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Effect of Ni substitution on the microwave dielectric properties of cordierite

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Abstract

Cordierite ($Mg_2Al_4Si_5O_{18}$) is one of the silicates with low dielectric constant (ε_r), which are expected for good candidate of millimeter wave dielectrics. Microwave dielectric properties of Ni substituted cordierite solid solutions; $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ have been investigated. $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ with no secondary phase was obtained in the compositions x range from 0 to 0.1. It was found that a very small amount of Ni substitution was effectively increased of the quality factor (Qf) value and the highest Qf value of 99,110 GHz was obtained in the composition $x = 0.1$. No remarkable composition dependence of the temperature coefficient of resonance frequency (τ_f) was observed in the range from $x = 0.05$ to 0.2, On the other hand, τ_f abruptly shifted toward negative value with increasing x from 0.3 to 0.5. The correlation between the crystal structure of cordierite and the microwave dielectric properties, particularly Qf is discussed.

Keywords: Microwave dielectric properties; Silicate; Cordierite

1. Introduction

The recent advances in wireless communication technology has considerably increased the demand for microwave dielectric materials. The important characteristics required for a dielectric material are suitable dielectric constant (ε_r), high quality factor (Qf) and a nearly zero temperature coefficient of resonance frequency (τ_f). With the utilizable region of communication frequency expands to millimeter wave, a low ε_r is necessary to decrease the time for electronic signal transition. For this reason, microwave dielectric properties of silicates were investigated for millimeter wave applications. Silicates are composed of silica tetrahedron with approximately 55% of covalent bonding. Consequently, silicates reveal a low ε_r, which are expected for good candidate of millimeter wave dielectrics.

Among the systems of $MgO–Al_2O_3–SiO_2$, cordierite ($Mg_2Al_4Si_5O_{18}$) is characterized by a lower ε_r[1] and low coefficient of thermal expansion. The ε_r of cordierite ceramics prepared by standard solid state reaction method showed 6.19 and its τ_f exhibited -24 ppm/°C, which was more close to zero compared to other isotropic silicates. The crystal structure of cordierite consists of hexagonal rings formed by corner sharing $(Si,Al)O_4$ tetrahedron in the a–b plane. Because of the structural anisotropy, the cordierite reveals large anisotropy in coefficients of thermal expansion, characterizing by negative value for c-axis and positive value for a- or b-axis.[2]

This study investigated the effects of Ni substitution on the microwave dielectric properties of cordierite ceramics. In addition, we discussed the relationship between crystal structure and microwave dielectric properties, particularly Qf from the viewpoint of crystal structure refined by Rietveld analysis.

2. Experimental

Ni substituted cordierite solid solutions were synthesized by conventional solid-state reaction method. General formula $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ $(0 \le x \le 0.5)$ was synthesized using a mixed oxide route with raw materials of $Mg(OH)_2$ (purity of 99.98%), NiO (purity of 99.9%), Al_2O_3 (purity of 99.99%) and SiO_2 (purity of 99.9%). These powders were weighed in their appropriate ratios. Then they were mixed for 24 h in ethanol using ZrO_2 ball. The slurry was then dried calcined at 1300–1355 °C for 3 h in air. The calcined powders were re-

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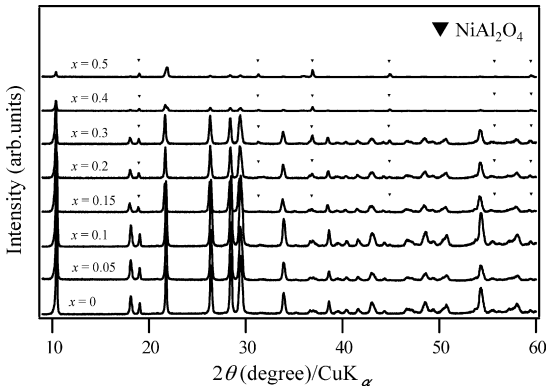

