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Dielectric properties and crystal structure of Mg_2TiO_4 ceramics substituting Mg^{2+} with Zn^{2+} and Co^{2+}

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ABSTRACT

Solid solutions of $[(Mg, Zn)]_2TiO_4$–Co_2TiO_4 were used to prepare $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ have been fabricated using solid-state synthesis for mobile communications. The effect of Zn^{2+} and Co^{2+} substitution were to enhance $Q \times f$ value and densification sintering at lower temperature compared to Mg_2TiO_4 which sintered at 1450 °C. As an optimal compose, $[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4$ successfully demonstrated a dielectric constant of 18.18, a $Q \times f$ of 206,000 GHz and a τ_f value of −20.8 ppm/°C sintered at 1225 °C. The maximum quality factor multiples resonant frequency ($Q \times f$) value of around 2100,000 GHz was obtained for the $[(Mg_{0.6}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4$, and added more Zn^{2+}, the $Q \times f$ decrease $[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4$.

1. Introduction

The rapid growth of recent wireless communication systems led to an increasing demand for small-scale high-frequency resonators, filters and antennas capable of operating in the GHz range [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 [3–6]. At the same time, in order to work with high efficiency and stability, many researches have been focusing on developing new dielectric materials with a high quality factor ($Q \times f$) and a near-zero temperature coefficient of resonant frequency (τ_f) for use as dielectric resonator and microwave device substrate [7–9].

Mg_2TiO_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_2TiO_4 has a spinel-type structure and a space group of $Fd\bar{3}m(227)$ [10].

In this paper, the Zn^{2+} and Co^{2+} substitution content Mg_2TiO_4 to formed $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$. Because the ionic radius of Mg (0.78 Å) are similar to that of Zn (0.83 Å) and Co (0.82 Å). Consequently, not only did the substitution tremendously boost the $Q \times f$ to an even higher value, it also ensured an extremely reliable process to achieve material of 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 ($[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ($x = 0.1$–0.5) were prepared by the solid-state mixed oxides route with starting materials of high-purity oxide powders (>99.9%): MgO, ZnO, CoO and TiO_2. Because MgO is hygroscopic, it was first fired at 600 °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 °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 1175–1300 °C for 4 h in air.

The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) spectra were collected using Cu Kα radiation (at 30 kV and 20 mA) and a graphite monochrometer in the 2θ range of 10–80°. The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα ($\lambda = 0.15406$ nm) radiation with a Siemens D5000 diffractometer (Munich, Germany) operated at 40 kV and 40 mA. The latttice constant calculation was accomplished using GSAS software with Rietveld method to fit the XRD patterns [11]. The microstructural observations and analysis of the sintered surface were performed using a scanning electron microscope (SEM, Philips XL-40FEG).

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 [12]. This method utilizes parallel conducting plates and coaxial probes in TE_{011} 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 20–80 °C. A HP8757D network analyzer and a HP8350B sweep oscillator were employed in the measurement.

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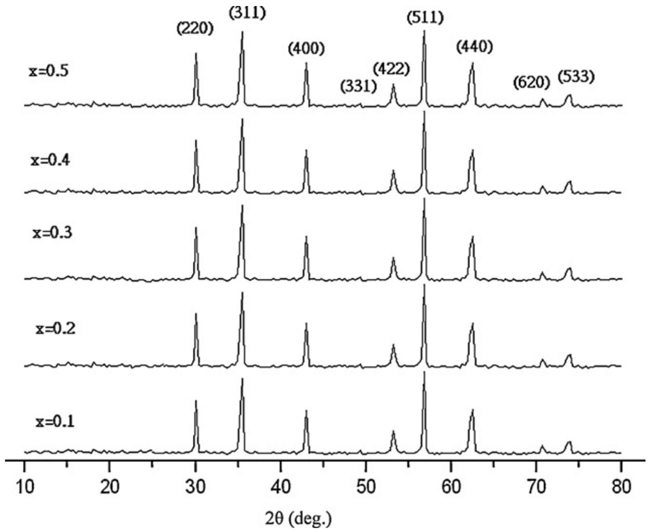


Fig. 1. X-ray diffraction patterns of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics sintered at 1225 °C.

