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Dielectric Properties and Crystal Structure of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ Ceramics

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Abstract

The prepared $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.01~0.009) ceramics are sintered at 1275-1425ºC, the needed sintering temperatures of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics slightly increased with the increase of Co^{4+} content. The sintering characteristics of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ 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 Co^{4+} content and sintering temperatures on the quality values ($Q\times f$) and the temperature coefficient of resonant frequency (τ_f values) of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics at microwave frequency are well developed in this study. As an optimal compose, $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.05) successfully demonstrated a dielectric constant of 14.70, a $Q\times f$ of 330,000 GHz and a temperature coefficient of resonent frequency value of -48.18 ppm/ºC sintering at 1350ºC.

Keywords: Dielectric; Microwave ceramics; Dielectric resonators

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-3m (227) [10].

Since the ionic radius of Mg^{2+} ions (0.78 Å) is similar to that of Co^{2+} ions (0.82 Å), the Mg^{2+} ion can be replaced by the Co^{2+} ion to form $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$. In this investigation, $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ were synthesized and some of the Sn^{4+} ions were substituted with Ti^{4+} ions to improve their microwave dielectric properties. More recently, many researchers, minor replaced similar ionic radius to boost of $Q\times f$ [11-14].

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 Qxf value were also investigated. As with conductivity, we will start with macroscopic property and connect to the microscopic • All aspects of free electrons have been covered: only bound electrons left • Capacitance, Optical properti es --> ε,n --> molecules and atoms. A few simplified definitions of dielectric properties are necessary for meaningful discussion of their measurement and applications. They have been defined previously in terms of electrical circuit concepts and electromagnetic field concepts.

Experimental Procedures

The $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.01~0.09) were prepared by the solid-state mixed oxides route with starting materials of high-purity oxide powders (>99.9%): MgO, CoO SnO_2 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 1275-1425°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 to 80º. The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα (λ=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 [15]. 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

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by the post-resonant method as suggested by Hakki and Coleman [16,17]. 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 to 80°C. A HP8757D network analyzer and a HP8350B sweep oscillator were employed in the measurement.

Results and Discussion

XRD patterns recorded from the $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.01~0.09) ceramics sintered at different temperatures for 4 h are shown in Figure 1. The cubic-structured $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (which can be indexed as Mg_2TiO_4, 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 $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$, without any second phase was observed. Moreover, significant variation was not detected from the XRD patterns of the specimens at different x values (x=0.01–0.09) in our experiment.

In order to confirm the formation of the solid solution, the lattice parameters of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics sintered at 1350°C were measured and are demonstrated in Table 1. An increase in the lattice parameters was found for $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics in comparison with that of Mg_2TiO_4. The results indicated that with the partial replacement of Mg^{2+} by Co^{2+}, Mg_2TiO_4–Co_2TiO_4 ceramics would form solid solutions. Moreover, formation of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ would lead to an increase in the lattice parameters from $a=b=c$=8.4415 Å in Mg_2TiO_4 to $a=b=c$=8.4676 Å in $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.09). This is because the ionic radii of Co^{2+} (0.82 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.

SEM micrographs of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics sintered at various temperatures for 4 h are shown in Figure 2. The grain size increased with increasing sintering temperatures. However, rapid grain growth was observed at 1375°C and the pores were almost eliminated for the specimen sintered at 1350°C. The relative density and dielectric constant of the $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ solid solutions as a function of the sintering temperature for 4h are illustrated in Figure 3. Notice

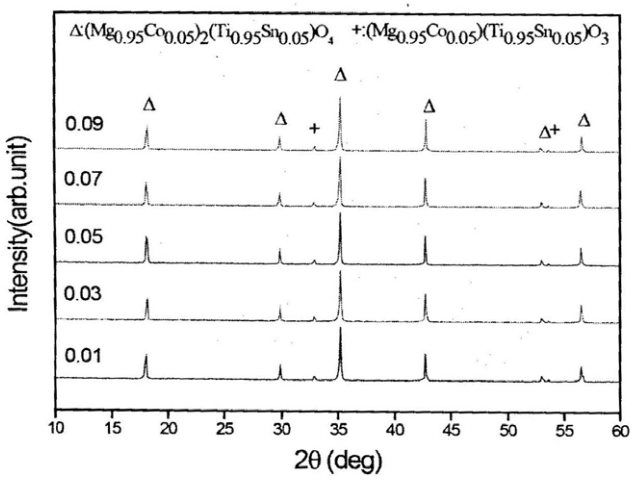

Figure 1: X-ray diffraction patterns of$(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.01~0.09) ceramics sintered at 1350°C temperatures.

