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Dielectric Properties and Crystal Structure of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1}-Xta_x)_2O_9$ Ceramics

Bing-Jing Li[1], Sih-Yin Wang[1] and Yuan-Bin Chen[2]*

[1]Department of Electrical Engineering, National Cheng Kung University, 1 University Rd., Tainan 70101, Taiwan
[2]Department of Engineering and Management of Advanced Technology, Chang Jung Christian University, Tainan 71101, Taiwan

Abstract

The microstructure of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ is analyzed using X-ray diffractometry and scanning electron microscopy. The Qxf values of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ increases with increasing sintering temperature; and then up to a temperature of 1375°C significantly decreased. The maximum values of the electric permitivity and the quality factor (Qxf) can be obtained 12.76 and 442,000 GHz is obtained for $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ sintered at 1375°C for 4 h. The temperature coefficient of resonant frequency (τ_f) measured for $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ is −54 ppm/°C.

Keywords: Crystal structure; X-ray diffractometry; Wireless communication

Introduction

The rapid growth of recent wireless communication systems led to an increasing demand for small-scale high-frequency resonators, filters and antennas capable of operating 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]. At the same time, in order to work with high efficiency and stability, many researches have been focusing on developing new dielectric materials with a high quality factor ($Q \times f$) and a near-zero temperature coefficient of resonant frequency (τ_f) for use as dielectric resonator and microwave device substrate [6-8].

$Mg_4Nb_2O_9$ has been found to have an electric permittivity of 12.4, a temperature coefficient of resonant frequency τ_f of ~ -70 ppm/°C and a high Qxf of ~194,000 GHz [9]. However, a sintering temperature of as high as 1350-1400°C and a sintering time of 10 h are required. The high sintering temperature limits the application of these ceramics will limit its applications for practical cases. In addition, the Qxf value needs to be increased for high-frequency applications.

In this paper, the Ni^{2+} are doped into $Mg_4Nb_2O_9$ to form $(Mg_{0.95}Ni_{0.05})_4Nb_2O_9$. Because the ionic radius of Mg^{2+} (0.78 Å) is similar to those of Ni^{2+} (0.69 Å). Ni^{2+} substitutes Mg^{2+} to improve the quality factor. The Ta^{5+} substitution content Nb^{5+} to formed $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$, we discovered it improved the microwave dielectric properties. The effect of Ta^{5+} substituting Nb^{5+} on the structure and microwave dielectric properties of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ is investigated.

Experimental Procedures

$(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ 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 content 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 Cu Kα radiation (at 30 kV and 20 mA) and a graphite monochrometer in the 2θ range of 20 to 60°C. The microstructural observations and analysis of the sintered surface were performed by a 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-resonant method as suggested by Hakki and Coleman [10]. This method uses parallel conducting plates and coaxial probes on 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 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 were employed in the measurement.

Results and Discussion

Microwave dielectric properties of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ (x=0-1.0) ceramic system sintered at various temperatures for 4 h are illustrated in Table 1 and Figure 1 shown the room-temperature X-ray diffraction (XRD) patterns recorded from the $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ (x=0-1.0) ceramics sintered at 1375°C for 4 h. The single trigonal-structured $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ (x=0-1.0), belonging to the space group P3c1 (165), was identified throughout the entire tested range. The position and relative intensity of the XRD peaks varied slightly, implying that the compound tends to form a continuous solid solution. In order to confirming the formation of solid solution, the lattice parameters of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ (x=1) ceramics

***Corresponding author:** Yuan-Bin Chen, Department of Engineering and Management of Advanced Technology, Chang Jung Christian University, Tainan 71101, Taiwan, Tel: +886-6-2785123-6112; E-mail: cubnck@yahoo.com.tw

X value	Bulk density (g/cm³)	Relative density (%)	ε_r	Q×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

Table 1: The microwave dielectric properties of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$.
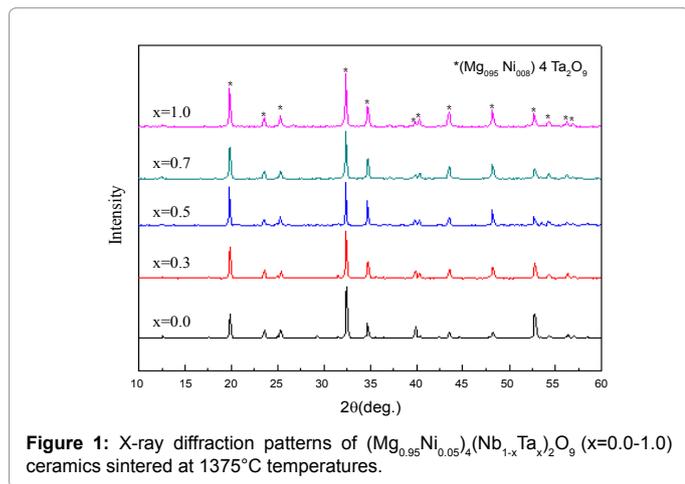

Figure 1: X-ray diffraction patterns of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ (x=0.0-1.0) ceramics sintered at 1375°C temperatures.

sintered at various temperatures XRD pattern shown in Figure 2. It is also belonging to the space group P3c1 (165) and the single trigonal-structured without any secondary phase.

