The effects of the substitution of Mn$^{2+}$ at Mg$^{2+}$ sites on the structural characteristics and microwave dielectric properties of (Mg$_{1-x}$Mn$_x$)$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$ ($x = 0.01-0.009$) ceramics were investigated. Second phase of (Mg$_{1-x}$Mn$_x$)$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$ was observed. The sintering characteristics of (Mg$_{1-x}$Mn$_x$)$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$ ceramics are developed by the X-ray diffraction patterns and SEM observations to find the influence of sintering temperatures and Sn$^{4+}$ content on the crystal structure and the grain growth. The influence Mn$^{2+}$ content and sintering temperatures on the quality values ($Q\times f$) and the temperature coefficient of resonant frequency ($\tau$ values) of (Mg$_{1-x}$Mn$_x$)$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$ ceramics at microwave frequency are well developed in this study. As an optimal compoese, (Mg$_{1-x}$Mn$_x$)$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$ ($x = 0.05$) successfully demonstrated a dielectric constant of 14.21, a $Q\times f$ of 347,000 GHz and a temperature coefficient of resonant frequency value of $-57.94$ ppm/$^\circ$C sintering at 1325$^\circ$C.

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1. Introduction

MgO–TiO$_2$ system has been studied extensively and the existence of three stable phases (MgTiO$_3$, Mg$_2$TiO$_4$ and MgTi$_2$O$_5$)$_3$1 has been reported in literatures. The two magnesium titanates are good candidates for use in microwave dielectrics: MgTiO$_3$ ($\varepsilon_r = 13-17$, $Q\times f = 80,000-200,000$ GHz),2–11 Mg$_2$TiO$_4$ ($\varepsilon_r = 13-14$, $Q\times f = 50,000$ GHz)7–9). There were a number of methods to synthesize MgTiO$_3$ ceramics, such as solid state reaction, sol–gel,12,13) and chemical-reactive precipitation methods.14) The possibility of using materials based on MgTiO$_3$ in the low-temperature cofired ceramic (LTCC) technique has been reported.2–14) However, the available literatures contain seldom data about the synthesis and properties of MgO–TiO$_2$ dielectric materials based on Mg$_2$TiO$_4$. Usually, solid state reaction method for preparing Mg$_2$TiO$_4$ phase needs high temperature (more than 1300$^\circ$C), and Mg$_2$TiO$_4$ as secondary phase are almost inevitable.8) Presently active investigations are being done to improve its microwave dielectric properties or reduce the sintering temperature by suitable substitution with ions.15)–17) Up to date, how to obtain pure Mg$_2$TiO$_4$ phase and sintering the ceramics at low sintering temperature is still a challenging issue.

In this paper, the Mn$^{2+}$ substitution content (Ti$_{0.95}$Sn$_{0.05}$)O$_4$ to form (Mg$_{1-x}$Mn$_x$)$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$ to improve dielectric properties. It was seen that with substitution of a slightly larger Mn$^{2+}$ (0.83 Å) for a smaller Mg$^{2+}$ (0.72 Å),18) Consequently, not only did the substitution tremendously boost the $Q\times f$ to an even higher value, it also achieved an extremely reliable process to achieve material of stable dielectric properties. In addition, the formation of the second phases (Mg$_{1-x}$Mn$_x$) (Ti$_{0.95}$Sn$_{0.05}$)O$_4$ did not degrade the dielectric properties of the host materials because they possessed properties compatible with those of the primary phases. Consequently, not only did the substitution tremendously boost the $Q\times f$, it also represented an extremely reliable process to achieve a material with stable dielectric properties. The resultant microwave dielectric properties were analyzed based upon the densification, the X-ray diffraction (XRD) patterns and the microstructures of the ceramics. The correlation between the microstructure and the $Q\times f$ value were also investigated.