x	$a=b=c$(Å)	Vm ((Å^3)
0.01	8.4591 ± 0.0061	605.3025
0.03	8.4622 ± 0.0119	605.9682
0.05	8.4634 ± 0.0145	606.2260
0.07	8.4651 ± 0.0105	606.5914
0.09	8.4676 ± 0.0226	607.1290

Table 1: Lattice parameters data for sintered $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ sintered at 1350°C.

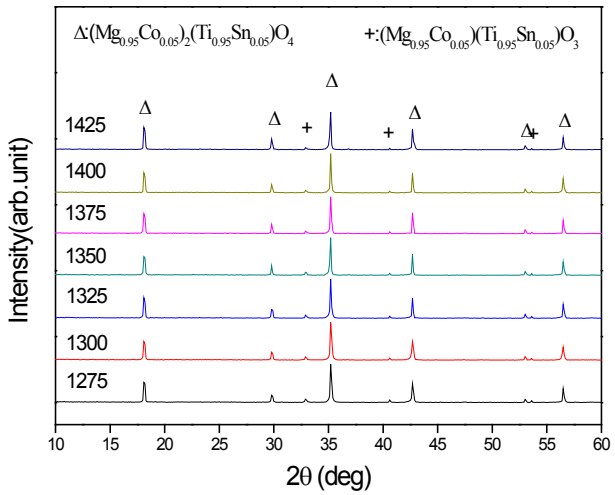

Figure 2: X-ray diffraction patterns of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.05) ceramics sintered at various temperatures.

Elements	Mg	Co	Ti	Sn	O
A	27.30	2.13	13.06	1.03	56.48
B	20.45	1.41	18.72	1.07	58.35

Table 2: EDX data of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.05) ceramics for spot A (atom%) and B (atom%).

that the densities apparently increased with increasing sintering temperature to a maximum at 1350°C and slightly decreased thereafter. Based on EDS as shown in Table 2, large grains (Figure 4, spot A) were identified as $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.05), small grains $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (Figure 4, spot B).

The bulk density and dielectric constant of the $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics as a function of its sintering temperature for 4 h are shown in Figure 5. Note that the densities initially increased with increasing sintering temperature, reaching their maximum at 1350°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 Figure 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 $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ are illustrated in Figure 6. $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ 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 bulk densities and sintering temperatures since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature.

Figure 7 shows the $Q\times f$ values of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics sintered at various temperatures as a functions of the x value.