SEM photographs of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ (x=1) ceramics sintered at various temperatures for 4 h are shown in Figure 3. The grain size increases with increasing sintering temperature. The grain size growth the most uniform sintered at 1375°C and obtained the best microwave dielectric properties as shown in Figure 4, however sinter above the 1375°C, the grain over-sintering.

The relative density and electric permittivity of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ ceramics as functions of sintering temperature are shown in Figures 5 and 6. Note that the relative density initially increased with increasing sintering temperature, reaching its maximum at 1325°C (<0x<0.03), with increasing more Ta⁵⁺ content and the saturated relative density sintering at 1375°C (x=1) and then relative density decreased sintering at high temperature. The relative density of all the specimens was high above 94% of the theoretical density. The relative density increased with increasing sintering temperature due to increased Ta⁵⁺ content at higher sintering temperature. The increase in relative density mainly resulted from grain growth as, shown in from Figure 3.

The dielectric properties of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ are shown in Figure 6. With 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 electric permittivity and quality factor of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ for various values of x is shown in Figure 5. The electric permittivity values of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ slightly decreased with increasing value of x; These values for $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ are very similar to those for Al_2O_3 and SAT [11,12].

The electric permittivity of microwave dielectric ceramics is affected by ionic polarizability [13]; The electric permittivity values of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ decreased with increasing Ta⁵⁺ substitution for Nb⁵⁺. Similar result was reported for SAN and SAT; Guo et al. [14] suggest that the differences between SAT and SAN are not unique to these two materials, but are common to all Nb⁵⁺ compounds and their analogous Ta compounds. It is insufficient to explain the reason for those differences by, for instance, simply considering the bonding strength (as they have the same valence and coordination numbers), or on the basis of available ionic polarizability data (α_i^{Ta5+} = 4.73 Å³ and α_i^{Nb5+} = 3.97 Å³ that would predict a lesser polarizability for SAN than SAT). It seems to us that the electronic structure differences may have caused the Ta-O bonding to be less ionic in nature and somehow enhanced the bonding strength in the crystal structures of SAN and SAT may exert an influence on the decrease in the electric permittivity value. Thus, it is considered the observed ionic polarizability (α_{obs}) of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ was estimated in order to clarify the effects of the Ta substitution for Nb on the ε_r by using the Clausius-Mosotti equation:

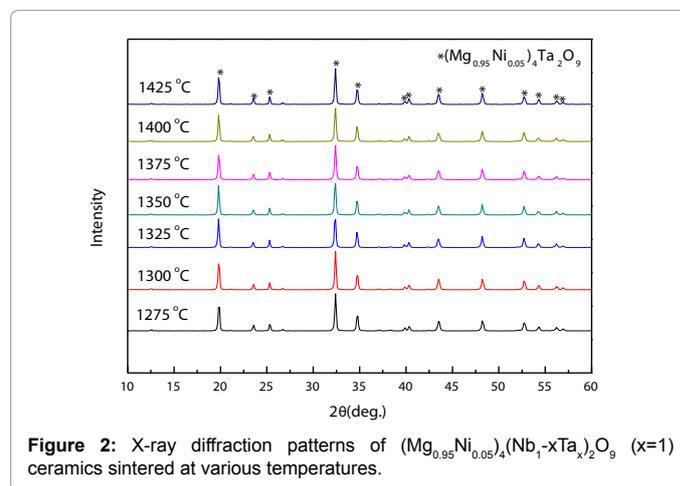**Figure 2:** X-ray diffraction patterns of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1}-xTa_x)_2O_9$ (x=1) ceramics sintered at various temperatures.
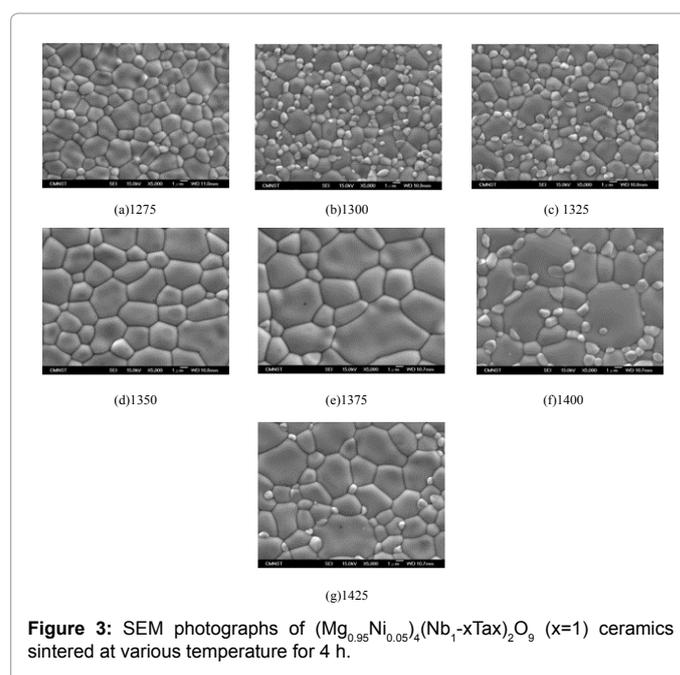