2. Experimental procedures

The (Mg$_{1-x}$Mn$_x$)$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$ ($x = 0.01–0.009$) were prepared by the solid-state mixed oxides route with starting materials of high-purity oxide powders (>99.9%): MgO, MnO, SnO$_2$ and TiO$_2$. Because MgO is hygroscopic, it was first fired at 600$^\circ$C to avoid moisture contain. The weighed raw materials were mixed by ball milling with agate media in distilled water for 24 h, and the mixtures were dried and calcined at 1100$^\circ$C for 4 h. Prepared powders were dried, ball-milled for 24 h with 5 wt% of a 10% solution of PVA as a binder, granulated by sieving through 100 mesh, and pressed into pellets with 11 mm in diameter and 5 mm in thickness. All samples were prepared using an automatic uniaxial hydraulic press at 2000 kg/cm$^2$. These pellets were sintered at 1275–1425$^\circ$C for 4 h in air.

The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) spectra were collected using Cu K$\alpha$ radiation (at 30 KV and 20 mA) and a graphite monochromator in the 2$\theta$ range of 10 to 80°. The crystalline phases of the sintered ceramics were identified by XRD using Cu K$\alpha$ ($\lambda = 0.15406$ nm) radiation with a Siemens D5000 diffractometer (Munich, Germany) operated at 40 KV and 40 mA. The lattice constant calculation was accomplished using GSAS software with Rietveld method to fit the XRD patterns.15) The microstructural observations and analysis of the sintered surface were performed using a scanning electron microscope (SEM, Philips XL–40EG). The bulk densities of the sintered pellets were measured by the Archimedes method. Microwave dielectric properties, such as the

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dielectric constant and unloaded Q, were measured at 6–12 GHz by the post-resonant method as suggested by Hakki and Coleman.20,21 This method utilizes parallel conducting plates and coaxial probes in TE₀₁₁ mode, TE means transverse electric waves, the first two subscript integers denote the wave guide mode, and the subscript 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 to 80°C. A HP8757D network analyzer and a HP8350B sweep oscillator were employed in the measurement.

3. Results and discussion

XRD patterns recorded from the (Mg₉₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ (x = 0.01–0.09) ceramics sintered at different temperatures for 4 h are shown in Fig. 1. The cubic-structured (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ (which can be indexed as Mg₂TiO₄, ICDD-PDF#00-025-1157), belonging to the space group Fd-3m(227), was identified as the main phase, implying the forming of a solid solution. In addition to (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄, second phase of (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₃ was observed. Additional phase formation was not detected throughout the complete range of mixtures. The formation of the second phase was attributed to the fact that MgO is hygroscopic, which would lead to a Ti-rich compound. It is usually difficult to eliminate completely from the samples prepared by the mixed oxide route. However, its presence became less because the MgO was fired at 600°C before the synthesis of the compounds. Moreover, Petrova et al. proposed the following thermal decomposition mechanism to further explain the formation of the (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₃ phase.

\[ \text{Mg}_2\text{TiO}_4 \rightarrow \text{Mg}_{2+2x}\text{Ti}_{1-2x}\text{O}_4 + \text{MgTiO}_3 \]

The thermal decomposition of Mg₂TiO₄, however, becomes negligible at temperatures exceeding 1400°C.22 Moreover, significant variation was not detected from the XRD patterns of the specimens at different x values (x = 0.01–0.09) in our experiment. XRD patterns recorded from the (Mg₀.₉₅Mn₀.₀₅)(Ti₀.₉₅Sn₀.₀₅)O₄ ceramics sintered at different temperatures for 4 h are shown in Fig. 2. (Mg₀.₉₅Mn₀.₀₅)(Ti₀.₉₅Sn₀.₀₅)O₄ was the main phase, second phase of Mg₀.₉₅Mn₀.₀₅(Ti₀.₉₅Sn₀.₀₅)O₃ was observed at various temperatures.

