Low loss dielectric material system of 

\((1 - x)(\text{Mg}_{0.95}\text{Co}_{0.05})_2(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_4 - x(\text{Ca}_{0.8}\text{Sm}_{0.4/3})\text{TiO}_3\) at microwave frequency with a near-zero temperature coefficient of the resonant frequency

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1. Introduction

Wireless telecommunications is perhaps the sector of electronic industry showing the more dramatic growth in the past two decades. The use of ceramic materials in the fabrication of modern high-frequency filters and resonators has stimulated the search for new low-cost materials for technological applications. The improvement of dielectric materials has been focused on the tailoring of systems showing high unloaded quality factors (Q), high dielectric permittivity, a low dielectric loss (\(\tan \delta\)), high dielectric constant (\(\varepsilon_r\)) and near zero temperature coefficients of the resonant frequency (\(T_r\), \(f_r\)) and frequency stability and selectivity of the components under different atmospheric conditions. Nevertheless to achieve these requirements it is usually necessary to reach a compromise.\(^1,2\)

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. The use of dielectric resonators makes the size reduction of microwave components possible. Requirements for these dielectric resonators are a high dielectric constant, a low dielectric loss (\(Q > 5000\), where \(Q = 1/\tan \delta\)), and a near-zero temperature coefficient of resonant frequency (\(T_r\)).\(^3\) The high-quality factor (inverse of the dielectric loss, \(Q = 1/\tan \delta\)) plays a prominent role as \(Q\times f\) is almost constant in the microwave region.

0.95MgTiO\(_3\)–0.05CaTiO\(_3\) ceramic has an \(\varepsilon_r \approx 21\), a \(Q\times f\) of 56,000 (at 7 GHz), and a zero \(T_r\) value.\(^4\) However, it requires sintering temperatures as high as 1400–1450°C. For practical applications, their sintering temperature needs to be reduced.\(^5\)–\(^9\)

For example, MgTiO\(_3\) and Mg\(_2\)TiO\(_4\), belonging to the MgO–TiO\(_2\) binary system, are both recognized as good candidates for high frequency applications.

Mg\(_2\)TiO\(_4\)-based ceramics have wide applications as dielectrics in resonators, filters and antennas for communication, radar and global positioning systems operating at microwave frequencies. Mg\(_2\)TiO\(_4\) has a spinel-type structure and a space group of Fd-3m (227).\(^10\) Partially replacing Mg by Co and Ti replacing by Sn, the MCTS ceramic possesses a high-dielectric constant (\(\varepsilon_r\)) of \(\sim 14.7\), a high \(Q\times f\) of \(\sim 330,134\) GHz and a negative \(T_r\) of \(-46\) ppm/°C.\(^11\) The CST has a high \(\varepsilon_r\) of 120, a \(Q\times f\) value higher than 13,800 GHz and a \(T_r\) value of \(+46\) ppm/°C.\(^12\) The present work thus aims to investigate the microstructures and microwave dielectric of \((1 - x)\text{MCTS} - x\text{CST}\).

2. Experimental procedure

The starting materials were high-purity oxide powders (>99.9%): MgO, CoO, TiO\(_2\), Sm\(_2\)O\(_3\), CaO, Sm\(_2\)O\(_3\). The powders were separately prepared according to the desired stoichiometry of MCTS and CST. They were then ground in distilled water for 12 h in a ball mill with agate balls. The prepared powders were dried and calcined at 925 and 1000°C for 4 h in air. After calcination, the calcined powders were combined according to the molar fraction \((1 - x)\text{MCTS} - x\text{CST}\) 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 1100–1225°C for 4 h in air. The heating and the cooling rates were both set at 10°C/min.
The crystalline phases of the calcined powder and the sintered ceramics were identified using X-ray diffraction pattern analysis. The microstructure observations and analysis of sintered surface were performed using a scanning electron microscope (SEM, Philips XL-40FEI). Energy dispersive spectroscopy (EDS) was used to identify the existence of second phases. The apparent density of the sintered pellets were measured using the Archimedes method. The dielectric constant \( \varepsilon_r \) and the quality factor values \( Q \) at microwave frequencies were measured using the Hakki-Coleman\(^{(3)} \) dielectric resonator method under TE011 and TE016 modes as modified and improved by Courtney.\(^{(14)} \) The dielectric resonator was positioned between two brass plates. A system combined with an HP8757D network analyzer and an HP8350B sweep oscillator was employed in the measurement. The same technique was applied in measuring the temperature coefficient of resonant frequency \( \tau_f \). The test set was placed over a thermostat in the temperature range of +25 to +80°C. The \( \tau_f \) value (ppm/°C) was calculated by noting the change in resonant frequency \( \Delta f \).

