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Microwave dielectric properties of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ (M = Zn and Mg) ceramics

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Abstract

The influence of M (M = Zn and Mg) substitution for Ni on the microwave dielectric properties and the crystal structure of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics was investigated in this study. The $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ (BTNZ) solid solutions showed a single phase in the composition range of 0–1, whereas the limit of $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ (BTNM) solid solutions was approximately $x = 0.75$; the lattice parameters of both solid solutions increased linearly, depending on the composition x. Although the dielectric constants (ε_r) of BTNZ were almost constant over the whole composition range, those of BTNM slightly decreased from 27.8 to 24.3; the decrease in the dielectric constant of BTNM is due to the change in relative density of the sample. The quality factors ($Q \times f$) of both solid solutions were improved by the M substitution for Ni; the maximum $Q \times f$ values of BTNZ and BTNM were 91729 and 93127 GHz, respectively. Moreover, the temperature coefficients of resonant frequency (τ_f) of BTNZ and BTNM varied from 33 to 40 ppm/°C and from 33 to 26 ppm/°C, respectively.

Keywords: Powder-solid state reaction; Grain size; Dielectric properties; Perovskites

1. Introduction

In the area of wireless communication systems, a variety of microwave dielectric ceramics have been extensively used as the resonator and the filter etc. Much attention has been paid to the compounds which have a complex perovskite-type structure in the commercially used microwave dielectric ceramics. Thus, most of recent researches have focused on the complex perovskite compounds, such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT);[1,2] moreover, Molodetsky et al.[3] have reported the microwave dielectric properties of 1:1 or 1:2 cation ordering perovskites such as $Ba(Y_{1/2}Nb_{1/2})O_3$ and $Ba(Co_{1/3}Nb_{2/3})O_3$ with a dielectric constant of 31 and 37. However, there is a considerable interest in the development of new dielectric ceramics because various kinds of dielectric ceramics may be required for application in wireless communication systems.

According to the crystal structure analysis of $Ba_8Ta_6NiO_{24}$ ceramic reported by Abakumov et al.,[4] it is found that the crystal structure of $Ba_8Ta_6NiO_{24}$ ceramic has a hexagonal perovskite structure with a space group of $P6_3cm$ in which Ta and Ni cations has the symmetric sixfold oxygen coordination in the TaO_6 and NiO_6 octahedra. The microwave dielectric properties of $Ba_8Ta_6ZnO_{24}$ ceramic was reported to have a ε_r of 29, a $Q \times f$ value of 68224 GHz and τ_f value of 29.4 ppm/°C.[5] However, since the $Q \times f$ value of $Ba_8Ta_6ZnO_{24}$ ceramic is lower than that of BZT ceramic, an improvement in the $Q \times f$ value of $Ba_8Ta_6ZnO_{24}$ ceramic is required for a commercial application. Moreover the τ_f value of $Ba_8Ta_6ZnO_{24}$ ceramic has been reported to possess a positive value; the improvement in τ_f value is also required. Thus, in order to improve these dielectric properties, the $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics (where M = Zn and Mg) were prepared; the effect of M substitution for Ni on the microwave dielectric properties and crystal structure of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics was investigated in this study.

2. Experimental method

Ceramic pellets of the $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics were prepared via the solid-state reaction method, using $BaCO_3$, Ta_2O_5, NiO, ZnO and MgO powders with high purity (>99.9%). These materials were weighed on the basis of stoichiometric composition of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics in the compositions ranging from 0 to 1.0. The powders were mixed with acetone and calcined at a temperature of 1150 °C for 10 h in air. The calcined powders were crushed and ground with an

