Sintering temperature dependences of $x[(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4-(1-x)\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ microwave dielectric ceramics with a zero temperature coefficient of resonant frequency

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High-quality $x[(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4-(1-x)\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramics were prepared by solid-state reaction. The products were characterized by scanning electron microscopy, X-ray diffraction, and network analyzer. $[(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$ has a dielectric constant ($\varepsilon_r$) of 18.24, a high quality factor ($Q\times f$) of $\sim$206,000 GHz, and a temperature coefficient of resonant frequency ($\tau_r$) of $\sim$20.8 ppm/°C. To produce a temperature-stable material, Ca$_{0.8}$Sr$_2$TiO$_3$, which has a large positive $\tau_r$ value of 400 ppm/°C, was added to $[(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$. 0.93[$(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$–0.07Ca$_{0.8}$Sr$_2$TiO$_3$ has an excellent combination of microwave dielectric properties: $\varepsilon_r$ $\sim$18.24, $Q\times f$ $\sim$130,000 (at 9 GHz), and $\tau_r$ $\sim$1 ppm/°C sinter at 1175°C, and can be utilized in the fabrication of microwave devices. Therefore, a band-pass filter is designed and simulated using the proposed dielectric to study its performance.

Key-words : Dielectric, Microwave ceramics, Dielectric resonators

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 ($\varepsilon_r$) and near zero temperature coefficients of the resonant frequency ($\tau_r$), because these qualities are necessary to decrease the size of the devices and assure the 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 ($\tau_r$).\(^{3,4}\) 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.\(^{5-7}\)

Mg$_2$TiO$_4$ and Mg$_3$TiO$_4$, belonging to the MgO–TiO$_2$ binary system, are both recognized as good candidates for high-frequency applications.

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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 $Fd\overline{3}m$ ($227$).\(^{8-10}\) Partially replacing Mg by Zn and Co, the $[(\text{Mg}_{0.x}\text{Zn}_{0.5})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$ ceramic possesses a high-dielectric constant ($\varepsilon_r$) of $\sim$18, a high $Q \times f$ value of $\sim$206,000 GHz (at 10.4 GHz) and a negative $\tau_r$ value of $\sim$20.8 ppm/°C.\(^{11}\) The Ca$_{0.8}$Sr$_2$TiO$_3$ has a high $\varepsilon_r$ of around 181, a $Q \times f$ value higher than 8,300 GHz and a $\tau_r$ value of 991 ppm/°C.\(^{12}\)

It is clear that the $\tau_r$ of the $[(\text{Mg}_{0.x}\text{Zn}_{0.5})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$ ceramics needs an appropriate modification before putting it to practical applications. Consequently, Ca$_{0.8}$Sr$_2$TiO$_3$, having a large positive $\tau_r$ ($\sim$991 ppm/°C)\(^{12}\) as selected as a $\tau_r$ compensator and added to the $[(\text{Mg}_{0.x}\text{Zn}_{0.5})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$ ceramics to achieve a near-zero $\tau_r$.

In this paper, Ca$_{0.8}$Sr$_2$TiO$_3$ was added to $[(\text{Mg}_{0.x}\text{Zn}_{0.5})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$ as a ceramic system of $x[(\text{Mg}_{0.x}\text{Zn}_{0.5})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4-(1-x)\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$, which demonstrated an effective compensation in its $\tau_r$ value. 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 was also investigated.