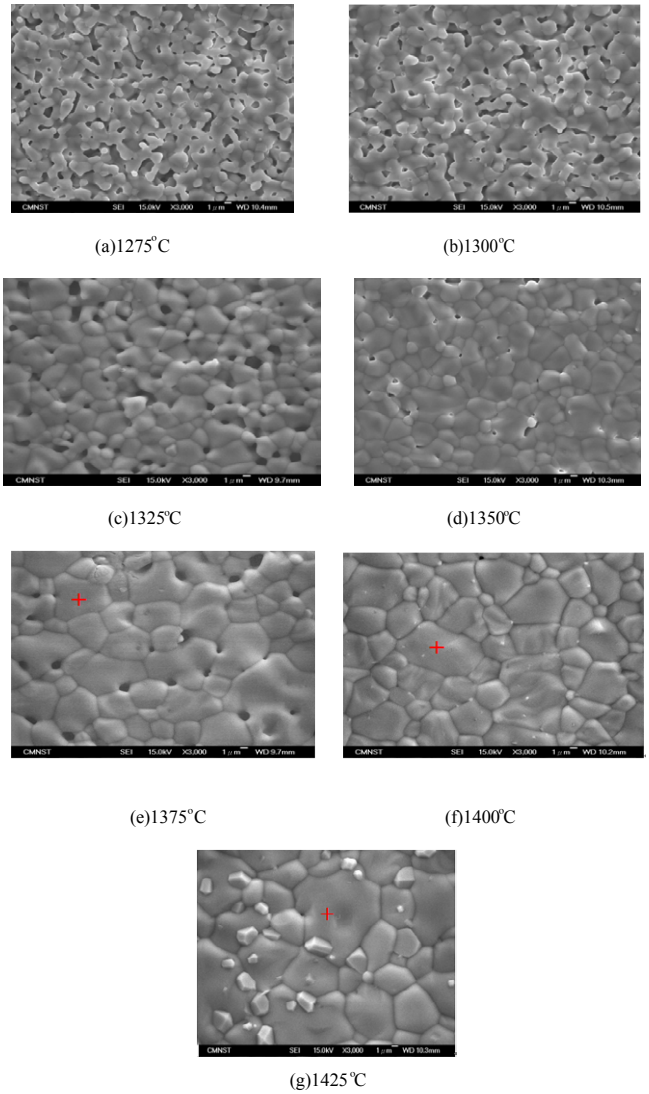

Figure 3: SEM photographs of$(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.05)ceramics sintered at various temperature 4 h.

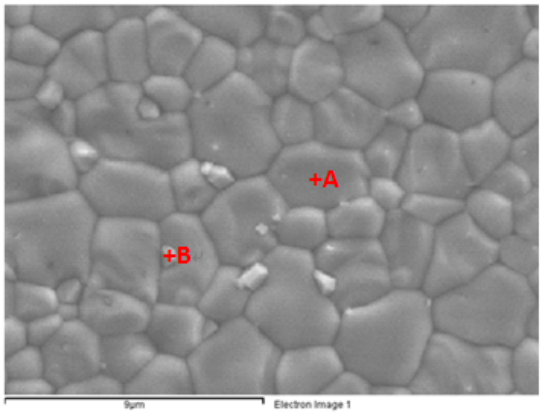

Figure 4: The marks of SEM for the $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.05) ceramics sinter at 1350°C for 4 h.

The quality factor values ($Q\times f$) of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramic at various sintering temperatures are shown in Figure 7. With increasing sintering temperature, the $Q\times f$ value increased to a maximum value and then decreased. A maximum Q×f value of 330,000 GHz was obtained for $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.05) ceramic at 1350°C. The degradation of the $Q\times f$ value can be attributed to abnormal grain growth at higher sintering temperatures, as shown in Figure 3. 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 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

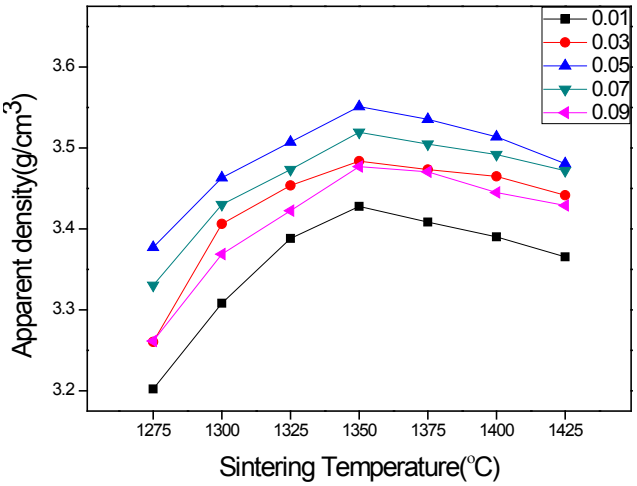

Figure 5: Bulk density of$(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.01~0.09) ceramics system sintered at different temperatures addition.

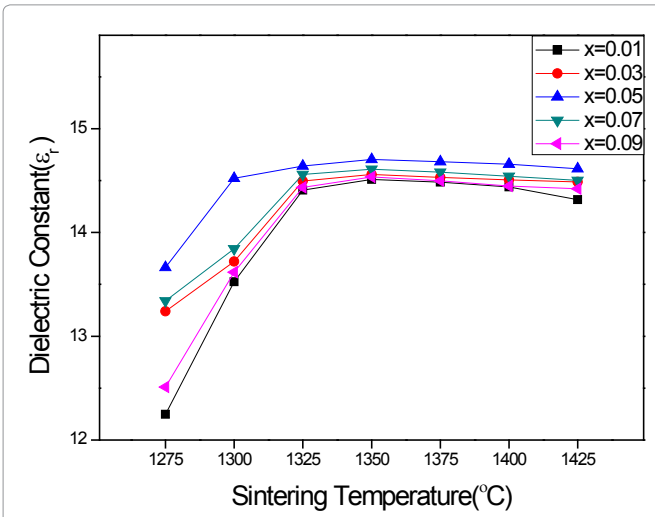

Figure 6: ε_r values of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.01~0.09) ceramics system sintered at different temperatures.