3. Results and discussion

XRD patterns recorded from the $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics sintered at different temperatures for 4 h are shown in Fig. 1. The cubic-structured $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ (which can be indexed as Mg_2TiO_4, ICDD-PDF#00-025-1157), belonging to the space group $Fd\bar{3}m(227)$, was identified as the main phase, implying the forming of a solid solution. In addition to $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$, without any second phase was observed. Moreover, significant variation was not detected from the XRD patterns of the specimens at different x values ($x = 0.1$–0.5) in our experiment.

In order to confirm the formation of the solid solution, the lattice parameters of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics sintered at 1225 °C were measured and are demonstrated in Table 1. An increase in the lattice parameters was found for $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics in comparison with that of Mg_2TiO_4. The results indicated that with the partial replacement of Mg^{2+} by Zn^{2+} and Co^{2+}, $[(Mg, Zn)]_2TiO_4$–Co_2TiO_4 ceramics would form solid solutions. Moreover, formation of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ would lead to an increase in the lattice parameters from $a = b = c = 8.4415$ Å in Mg_2TiO_4 to $a = b = c = 8.4498$ Å in $[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4$. This is because the ionic radii of Co^{2+} (0.82 Å) and Zn^{2+} (0.83 Å) are larger than that of Mg^{+2} (0.78 Å). The Co_2TiO_4 and Zn_2TiO_4 phase are formed at a significantly lower temperature 1225 °C than that of the Mg_2TiO_4 [13].

SEM micrographs of $[(Mg_{0.6}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4$ ceramics sintered at various temperatures for 4 h are shown in Fig. 2. The grain size increased with increasing sintering temperatures. However, rapid grain growth was observed at 1225 °C and the pores were almost eliminated for the specimen sintered at 1200 °C. The relative density and dielectric constant of the $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ($x = 0.1$–0.5) solid solutions as a function of the sintering temperature for 4 h are illustrated in Fig. 3. Notice that the densities apparently increased with increasing sintering temperature to a maximum at 1200 °C and slightly decreased thereafter. Based on EDS, large grains (Fig. 3(a), spot A) were identified as $[(Mg_{0.}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4$ (Mg K: 19.42, Co K: 3.67, Zn-L: 10.18, Ti K: 25.31, O K: 41.42). Moreover, the Zn^{2+} content slightly decreased from 10.83 at.% at 1175 °C to 7.82 at.% at 1300 °C and dramatically drop off thereafter. Zn^{2+} would begin to evaporate at sintering temperatures higher than 1275 °C. Similar result was reported previously.

The bulk density and dielectric constant of the $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics as a function of its sintering temperature for 4 h are shown in Fig. 4. Note that the densities initially increased with increasing sintering temperature, reaching their maximum at 1250 °C with x from 0.1 to 0.4, and decreased 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 an abnormal grain growth. With increased Zn^{2+} content ($x = 0.5$), the sintering temperature decreased. $[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4$ could be sintered at 1200 °C due to more Zn^{2+} content.

The dielectric properties of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ are illustrated in Fig. 5. $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics sintered temperatures as a functions of the x value. The relationships between ε_r values and sintering temperatures revealed the same trend with those between relative densities and sintering temperatures 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 [14]; the ε_r values of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ decreased with Zn^{2+} substitution for Mg^{2+} as mentioned above. A similar result was reported for SAN and SAT; Guo et al. [15] suggested that the electronic changes which arose from the variation of the Nb–O and Ta–O bond strengths in the crystal structures of SAN and SAT may decrease the ε_r value. The ionic polarizabilities (α_{obs}) of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ were estimated in order to clarify the effects of Zn^{2+} substitution for Mg^{2+} on the dielectric constant by using the Clausius–Mosotti equation:

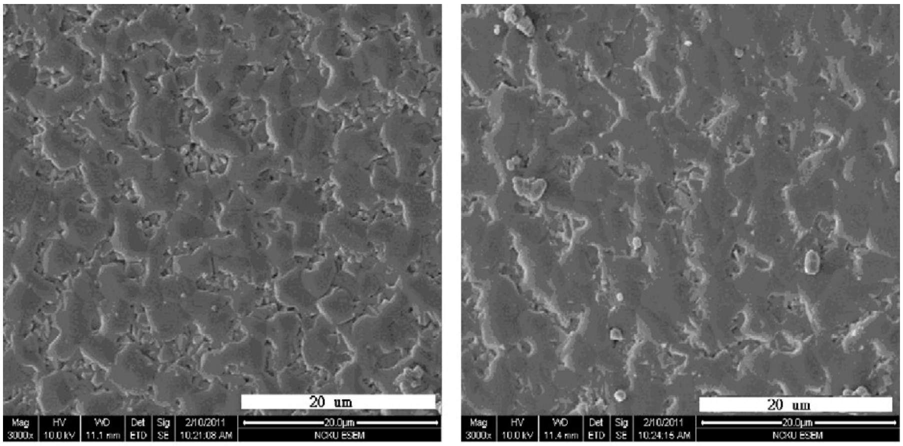
$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_m}{3V_m - 4\pi\alpha_m} \tag{1}$$

