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Origin of improvement of *Q* based on high symmetry accompanying Si–Al disordering in cordierite millimeter-wave ceramics

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Abstract

Cordierite ($Mg_2Al_4Si_5O_{18}$) is a candidate for millimetre-wave dielectrics because of the low dielectric constant ε_r of 6.19. This study has been focused on the effects of substituting Ni for Mg in octahedron. In the case of octahedral substitution, the quality factor *Qf* of the Ni-substituted analogue with single phase was improved from 39,900 to 99,110 GHz up to $x = 0.1$ in $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$. Though Ni-substituted cordierite is single phase up to $x = 0.1$, compositions substituted with more than $x = 0.15$ have a secondary phase. The origin of improvement of *Q* comes from changing to the high symmetry which is from orthorhombic to hexagonal. Here, cordierite with orthorhombic crystal system *Cccm* (no. 66) transforms to indialite with hexagonal crystal system *P6/mcc* (no. 192). It is confirmed, based on the crystal structure obtained by Rietveld method, that the configuration of the $(Si_4Al_2)O_{18}$ ring changes to an equilateral hexagonal ring from a distorted ring according to the substitution Ni for Mg. The volumes and covalencies of SiO_4 and AlO_4 tetrahedra also change to similar values according to the substitution. The crystal structure shows a tendency to higher symmetry of a hexagonal ring accompanying Si–Al disordering. In this case, contribution of high symmetry to *Q* might be greater than that of ordering.

Keywords: Microwave; Millimeter-wave; Dielectric properties; Quality factor; High *Q*; Dielectric losses; Silicate; Cordierite; Indialite; Ordering; Disordering

1. Introduction

Millimeter-wave dielectric ceramics have been expected for wide applications in fields such as wireless communication, ultrahigh speed wireless LAN, Engineering Test Satellite (ETS) for high-speed mobile satellite communication and Pri-Crushed Safety (PCS) System on the Intelligent Transport System (ITS). The dielectric ceramics for telecommunication devices are with need to have three important characteristics: a low dielectric constant ε_r to reduce the delay time of electronic signal transmission, a high quality factor *Qf* to achieve high selectivity, and nearly zero temperature coefficient of resonant frequency τ_f for thermal stability of the device frequency. Silicates are one of the good candidates for the millimeter-wave dielectric ceramics, because of their low dielectric constant ε_r.[1,2] Among the silicates, i.e. forsterite (Mg_2SiO_4),[3] willemite (Zn_2SiO_4),[1,4] cordierite ($Mg_2Al_4Si_5O_{18}$),[5] diopside ($CaMgSi_2O_6$), mullite ($Al_6Si_2O_{13}$) and akermanite ($Ca_2MgSi_2O_6$), the cordierite ceramic is the one that has a very low dielectric constant ε_r of 6.19. The crystal structure of cordierite ceramic consists of distorted hexagonal rings formed by corner sharing $(Si,Al)O_4$ tetrahedra in the *a*–*b* plane, as shown in Fig. 1(a), which has orthorhombic crystal system of space group *Cccm* (no. 66).[6] The cordierite has a high temperature type polymorph that is indialite as shown in Fig. 1(c), with equilateral hexagonal rings, which has hexagonal crystal system of space group *P6/mcc* (no. 192). It possesses a low coefficient of thermal expansion.[7] It has been reported that the quality factor *Qf* value improved to 99,110 GHz in Ni-substituted cordierite ceramics.[5] The present study was conducted to study the effects of cation substitutions such as Ni on the microwave dielectric properties (ε_r, *Qf*, τ_f) of cordierite ceramics. *Qf* is particularly discussed from the crystal structure viewpoints. The improvement of *Q* originates from the transformation to high symmetry.