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organic binder (polyvinyl alcohol). The ground powders were pressed into a pellet of 12 mm in diameter and 7 mm thick under a pressure of 100 MPa. Subsequently, the pellets were sintered in the temperature range of 1450–1650 °C for 10 h in air. The sintered pellets were polished and annealed at a temperature of 850 °C for 2 h in air. The phases of the synthesized materials were identified in terms of the X-ray powder diffraction (XRPD) with a Rigaku diffractmeter, using the Cu Kα radiation filtered through the Ni foil. The crystal structure and lattice parameters of the samples were refined using the Rietveld analysis program, i.e., RIETAN,[6,7] and the atomic distances of the polyhedra were determined. The XRPD data for the Rietveld analysis were obtained in terms of a step scanning method in the range of $10° \leq 2\theta \leq 90°$ with a step size of 0.03°/step and a counting time of 1.0 s. The dielectric constant and $Q \times f$ values at TE_{011} mode were evaluated by using the Hakki and Coleman method;[8] the temperature coefficient of resonant frequency was determined from the resonant frequencies at the two temperatures of 20 and 80 °C. The microstructure of the samples was investigated by using the field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDX).

3. Results and discussion

Figs. 1 and 2 show the XRPD patterns of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics in the composition range of 0–1. The XRPD results of $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ solid solutions showed that any secondary phase was not obtained over the whole composition range as shown in Fig. 1. From the XRPD profile of $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ceramic at $x = 1$, it was shown that three phases, $Ba(Mg_{0.33}Ta_{0.67})O_3$, $Ba_5Ta_4O_{15}$ and unknown phase were present as shown in Fig. 2, whereas the samples showed a single phase in the composition range from 0 to 0.75. Moreover, the peak shifts of the diffraction peak toward the lower 2θ values were observed with the Zn and Mg substitutions for Ni; these shifts were due to the differences in the ionic radii of Zn^{2+}, Mg^{2+} and Ni^{2+} ions. According to the ionic radii reported by Shannon,[9] those of Zn^{2+}, Mg^{2+} and Ni^{2+} ions with sixfold oxygen coordination are 0.74, 0.72 and 0.69 Å, respectively. The Zn and Mg substitutions for Ni lead to the increase in the lattice parameters of the solid solutions. Thus, in order to clarify the effect of Zn and Mg substitutions for Ni on the crystal structure of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ (M = Zn and Mg) ceramics, the lattice parameters of the ceramics are refined in terms of the Rietveld analysis; the results obtained in this study are shown in Fig. 3. The lattice parameters, a and c, of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics increased linearly, depending on the composition x; the increases in the lattice parameters depended on the differences in the ionic radii between the Ni and the M ions because the ionic radii of Zn^{2+} and Mg^{2+} ions are larger than that of Ni^{2+} ion as decreased above. Since the linear variations in the lattice parameters of the Zn-substituted samples over the whole composition range satisfy Vegard's rule, it is considered that the $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ceramics form a solid solution. Although the influences of M substitution for Ni on the lattice parameters were clarified, the interrelationships between the variations in the atomic distances of the polyhedra and the M substitution for Ni have not been evaluated. On the basis of the refined crystal structure parameters of the samples, the atomic distances in the polyhedra were determined in this study; the variations in the atomic distances of AO_6 (A = Ta, Ni, Zn and Mg) octahedra caused by the M substitution for Ni are shown in Fig. 4, as well as listed in Table 1. In the AO_6 octahedra, the atomic distance of A–O(4) was decreased by the Zn and Mg substitutions for Ni, whereas that of A–O(6) increased. Thus, the