\[
\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}
\]

where \( f_1 \) and \( f_2 \) represent the resonant frequencies at \( T_1 \) and \( T_2 \), respectively.

3. Results and discussion

Figure 1 shows the XRD patterns of the \((1-x)\)MCTS–xCST ceramic sintered at 1325°C for 4 h. The XRD patterns showed that peaks indicating the presence of MCTS as the main crystalline phase, in association with CST as minor phases. According to the XRD patterns, the MCTS phase exists in these specimens. The second phase \((\text{Mg}_{0.95}\text{Co}_{0.05})\text{Ti}_0.95\text{Sn}_{0.05}\text{O}_3\) (can be indexed as MgTiO\(_3\)) was detected and the XRD patterns showed a three-phase system with a MCTS phase, in association with a CST phase. Moreover, it is understood that MCTS has a ilmenite type structure and its XRD pattern is also included in Figs. 1 and 2.

Figure 2 shows the XRD patterns of the 0.84MCTS–0.16CST ceramic sintered at various temperatures for 4 h. The XRD patterns showed that peaks indicating the presence of MCTS as the main crystalline phase, in association with CST as minor phases. According to the XRD patterns, the MCTS phase exists in these specimens. The X-ray diffraction patterns of the 0.84MCTS–0.16CST ceramic systems have not been changed significantly with sintering temperatures in the range 1250–1400°C. The XRD patterns show peaks indicating the presence of MCTS as the main crystalline phase. The formation of mixed phases in the 0.84MCTS–0.16CST ceramic system was due to structural differences; therefore, a solid solution could not be obtained. The XRD patterns of the 0.84MCTS–0.16CST ceramic did not significantly change with sintering temperature in the range 1250–1400°C.

According to their report, the thermal decomposition of Mg\(_2\)TiO\(_4\) would become negligible at temperatures exceed 1400°C. However, the \((\text{Mg}_{0.95}\text{Co}_{0.05})\text{Ti}_0.95\text{Sn}_{0.05}\text{O}_3\) phase also presented as a second phase at temperatures >1400°C. It implies that the thermal decomposition mechanism is still ongoing, which might be due to the modified composition. There is also the possibility that the second phase might reappear during the cool down, even if it does not exist above 1400°C. It may be verified by using the high-temperature XRD in the future. Moreover, significant variation was not detected from the XRD patterns of the specimens at different \( x \) values, even for the \((\text{Mg}_{0.95}\text{Co}_{0.05})\text{Ti}_0.95\text{Sn}_{0.05}\text{O}_3\) phase, in our experiment. It tends to suggest that the second mechanism might be also important. The individually prepared \((\text{Mg}_{0.95}\text{Co}_{0.05})\text{Ti}_0.95\text{Sn}_{0.05}\text{O}_3\) specimen (exhibits ilmenite type structure and its XRD pattern is also included in Figs. 1 and 2.)

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for the non-uniform grain morphology, which could increase the probability of formation of pores. At 1250 and 1275°C, porous microstructures were observed again due to the inhomogeneous grain growth. The energy dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to distinguish every grain for 0.84MCTS–0.16CST ceramics sintered at 1325°C, as shown in Fig. 4. The EDX datum and data of corresponding spots A–B were showed in Table 1, respectively. The grain morphology of well developed 0.84MCTS–0.16CST ceramics could be grouped into two types: both large grains (spot A and spot B), indicating Mg–Ti phase, were MCTS, and small grains (spot B) were CST. In contrast to that of pure MCTS, CST shows a lower sintering temperature. It is because the grain size of CST is smaller than that of MCTS and adding CST to MCTS would benefit the densification of the ceramics.