(a)1275
(b)1300
(c) 1325
(d)1350
(e)1375
(f)1400
(g)1425

Figure 3: SEM photographs of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1}-xTax)_2O_9$ (x=1) ceramics sintered at various temperature for 4 h.
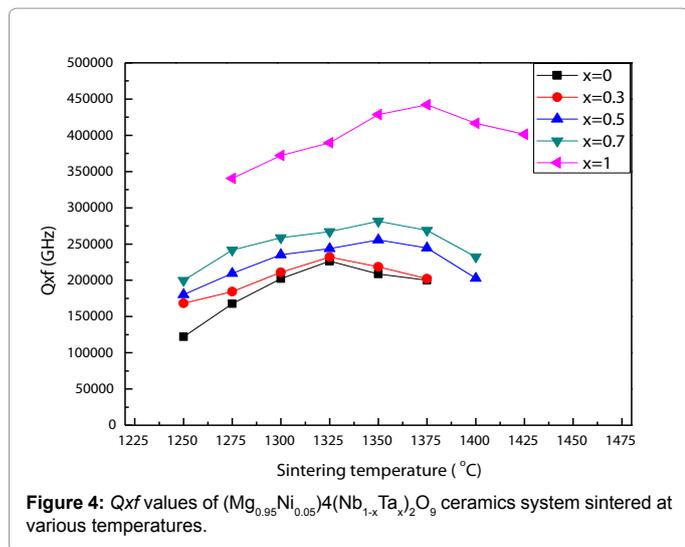
Figure 4: Qxf values of $(Mg_{0.95}Ni_{0.05})4(Nb_{1-x}Ta_x)_2O_9$ ceramics system sintered at various temperatures.
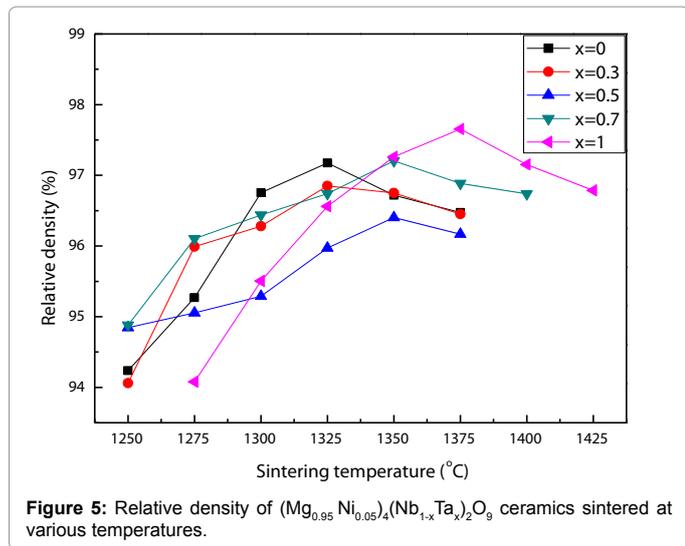