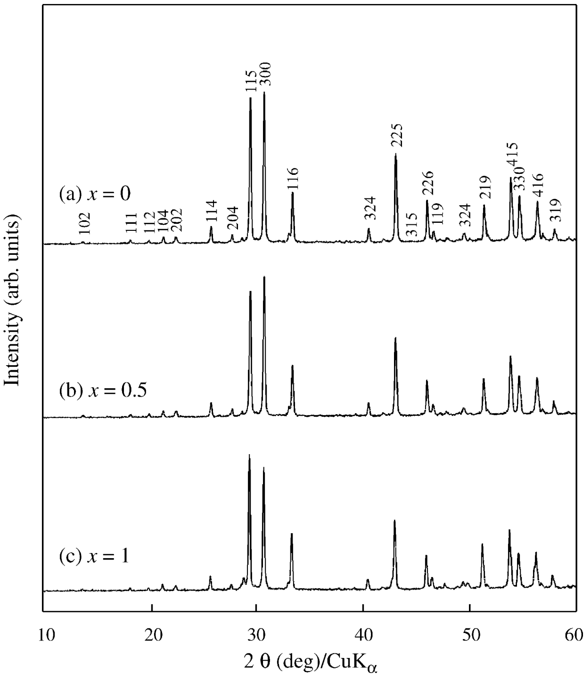


Fig. 1. XRPD patterns of $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ ($x = 0 \sim 1$) ceramics.

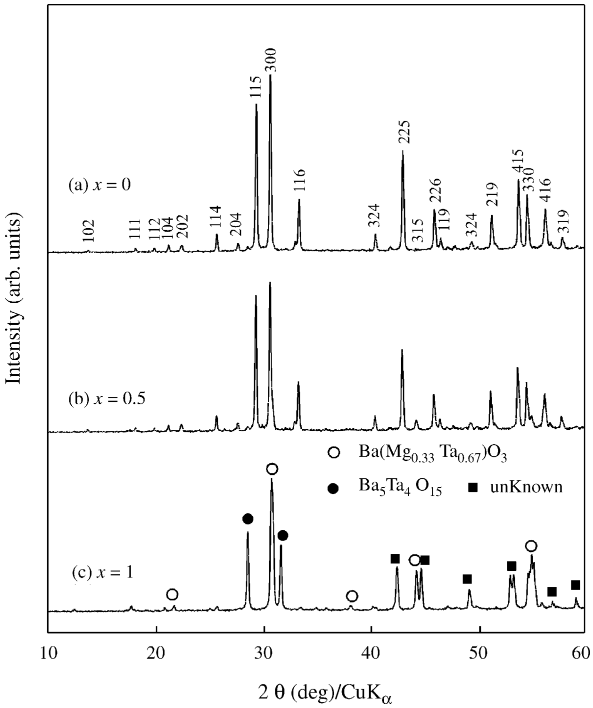


Fig. 2. XRPD patterns of $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ($x = 0 \sim 1$) ceramics.

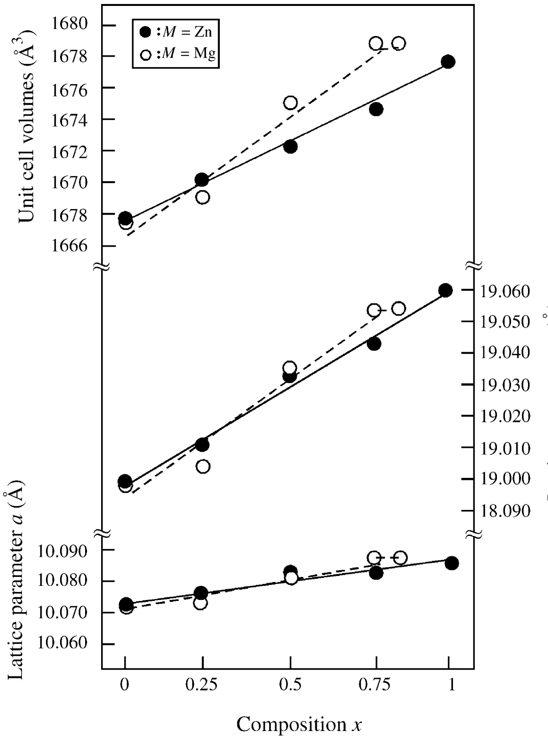
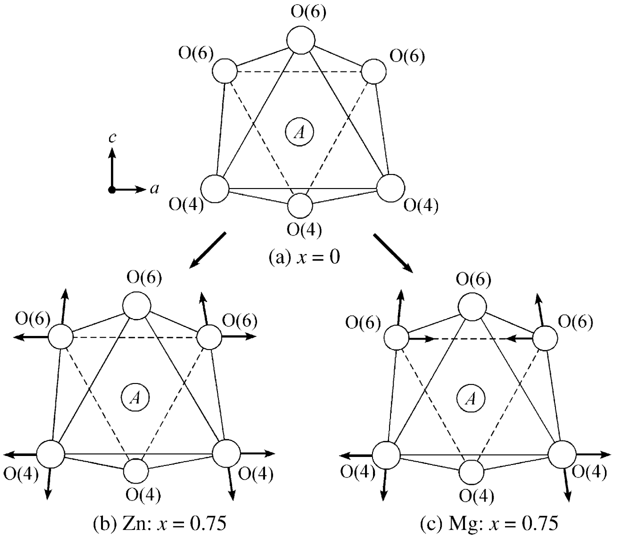


