Microwave dielectric properties and microstructure of \([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3.02\) ceramics

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\([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3.02\) ceramics were fabricated using solid-state synthesis for mobile communications. Zn\(^{2+}\) and Co\(^{3+}\) substitution enhanced the Q\(_{xf}\) value and allowed densification sintering at lower temperature compared to that for \([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3.02\), which must be sintered at 1175°C. \([(\text{Mg}_{6.8}\text{Zn}_{3.2}\text{Co}_{0.05}\text{TiO}_3)_{1.02}\) sintered at 1175°C has a dielectric constant of 20.1, a Q\(_{xf}\) value of 280,000 GHz, and a \(\tau_f\) value of -64.7 ppm/°C. The maximum quality factor multiples resonant frequency (Q\(_{xf}\)) value of around 280,000 GHz was obtained for the \([\text{Mg}_{6.6}\text{Zn}_{3.4}\text{Co}_{0.05}]_{1.02}\text{TiO}_4\).

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1. Introduction

The rapid growth of wireless communication systems has led to increasing demand for small-scale high-frequency resonators, filters, and antennas capable of operating in the GHz range.\(^7\) 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.\(^7\) For high efficiency and stability, many studies have focused on developing new dielectric materials with a high quality factor (Q\(_{xf}\)) and a near-zero temperature coefficient of resonant frequency (\(\tau_f\)) for use as dielectric resonator and microwave device substrates.\(^7\)–\(^9\)

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. The non-stoichiometric Mg\(_{1.1}\)TiO\(_{3.8}\) (Q\(_{xf}\) ~ 357600 GHz, dielectric constant of 18.3, \(\tau_f\) of -50 ppm/°C) ceramics were first reported by Huang.\(^10\) The high Q\(_{xf}\) value is associated with the single MgTiO\(_2\) phase. However, Mg\(_{1.1}\)TiO\(_{3.8}\) sintering temperature at as high as 1450°C.

In this paper, the Zn\(^{2+}\) and Co\(^{3+}\) substitution Mg\(^{2+}\) to form \([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3.02\). The ionic radius of Mg (0.78 Å) is similar to that of Zn\(^{2+}\) (0.83 Å) and Co\(^{3+}\) (0.82 Å). Consequently, the substitution greatly increased the Q\(_{xf}\) and is an extremely reliable process for obtaining materials with stable dielectric properties. The microwave dielectric properties of the synthesized ceramics were analyzed in terms of densification, X-ray diffraction (XRD) patterns, and microstructures. The correlation between the microstructure and the Q\(_{xf}\) value was also investigated.

2. Experimental procedure

\([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3.02\) \((x = 0.1–0.5)\) was prepared via the solid-state mixed oxide route with starting materials of high-purity oxide powders (>99%): MgCO\(_3\)·0.2708H\(_2\)O. The decomposition reaction of MgCO\(_3\)·0.2708H\(_2\)O at temperatures of 600–700°C for 5 h can be represented as follows:\(^10\)

\[
\text{MgCO}_3 \cdot 0.2708\text{H}_2\text{O} \rightarrow \text{MgO} + \text{CO}_2 + x\text{H}_2\text{O}
\]

The ceramics was first fired at 650°C to avoid moisture contain. The weighed raw materials were mixed by ball milling with agate media in distilled water for 24 h. The mixtures were then dried and calcined at 1000°C for 4 h. The 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 a 100 mesh, and pressed into pellets, 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 1075–1200°C for 4 h in air.

The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III-V) patterns 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\(_\alpha\) radiation (\(\lambda = 0.15406\) nm) with a Siemens D5000 diffractometer (Munich, Germany) operated at 40 kV and 40 mA. The lattice constant calculation was accomplished using GSAS software with the Rietveld method to fit the XRD patterns.\(^11\) The microstructural observations and analysis of the sintered surfaces were performed using scanning electron microscopy (SEM, Philips XL-40FEG).

The bulk densities of the sintered pellets were measured by the Archimedean method. The 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.\(^12\) This method utilizes parallel conducting plates and coaxial probes in T\(_{011}\) mode, where TM 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.

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3. Results and discussion

Figure 1 shows the XRD patterns of the [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} ceramic sintered at various temperatures for 4 h. The XRD patterns show peaks indicating the presence of [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} as the main crystalline phase (rhombohedral, ICDD-PDF 01-0737-7552). According to the XRD patterns, the [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} phase exists in these specimens. The XRD patterns of the [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} ceramics system did not change significantly with sintering temperature in the range 1075–1200°C, without finding any secondary phase. Figure 2 shows XRD patterns for [(Mg\textsubscript{0.6}Zn\textsubscript{0.4})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} at 1200°C. The secondary phase MgTi\textsubscript{0.5}O\textsubscript{4} (ICDD#00-035-0792) appeared at δ = 0.01; this phase degraded the microwave dielectric properties. When δ was 0.02, only a single phase (MgTiO\textsubscript{3}) was observed. The insertion of Zn\textsuperscript{2+} decreased the Zn\textsuperscript{2+} content. The results indicate that with the partial replacement of Mg\textsuperscript{2+} by Zn\textsuperscript{2+} and Co\textsuperscript{2+}, [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} ceramics form solid solutions. Moreover, the formation of [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} leads to an increase in the lattice parameters from a = b = 5.0581 Å and c = 13.9072 Å for [(Mg\textsubscript{0.9}Zn\textsubscript{0.1})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02} to a = b = 5.0672 Å and c = 13.9221 Å for [(Mg\textsubscript{0.5}Zn\textsubscript{0.5})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}. This is due to the ionic radius of Zn\textsuperscript{2+} (0.83 Å) being larger than that of Mg\textsuperscript{2+} (0.78 Å).