In order to confirm the formation of the solid solution, the lattice parameters of (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ ceramics sintered at 1325°C were measured and are demonstrated in Table 1. In addition to Mn²⁺, other ions, such as Mn³⁺ or Mn⁴⁺, may possibly exist to form other compositions. Consequently, the presence of lattice parameters becomes necessary because the detection of a minor phase by XRD is extremely difficult. The measured lattice parameters increased linearly with an increase in the Mn content, implying the formation of a solid solution. An increase in the lattice parameters was found for (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ ceramics in comparison with that of Mg₂TiO₄. The results indicated that with the partial replacement of Mg²⁺ by Mn²⁺, Mg₂(Ti₀.₉₅Sn₀.₀₅)O₄–Mn₂(Ti₀.₉₅Sn₀.₀₅)O₄ ceramics would form solid solutions. Moreover, formation of (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ the lattice parameters increased from a=b=c = 8.4415 Å in Mg₂TiO₄ to a=b=c = 8.4784 Å in (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ (x = 0.09).

SEM micrographs of (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ (x = 0.05) ceramics sintered at various temperatures for 4 h are shown in Fig. 3. The grain size increased with increasing sintering temperatures. However, rapid grain growth was observed at 1350°C and the pores were almost eliminated for the specimen sintered at 1325°C. The relative density and dielectric constant of the (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ solid solutions as a function of the sintering temperature for 4 h are illustrated in Fig. 5. Notice that the densities apparently increased with increasing sintering temperature to a maximum at 1325°C and slightly decreased thereafter. Based on EDS as shown in Table 2, large grains (Fig. 4, spot A) were identified as (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ (x = 0.05), small grains (Mg₀.₉₅Mn₀.₀₅)(Ti₀.₉₅Sn₀.₀₅)O₃ (x = 0.05) (Fig. 4, spot B).

The bulk density and dielectric constant of the (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ ceramics as a function of its sintering temperature

![Fig. 2. X-ray diffraction patterns of (Mg₀.₉₅Mn₀.₀₅)(Ti₀.₉₅Sn₀.₀₅)O₄ sintered at 1325°C temperatures.](image)

![Table 1. Lattice parameters, cell volumes, and ionic polarizabilities for (Mg₁₋ₓMnₓ)(Ti₀.₉₅Sn₀.₀₅)O₄ ceramics sintered at 1325°C temperatures.](table)

| x       | a (Å)      | b (Å)      | c (Å)      | Vm (Å³)   |
|---------|------------|------------|------------|-----------|
| 0.01    | 8.4518 ± 0.0065 | 605.1307  |
| 0.03    | 8.4662 ± 0.0043 | 605.9037  |
| 0.05    | 8.4669 ± 0.0100 | 605.9682  |
| 0.07    | 8.4727 ± 0.0102 | 606.0326  |
| 0.09    | 8.4784 ± 0.0044 | 606.3550  |
The densities initially increased with increasing sintering temperature, reaching their maximum at 1325°C with $x$ form 0.01 to 0.09, and decreased sintering at higher temperature. The increase in density mainly resulted from the grain growth as shown in Fig. 3. The reduction of the density of the specimen was due to the appearance of pores resulting from an abnormal grain growth.

The dielectric properties of $(\text{Mg}_1-x\text{Mn}_x)_2(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4$ are illustrated in Fig. 6. $(\text{Mg}_1-x\text{Mn}_x)_2(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4$ ceramics sintered temperatures as a functions of the $x$ value. The relationships between $\varepsilon_r$ values and sintering temperatures revealed the same trend with those between bulk densities and sintering temperatures since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. A maximum $\varepsilon_r$ value of 14.21 was obtained for the specimen sintered at 1325°C for 4 h.

Table 2. EDX data of $(\text{Mg}_1-x\text{Mn}_x)_2(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4$ ($x = 0.05$) ceramics for spot A (atom %) and B (atom %)

| At%       | elements | Mg | Mn | Ti | Sn | O      |
|-----------|----------|----|----|----|----|--------|
| Spot A    |          | 26.98 | 1.70 | 14.27 | 0.66 | 56.40   |
| Spot B    |          | 27.29 | 1.43 | 13.76 | 0.61 | 56.48   |

Fig. 5. Relative density of $(\text{Mg}_{1-x}\text{Mn}_x)(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4$ ($x = 0.01$–0.09) ceramics system sintered at different temperatures addition.