Fig. 3. Lattice parameters and unit cell volume of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ (M = Zn and Mg) solid solutions as a function of composition x.



(a) $x = 0$

(b) Zn: $x = 0.75$

(c) Mg: $x = 0.75$

Fig. 4. Variations in atomic distances in AO_6 (A = Ta, Ni, Zn and Mg) octahedra of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ (M = Zn and Mg) solid solutions caused by M substitution for Ni.

Table 1
Atomic distances in AO_6 (A = Ta, Ni, Zn and Mg) octahedra

Atomic distances (Å)	$x = 0$	$x = 0.75$ (Zn)	$x = 0.75$ (Mg)
A—O(4)	2.258	2.053	2.155
A—O(6)	1.952	2334	2.097
O(4)—O(4)	2.976	3.209	3.119
O(4)—O(6)	2.876	3.060	3.048
O(6)—O(6)	3.082	3.140	3.043

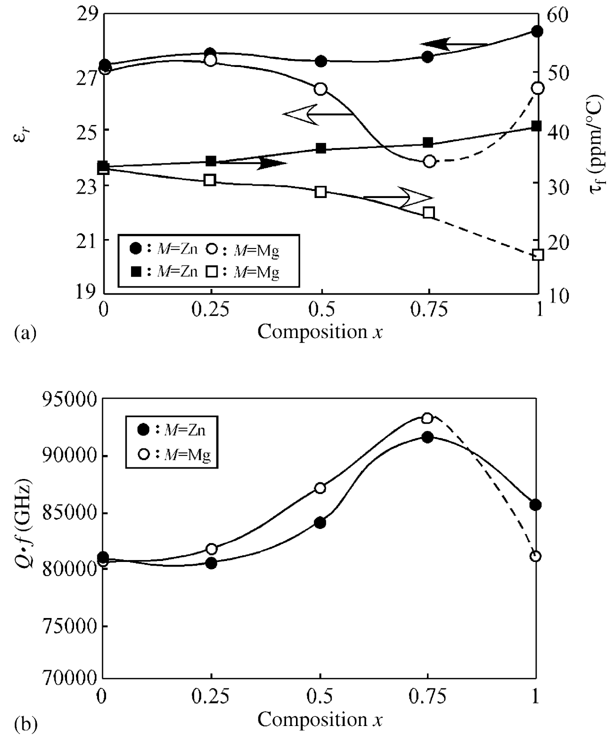


Fig. 5. Effect of M substitution for Ni on (a) dielectric constant (ε_r) and temperature coefficient of resonant frequency (τ_f), (b) quality factor ($Q \times f$) of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ (M = Zn and Mg) ceramics.