2. Experimental

Ni-substituted cordierite solid solutions were synthesized by conventional solid state reaction method. High purity $Mg(OH)_2$ (99.98%), NiO (99.9%), Al_2O_3 (99.99%) and SiO_2 (99.9%) were used as raw materials. These powders were weighed in their appropriate ratios with the general formula

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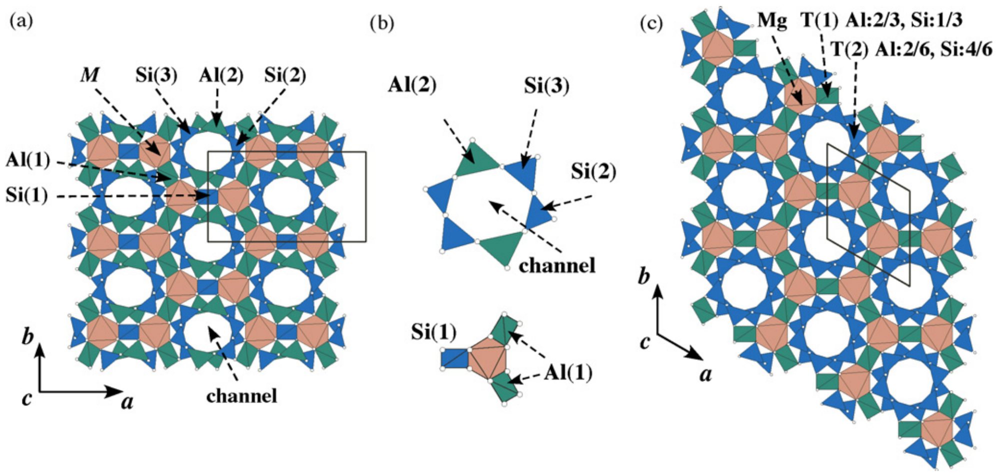

Fig. 1. Crystal structure of the low temperature form of cordierite with orthorhombic system *Cccm* (no. 66) (a), (Si,Al)O_4 ordered tetrahedra located in hexagonal rings and among the rings (b), and high temperature form indialite with hexagonal system, *P*6/*mcc* (no. 192) (c).

$(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x = 0$–0.5). The weighed powders were ball-milled in a polyethylene bottle with ZrO_2 balls for 24 h using ethanol as medium. Then the slurry was dried followed by calcination at 1355 °C for 3 h. The calcined powders were remilled for 24 h in ethanol. After drying and grinding, the powders were pelletized into a cylindrical compact by using an uniaxial press at 20 MPa and a cold isostatic press (CIP) at 200 MPa. Then the pellets were sintered at 1430–1440 °C for 2 h. The calcining and sintering atmospheres were in air. Densities of the samples were measured by the Archimedes' method. Crystalline phases were identified by X-ray powder diffraction (XRPD) method (X'pert MPD, Philips) using Cu Kα radiation. Lattice constants were refined by the whole-powder-pattern decomposition (WPPF) program.[8] Crystal structures of the selected samples were refined by using the Rietveld analysis (RIETAN-2000 program).[9] The lattice constants and the Rietveld refinement were carried out using a synchrotron radiation powder diffraction data obtained by a multiple two theta detector system (MDS, in PF-KEK, Tsukuba, Japan).[10] Microwave dielectric properties (ε_r, *Qf*, τ_f) were measured by Hakki and Coleman's method[11,12] in the TE_{011} resonant mode using a network analyzer (8720ES, Agilent). The τ_f was measured at the temperatures of 20 and 80 °C.

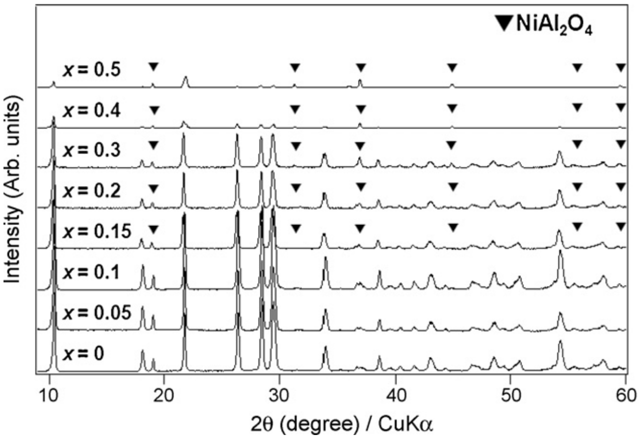

Fig. 2. Synchrotron XRPD patterns of Ni-substituted cordierite $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x = 0$–0.5).

