Dielectric properties and crystal structure of Mg$_4$Ta$_2$O$_9$ ceramics with Mg$^{2+}$ substituted by Co$^{2+}$

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Dielectric properties of (Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$ ($x = 0.01$ to $0.09$) prepared by solid state reaction were investigated. The maximum properties of the (Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$ ($x = 0.05$) system were namely, an obtained $\varepsilon_r$ value of 12.27, a $Q_xf$ value of 440,000 GHz, and a $\tau_f$ value of $-59$ ppm/$^\circ$C sintered at 1325$^\circ$C. The theoretical polarizability of (Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$ increased with Co substitution, $x$. (Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$ with Mg$^{2+}$ substituted by and Co$^{2+}$ not only improved the microwave dielectric properties, but also decreased sintering temperature. From the calculation of the covalency of cation–oxygen bonds, it is found that the covalency of the Co–O bond is lower than that of the Mg–O bond and the difference in the covalency between these cation–oxygen bonds influences the temperature dependence of dielectric constant on the compounds. From our experiment, the best microwave dielectric property happens in (Mg$_{0.95}$Co$_{0.05}$)$_4$Ta$_2$O$_9$ sintered at 1325$^\circ$C for 4 h, and it’s $Q_xf$ is 440,000 GHz with $\tau_f = 59.5$ ppm/$^\circ$C.

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 ($Q_xf > 15,000$), permittivity, have and a temperature coefficient of resonant frequency ($\tau_f = \pm 3$ ppm/$^\circ$C).

Mg$_5$Nb$_2$O$_{12}$ ceramics$^{3-3}$ has been of great interest to the electronics and communication industries in the last few years.$^{11-11}$ They have been found to exhibit superior microwave dielectric properties by Khalam et al.$^{12}$ An $\varepsilon_r$ of $\sim 16$, a $Q_xf$ of $116,000$ GHz, and a $\tau_f$ of $-66$ ppm/$^\circ$C were also reported for sintering at $1400^\circ$C.

Further research was carried out to improve $Q_xf$ by partially substituting Nb with Sb, Ta, or V to form a solid solution and the pellets obtained were sintered in the temperature range of 1350–1400$^\circ$C for 10 h in air.$^{13-16}$ (Kan et al. reported that a dielectric constant of 11.6 and a $Q_xf$ of 160,256 GHz were obtained for Mg$_5$(Nb$_2$-xSbx)O$_{12}$ at $x = 0.0625$ sintered at $1025^\circ$C.) Among those solid solutions, an extremely high $Q_xf$ ($\sim 350,000$ GHz) could be achieved from specimens using Mg$_5$(Nb$_2$-xSbx)O$_{12}$. In the present study, the Co substitution content for Mg$_4$Ta$_2$O$_9$ to form (Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$ was carried out. Mg$^{2+}$ (0.72A), and Co$^{2+}$ (0.745 A) have similar ionic radius.17-20 The effects of Co$^{2+}$ substitute on for Mg$^{2+}$ on the structure and microwave dielectric properties of (Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$ are investigated.

2. Experimental procedure

(Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$ powders were prepared using the solid-state reaction method by mixing individual high-purity oxides MgO, CoO, and Ta$_2$O$_5$. The starting materials were stoichiometrically weighed after heating MgO at 800$^\circ$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 between 1100$^\circ$C. The calcined powder with the organic binder polyvinyl alcohol was pressed into pellets by using a uniaxial press and the binder was evaporated at 650$^\circ$C for 12 h. Sintering was carried out at 1175–1275$^\circ$C for 4 h. The powder and bulk X-ray diffraction (Rigaku D/max III-V XRD) patterns were collected using Cu K$\alpha$ radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2$\theta$ range of 20 to 60$^\circ$. The microstructural observations and analysis of the sintered surface were performed by scanning electron microscopy (SEM; Philips XL–40FE). 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.21 By this method, parallel conducting plates and coaxial probes were used in the T$_{011}$ 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$^\circ$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 (Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$ ($x = 0.01$–0.09) ceramics sintered at 1325$^\circ$C for 4 h. The main trigonal-structured (Mg$_{1-x}$Co$_x$)$_4$Ta$_2$O$_9$, belonging to the space group P3c1 (165), was identified throughout the entire tested range. The positions and there relative intensities of the XRD peaks varied slightly implying that the compound tends to form a continuous solid solution. In order to confirming the formation of a solid solution, the lattice pattern.