Fig. 6. $\varepsilon_r$ values of $(\text{Mg}_{1-x}\text{Mn}_x)(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4$ ($x = 0.01$–0.09) ceramics system sintered at different temperatures.

resulted from the grain growth as shown in Fig. 3. The reduction of the density of the specimen was due to the appearance of pores resulting from an abnormal grain growth.

The dielectric properties of $(\text{Mg}_1-x\text{Mn}_x)_2(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4$ are illustrated in Fig. 6. $(\text{Mg}_1-x\text{Mn}_x)_2(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4$ ceramics sintered temperatures as a functions of the $x$ value. The relationships between $\varepsilon_r$ values and sintering temperatures revealed the same trend with those between bulk densities and sintering temperatures since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. A maximum $\varepsilon_r$ value of 14.21 was obtained for the specimen sintered at 1325°C for 4 h. It only shows a small variance in comparison with that of $(\text{Mg}_{0.95}\text{Mn}_{0.05})(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4$ ($\varepsilon_r ~15.86$) in our experiment, implying that the influence of the presence of the second phase on the $\varepsilon_r$ is almost negligible.
loss of ceramics. Kim et al.\(^{26}\) reported that the \(Q \times f\) value was closely related to the packing fraction of the structure. With the increase of the packing fraction, the lattice vibrations decreased, and then the \(Q \times f\) value would increase. As a result, the intrinsic loss decreases and \(Q \times f\) value increases.\(^{27}\) This work, the packing fraction depended on the composition of (Mg\(_{1-x}\)Mn\(_x\))(Ti\(_{0.95}\)Sn\(_{0.05}\))O\(_4\) solid solutions.

Figure 8 shows the \(\tau_f\) values of (Mg\(_{1-x}\)Mn\(_x\))(Ti\(_{0.95}\)Sn\(_{0.05}\))O\(_4\) ceramics sintered at various temperatures as a functions of Mn\(^{2+}\) content. The remarkable variations in the \(\tau_f\) values of (Mg\(_{1-x}\)Mn\(_x\))(Ti\(_{0.95}\)Sn\(_{0.05}\))O\(_4\) were recognized by the Mn\(^{2+}\) substitution for Mg\(^{2+}\) and these values ranged from \(-61\) to \(-49\) ppm/°C. Thus, it is considered that the additional improvement in the \(\tau_f\) value is required for the dielectric resonator applications at high frequency.

4. Conclusions

The dielectric properties of (Mg\(_{1-x}\)Mn\(_x\))(Ti\(_{0.95}\)Sn\(_{0.05}\))O\(_4\) solid solutions were investigated. The effect of Mn\(^{2+}\) substitution were to enhance \(Q \times f\) value from 116,000 to 347,000 GHz and densification sintering at lower temperature compared to Mg\(_2\)TiO\(_4\) which sintered at 1450°C. An inexpensive, reliable, and easy-to-process dielectric using (Mg\(_{1-x}\)Mn\(_x\))(Ti\(_{0.95}\)Sn\(_{0.05}\))O\(_4\) ceramics was achieved. Especially, it provides a very wide process window, which will be highly beneficial for practical applications. At 1325°C, the (Mg\(_{0.95}\)Mn\(_{0.05}\))(Ti\(_{0.95}\)Sn\(_{0.05}\))O\(_4\) (x = 0.05) ceramics possess a maximum \(Q \times f\) of 347,000 GHz associated with an \(\varepsilon_r\) of 14.21 and a\(\tau_f\) of \(-57.94\) ppm/°C. The Mn\(^{2+}\) substitution for Mg\(^{2+}\) improves the \(Q \times f\) value sintering at lower temperature compare with pure Mg\(_2\)TiO\(_4\). The proposed dielectric, has an extremely low loss has made it a very promising material for microwave and millimeter wave applications.

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