3. Results and discussion

Fig. 2 shows the synchrotron XRPD patterns of samples substituted with $x = 0.05$–0.5 Ni. The result of $Mg_2Al_4Si_5O_{18}$ is also given as for comparison. It can be seen that no secondary phase

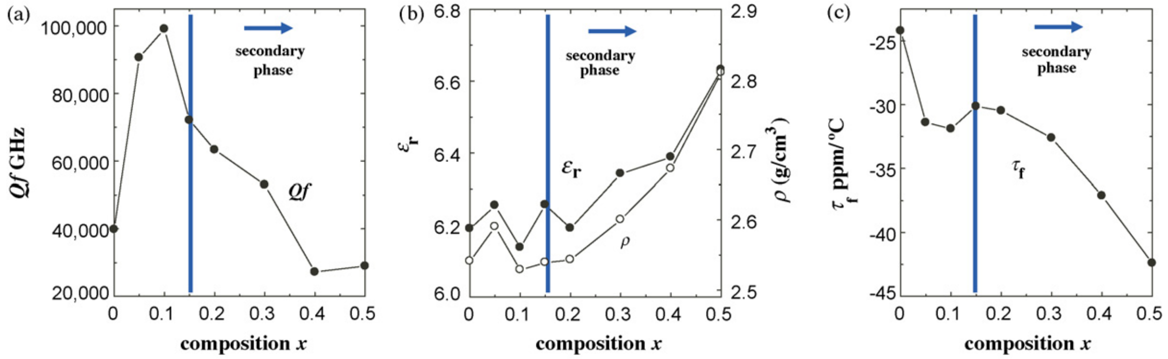

Fig. 3. Microwave dielectric properties of Ni-substituted $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x = 0$–0.5) ceramics. Quality factors *Qf* (a), dielectric constants ε_r and apparent densities ρ (b) and temperature coefficients of resonant frequency τ_f (c).

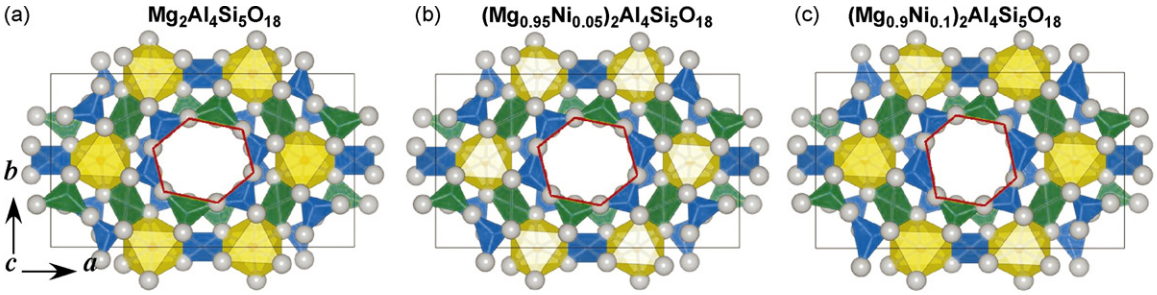

Fig. 4. Crystal structure on Ni-substituted cordierite $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x = 0$, 0.05, 0.1, 0.15).