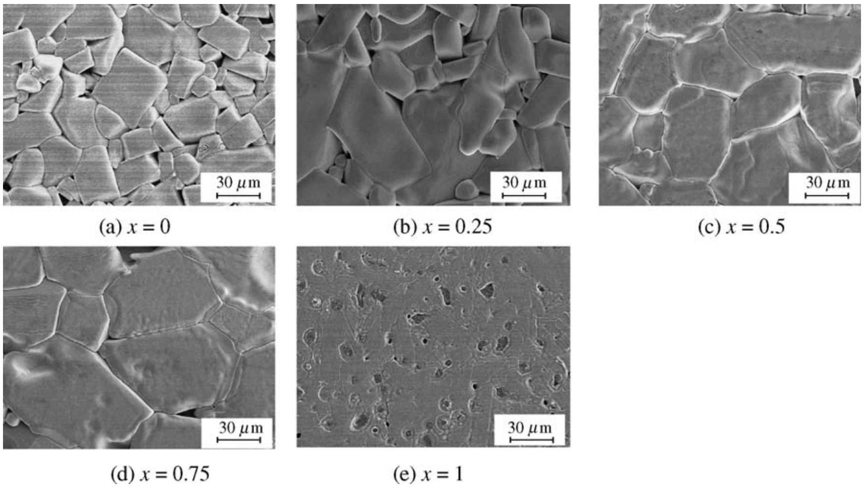
atomic distances of O(4)–O(4) and O(6)–O(6) in the direction of the a-axis and that of O(4)–O(6) in the direction of the c-axis are increased by the Zn substitution for Ni. Therefore, it is considered that the increases in the atomic distances of O(4)–O(4), O(6)–O(6) and O(4)–O(6) exert an influence on those of the lattice parameters a and c.

The effect of M substitution for Ni on the microwave dielectric properties of the $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics is shown in Fig. 5; the details on these values are also listed in Table 2. The ε_r values of the $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ and $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ceramics varied from 27.0 to 28.9 and from 24.4 to 28.8, respectively; any significant variations in the dielectric constant were not observed with the Zn substitution

Table 2
Microwave dielectric properties of Ba_8Ta_6 $(Ni_{1-x}M_x)O_{24}$ (M = Zn and Mg) solid solutions

x	D_r (%)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0	93.68	27.45	81758	33
M = Zn				
0.25	93.02	27.95	80631	34
0.5	92.45	27.35	83814	36
0.75	92.66	27.65	91729	37
1	94.01	28.85	85030	40
M = Mg				
0.25	95.63	27.87	81542	32
0.5	93.83	26.56	86821	31
0.75	89.39	24.32	93127	26
1	90.75	26.58	80947	18

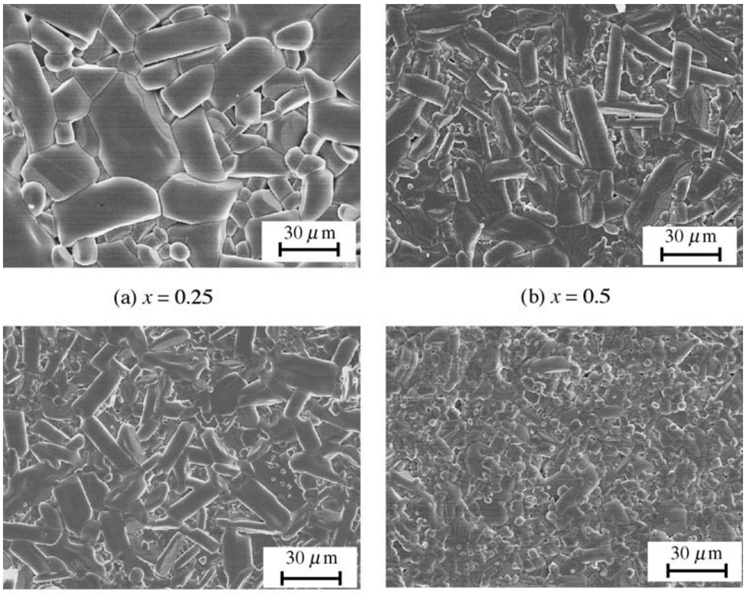
x: composition, D_r: relative density, ε_r: dielectric constant, $Q \times f$: quality factor, τ_f: temperature coefficient of resonant frequency.