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 show in Table 1 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 $3V_m/4\pi$, 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,

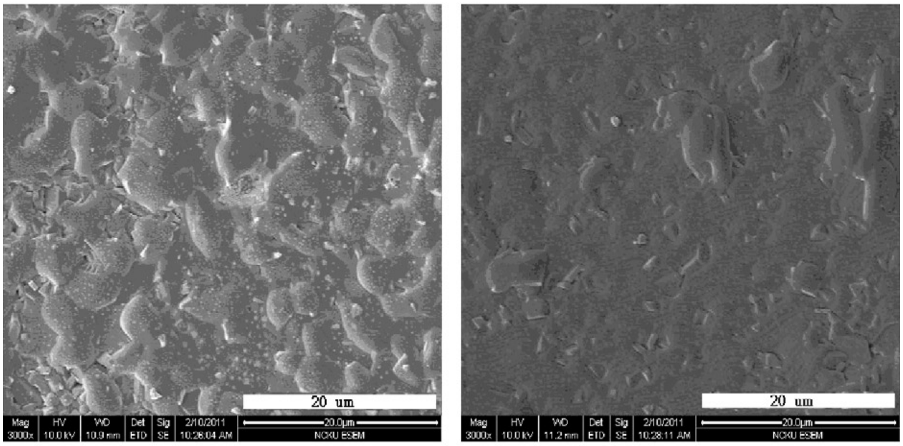
$$\alpha_m = \sum \alpha(\text{ions}) \tag{2}$$

The theoretical polarizability (denoted as α_m(theory)) values calculated according Eq. (2) are compared with the "experimental" polarizability denoted as α_m(exp) determined using the Claussius–Mossotti relation, Eq. (2) in Table 1. It is noted that α_m(exp) for the $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ end member is large than the α_m(theory) value, the α_m(exp) values are larger than α_m(theory). Shannon [14] suggested that deviations from additivity of ionic polarizability arise when the compression or rattling of cations occur in the structural sites as the cation sizes are varied. The lower α_m(exp) value for $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ may thus be due to compression effects caused by the large difference between the ionic polarizabilities of Mg^{2+} and Zn^{2+}. This agrees with the harmonic-oscillator model [16].

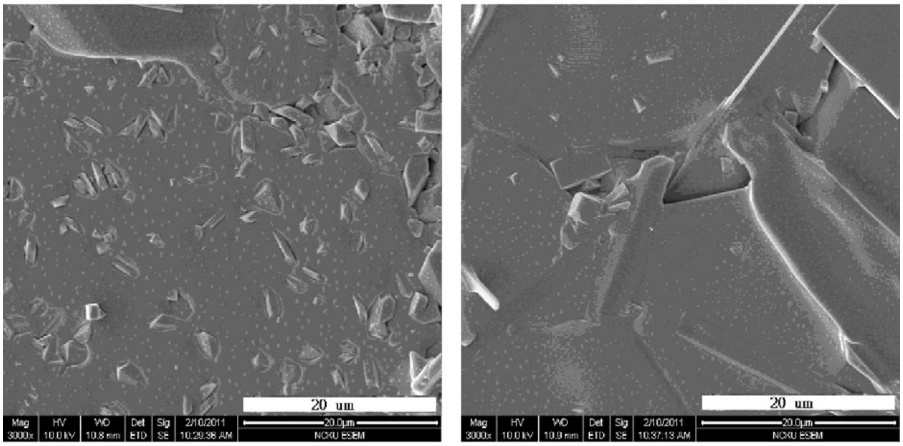
Fig. 6 shows the $Q \times f$ values of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics sintered at various temperatures as a functions of the x value. The quality factor values ($Q \times f$) of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramic at various sintering



