Dielectric properties and crystal structure of 
(1−y)(Mg0.95Ni0.05)4Ta2O9−y(Ca0.8Sr0.2)TiO3 ceramics

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The microwave dielectric properties and microstructures of (1−y)(Mg0.95Ni0.05)4Ta2O9−y(Ca0.8Sr0.2)TiO3 ceramics prepared using a mixed oxide route were investigated. (Mg0.95Ni0.05)4Ta2O9 has a dielectric constant (εr) of ~12.23, a high quality factor (Qf) of ~442,092 GHz, and a temperature coefficient of resonant frequency (τf) of ~−55 ppm/°C. To produce a temperature-stable material, Ca0.8Sr0.2TiO3, which has a large positive τf value of 990 ppm/°C, was added to (Mg0.95Ni0.05)4Ta2O9. The temperature coefficient of resonant frequency increased with increasing Ca0.8Sr0.2TiO3 content, going through nearly zero at y = 0.7. The microwave dielectric material 0.3(Mg0.95Ni0.05)4Ta2O9−0.7(Ca0.8Sr0.2)TiO3 has an excellent combination of microwave dielectric properties: εr ~ 29.8, Qf ~ 226,000 GHz (at 9 GHz), and τf ~ −2.38 ppm/°C sinter at 1350°C. It is proposed as a candidate material for industrial, scientific and medical band components and Global Position System antennas.

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Key-words : Dielectric, Microwave ceramics

1. Introduction

High-quality devices are important for mobile communication applications. In order to minimize the dimensions of devices and for high efficiency and stability, microwave resonators materials are required to have the following three dielectric characteristics: high quality factor (Qf), permittivity, have and a temperature coefficient of resonant frequency (τf). Mg0.95Nb0.05O3 ceramics have been of great interest to the electronics and communication industries in the last few years. Mg4Nb2O9 ceramics have similar ionic radius. (1−y)(Mg0.95Ni0.05)4Ta2O9−y(Ca0.8Sr0.2)TiO3 ceramics had high quality factor (Qf) of ~442,092 GHz, and a temperature coefficient of resonant frequency (τf) of ~−55 ppm/°C.

In the present study, the Ni substitution content for Mg4Ta2O9 to form (Mg0.95Ni0.05)4Ta2O9 was carried out. Mg2+(0.72 Å), and Ni2+(0.69 Å) have similar ionic radius. The effects of Ni2+ substitute on for Mg2+ on the structure and microwave dielectric properties of (Mg0.95Ni0.05)4Ta2O9 and Ca0.8Sr0.2TiO3 are investigated. (Mg0.95Ni0.05)4Ta2O9 has a dielectric constant (εr) of ~12.23, a high quality factor (Qf) of ~442,092 GHz, and a temperature coefficient of resonant frequency (τf) of ~−55 ppm/°C.

In stead of SrTiO3, (Ca0.8Sr0.2)TiO3 ceramics have been of great interest to the electronics and communication industries in the last few years. Mg4Ta2O9 ceramics have similar ionic radius. (1−y)(Mg0.95Ni0.05)4Ta2O9−y(Ca0.8Sr0.2)TiO3 and then remilled for 12 h. A fine powder with 3 wt% of a 10% solution of polyvinyl alcohol (PVA 500, Showa, Japan) used as a binder was pressed into pellets, 11 mm in diameter and 5 mm thick, under a pressure of 200 MPa. The pellets were sintered at temperatures of 1275−1475°C for 4 h in air. The heating and the cooling rates were both set at 10°C/min.

The powder and bulk X-ray diffraction (Rigaku D/max 11-V XRD) 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°. The microstructural observations and analysis of the sintered surface were performed by using scanning electron microscopy (SEM; Philips XL−40FEG).

The bulk densities of the sintered pellets were measured by the Archimedes method. Microwave dielectric properties such as the dielectric constant and unloaded Q were measured at 6−12 GHz by the post resonant method as suggested by Hakki and Coleman. By this method, parallel conducting plates and coaxial probes were used in the TE011 mode. TE means transverse electric waves and the first two subscript integers denote the wave guide mode, while 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 equipped with a HP8757D network analyzer and a HP8350B sweep oscillator were employed in the measurement.

3. Results and discussion

Figure 1 shows the room-temperature XRD patterns recorded from the $(1 - y)(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-y(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics sintered at 1350°C for 4 h. The main trigonal-structured $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$, belonging to the space group P3c1 (165), was identified throughout the entire tested range, in association with $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ as minor phases. It is understood that crystal structures of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$ and $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ are trigonal-structured phase (PDF-card #01-079-0381) and orthorhombic (PDF-card #01-070-8504), respectively. According to the XRD patterns, the $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$ phase exists in these specimens. X-ray diffraction patterns of $(1 - y)(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-y(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics system have not been changed significantly with sintering temperatures at 1350°C. The XRD patterns show peaks indicating the presence of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$ as the main crystalline phase, a minor phase of $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$. The formation of mixed phases in the $(1 - y)(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-y(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramic system was due to structural differences; therefore, a solid solution could not be obtained. The XRD patterns of the $0.3(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-0.7(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramic did not significantly change with sintering temperature in the range 1275–1425°C as shown in Fig. 2.