Fig. 1. XRD patterns of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ solid solutions.

milled for 24 h in ethanol. After drying and granulation, the powders were uniaxially pressed at 20 MPa into pellets. The pellets were cold isostatically pressed under pressure of 200 MPa and sintered at 1390–1440 °C for 2 h. Densities of the samples were measured by the Archimedes' method. Crystalline phases were identified by X-ray powder diffraction method (XRD; X'pert MPD, Philips) using Cu Kα radiation. Lattice constants were refined by the whole-powder-pattern decomposition (WPPF[3]) program. Crystal structure of the selected samples; $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ $(0 \le x \le 0.5)$ with x of 0, 0.1 were refined by using the Rietveld analysis (RIETAN-2000 program[4]). Rietveld analysis was performed using approximately 29,800 intensity data collected in the 2θ range from 3° to 152° in the composition $x = 0$ and approximately 25,200 intensity data collected in the 2θ range from 4° to 130° in the composition $x = 0.1$. Temperature factor of each ion determined by Gibbs[5] was used for this analysis. Lattice constants and the Rietveld refinement was carried out using a synchrotron radiation powder diffraction data obtained by a multiple 2θ detector system (MDS) at BL-4B2 in photon factory of the high energy accelerator research organization (PF-KEK), Tsukuba, Japan. Microwave dielectric properties were measured by Hakki and Coleman's method[6] in the $TE_{01\delta}$ mode using a network analyzer (HP-8757, Hewlett Packard). The τ_f was measured in the temperature range between 20 and 80 °C.

3. Results

XRD patterns of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ $(0 \le x \le 0.5)$ solid solutions are shown in Fig. 1. It can be seen that cordierite with no secondary phase was obtained in the compositions x range from 0 to 0.1, whereas the cordierite solid solutions at a higher compositions higher than $x = 0.15$ contained $NiAl_2O_4$ phases. This secondary phase remarkably increased with increasing x from 0.3. The lattice parameters of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ $(0 \le x \le 0.1)$ solid solutions were determined by the WPPF (Fig. 2). Slight composition dependence of lattice constants was observed. The lattice constants were decreased with increasing the composition x, because the ionic radii of Ni^{2+} is smaller than that of Mg^{2+}[7]. Structure parameters of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ $(x = 0, 0.1)$ were refined by the Rietveld method as listed in Table 1.

Table 1
$(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ $(x = 0)$, S.G. *Cccm* No.66 orthorhombic, $a = 17.063(2)$ Å, $b = 9.745(1)$ Å, $c = 9.337(1)$ Å, $V = 1552(1)$ Å^3

Atom	x	y	z	B (Å)
Mg	0.3358(2)	0	1/4	0.23
Al (1)	1/4	1/4	0.2505(5)	0.22
A1 (2)	0.0531(2)	0.3060(3)	0	0.25
Si (1)	0	1/2	1/4	0.2
Si (2)	0.1933(2)	0.0830(3)	0	0.26
Si (3)	0.1347(2)	0.7654(3)	0	0.23
O (1)	0.2394(2)	0.9024(4)	0.3766(4)	0.27
O (2)	0.0648(2)	0.5830(4)	0.3349(4)	0.24
O (3)	0.8223(2)	0.6922(4)	0.3602(5)	0.31
O (4)	0.0465(3)	0.7556(6)	0	0.25
O (5)	0.1304(4)	0.1760(6)	0	0.65
O (6)	0.1651(3)	−0.0723(6)	0	0.54

$R_{wp} = 29.63\%$, $R_I = 13.03\%$, $R_F = 3.56\%$, $S = 1.4753\%$.

Densities (ρ) and microwave dielectric properties of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ solid solutions as a function of composition x are shown in Fig. 3. Both ε_r and ρ monotonously increased with increasing composition x from 0 to 0.5. Qf was improved in the range of $0 < x \le 0.1$. The highest value of 99,110 GHz was obtained at the composition $x = 0.1$. The value decreased with increasing x from 0.15. No remarkable composition dependence of τ_f was observed in the ranges $x = 0.05$–0.2, On the other hand, τ_f abruptly shifted toward negative value in the compositions x higher than 0.3.