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parameters of (Mg(1-x)Co)xTa2O9 (x = 0.01–0.09) ceramics sintered at 1325°C were measured and are shown demonstrated in Table 1. The lattice parameters linearly increased from a = 5.1487 ± 0.0056 Å at x = 0.01 to a = 5.1562 ± 0.0065 Å at x = 0.09 for the (Mg0.95Co0.05)4Ta2O9 composition (Table 1). The variation of the lattice parameters of the specimens resulted from the incorporation of larger Co3+ (0.74 Å, CN = 6) in place of Mg2+ (0.72 Å, CN = 6) under the same coordination number. The X-ray diffraction patterns of (Mg0.95Co0.05)4Ta2O9 ceramics sintered at various temperature. Figure 2 shows SEM images of (Mg0.95Co0.05)4Ta2O9 ceramics sintered at various temperature without any second phase as shown in Fig. 2. It is also the trigonal-structured phase.

Figure 3 shows SEM images of (Mg0.95Co0.05)4Ta2O9 ceramics sintered at various temperatures for 4h. The grain size increased with increasing sintering temperatures markedly obviously. The (Mg0.95Co0.05)4Ta2O9 ceramic system was not dense and the grains did not grow at 1250°C. However, rapid grain growth was observed at 1375°C and the pores were almost eliminated for the specimen sintered at 1325°C. Based on EDS, large grains were identified as (Mg0.95Co0.05)4Ta2O9 (x = 0.05) ceramics for Fig. 3(d). EDX data of (Mg0.95Co0.05)4Ta2O9 ceramics: Mg K: 29.29, Co K: 2.59, Ta k 15.52, O K: 45.69. The relative density and dielectric constant of the (Mg0.95Co0.05)4Ta2O9 solid solutions as a function of sintering temperature for 4h are shown in Fig. 4. Note that the relative densities initially increased with increasing sintering temperature, reaching their maximum at 1325°C, and decreased sintering at higher temperature. The increase in relative density mainly resulted from the grain growth as shown in Fig. 3. The reduction of the relative density of the specimen was due to the appearance of pores resulting from an abnormal grain growth sintering above 1325°C.

The dielectric properties of (Mg0.95Co0.05)4Ta2O9 are illustrated in Fig. 5. The variation in the relative permittivity with composition is often explained using the Clausius–Mossotti relation, which shows how the relative permittivity depends on the composition and crystal structure through polarizability and molar volume:

\[
\varepsilon_r = \frac{3V_m + 8\pi\alpha_m}{3V_m - 4\pi\alpha_m},
\]

Here, \(\varepsilon_r\), \(V_m\), and \(\alpha_m\) represent the relative permittivity, molar volume, and macroscopic polarizability, respectively. Using the experimental relative permittivity data and unit-cell volume data, the macroscopic polarizability \(\alpha_m\) was calculated. The theoretical polarizability data show an almost sigmoidal increase with increasing in Zn content. The unit-cell volume increased with x. The relative permittivity increases with \(\alpha_m\). When the value of \(\alpha_m\) 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 such that display

\[
\alpha_m = \Sigma\alpha(\text{ions}).
\]