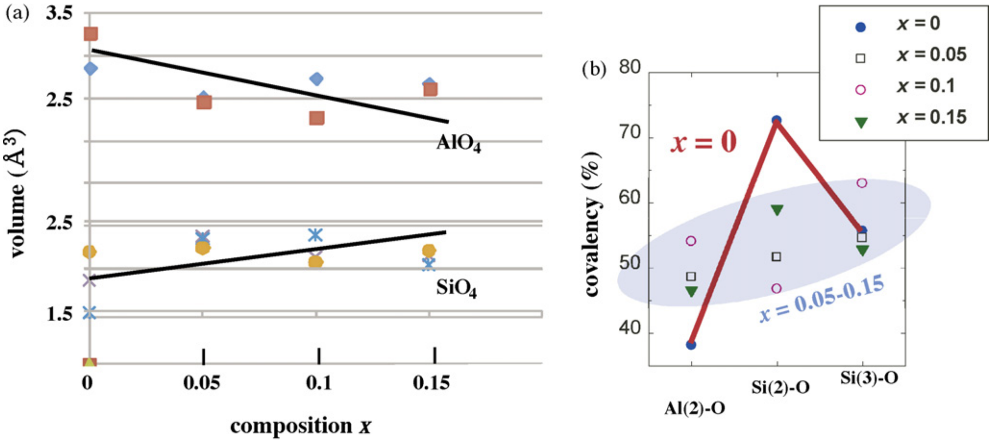

Fig. 5. Volumes (a) of SiO_4 and AlO_4, and covalencies (b) of Si and Al as a function of composition x on $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$.

was obtained up to $x = 0.1$ in Ni-substituted cordierite ceramics. The compositions substituted with more than $x = 0.15$ have a secondary phase of $NiAl_2O_4$.

Fig. 3 represents the microwave dielectric properties (Qf, ε_r, τ_f) of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x = 0$–0.5) ceramics. Quality factors Qf of Ni-substituted cordierite ceramics up to $x = 0.1$ were highly improved from 39,900 to 99,110 GHz. This suggests that the existence of secondary phases over $x = 0.15$ might reduce the Qf values. On the other hand, for the cation substitutions in all compounds, dielectric constants ε_r and the temperature coefficients of resonant frequency τ_f show tendency to shift toward high value (6.19–6.63) and negative value (−24 to −43 ppm/°C), respectively.

In order to clarify the origin of the improved Qf value of cation substituted cordierite ceramics, the crystal structure has been investigated by Rietveld analysis.[9] We focused on Ni-substituted cordierite ceramics, particularly the one without secondary phases. Fig. 4 illustrates the crystal structure of Ni-substituted cordierite ceramics with general formula $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ with compositions $x = 0$, 0.05 and 0.1. The structure parameters were refined by the Rietveld method as listed in Table 1. It can be seen that the symmetry of hexagonal rings composed of corner sharing $(Si,Al)O_4$ tetrahedra in the a–b plane of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ with composition $x = 0.1$ (see Fig. 4(c)) was obviously closed to equilateral hexagonal rings compared to $(Mg_{0.95}Ni_{0.05})_2Al_4Si_5O_{18}$ (Fig. 4(b)) and $Mg_2Al_4Si_5O_{18}$ (Fig. 4(a)).

Table 1
Refined structure parameters of $Mg_2Al_4Si_5O_{18}$ (a), $(Mg_{0.95}Ni_{0.05})_2Al_4Si_5O_{18}$ (b), and $(Mg_{0.9}Ni_{0.1})_2Al_4Si_5O_{18}$ (c). Space group: *Cccm* (no. 66), orthorhombic.

Atom	*x*	*y*	*z*	*B* (Å)
(a) $Mg_2Al_4Si_5O_{18}$ [a]				
M	0.3358(2)	0	1/4	0.23
Al(1)	1/4	1/4	0.2505(5)	0.22
Al(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	0.2394(2)	0.9024(4)	0.3766(4)	0.27
O	0.0648(2)	0.5830(4)	0.3349(4)	0.24
O	0.8223(2)	0.6922(4)	0.3602(5)	0.31
O	0.0465(3)	0.7556(6)	0	0.25
O	0.1304(4)	0.1760(6)	0	0.65
O	0.1651(3)	−0.0723(6)	0	0.54

Atom	*g*	*x*	*y*	*z*	*B* (Å)
(b) $(Mg0._{95}Ni_{0.05})_2Al_4Si_5O_{18}$ [b]					
Mg	0.938(3)	0.3369(2)	0	1/4	0.23
Ni	0.061(2)				
Al(1)	1	1/4	1/4	0.2505(4)	0.22
Al(2)	1	0.0511(2)	0.3132(3)	0	0.25
Si(1)	1	0	1/2	1/4	0.2
Si(2)	1	0.1907(2)	0.0774(3)	0	0.26
Si(3)	1	0.1340(2)	0.7607(3)	0	0.23
O	1	0.2486(3)	0.8957(4)	0.3576(4)	0.27
O	1	0.0642(3)	0.5837(3)	0.3552(4)	0.24
O	1	0.8278(2)	0.6872(3)	0.3545(4)	0.31