(a)1175 (b)1200



(c)1225 (d)1250



(e)1275 (f) 1300

Fig. 2. SEM photographs of $[(Mg_{0.6}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4$ ceramics: (a) 1175 °C, (b) 1200 °C, (c)1225 °C, (d) 1250 °C, (e) 1275 °C, (f) 1300 °C sintered at various temperatures for 4 h.

temperatures are shown in Fig. 6. With increasing sintering temperature, the $Q \times f$ value increased to a maximum value and then decreased. A maximum $Q \times f$ value of 210,000 GHz was obtained for $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ($x = 0.4$) ceramic at 1225 °C. The degradation of the $Q \times f$ 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. Relative density also plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials. As well known, factors that influence the dielectric Q fall into two categories: intrinsic and extrinsic. The

Table 1
Lattice parameters, cell volumes, ionic polarizablities, and ε_r data for sintered $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$.

	x					
	0	0.1	0.2	0.3	0.4	0.5
$a = b = c$ (Å)	8.445	8.4452	8.4463	8.4474	8.4486	8.4498
V_m (Å^3)	602.2807	602.3235	602.5589	602.7943568	603.0512842	603.3083
α_m(theory)	107.824	110.2384	111.3328	112.4272	113.5216	114.616
α_m(exp)	116.8837	118.2831	119.349	120.1812721	121.5696307	122.6798
Dielectric(cal.)	11.99532	12.83432	13.24833	13.68958939	14.15899342	14.66128
Dielectric(measured)	14.1	14.87	15.57	16.15	17.23	18.18

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 pure 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 between $Q \times f$ and the dielectric constant could be obtained as

$$Q \times f \propto \varepsilon^{-1} \tag{2′}$$

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 evidenced that the extrapolation of Eq. [2] from microwave frequencies down to megawatt frequencies (1–4 magnitude orders below the optical phonon engine fre-quency) at room temperature could also give a satisfying magnitude order

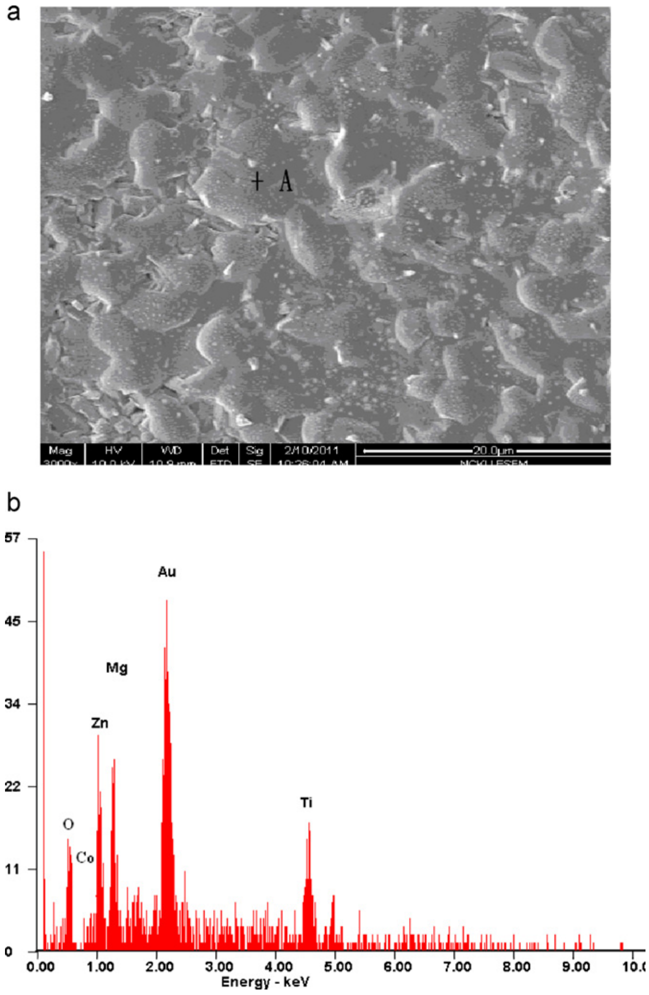


Fig. 3. (a) The marks of SEM for the $[(Mg_{0.6}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4$ ceramics sinter at 1225 °C and (b) EDX data of $[(Mg_{0.6}Zn_{0.4})_{0.95}Co_{0.05}]_2TiO_4$ ceramics for spot A. Spot A (at.%): Mg K: 19.42, Co K: 3.67, Zn-L: 10.18, Ti K: 25.31, O K: 41.42.

