Dielectric properties and crystal structure of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics

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The microstructure of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics was analyzed using X-ray diffractometry and scanning electron microscopy. The quality factor ($Q \times f$) values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics increase with increasing sintering temperature, with the maximum value obtained at 1375°C. The maximum values of electric permittivity (ϵ) and $Q \times f$ were 12.76 and 442,000 GHz, respectively, for $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics sintered at 1375°C for 4 h. Furthermore, the temperature coefficient of resonant frequency (τ_f) measured for $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics is $-54 \text{ ppm}/^\circ\text{C}$.

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1. Introduction

The rapid growth of wireless communication systems has led to an increasing demand for small-scale high-frequency resonators, filters, and antennas that can be operated in the GHz range.^{1)–3)} The unique electrical properties of ceramic dielectric resonators have revolutionized the microwave-based wireless communications industry by reducing the size and cost of filter and oscillator components in circuit systems.^{4)–5)} Many studies have focused on the development of dielectric materials with a high quality factor ($Q \times f$) and a near-zero temperature coefficient of resonant frequency (τ_f) for dielectric resonators and microwave device substrates due to their high efficiency and stable performance.

$\text{Mg}_4\text{Nb}_2\text{O}_9$ -based ceramics have been utilized as dielectrics in resonators, filters and antennas for communication, and radar and global positioning systems operating at microwave frequencies. Several corundum ceramics, such as the $\text{A}_4\text{M}_2\text{O}_9$ (where $\text{A} = \text{Mg}^{2+}$, Co^{2+} , Zn^{2+} , or Ni^{2+} , and $\text{M} = \text{Nb}^{5+}$ or Ta^{5+}) series, with negative τ_f values were reported by Kan et al.^{6)–8)} Corundum magnesium niobium ($\text{Mg}_4\text{Nb}_2\text{O}_9$) ceramics have attracted a lot of attention due to their high Q values and low dielectric constants, which arise from the isolation of the NbO_6 octahedron by the MgO_6 octahedron layer and the cation vacancy layer in comparison with perovskite titanates. In the corundum structure, each NbO_6 octahedral layer sandwiched by two layers of MgO_6 octahedron is a modified $\alpha\text{-Al}_2\text{O}_3$ structure. $\text{Mg}_4\text{Nb}_2\text{O}_9$ ceramics have a corundum structure, which is a trigonal crystal system with a space group of $(P\bar{3}c1)$.^{9)–10)} Many experiments have been conducted to study the preparation and properties of $\text{Mg}_4\text{Nb}_2\text{O}_9$ ceramics.^{11)–15)} Among them, $\text{Mg}_4\text{Nb}_2\text{O}_9$ ceramics have a high dielectric constant ϵ_r of ~ 12.9 , high quality factor $Q \times f$ of $\sim 210,000$ (at 11.7 GHz), and negative τ_f of $\sim -70 \text{ ppm}/^\circ\text{C}$.

In this paper, Ni^{2+} ions were doped into $\text{Mg}_4\text{Nb}_2\text{O}_9$ ceramics to form $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Nb}_2\text{O}_9$ ceramics. Because the ionic radius

of Mg^{2+} ($0.78 \text{ \AA}$) is similar to that of Ni^{2+} ($0.69 \text{ \AA}$), Ni^{2+} substitutes Mg^{2+} , improving the quality factor. Maximum values of electric permittivity (ϵ) and quality factor ($Q \times f$) were 12.76 and 442,000 GHz (at 12.99 GHz) for $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$ ceramic solid solutions and $\tau_f = -55.63 \text{ ppm}/^\circ\text{C}$ for ceramics sintered at 1375°C for 4 h. When Nb^{5+} was replaced by Ta^{5+} to form $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics, the microwave dielectric properties improved significantly. The effect of Ta^{5+} substituting Nb^{5+} on the structure and microwave dielectric properties of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics was investigated.

2. Experimental procedures

$(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramic powders were prepared using the solid-state reaction method by mixing individual high-purity oxides MgO , NiO , Ta_2O_5 , and Nb_2O_5 . The starting materials were stoichiometrically weighed after MgO was sintered at 800°C for 6 h to remove moisture and carbonates. The powders were then dry-mixed with an agate mortar and pestle and subsequently wet-mixed using distilled water. The calcination temperature was varied in the range of 900 to 1100°C. The calcined powder with the organic binder polyvinyl alcohol was pressed into pellets using a uniaxial press. The binder was then evaporated at 650°C for 12 h. Sintering was carried out at 1250–1425°C for 4 h. The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) patterns were collected using $\text{Cu K}\alpha$ radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2θ range of 20 to 60°. The microstructural observations and analysis of the sintered surface were performed using scanning electron microscopy (SEM, Philips XL-40FEG).