Figure 5: Relative density of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ ceramics sintered at various temperatures.
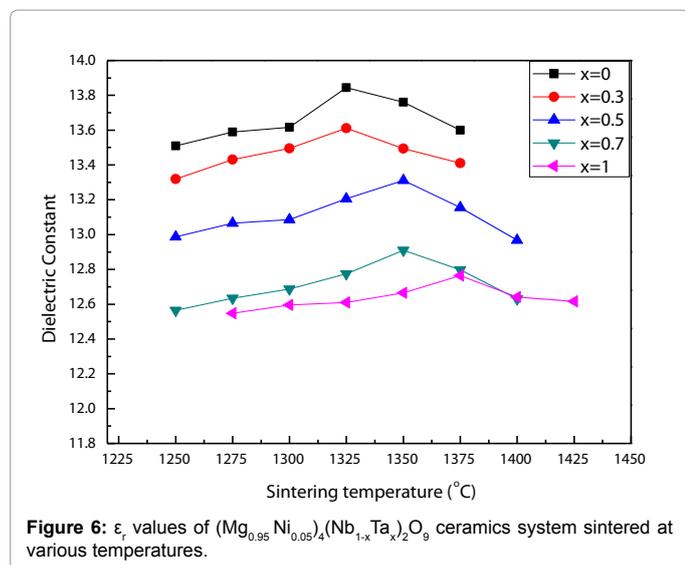

Figure 6: ε_r values of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ ceramics system sintered at various temperatures.

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_m}{3V_m - 4\pi\alpha_m} \tag{1}$$

where ε_r, V_m, and α_m represent the relative permittivity, molar volume, and macroscopic polarizability, respectively. Using the experimental relative permittivity data and unit-cell volume data, the macroscopic polarizability, α_m, was calculated. The theoretical polarizability data show an almost sigmoidal increase with increasing in Zn content and the unit-cell volume increasing with x. The relative permittivity increases with α_m. When the value of α_m approaches $3V_m/4\pi$, the relative permittivity increases very rapidly. It has also been reported that the macroscopic polarizability of complex systems with an ideal symmetry can be determined from the summation of the polarizability of the constituent cations:

$$\alpha_m = \Sigma\alpha_{(ions)} \tag{2}$$

The theoretical polarizability values (denoted as α_m(theory)) values calculated using Eq. (2) are compared with the experimental polarizability values (determined using the Claussius–Mossotti relation, Eq. (1). It is noted that α_m(exp) for the $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ end member is less than the α_m(theory) value. Shannon [12] suggested that deviations from the additivity of ionic polarizability arise when compression or rattling of cations occurs at the structural sites as the cation sizes are varied. The lower α_m(exp) value for $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ may thus be due to compression effects caused by the large difference between the ionic polarizabilities of Nb^{5+} and Ta^{5+}. This correlation agrees with the harmonic-oscillator model [14]. The unique relationship between permittivity and internal lattice stress is analogous to the reversible changes in permittivity with applied external stress reported by Steiner et al. [15].

Figure 4 shows the Qxf value of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ ceramics at various sintering temperatures as a function of the x value. The Qxf value increased with increasing Ta^{5+} content and sintering temperature. Many factors can affect the microwave dielectric loss of dielectric resonators, such as the lattice vibration modes, pores, and secondary phases. Generally, a larger grain size, i.e., a smaller grain boundary, indicates a reduction in lattice imperfection and thus reduced dielectric loss. When the x value was increased from 0 to 1, the Qxf values of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ increased dramatically from 226,000GHz (x=0~1325°C) to 442,000GHz (x=1~1375°C) GHz; which is comparable to that of Al_2O_3. Relative density also plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials. As well known, factors that influence the dielectric Q fall into two categories: intrinsic and extrinsic. The former is due to the interaction between polar phonon vibration with the microwave electric field in crystals, while the latter includes order-disorder transformation, pore density, grain size, oxygen vacancy, and impurity phases in ceramics. 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 microwave frequency range. In this model, when employing one-phonon absorption approximation, a roughly reciprocal relationship between Qxf and the ε_r could be obtained as

$$Qxf \alpha \varepsilon^{-1} \tag{3}$$

where the frequency f should be limited to the vicinity of the phonon engine frequencies, of 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 microwave frequencies down to megawatt frequencies (1-4 magnitude orders below the optical phonon
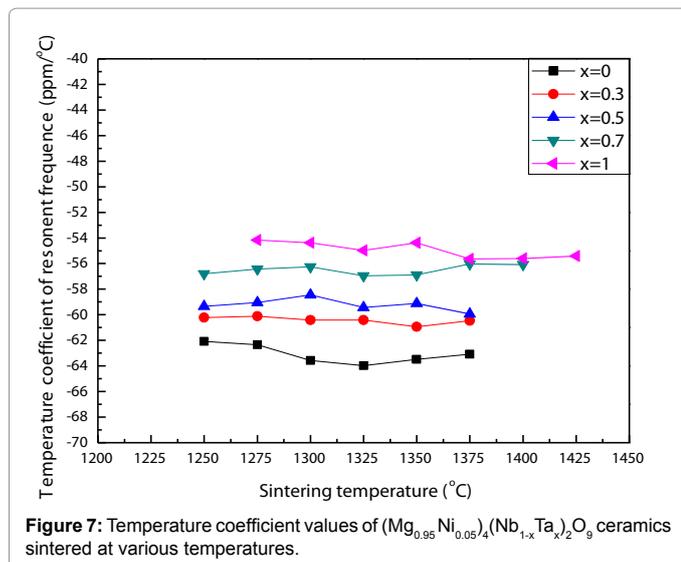
Figure 7: Temperature coefficient values of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ ceramics sintered at various temperatures.