Figure 3 shows SEM images of $0.3(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-0.7(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics sintered at various temperatures for 4 h. The grain size increased with increasing sintering temperatures markedly obviously. The $0.3(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-0.7(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramic system was not dense and the grains did not grow at 1275°C. However, rapid grain growth was observed at 1475°C and the pores were almost eliminated for the specimen sintered at 1350°C. The EDX datum and data of corresponding spots A–B were showed in Fig. 4 and Table 2, respectively. The grain morphology of well developed $0.3(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-0.7(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics could be grouped into two types: both large grains (spot A), indicating $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$ phase, and small shape grains (spot B) were $(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$. The EDX evidences are in agreement with the XRD results obtained from $0.3(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-0.7(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics. It is because the grain size of $(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ is smaller than that of $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$ and adding $(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ to $(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9$ would benefit the densification of the ceramics. Figure 5 shows the bulk densities of the $(1 - y)(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-y(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics sintered at various temperatures for 4 h.

![Fig. 1. X-ray diffraction patterns of $(1 - y)(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-y(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics sintered at 1350°C for 4 h.](image1)

![Fig. 2. X-ray diffraction patterns of $0.3(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-0.7(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics sintered at various temperatures for 4 h.](image2)

![Fig. 3. SEM images of $0.3(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-0.7(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ceramics sintered at (a) 1275, (b) 1300 (c) 1325, (d) 1350°C (e) 1350°C (f) 1400°C and (g) 1425°C respectively for 4 h.](image3)
ious temperatures for 4 h. With increasing temperature, the bulk density increased to a maximum value of 6 g/cm³ at 1350°C, and then it decreased. The reduction of density due to the abnormal grain growth is shown in Fig. 3.

The dielectric properties of (1 − y)(Mg0.95Ni0.05)4Ta2O9−y(Ca0.8Sr0.2)TiO3 are illustrated in Fig. 6.

The relationship between εᵣ values and sintering temperature revealed the same trend as that between density and sintering temperature since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. A maximum εᵣ value of 42.1 was obtained for y = 0.5(Mg0.95Ni0.05)4Ta2O9−0.8(Ca0.8Sr0.2)TiO3 ceramics sintered at 1350°C for 4 h.

The quality factor values (Q × f) of (1 − y)(Mg0.95Ni0.05)4Ta2O9−y(Ca0.8Sr0.2)TiO3 ceramic at various sintering temperatures are shown in Fig. 7. With increasing sintering temperature, the Q × f value increased to a maximum value and then decreased. The maximum Q × f value of 250,000 (GHz) for y = 0.5 was achieved at a sintering temperature of 1350°C and then decreased sintering at higher temperature. The degradation of the Q × f value can be attributed to the abnormal grain growth at higher sintering temperatures, as shown in Fig. 3. The microwave dielectric loss is mainly caused by the lattice vibrational modes, pores, second phases, impurities, and lattice defects. Relative density also plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials. As is 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.

The temperature coefficient of resonant frequency (τᵣ) of (1 − y)(Mg0.95Ni0.05)4Ta2O9−y(Ca0.8Sr0.2)TiO3 ceramics subjected to various sintering temperatures is shown in Fig. 8. The temperature coefficient of resonant frequency is related to the composition, additives, and second phase of the material. Because the τᵣ values of (Mg0.95Ni0.05)4Ta2O9 and Ca0.8Sr0.2TiO3 are −55 and 990 ppm/°C, respectively, increasing Ca0.8Sr0.2TiO3 content makes the τᵣ value more positive. This implies that a zero τᵣ value can be achieved by tuning the amount of Ca0.8Sr0.2TiO3 content. In fact, with y = 0.7, a nearly zero τᵣ value was achieved for the 0.3(Mg0.95Ni0.05)4Ta2O9−0.7(Ca0.8Sr0.2)TiO3 ceramic system sintered at 1350°C for 4 h.

Table 1 summarizes the microwave dielectric properties of (1 − y)(Mg0.95Ni0.05)4Ta2O9−y(Ca0.8Sr0.2)TiO3 ceramic system. These dielectric properties and densities vary substantially.
phases of \((\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9\) as the main phase with some minor phases of \((\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3\). With the partial replacement of \(\text{Mg}^{2+}\) by \(\text{Ni}^{2+}\), \((\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9\) had excellent dielectric properties with an \(\varepsilon_r \sim 12.23\), \(Q \times f \sim 440,000\) GHz, and a \(\tau_f \sim -55\) ppm/C after being sintered at a low temperature of 1375°C. The \((1-y)(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-y(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3\) ceramic system showed mixed phases of \((\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9\) as the main crystalline phase, a minor phase of \((\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3\). At 1350°C, the \(0.3(\text{Mg}_{0.95}\text{Ni}_{0.05})_4\text{Ta}_2\text{O}_9-0.7(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3\) ceramic has been developed, exhibiting excellent microwave dielectric properties: \(\varepsilon_r \sim 29.86\), \(Q \times f \sim 226,000\) GHz, and \(\tau_f \sim -2.38\) ppm/C, which make it a suitable candidate material with a relatively low sintering temperature for ISM band components and GPS antennas.

### Acknowledgement
This work was supported by the National Science Council of Taiwan.

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