2. Experimental procedure

The starting materials were high-purity oxide powders (>$99.9\%$): MgO, ZnO, TiO$_2$, CoO, CaO, and SrO. The powders were separately prepared according to the desired stoichiometry of $[(\text{Mg}_{0.x}\text{Zn}_{0.5})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$ and Ca$_{0.8}$Sr$_2$TiO$_3$. 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°C.
1000°C for 4 h in air. After calcination, the calcined powders were mixed according to the molar fraction $x[(Mg_{0.6}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4-(1-x)Ca_0.8Sr_2TiO_3$ 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-40FEG). Energy dispersive spectroscopy (EDS) was used to identify the existence of second phases. The bulk densities 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 dielectric resonator method under TE011 and TE01\sigma modes as modified and improved by Courtney. 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 ($\Delta f$).

$$\Delta f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}$$

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 $x[(Mg_{0.6}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4-(1-x)Ca_0.8Sr_2TiO_3$ ceramic sintered at various temperatures for 4 h. The XRD patterns showed that peaks indicating the presence of $[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4$ as the main crystalline phase, in association with $Ca_0.8Sr_2TiO_3$ as minor phases. According to the XRD patterns, the $[(Mg_{0.5}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4$ phase exists in these specimens. The X-ray diffraction patterns of the 0.93$[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4-0.07Ca_0.8Sr_2TiO_3$ ceramic systems have not been changed significantly with sintering temperatures in the range 1100–1200°C. The XRD patterns show peaks indicating the presence of $[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4$ as the main crystalline phase, a minor phase of $Ca_0.8Sr_2TiO_3$. The formation of mixed phases in the 0.93$[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4-0.07Ca_0.8Sr_2TiO_3$ ceramic system was due to structural differences; therefore, a solid solution could not be obtained. The XRD patterns of the 0.93$[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4-0.07Ca_0.8Sr_2TiO_3$ ceramic did not significantly change with sintering temperature in the range 1100–1200°C.

The surface microstructure photographs of 0.93$[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4-0.07Ca_0.8Sr_2TiO_3$ ceramics for various sintering temperatures are presented in Fig. 2. Porous microstructures were observed at 1100°C the grains; however, started to grow at 1175°C and a significant increase in the grain size was observed at 1175°C. Inhomogeneous grain growth was observed at temperatures higher than 1200°C, which might degrade the microwave dielectric properties of the ceramics.

The energy dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to distinguish every grain for 0.93$[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4-0.07Ca_0.8Sr_2TiO_3$ ceramics sintered at 1175°C, as shown in Fig. 3(a). The EDX datum and data of corresponding spots A–B were showed...
in Fig. 3(b), respectively. The grain morphology of well-developed 0.93[(Mg0.6Zn0.4)0.95Co0.05]2TiO4-0.07Ca0.8Sr2TiO3 ceramics could be grouped into two types: both large grains (spot A), indicating Mg-Ti phase, were [(Mg0.6Zn0.4)0.95Co0.05]2TiO4, and small cubic-shape grains (spot B) were Ca0.8Sr2TiO3. In contrast to that of pure [(Mg0.6Zn0.4)0.95Co0.05]2TiO4, Ca0.8Sr2TiO3 shows a lower sintering temperature. It is because the grain size of Ca0.8Sr2TiO3 is smaller than that of [(Mg0.6Zn0.4)0.95Co0.05]2TiO4 and adding Ca0.8Sr2TiO3 to [(Mg0.6Zn0.4)0.95Co0.05]2TiO4 would benefit the densification of the ceramics.

Figure 4 shows the bulk densities of the x[(Mg0.6Zn0.4)0.95Co0.05]2TiO4-(1-x)Ca0.8Sr2TiO3 ceramics sintered at various temperatures for 4h. With increasing temperature, the bulk density increased to a maximum value of 3.66 g/cm³ at 1175°C, and then it decreased. The reduction of density due to the abnormal grain growth is shown in Fig. 2. The variation of εr was consistent with that of density. The dielectric constant also increased with sintering temperature. After reaching a maximum at 1175°C, it decreased.