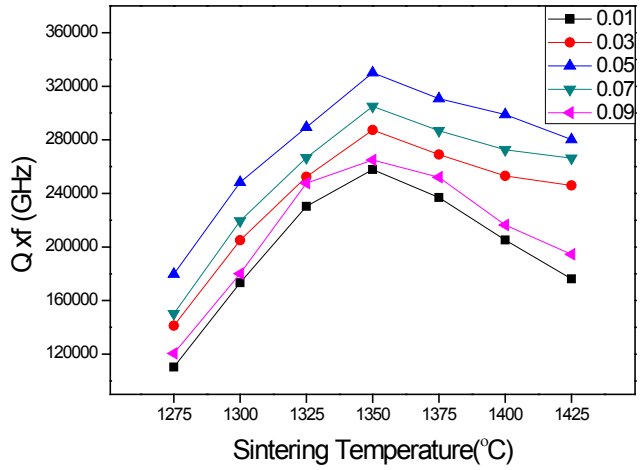

Figure 7: $Q\times f$ values of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.01~0.09) ceramics system sintered at different temperatures.

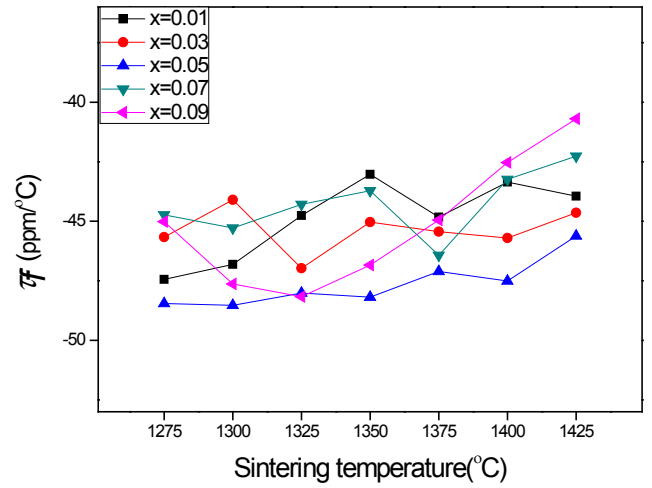

Figure 8: Temperature coefficient of resonant frequency values of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$($x$=0.01~0.09) ceramics system sintered at different temperatures.

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

$$Qxf \alpha \varepsilon^{-1} \quad (2)$$

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 of dielectric Q for well processed ceramics. The result, however, showed that the dependence of $Q\times f$ on ε_r only yielded $Q\times f$ α $\varepsilon_r^{-0.6}$, indicating a rather smoother increasing rate of $Q\times f$ 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

$$Q=(1-1.5P), \quad (3)$$

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

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

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 $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ end component in the present study. The maximum $Q\times f$ value sintered at 1350°C with x form 0.01 to 0.09. The $Q\times f$ value increased with increasing of Co^{2+} content, but the x value is above 0.05, $Q\times f$ value decreased due to the Co^{2+} sintering at higher 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 0.01 to 0.05, the $Q\times f$ value of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ increased dramatically from 24,000 to 330,000 GHz.

Figure 8 shows the τ_f values of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics sintered at various temperatures as a functions of the Co^{2+} content. The remarkable variations in the τ_f values of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ were recognized by the Co^{2+} substitution for Mg^{2+} and these values ranged from -48 to -41 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.

Conclusions

The dielectric properties of $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ solid solutions were investigated. The effect of Co^{2+} substitution were to enhance $Q\times f$ value from 150000 GHz to 330000 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 $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics was achieved. Especially, it provides a very wide process window, which will be highly beneficial for practical applications. At 1350°C, the $(Mg_{1-x}Co_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x=0.05) ceramics possess a maximum $Q\times f$ of 330,000 GHz associated with an ε_r of 14.7 and aτ_f of -48.18 ppm/°C. The 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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