SEM micrographs of [(Mg\textsubscript{0.6}Zn\textsubscript{0.4})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} ceramics sintered at various temperatures for 4 h are shown in Fig. 3. The grain size increased with increasing sintering temperature. However, rapid grain growth was observed at 1200°C and the pores were almost eliminated for the specimen sintered at 1100°C. The relative density and dielectric constant of the [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} (x = 0.1–0.5) solid solutions as functions of the sintering temperature are shown in Fig. 3. Notice that the relative densities increase with increasing sintering temperature to a maximum at 1175°C and slightly decrease thereafter. Based on energy-dispersive X-ray spectroscopy spectra, large grains (Fig. 4, spot A) were identified as [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} (Mg K: 19.12, Co K: 2.78, Zn L: 9.27, Ti K: 26.42, O K: 42.41 as shown in Table 2) and some small grains is also identified as [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} (Fig. 4, spot B, Mg K: 10.13, Co K: 1.51, Zn L: 6.89, Ti K: 27.53, O K: 53.94 as shown in Table 2).

The relative density of the [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} ceramics as a function of sintering temperature is shown in Fig. 5. Note that the densities initially increase with increasing sintering temperature, reaching their maximum at 1175°C with x = 0.4, and then decreased with sintering at higher temperature. The increase in density mainly resulted from the grain growth, as shown in Fig. 2. The reduction of the density of the specimen was due to the appearance of pores resulting from abnormal grain growth. With increased Zn\textsuperscript{2+} content (x = 0.5), the sintering temperature decreased. The increased Zn\textsuperscript{2+} content would decrease relative density sintering at higher temperatures, due to the [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} with more Zn\textsuperscript{2+} content would be evaporate.

The dielectric properties of [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} are shown in Fig. 6. [(Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1.02}Ti\textsubscript{0.02} ceramics sintered at various temperatures as a function of the x value. The relationship between dielectric constant and the sintering temperature has the same nature.
trend as those between ionic polarizability (Table 1), relative density, and sintering temperature since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. The dielectric constant of a microwave dielectric ceramic is known to be affected by ionic polarizability.13) The ε_r values of [(Mg_1-xZn_x)_{0.95}Co_{0.05}]_{1.02}TiO_{3.02} decreased with Zn^{2+} substitution for Mg^{2+}, as mentioned above. The ionic polarizabilities (α_m) of [(Mg_1-xZn_x)_{0.95}Co_{0.05}]_{1.02}TiO_{3.02} were estimated in order to clarify the effects of Zn^{2+} substitution for Mg^{2+} on the dielectric constant by using the Clausius-Mossotti equation:

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

where ε_r, V_m, and α_m are the relative permittivity, molar volume, and macroscopic polarizability, respectively. Using the experimental relative permittivity data and unit-cell volume data, the macroscopic polarizability, α_m, was calculated. The theory polarizability data in Table 1 show an almost sigmoidal increase with increasing Zn^{2+} content, while the unit-cell volume increased with x. The relative permittivity increased with α_m. When the value of α_m approached 3V_m/4π, the relative permittivity increased very rapidly. It has also been reported that the

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**Fig. 3.** SEM photographs of [(Mg_0.6Zn_0.4)_{0.95}Co_{0.05}]_{1.02}TiO_{3.02} ceramics (a) 1075, (b) 1100, (c) 1125, (d) 1150, (e) 1175°C, (f) 1200 sintered at various temperatures for 4 h.

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**Table 2.** The EDX Data of the [(Mg_1-xZn_x)_{0.95}Co_{0.05}]_{1.02}TiO_{3.02} Ceramics for Spots A and B Shown in Fig. 4

| Spots | Atom (%) |
|-------|----------|
|       | Mg (K)   | Co (K) | Zn (L) | Ti (K) | O (K) |
| A     | 11.12    | 2.78   | 6.27   | 26.42  | 53.41 |
| B     | 10.13    | 1.51   | 6.89   | 27.53  | 53.94 |

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**Fig. 4.** The marks of SEM for the [(Mg_0.6Zn_0.4)_{0.95}Co_{0.05}]_{1.02}TiO_{3.02} ceramics sinter at 1200°C.