The bulk densities of the sintered pellets were measured using the Archimedes method. Microwave dielectric properties such as the electric permittivity and unloaded Q were measured at 6–12 GHz using the post-resonance method as suggested by Hakki and Coleman.¹⁶⁾ This method uses parallel conducting plates and coaxial probes in TE_{011} mode, where TE means transverse electric waves, the first two subscript integers denote the wave guide mode, and the third integer denotes the order of resonance in an increasing set of discrete resonant lengths. The temperature

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coefficient of resonant frequency was measured in the temperature range of 20–80°C. A system that combines an HP8757D network analyzer and an HP8350B sweep oscillator was employed in the measurements.

3. Results and discussion

The microwave dielectric properties of the $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 0-1.0$) ceramic system sintered at various temperatures for 4 h are shown in **Table 1**. **Figure 1** shows the room-temperature XRD patterns recorded from the $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 0-1.0$) ceramics sintered at 1375°C for 4 h. The single trigonal-structured $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics ($x = 0-1.0$), belonging to the space group $P3c1$ (165), were identified throughout the entire tested range. The position and relative intensity of the XRD peaks varied slightly, implying that the compounds tend to form a continuous solid solution. In order to confirm the formation of solid solution, the XRD patterns of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics sintered at various temperatures are shown in **Fig. 2**. These ceramics also belong to the space group $P3c1$ (165) and have a single trigonal structure without any secondary phases.

In order to confirm the formation of solid solution, the lattice parameters of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 0-1.0$) ($x = 0.1-1$) ceramics sintered at 1375°C were determined. The XRD patterns shown in **Fig. 2** are listed in **Table 2**. The lattice parameters were almost constant over the whole composition range because the ionic radii of Nb^{5+} and Ta^{5+} cations are similar.¹⁷⁾

SEM images of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics sintered at various temperatures for 4 h are shown in **Fig. 3**. The grain size increased with increasing sintering temperature. With sintering at 1375°C, the grain size growth was uniform and good microwave dielectric properties were obtained; however, with

sintering at above this temperature, the grain size growth was non-uniform. In order to confirm the formation of solid solution, typical energy-dispersive X-ray spectroscopy (EDX) data (**Table 3**) for spots A–C in **Fig. 3(g)** were obtained. All the grains under test showed a $(\text{Mg}_{0.95}\text{Ni}_{0.05}):(\text{Nb}_{1-x}\text{Ta}_x)$ ratio of 4:2, suggesting the formation of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics, which is consistent with the measured lattice parameters and XRD patterns. Moreover, the corresponding EDX data of the $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics sintered at temperatures of 1275–1425°C are shown in **Table 4**. The surface of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics contained Mg, Ni, Nb, Ta, and O ions, with no significant variance observed throughout the entire temperature range.

The relative density and electric permittivity of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics as functions of sintering temperature are shown in **Figs. 4** and **5**, respectively. Note that the relative density initially increased with increasing sintering temperature, reaching its maximum value at 1325°C ($0 < x < 0.03$), with increasing Ta^{5+} content and the saturated relative density sintering at 1375°C ($x = 1$) and then relative density decreased sintering at high temperature. The relative densities of all the specimens were above 94% of the theoretical density. The relative density increased with increasing sintering temperature due to increased Ta^{5+} content at higher sintering temperature. The increase in relative density mainly resulted from grain growth, as shown in **Fig. 3**.

The dielectric properties of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics are shown in **Fig. 5**. When the x value was increased from 0 to 1, the electric permittivity decreased from 13.84 ($x = 0$ sintered at 1225°C) to 12.76 ($x = 1$ sintered at 1375°C). The influence of Ta substitution for Nb on the dielectric constants of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics as a function of composition x was determined. The electric permittivity values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics slightly decreased with increasing value of x . These values for $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics are very similar to those for Al_2O_3 .

Table 1. Microwave dielectric properties of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics sintered at 1350°C

x	Bulk density (g/cm ³)	Relative density (%)	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0	4.34	97.17	13.84	226,403	−63.98
0.3	4.85	96.85	13.61	231,913	−60.41
0.5	5.18	96.40	13.31	255,577	−59.10
0.7	5.57	97.20	12.91	281,344	−56.88
1	6.15	97.66	12.76	442,092	−55.63

Fig. 1. XRD patterns of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 0.0-1.0$) ceramics sintered at 1375°C.

Fig. 2. XRD patterns of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics sintered at various temperatures.

Table 2. Lattice parameters and cell volume data for sintered $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics

x	0.1	0.3	0.5	0.7	1
a (Å)	5.1599	5.1598	5.1594	5.1593	5.1590
c (Å)	14.0208	14.0205	14.0204	14.0203	14.0109
V_m	323.43	323.25	323.21	323.19	323.15

Fig. 3. SEM images of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics sintered at various temperatures for 4 h.