4. Discussion

The behavior of ε_r as a function of the composition was similar to that of ρ. ε_r depended on the sintering temperature, meaning that dense ceramics reveals the high ε_r[8]. Therefore, ε_r of the cordierite solid solutions are mainly affected by the bulk density. In order to investigate the origin of improved Qf value of Ni substituted cordierite, the crystal structure of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ $(x = 0.1)$ was compared to

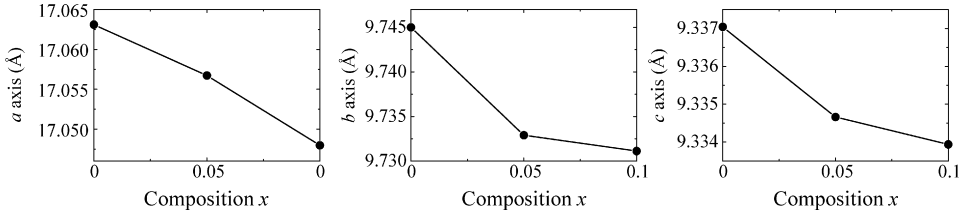

Fig. 2. Lattice constants of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ solid solutions as a function of composition x.

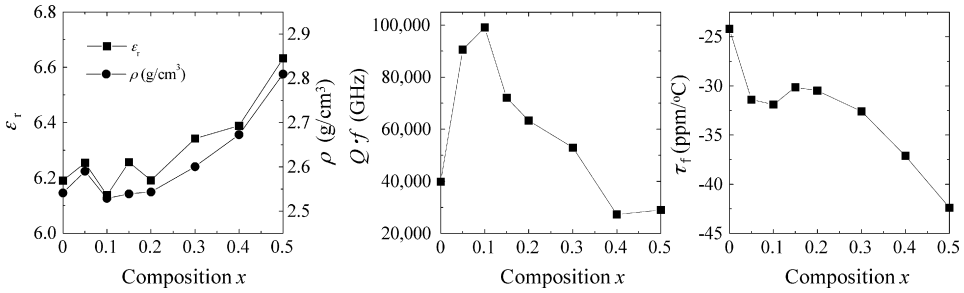

Fig. 3. Densities and microwave dielectric properties of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ solid solutions as a function of composition x.