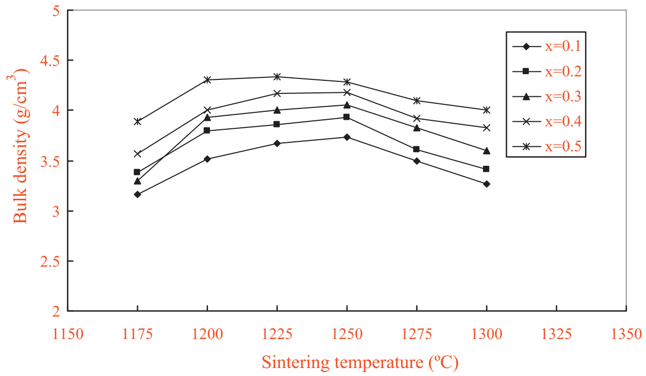


Fig. 4. Bulk density of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics system sintered at different temperatures addition.

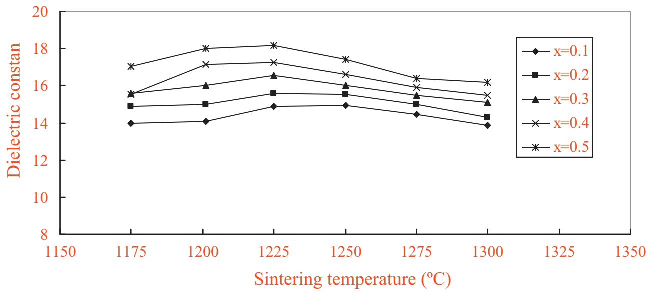


Fig. 5. ε_r values of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics system sintered at different temperatures.

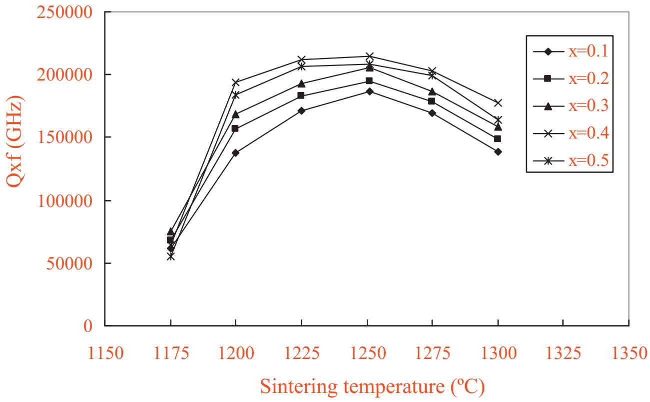


Fig. 6. $Q \times f$ values of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics system sintered at different temperatures.

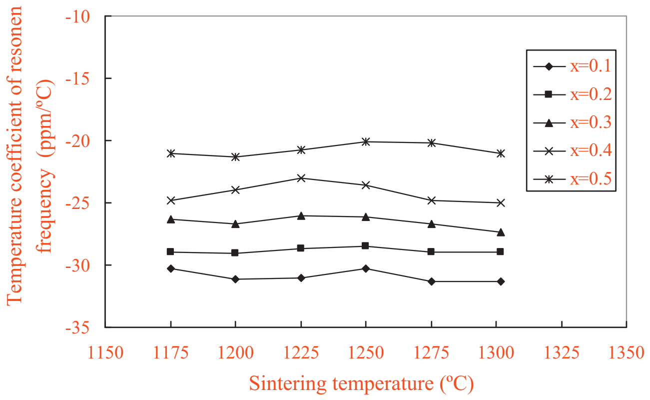


Fig. 7. Temperature coefficient of resonant frequency values of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics system sintered at different temperatures.

of dielectric Q for well-processed ceramics. The result, however, showed that the dependence of $Q \times f$ on ε_r only yielded $Q \times f \propto \varepsilon_r^{-0.6}$, indicating a rather smoother increasing rate of $Q \times f f$ value with ε_r compared with Eq. [2]. The most probable reason for this phenomenon could be associated with the extrinsic origins. As acknowledged by many authors, the porosity in dielectrics had deleterious effects on dielectric $Q \times f$ values, whose influencing degree, however, varied with different dielectrics. For low dielectric $Q \times f$ ceramics with 10^3 GHz magnitude order, the effect of porosity on dielectric Q could be described as