Figure 5 shows the dielectric constants curves of the x[(Mg0.6Zn0.4)0.95Co0.05]2TiO4-(1-x)Ca0.8Sr2TiO3 ceramic system at various sintering temperatures for 4h. The relationship between εr values and sintering temperature shows 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. εr values of 0.93[(Mg0.6Zn0.4)0.95Co0.05]2TiO4-0.07Ca0.8Sr2TiO3 ceramics increased from 17.90 to 18.24 when the sintering temperature was increased from 1100 to 1175°C. A maximum εr value of 20.00 was obtained for 0.89[(Mg0.6Zn0.4)0.95Co0.05]2TiO4-0.11Ca0.8Sr2TiO3 ceramics sintered at 1175°C for 4h.

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©f) of x[(Mg0.6Zn0.4)0.95Co0.05]2TiO4-(1-x)Ca0.8Sr2TiO3 ceramic at various sintering temperatures are shown in Fig. 6. With increasing sintering temperature, the Q © f value increased to a maximum value and then decreased. A maximum Q © f value of 160,000 GHz was obtained for 0.95[(Mg0.6Zn0.4)0.95Co0.05]2TiO4-0.05Ca0.8Sr2TiO3 ceramic at 1175°C. The degradation of the Q © f value can be attributed to abnormal grain growth at higher sintering temperatures, as shown in Fig. 2. The microwave dielectric loss is mainly caused by the lattice vibrational modes, pores, second phases, impurities, and lattice defects.
density also plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials.

Figure 7 shows the $\tau_f$ values of the $x\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - (1-x)\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ 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 $\text{[(Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$ and $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ are $-20.8$ and $991$ ppm/°C, respectively, increasing $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ content makes the $\tau_f$ value more positive. This implies that a zero $\tau_f$ value can be achieved by tuning the amount of $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ content. In fact, with $x = 0.93$, a near zero $\tau_f$ value was achieved for the $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic system sintered at $1175°C$ for 4 h.

Table 1 shows the microwave dielectric properties of the $x\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - (1-x)\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic system sintered at $1175°C$ for 4 h. When the $(1-x)$ value increased from 0.05 to 0.11, the $\tau_f$ values of the $x\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - (1-x)\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic system changed from $-13$ to $18$ ppm/°C. The $\tau_f$ curves went through zero, which indicates that a zero $\tau_f$ value can be obtained by appropriately adjusting the $x$ value of the $x\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - (1-x)\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic system. With $x = 0.93$, the $0.93\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - 0.07\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic system showed good temperature stability with $\tau_f \approx 1$ ppm/°C. However, when the $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ content was increased, the $Q \times f$ value decreased because the $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic has a low $Q \times f$ value of $8,000$ GHz.

Figure 8 shows the physical layout of the designed filter with a center frequency of $2.4$ GHz. The simulation results are listed in Table 2. Compared to FR4 and alumina, the filter using the 0.93$\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - 0.07\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic shows a tremendous reduction in the insertion loss and demonstrates a large reduction in its size. This design approach enables one to use an EM simulator (IE3D) to complete the filter design in order to determine the physical dimensions of the filters.

4. Conclusion

In this paper, $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ was added to $\text{[(Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Co}_{0.05}]_2\text{TiO}_4$ to adjust $\tau_f$ values and improve the dielectric constant. 0.93$\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - 0.07\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic exhibited mixed phases of $\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4$ as the main phase with some minor phases of $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$. The $x\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - (1-x)\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic system showed mixed phases of $\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4$ as the main crystalline phase, a minor phase of $\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$. At $1175°C$, the 0.93$\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - 0.07\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic demonstrated excellent microwave dielectric properties: $\varepsilon_r \approx 28.14$, $Q \times f \sim 130,000$ GHz (at $9$ GHz), and $\tau_f \sim 1$ ppm/°C sintered at $1175°C$. Their excellent dielectric properties make the 0.93$\{\text{Mg}_{0.6}\text{Zn}_{0.4}\}_{0.95}\text{Co}_{0.05}\}_2\text{TiO}_4 - 0.07\text{Ca}_{0.8}\text{Sr}_2\text{TiO}_3$ ceramic capable in the application of microwave devices.
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