The theoretical polarizability [denoted as \(\alpha_m(\text{theory})\)] values calculated using to Eq. (2) are compared with the “experimental” polarizabilities [determined using the Clausius–Mossotti
relation, Eq. (2) in Table 1. It is noted that $\alpha_m(\text{exp})$ for the $(\text{Mg}(1-x)\text{Co}_x)\text{Ta}_2\text{O}_9$ end member is less than the $\alpha_m(\text{theory})$ value. The $\alpha_m(\text{exp})$ values are smaller than $\alpha_m(\text{theory})$. Shannon23) suggested that deviations from the additivity of ionic polarizability arise when compression or rattling of cations occur in the structural sites as cation size varies. The lower $\alpha_m(\text{exp})$ value for $(\text{Mg}(1-x)\text{Co}_x)\text{Ta}_2\text{O}_9$ may thus be due to compression effects due to the large difference in size between the $\text{Mg}^{2+}$ and $\text{Co}^{2+}$ cations in the octahedral sites. A similar argument is that the larger $\alpha_m(\text{exp})$ in $\text{Co}^{2+}$ would be attributed to the rattling of the smaller $\text{Mg}^{2+}$ cations in the oxygen octahedra, which is characteristic of ferroelectric materials. The reduction in the lattice stress effectively induces a decrease in restoring force constant with a resultant increase in the vibrational anisotropy leading to an increase in the relative permittivity and its temperature dependence. This correlation also agrees with the harmonic-oscillator model.24) 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.25) The relative bulk density and dielectric constant of the $(\text{Mg}(1-x)\text{Co}_x)\text{Ta}_2\text{O}_9$ ceramics as a function of its sintering temperature for 4 h are shown in Fig. 4 and Fig. 5. The bulk density and dielectric constant have the same trend form Fig. 4 and Fig. 5. The dielectric constant is mainly affected by bulk density. The quality factor values ($Qf$) of $(\text{Mg}(1-x)\text{Co}_x)\text{Ta}_2\text{O}_9$ ceramic at various sintering temperatures are shown in Fig. 6. With increasing sintering temperature, the $Qf$ value increased to a maximum value and then decreased. The maximum $Qf$ value of 440,000 (GHz) for $x = 0.05$ was achieved at a sintering temperature of 1325°C and then decreased sintering at higher temperature. The degradation of the $Qf$ 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 perfect 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 of Q×f and the dielectric constant could be obtained as

\[ Q \times f = \alpha \varepsilon e^{-1}, \]  

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 showed that the extrapolation of Eq. (3) from 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 result, however, showed that the dependence of Q×f on εr only yielded Q×f α εr\(^{-0.6}\), indicating a rather smoother increasing rate of Q×f value with εr compared with Eq. (3). The most probable reason for this phenomenon could be associated with the extrinsic origin. As acknowledged by many authors, the porosity in dielectrics had deleterious effects on dielectric Q×f values, degree of whose influence, however, varied with different dielectrics. For low dielectric Q×f ceramics with 10^12 GHz magnitude order, the effect of porosity on dielectric Q could be described as

\[ Q = Q_d (1 - 1.5P), \]  

where Qd is the intrinsic dielectric Q measured by using the microwave reflective spectrum and P was the porosity. However, for high Q×f ceramics with 10^9–10^10 GHz order of magnitude such as polycrystalline Al2O3 ceramic, even a low porosity would considerably reduce the dielectric Q by

\[ \frac{1}{Q} = (1 - P) \frac{1}{Q_d} + A'P\left(\frac{P}{1 - P}\right)^{2/3}, \]  

where Qd was the full density dielectric quality factor, A' is obtained a constant of 9.277 × 10^-3, and P was the porosity. According to Eqs. (4) and (5), about 3% porosity was obtained, which was the porosity in (Mg(1-x)Co)xTa2O9 ceramics end component in the present study.

The temperature coefficient of resonant frequency (TCF) of (Mg(1-x)Co)xTa2O9 ceramics subjected to various sintering temperatures was shown in Fig. 7. The temperature coefficient of resonant frequency is related to the composition, additives, and second phase of the material. It seemed that a higher Co\(^{3+}\) content would shift TCF value to be more positive. It varied from -55.8 to -60.8 ppm/°C as the x value increased from 0.01 to 0.09 for sintering at 1325°C. In general, the temperature coefficient of resonant frequency was found to not be related to the composition, whereas increasing Co\(^{3+}\) content correlates to the increase in TCF, as shown in Fig. 7. In the tilted region, generally the increasing thermal energy is completely absorbed to recover the tilting. TCF values were found to increase with the content of Co\(^{3+}\), as shown in Fig. 7.

4. Conclusion

The dielectric properties of (Mg(1-x)Co)xTa2O9 ceramics were investigated. (Mg(1-x)Co)xTa2O9 ceramics exhibited a trigonal-structured structure. The improved dielectric properties of (Mg(1-x)Co)xTa2O9 (x = 0.05) system were, in fact, an obtained εr value of 12.27, a Q×f value of 440,000 GHz, and a TCF value of -59 ppm/°C sintered at 1325°C. By partial Mg substitution in MgTa2O9 ceramics by Co, the ceramics with a higher Q×f value could be obtained at a lower sintering temperature, compared with MgTa2O9 (εr = 16, Q×f ~ 116,000 GHz, and TCF ~ -66 ppm/°C). Therefore, the (Mg(1-x)Co)xTa2O9 ceramics are suitable for applications in microwave dielectric resonators and microwave devices owing to their superior microwave dielectric properties.

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