$$Q = Q_o(1 - 1.5P) \tag{3}$$

where Q_o was the intrinsic dielectric Q measured by microwave reflective spectrum and P was the porosity. However, as for high $Q \times f$ ceramics with 10^5–10^6 GHz magnitude order such as polycrystalline Al_2O_3 ceramic, even a small amount of porosity would considerably reduce the dielectric Q by

$$\frac{1}{Q} = (1 - P)\frac{1}{Q_o} + A'P\left(\frac{P}{1 - P}\right)^{2/3} \tag{4}$$

where Q_o was the full density dielectric quality factor (1.565×10^{-5}), A' was a constant of 9.277×10^{-3} and P was the porosity. According to Eqs. (3) and (4), 8% porosity, which was the porosity in $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ end component in the present study. The maximum $Q \times f$ value sintered at 1250 °C with x from 0.1 to 0.4, and more content Zn^{2+}, maximum $Q \times f$ value is 206,000 GHz sintered at 1225 °C. The $Q \times f$ value increased with increasing of Zn^{2+} content, but the x value is 0.5, $Q \times f$ value decreased due to the Zn^{2+} evaporate 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 $Q \times f$ value of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ increased dramatically from 55,000 to 210,000 GHz.

Fig. 7 shows the τ_f values of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics sintered at various temperatures as a functions of the Zn^{2+} content. The remarkable variations in the τ_f values of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ were recognized by the Zn^{2+} substitution for Mg^{2+} and these values ranged from −31 to −20.1 ppm/°C. Thus, it is considered that the additional improvement in the τ_f value is required for the dielectric resonator applications at high frequency.

The temperature coefficients of resonant frequency, TCF, could be defined as following:

$$TCF = -\alpha_l - \frac{1}{2}\tau_\varepsilon \tag{5}$$

where α_l is the linear thermal expansion coefficient and τ_ε is the temperature coefficient of permittivity. Because α_l of microwave dielectric is known to be in the range of 10 ppm/°C and assuming that α_l of $[(Mg, Zn)]_2TiO_4$–Co_2TiO_4 ceramic is independent on x value, TCF mainly depends on τ_ε. Using the Clausius–Mosotti equation, Bosman and Havinga [17] derived an expression for τ_ε at a constant pressure, as follows:

$$\tau_\varepsilon = \frac{1}{\varepsilon}\left(\frac{\partial\varepsilon}{\partial T}\right)_p = \frac{(\varepsilon - 1)(\varepsilon + 2)}{\varepsilon}(A + B + C) = \left(\varepsilon - \frac{2}{\varepsilon} + 1\right)(A + B + C)$$
$$A = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P$$
$$B = \frac{1}{3\alpha_m}\left(\frac{\partial\alpha_m}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$
$$C = \frac{1}{3\alpha_m}\left(\frac{\partial\alpha_m}{\partial T}\right)_V$$

The $(A+B+C)$ value could be extrapolated from Eqs. (1) and its value was about −10.95 ppm/°C. When $(A+B+C)$ value is negative, TCF value will increase with permittivity. When $(A+B+C)$ value is positive, TCF value will decrease with permittivity. Usually the absolute value of TCF will increase with permittivity. The sum of the A and B terms is approximately 6 ± 1 ppm/°C. For term C, the suggested value is in the range of −1 to −10 ppm/°C. The term C represents the direct dependence of the polarizability on temperature. Plotting the trend of TCF values versus permittivity of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics, it is found that TCF values decreased from −31 to −20.8 ppm/°C linearly independent on the x values as increased from 0.1 to 0.5. Hence, it is indicated that the TCF value has a linear relationship with the x value.

4. Conclusions

The dielectric properties of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ solid solutions were investigated. The effect of Zn^{2+} and Co^{2+} substitution were to enhance $Q \times f$ value from 150,000 GHz to 210,000 GHz and densification sintering at lower temperature compared to Mg_2TiO_4 which sintered at 1450 °C. An inexpensive, reliable, and easy-to-process dielectric using $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics was achieved. Especially, it provides a very wide process window, which will be highly beneficial for practical applications. At 1225 °C, the $[(Mg_{0.5}Zn_{0.5})_{0.95}Co_{0.05}]_2TiO_4$ ceramics possess a maximum $Q \times f$ of 206,000 GHz associated with an ε_r of 18.18 and a τ_f of −20.8 ppm/°C. The Zn^{2+} and Co^{2+} substitution for Mg^{2+} improves the $Q \times f$ value sintering at lower temperature compare with pure Mg_2TiO_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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