Figure 5 shows the bulk densities of the (1 − x)MCTS–xCST ceramics sintered at various temperatures for 4 h as a function of sintering temperature. With increasing sintering temperature, the bulk density was found to increase to a maximum (3.85 g/cm³) at 1325°C and thereafter decrease. The increase of bulk density may be due to the elimination of pores and grain growth which decreased the grain boundaries as observed in Fig. 3. While the bulk density decreased could be attributed to the abnormal grain growth. In addition, the variation trend of εr was in accordance with that of corresponding density. The reduction of apparent density due to the abnormal grain growth is shown in Fig. 3. The variation of εr was consistent with that of apparent density. The dielectric constant also increased with sintering temperature. After reaching a maximum at 1325°C, it decreased.

Figure 6 shows the dielectric constants curves of the (1 − x)MCTS–xCST ceramic system at various sintering temperatures for 4 h. The relationship between εr values and sintering temperature shows the same trend as that between apparent density and sintering temperature since higher apparent density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. εr values of 0.84MCTS–0.16CST ceramics is 21.19 sintered at 1325°C for 4 h. As
increased CST content the dielectric of (1–x)MCTS–xCST was increased. A maximum $\varepsilon_r$ value of 22.5 was obtained 0.2MCTS–0.8CST ceramics sintered at 1325°C for 4 h.

Microwave dielectric loss can be divided into intrinsic loss and extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes and densification or porosity. Interfacial polarization is thought to play an important role in porous materials. The quality factor values ($Q\times f$) of (1–x)MCTS–xCST ceramic at various sintering temperatures are shown in Fig. 7. With increasing sintering temperature, the $Q\times f$ value increased to a maximum value and then decreased. A $Q\times f$ value of 204,974 GHz (at 9.93 GHz) was obtained for 0.84MCTS–0.16CST ceramic at 1325°C. The microwave dielectric loss is mainly caused by the lattice vibrational modes, pores, second phases, impurities, and lattice defects. Relative apparent density also plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials.

Figure 8 shows the $\tau_f$ values of the (1–x)MCTS–xCST ceramics sintered at various sintering temperatures. The temperature coefficient of resonant frequency ($\tau_f$) is known to be governed by the composition, the additives, and the second phase of the material. Because the $\tau_f$ values of MCTS and CST are −46 and −400 ppm/°C, respectively, increasing CST content makes the $\tau_f$ value more positive.

According to the Lichtenecker empirical rule, the mixing rule of $\tau_f$ value can be described as:

$$\tau_f = V_1 \tau_{f1} + V_2 \tau_{f2}$$

(3)

where $V_1$ and $V_2$ are the volume fraction of MCTS and CST, $\tau_{f1}$ and $\tau_{f2}$ are the $\tau_f$ values of the MCTS and CST, respectively. The theoretical $\tau_f$ values of (1–x)MCTS–xCST composite ceramics are calculated by using the Eq. (3) and the results are also listed in Fig. 8. CST has a higher $\tau_f$ of +400 ppm/°C, while MCTS has a lower $\tau_f$ of −46 ppm/°C. It is observed that both the theoretical $\tau_f$ values and the measured $\tau_f$ values increase with the increasing x value, and the change of the theoretical and measured $\tau_f$ values exhibits similar behavior. This implies that a near zero $\tau_f$ value can be achieved by tuning the amount of CST content. In fact, with x = 0.16, a zero $\tau_f$ value was achieved for the CST ceramic system sintered at 1325°C for 4 h.

4. Conclusion

In this paper, CST was added to MCTS to adjust $\tau_f$ values and improve the dielectric constant. 0.84MCTS–0.16CST ceramic exhibited mixed phases of MCTS as the main phase with some minor phases of CST. At 1325°C, the 0.84MCTS–0.16CST has an excellent combination of microwave dielectric properties: $\varepsilon_r = 22.5$, $Q\times f$ = 206,000 GHz (at 9 GHz), and $\tau_f$ = −0 ppm/°C sinter at 1325°C.

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