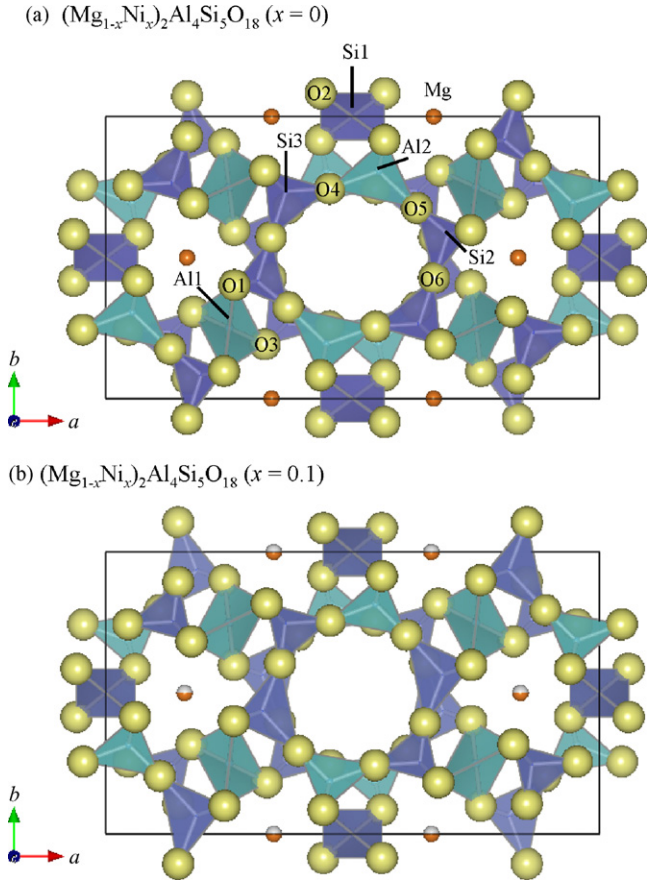

Fig. 4. Crystal Structures of (a) $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x=0$) and (b) $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x=0.1$).

that of the composition $x=0$. Fig. 4 illustrates the crystal structures obtained by using the crystal parameters listed on Tables 1 and 2. In this crystal structure, we focus on the symmetry of hexagonal rings composed of corner sharing $(Si,Al)O_4$ tetrahedron in the a–b plane. Fig. 4 shows that the rings of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ at the composition $x=0.1$ was close to equilateral hexagonal rings. In other word, the hexagonal rings of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ with $x=0.1$ are more isotropic than that of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ with $x=0$. We suggest that the slight change of the hexagonal ring cause improvement of Qf. It was considered that τ_f was influenced by slight variations of crystal structure in the range x of 0–0.1, since no secondary phase was observed. On the other hand, τ_f might be sensitive to the

Table 2
$(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x=0.1$), S.G. *Cccm* No.66 orthorhombic, $a=17.047(2)$ Å, $b=9.731(1)$ Å, $c=9.333(2)$ Å, $V=1548(1)$ Å^3

Atom	g	x	y	z	B (Å)
Mg	0.895(4)	0.3403(2)	0	1/4	0.23
Ni	0.104(4)	0.3403(2)	0	1/4	0.23
Al (1)	1	1/4	1/4	0.2473(5)	0.22
A1 (2)	1	0.0462(2)	0.3152(4)	0	0.25
Si (1)	1	0	1/2	1/4	0.2
Si (2)	1	0.1837(2)	0.0654(4)	0	0.26
Si (3)	1	0.1365(2)	0.7531(4)	0	0.23
O (1)	1	0.2405(3)	0.9008(4)	0.3759(5)	0.27
O (2)	1	0.0593(3)	0.5850(5)	0.3522(5)	0.24
O (3)	1	0.8262(2)	0.6830(5)	0.3424(5)	0.31
O (4)	1	0.0454(4)	0.7438(7)	0	0.25
O (5)	1	0.1096(4)	0.2055(7)	0	0.65
O (6)	1	0.1468(4)	−0.1061(6)	0	0.54

$R_{wp} = 26.54\%$, $R_I = 9.33\%$, $R_F = 2.88\%$, $S = 1.3802\%$.

secondary phase of $NiAl_2O_4$, in the range over $x=0.3$. According to other researchers, it has been reported that τ_f of $MgAl_2O_4$ and $ZnAl_2O_4$ show −75 and −79 ppm/°C, respectively[9,10]. We consider that τ_f of $NiAl_2O_4$ owing to same crystal structure, which results in the remarkable composition dependence.

5. Conclusion

Microwave dielectric properties of Ni substituted cordierite solid solutions; $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ have been investigated. Single phase cordierites were obtained in the compositions x range from 0 to 0.1. Secondary phase was observed at the compositions of larger than $x=0.3$. ε_r of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ solid solution slightly increased with increasing x. The highest Qf value of 99,110 GHz was obtained at the composition $x=0.1$. τ_f varied from −24 ppm/°C to approximately −30 ppm/°C in the ranges $x=0.05$–0.2 without the influence of secondary phase. From Rietveld analysis's result, hexagonal rings composed of corner sharing $(Si,Al)O_4$ tetrahedron in the a–b plane in the composition $x=0.1$ were more isotropic than that of $x=0$, suggesting that the Qf value was improved with the slight change of symmetry.

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