Table 1 (*Continued*)

Atom	x	y	z	B (Å)	
O	1	0.0420(3)	0.7490(4)	0	0.25
O	1	0.1199(3)	0.1930(5)	0	0.65
O	1	0.1638(3)	−0.0822(5)	0	0.54
(c) $(Mg_{0.9}Ni_{0.1})_2Al_4Si_5O_{18}$ [c]					
Mg Ni	0.895(4) 0.104(4)	0.3403(2)	0	1/4	0.23
Al(1)	1	1/4	1/4	0.2473(5)	0.22
Al(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	0.2405(3)	0.9008(4)	0.3759(5)	0.27
O	1	0.0593(3)	0.5850(5)	0.3522(5)	0.24
O	1	0.8262(2)	0.6830(5)	0.3424(5)	0.31
O	1	0.0454(4)	0.7438(7)	0	0.25
O	1	0.1096(4)	0.2055(7)	0	0.65
O	1	0.1468(4)	−0.1061(6)	0	0.54

[a] $a = 17.063(2)$ Å, $b = 9.745(1)$ Å, $c = 9.337(1)$ Å, $V = 1552(1)$ Å^3, $R_{wp} = 29.63$, $R_I = 13.03$, $R_F = 3.56$, $S = 1.4753$.

[b] $a = 17.056(2)$ Å, $b = 9.732(2)$ Å, $c = 9.334(2)$ Å, $V = 1549(1)$ Å^3, $R_{wp} = 16.39$, $R_I = 8.53$, $R_F = 2.90$, $S = 1.5671$.

[c] $a = 17.047(2)$ Å, $b = 9.731(1)$ Å, $c = 9.333(2)$ Å, $V = 1548(1)$ Å^3, $R_{wp} = 26.54$, $R_I = 9.33$, $R_F = 2.88$, $S = 1.3802$.

We have also calculated the volumes and covalency of SiO_4 and AlO_4 as shown in Fig. 5. On the cordierite $Mg_2Al_4Si_5O_{18}$ as shown in Fig. 1(a), SiO_4 and AlO_4 tetrahedra are located on the hexagonal rings and among sites of the rings as ordering as shown in Fig. 1(b); the volumes of these tetrahedra show different values as shown in Fig. 5(a). With increasing amount of Ni substitution in cordierite, those values (Fig. 5(a)) become similar and the rings have a tendency to become equilaterally hexagonal as shown in Fig. 1(c). The covalencies of Si and Al in the $(Si,Al)O_4$ tetrahedra also become similar as shown in Fig. 5(b). These phenomena mean the orthorhombic crystal system of cordierite (Fig. 1(a)) changes to the hexagonal one of indialite (Fig. 1(c)). The improvement of *Qf* should be based on the high symmetry instead of ordering by order–disorder transition.

4. Conclusions

Cordierite ceramics with Ni cation substitutions have been prepared by solid state reaction method. Quality factor *Qf* of Ni-substituted analogue with single phase up to 0.1 was improved to 99,110 GHz. Existence of secondary phases in samples with more than $x = 0.15$ might reduce the *Qf* values. The crystal structures of $(Mg_{1-x}Ni_x)_2Al_4Si_5O_{18}$ ($x = 0$, 0.05, 0.1) analyzed by Rietveld method are changing from orthorhombic crystal system of cordierite to hexagonal crystal system of indialite with high symmetry. As the volumes of SiO_4 and AlO_4 become similar and the covalencies of Si and Al are also similar, the crystal structure changes from ordered one with low symmetry to disordered one with high symmetry. The high *Qf* values are achieved by the high symmetry instead of ordering by order–disorder tradition.

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