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**Fig. 5.** Relative bulk density of [(Mg_1-xZn_x)_{0.95}Co_{0.05}]_{1.02}TiO_{3.02} ceramics system sintered at different temperatures addition.
macroscopic polarizability of complex systems with an ideal symmetry can be determined from the summation of the polarizability of the constituent cations:

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

The theoretical polarizability [denoted as \(\alpha_m(\text{theory})\)] values calculated according Eq. (2) are compared with the experimental polarizability [denoted as \(\alpha_m(\text{exp})\)] determined using the Clausius-Mossotti relation, Eq. (2) in Table 1. It is noted that \(\alpha_m(\text{exp})\) for the \([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3_{0.02}\) end member is larger than the \(\alpha_m(\text{theory})\) value, the \(\alpha_m(\text{exp})\) values are larger than \(\alpha_m(\text{theory})\). Shannon suggested that deviations from additivity of ionic polarizability arise when the compression or rattling of cations occurs in the structural sites as the cation sizes are varied. The lower \(\alpha_m(\text{exp})\) value for \([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3_{0.02}\) may thus be due to compression effects caused by the large difference between the ionic polarizabilities of \(\text{Mg}^{2+}\) and \(\text{Zn}^{2+}\). Therefore, the \([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3_{0.02}\) dielectric constant was leading by ionic polarizabilities.

\[\text{Figure 7}\] shows the Qxf values of \([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3_{0.02}\) ceramics sintered at various temperatures as a functions of the \(x\) value. With increasing sintering temperature, the Qxf value increased to a maximum value and then decreased. A maximum Qxf value of 280,000 GHz was obtained for \([(\text{Mg}_{1-x}\text{Zn}_x)_{0.95}\text{Co}_{0.05}]_{1.02}\text{TiO}_3_{0.02}\) (\(x = 0.4\)) ceramic at 1175°C. The degradation of the Qxf value can be attributed to abnormal grain growth at higher sintering temperatures, as shown in \[\text{Fig. 2}\]. The microwave dielectric loss is mainly caused by the lattice vibrational modes, pores, secondary 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, and 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 the microwave frequency range. In this model, when employing one-phonon absorption approximation, a roughly reciprocal relationship between Qxf and the dielectric constant is obtained:

\[Q_{\text{xf}}f = A^{-1}\]  

where the frequency \(f\) should be limited to the vicinity of the phonon engine frequencies, on 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
where \( Q_0 \) is the intrinsic dielectric Q measured from the microwave reflective spectrum and \( P \) is the porosity. However, for high-Qxf ceramics with a 10^6 GHz magnitude order, such as polycrystalline Al_2O_3 ceramic, even a small amount of porosity considerably reduces the dielectric Q by:

\[
Q = Q_0 (1 - 1.5P)
\]

(4)

where \( Q_0 \) is the full density dielectric quality factor (1.565 \times 10^3), \( A' \) is a constant (= 6.3 \times 10^{-3}), and \( P \) is the porosity. According to Eqs. (4) and (5), the porosity in the \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) end component is 8%. The maximum Qxf Qxf value is 280,000 GHz sintered at 1175°C with \( x = 0.4 \). The Qxf value increased with increasing Zn^{2+} content. However, when the \( x \) value was 0.5, the Qxf value decreased due to Zn^{2+} evaporating at higher sintering temperature. Many factors affect the microwave dielectric loss of dielectric resonators, such as the lattice vibration modes, pores, and secondary phases. Generally, a larger grain size, i.e., a smaller grain boundary, indicates a reduction in lattice imperfection and thus a reduction in the dielectric loss. When \( x \) was increased from 0.1 to 0.4, the Qxf value of \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) increased dramatically from 147,000 to 280,000 GHz.

Figure 8 shows the \( \tau_f \) values of \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) ceramics sintered at various temperatures as a function of the Zn^{2+} content. The remarkable variations in the \( \tau_f \) values of \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) are due to the Zn^{2+} substitution for Mg^{2+}; these values ranged from −54.3 to −65 ppm/C. Thus, additional improvement in the \( \tau_f \) value is required for dielectric resonator applications at high frequency.

The temperature coefficient of resonant frequency, TCF, can be defined as follows:

\[
TCF = -\alpha - \frac{1}{2} \tau_f
\]

(6)

A plot of the trend of TCF values versus permittivity of \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) ceramics shows that the TCF value decreased from −54 to −64.7 ppm/C when the \( x \) value was increased from 0.1 to 0.5. Hence, the TCF value has a linear relationship with the \( x \) value.

4. Conclusion

The dielectric properties of \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) solid solutions were investigated. The Zn^{2+} and Co^{2+} substitutions enhanced the Qxf value from 126,000 to 280,000 GHz and lowered the densification sintering temperature \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) sintered at 1175°C compared to MgTiO$_3$. An inexpensive, reliable, and easy-to-process dielectric using \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) ceramics was obtained. It provides a very wide process window, which will be highly beneficial for practical applications. At 1175°C, the \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) ceramics have a maximum Qxf of 280,000 GHz, an \( \varepsilon_r \) of 19.76, and a \( \tau_f \) of −61.3 ppm/C. \([\text{Mg}_1.0\text{Zn}_{0.95}\text{Co}_{0.05}]_1.02\text{TiO}_3.02\) ceramics sintering at lower temperature compared to pure MgTiO$_3$ (sintering at 1450°C) and obtained ultra low loss for microwave applications. The proposed dielectric has an extremely low loss, making it a very promising material for microwave and millimeter wave applications.

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