engine frequency) at room temperature could also give a satisfying magnitude order of dielectric Q for well processed ceramics. The result, however, showed that the dependence of Qxf on ε_r only yielded $Qxf \propto \varepsilon_r^{-0.6}$, indicating a rather smoother increasing rate of Qxf value with ε_r compared with Eq. (2). The most probable reason for this phenomenon could be associated with the extrinsic origins. As acknowledged by many authors, the porosity in dielectrics had deleterious effects on dielectric Qxf values, whose influencing degree, however, varied with different dielectrics. For low dielectric Qxf ceramics with 10^3 GHz magnitude order, the effect of porosity on dielectric Q could be described as

$$Q = Q_o(1-1.5P) \qquad (4)$$

where Q_o was the intrinsic dielectric Q measured by microwave reflective spectrum and P was the porosity. However, as for high Qxf ceramics with 10^5-10^6 GHz magnitude order such as polycrystalline Al_2O_3 ceramic, even a small amount of porosity would considerably reduce the dielectric Q by

$$\frac{1}{Q} = (1-P)\frac{1}{Q_o} + A'P\left(\frac{P}{1-P}\right)^{2/3} \qquad (5)$$

The τ_f values of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ ranged from -54 to -66 ppm/°C, as shown in Figure 7. The temperature coefficient of resonant frequency, τ_f (TCF), could be defined as following:

$$TCF = -\alpha_l - \frac{1}{2}\tau_\varepsilon \qquad (6)$$

Where α_l is the linear thermal expansion coefficient and τ_ε is the temperature coefficient of permittivity. Using the Clausius–Mosotti equation, Bosman and Havinga [16] derived the following expression for τ_ε at a constant pressure:

$$\tau_\varepsilon = \frac{1}{\varepsilon}\left(\frac{\partial \varepsilon}{\partial T}\right)_p = \frac{(\varepsilon-1)(\varepsilon+2)}{\varepsilon}(A+B+C) = \left(\varepsilon - \frac{2}{\varepsilon} + 1\right)(A+B+C)$$

$$A = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P,$$

$$B = \frac{1}{3\alpha_m}\left(\frac{\partial \alpha_m}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P,$$

$$C = \frac{1}{3\alpha_m}\left(\frac{\partial \alpha_m}{\partial T}\right)_V$$

The $(A+B+C)$ value can be extrapolated from Eq. (1) as -10.95 ppm/°C. When the $(A+B+C)$ value is negative, TCF value increases with permittivity. When the $(A+B+C)$ value is positive, the TCF value decreases permittivity. Usually, the absolute value of TCF increases with permittivity. The sum of the A and B terms is approximately 6 ± 1 ppm/°C. For term C, the suggested value is in the range of -1 to -10 ppm/°C. The term C represents the direct dependence of the polarizability on temperature.

Conclusions

The microwave dielectric properties of the $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ solid solutions were investigated. The quality factors of the $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ solid solutions was increased by Nb^{5+} substituting for Ta^{5+} and Ni^{2+} substituting for Mg^{2+}. When x was increased from 0 to 1, the Qxf value of $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ increased dramatically from 226,000 GHz (x=0~1325°C) to 442,000 GHz (x=1~1375°C) GHz. So $(Mg_{0.95}Zn_{0.05}Co_{0.05})_4(Nb_{0.1}Ta_{0.9})_2O_9$ improved the microwave dielectric properties and decreased the sintering temperatures compared to pure $Mg_4Nb_2O_9$. The $(Mg_{0.95}Ni_{0.05})_4(Nb_{1-x}Ta_x)_2O_9$ compound exhibits a good combination of $\varepsilon_r \sim 12.76$, $Q \times f \sim 442,000$ GHz, and $\tau_f \sim -55.63$ ppm/°C after sintering at 1375°C for 4 h. The proposed dielectric, having extremely low loss had made is a very promising material for microwave and millimeter-wave applications.

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