9] Moreover, the $Q{\cdot}f$ values of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions were improved by the partial Sb substitution for Nb.Thus, the $(Mg_{3.5}M_{0.5})$ $(Nb_{2-y}Sb_y)O_9$ (M = Zn and Ni) ($y=0$ to 1) solid solutions were investigated. The $Q{\cdot}f$ value of the $(Mg_{3.5}M_{0.5})(Nb_{2-y}Sb_y)O_9$ solid solutions are shown in Fig. 6. The quality factor of the Ni-substituted $(Mg_{3.5}Ni_{0.5})(Nb_{2-y}Sb_y)O_9$ solid solutions were slightly increased, whereas those of the Zn-substituted $(Mg_{3.5}Zn_{0.5})(Nb_{2-y}Sb_y)O_9$ solid solutions were extremely decreased with increasing the composition y. The decreases in the $Q{\cdot}f$ value of the $(Mg_{3.5}Zn_{0.5})(Nb_{2-y}Sb_y)O_9$ were attributed to the decrease in the density caused by Zn vaporization.

4. Conclusion

The microwave dielectric properties of the $(Mg_{4-x}M_x)(Nb_{2-y}Sb_y)O_9$ (M = Zn and Ni) solid solutions were investigated; the limits of the $(Mg_{4-x}M_x)Nb_2O_9$ and the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions were $x=2$ and $y=1.5$, respectively. The quality factors of the $(Mg_{4-x}M_x)Nb_2O_9$ solid solutions were decreased by the M substitutions for Mg, whereas those of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions were remarkably increased from 192 268 to 285 423 GHz. It was found that the increase in the $Q{\cdot}f$ values of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions may be related to the grain size decrease which is opposite to general results and this relation is consistent with that of Al_2O_3. Moreover, the partial Sb substitution for Nb in the $(Mg_{3.5}M_{0.5})(Nb_{2-y}Sb_y)O_9$ solid solutions was also effective in increasing the $Q{\cdot}f$ values. The optimum microwave dielectric properties were obtained for the $Mg_4(Nb_{z-y}Sb_y)O_9$ solid solutions; the properties at $y=1$ are: $\epsilon_r=10.0$, $Q{\cdot}f=285\ 423$ GHz and $\tau_f=-66.2$ ppm/°C. The microwave dielectric properties of the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions are comparable to those of Al_2O_3; it is considered that the $Mg_4(Nb_{2-y}Sb_y)O_9$ solid solutions are one of the suitable substrate for the integrate circuits.

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