Table 3. EDX data of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics for spots A–C in Fig. 3(g)

Spot	O K (at. %)	Mg K (at. %)	Ni K (at. %)	Ta M (at. %)
A	62.7	22.23	1.71	13.36
B	61.51	23.36	1.69	13.44
C	60.67	24.1	1.81	13.42

Table 4. EDX data of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics sintered at 1275 to 1425°C

Sintering temperature (°C)	O K (at. %)	Mg K (at. %)	Ni K (at. %)	Ta M (at. %)
1275	61.9	22.12	1.71	14.27
1300	60.89	23.41	1.65	14.05
1325	61.52	23.54	1.58	13.36
1350	60.58	23.1	1.57	14.75
1375	60.25	22.58	1.6	15.57
1400	61.02	22.05	1.59	15.34
1425	61.2	22.93	1.61	14.26

Figure 6 shows the $Q \times f$ values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics at various sintering temperatures as a function of the x value. With increasing x , the $Q \times f$ values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics increased dramatically from 226,000 GHz ($x = 0$, 1325°C) to 442,000 GHz ($x = 1$, 1375°C). The $Q \times f$ values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramic solid solutions for $x > 1$ are comparable to those of Al_2O_3 . Thus, with a high $Q \times f$ value and low dielectric constant, $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics are a suitable material for high-temperature superconductor devices. Relative density also plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials.

Fig. 4. Relative density of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics sintered at various temperatures.

As is well known, factors that affect the dielectric quality factor (Q) can be divided into two categories: intrinsic and extrinsic.^{18),19)} The intrinsic Q sets the upper limit value for a pure defect-free single crystal and can be quantitatively described by the well-known classical damped oscillator model in the microwave frequency range. In this model, when employing one-phonon absorption approximation, a roughly reciprocal relationship between $Q \times f$ and ϵ_r can be obtained:^{20)–25)}

$$Q \times f \propto f^{-1} \quad (1)$$

where the frequency f should be limited to the vicinity of the phonon engine frequencies, on the order of 10^{12} Hz at room temperature, to make the estimation valid. However, a series of experiments evidenced that the extrapolation of Eq. (2) from

Fig. 5. ϵ_r values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics sintered at various temperatures.

Fig. 6. $Q \times f$ values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics sintered at various temperatures.

microwave frequencies down to megawatt frequencies (1–4 orders of magnitude below the optical phonon engine frequency) at room temperature could also give a satisfying magnitude order of dielectric Q for well processed ceramics. The results, however, show that the dependence of $Q \times f$ on ϵ_r only yields $Q \times f \propto \epsilon_r^{-0.6}$, indicating a smoother increasing rate of $Q \times f$ value with ϵ_r compared with Eq. (2). The most probable reason for this phenomenon is associated with the extrinsic origins. As acknowledged by many authors, porosity in dielectrics has deleterious effects on dielectric $Q \times f$ values, whose influencing degree, however, varies with dielectric type. For low-dielectric $Q \times f$ ceramics with an order of magnitude of 10^3 , the effect of porosity on dielectric Q can be described as:^{20)–25)}

$$Q = Q_0(1 - 1.5P) \quad (2)$$

where Q_0 is the intrinsic dielectric Q measured from a microwave reflective spectrum and P is the porosity. However, for high $Q \times f$ ceramics with an order of magnitude of 10^5 – 10^6 GHz such as polycrystalline Al_2O_3 ceramic, even a small amount of porosity considerably reduces Q .^{20)–25)}

$$\frac{1}{Q} = (1 - P) \frac{1}{Q_0} + A' P \left(\frac{P}{1 - P} \right)^{2/3} \quad (3)$$

The τ_f values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ranged from -54 to -66 ppm/°C, as shown in Fig. 7. The temperature coefficient of resonant frequency, τ_f (TCF), can be defined as follows:

Fig. 7. Temperature coefficient values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics sintered at various temperatures.

$$\text{TCF} = -\alpha_1 - \frac{1}{2} \tau_\epsilon \quad (4)$$

where α_1 is the linear thermal expansion coefficient and τ_ϵ is the temperature coefficient of permittivity.

The remarkable variations in the τ_f values of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics were not recognized by the Nb^{5+} substitution for Ta^{2+} . These values ranged from -63.98 to -55.63 ppm/°C for ceramics sintered at 1350°C . Thus, an additional improvement in the τ_f value is required for high-frequency dielectric resonator applications.

4. Conclusion

The microwave dielectric properties of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ceramics were studied. $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$ ceramics exhibited a single phase with a corundum structure. The $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_9$ ($x = 1$) ceramics sintered at 1375°C for 4 h had a maximum $Q \times f$ of $\sim 442,000$ GHz, ϵ_r of ~ 12.76 , and τ_f of ~ -55.63 ppm/°C. The extremely low-loss dielectric is a very promising material for microwave and millimeter-wave applications.

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