(a) $x = 0$ (b) $x = 0.25$ (c) $x = 0.5$ (d) $x = 0.75$ (e) $x = 1$

Fig. 6. FE-SEM photographs of $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ ($x = 0 \sim 1$) ceramics.

for Ni, though the dielectric constant of Mg-substituted samples slightly decreased because of the decrease in the relative densities as listed in Table 2. Moreover, when comparing the dielectric constant of Mg-substituted sample at $x = 0.75$ with that of the sample at $x = 1$, the dielectric constant of the sample at $x = 1$ is higher than that of the sample at $x = 0.75$; this result is due to the formation of a secondary phase which is detected in XRPD patterns as described above. As for the influence of M substitution for Ni on the $Q \times f$ values, as shown in Fig. 5(b), the $Q \times f$ values of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramic increased with increased composition up to $x = 0.75$; therefore, the maximum $Q \times f$ values of $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ and $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ceramics were 91729 and 93127 GHz, respectively. Although the $Q \times f$ values of $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ and $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ceramics at the compositions higher than $x = 0.75$ decreased together, these results may be caused by the different phenomena. In Zn-substituted samples, the vaporization of Zn may have exerted an influence on the decrease in the $Q \times f$ value because of the higher sintering temperature, whereas the secondary phases which are identified from XRPD have a detrimental effect on the $Q \times f$ value in the Mg-substituted samples. The $Q \times f$ values of dielectric ceramics is generally known to be effected by defect concentration, impurity phase, grain size, porosity etc.[10,11] Thus, in order to clarify the relationship between the microwave dielectric properties and the morphological change in the samples caused by the M substitution for Ni, the microstructures of the samples have been investigated by using FE-SEM; the results are shown in Figs. 6 and 7. The grain size of the Zn-substituted samples increased with increasing the composition from 0 to 0.75, and then that of the sample decreased at $x = 1$ as shown in Fig. 6. As the increase of grain size obtained by the Zn-substituted samples leads to that of $Q \times f$ value in this



(a) $x = 0.25$ (b) $x = 0.5$ (c) $x = 0.75$ (d) $x = 1$

Fig. 7. FE-SEM photographs of $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ($x = 0 \sim 1$) ceramics.

study, the morphological changes may play an important role in improving $Q \times f$ value. In the case of Mg substitution for Ni, the column-like grain structure was observed; the volume of these grain structure increased with increasing composition x. Thus, it is considered that the morphological changes in the samples are due to the chemical composition of $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ceramics, though the $Q \times f$ values of the Mg-substituted sample in the single phase region increased as described above.

The plots of τ_f value versus composition x for $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramic are also shown in Fig. 5(a). The τ_f values of the samples with Zn substitution for Ni slightly increased from 33 to 40 ppm/°C, whereas those of Mg-substituted samples in the single phase region decreased from 33 to 26 ppm/°C, depending on the composition x. However, a near-zero τ_f value was not obtained by the M substitution for Ni in this study; a τ_f which is close to 0 ppm/°C is required for the commercial applications.

4. Conclusions

The $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ (M = Zn and Mg) ceramics were prepared by using the solid-state reaction method. From the XRPD patterns, it was found that the $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ solid solutions were a single phase over the whole composition range, whereas the limit of the $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ was approximately $x = 0.75$. The lattice parameters of the samples linearly increase, depending on the difference in the ionic radii of Mg^{2+}, Ni^{2+} and Zn^{2+} ions; it is considered that the increase in the lattice parameters of the samples closely relates with those of atomic distances of O(4)–O(4), O(6)–O(6) and O(4)–O(4) in AO_6 (A = Ta, Ni, Zn and Mg) octahedron.

As for the microwave dielectric properties of $Ba_8Ta_6(Ni_{1-x}M_x)O_{24}$ ceramics, although any remarkable variations in dielectric constant was not recognized by M substitution for Ni, the $Q \times f$ values of the samples increased in the composition range of 0–0.75. As a result, the maximum $Q \times f$ values of $Ba_8Ta_6(Ni_{1-x}Zn_x)O_{24}$ and $Ba_8Ta_6(Ni_{1-x}Mg_x)O_{24}$ ceramics were 91729 and 93127 GHz, respectively; the improvement in $Q \times f$ values may be related to the morphological changes in the samples caused by the Zn substitution for Ni and the composition dependence of the samples obtained by the Mg substitution for Ni, respectively.

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