Ultra low loss microwave dielectric properties of Non-stoichiometry [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]_{1+\delta}(Ti_{1-x}Sn_x)O_3+\delta ceramics

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The prepared [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]_{1+\delta}(Ti_{1-x}Sn_x)O_3+\delta (\delta = 0.02) (x = 0, 0.03, 0.05, 0.07, 0.09, 0.1 and 0.2) ceramics are sintered at 1175-1300°C, the needed sintering temperatures of [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]_{1+\delta}(Ti_{1-x}Sn_x)O_3+\delta (\delta = 0.02) ceramics slightly increased with the increase of Sn^{4+} content. The sintering characteristics of [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]_{1+\delta}(Ti_{1-x}Sn_x)O_3+\delta (\delta = 0.02) 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 Sn^{4+} content and sintering temperatures on the quality values (Q x f) and the temperature coefficient of resonant frequency (f values) of [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]_{1+\delta}(Ti_{1-x}Sn_x)O_3+\delta (\delta = 0.02) ceramics at microwave frequency are well developed in this study. As an optimal compose, [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]_{1+\delta}(Ti_{1-x}Sn_x)O_3+\delta (\delta = 0.02) successfully demonstrated a dielectric constant of 16.1, a Qxf of 300,000 GHz and a temperature coefficient of resonant frequency value of -53.8 ppm/°C after firing at a relatively lower sintering temperature of 1250°C.

Key-words : Dielectric, Microwave ceramics, Dielectric resonators

1. Introduction

High quality devices are important for mobile communications, such as filters and oscillators, materials with a low dielectric loss (high quality factor Q = \tan \delta) in the microwave (MW) range are used. The use of high-Q dielectrics as passive MW components dielectric resonators, dielectric substrates, waveguides, and antennas makes possible a significant improvement in the performance of communications equipment, in particular, better sensitivity and selectivity. This is particularly relevant with the current tendency to expand the operating frequency ranges of MW wireless communications, for instance, up to 20-30 GHz in Very Small Aperture Terminals (VSAT), 26-38 GHz in PtP Radiolinks, or 28-40 GHz in Local Multipoint Distribution Services (LMDIS), and applications at frequencies as high as 60 GHz have also been reported. A variety of microwave dielectric components are used in equipment like Low-noise Block (LNB), Block-Up-Converter (BUC) for LMDS, or VSAT terminals. In this case, in addition to the high-quality factor of a material, its price becomes an important factor. Therefore, for the above applications, new, low-cost dielectric materials with a dielectric constant of 10-20 and extremely low dielectric losses are urgently required.1

In the binary system, two magnesium titanates, which are good candidates for use in MW dielectrics, are known: Mg_2TiO_4 and MgTiO_3. Polycrystalline materials based on Mg_2TiO_4 and MgTiO_3 are characterized by the dielectric constants \(\varepsilon = 14\) and 16, respectively, a negative coefficient of the resonant frequency (\(\tau_f = -40\) and -50 ppm/°C), and a low dielectric loss (high Q), whose magnitude reaches Q = 20,000 at 10 GHz for MgTiO_3.2-5 For the temperature compensation of the negative values of the \(\tau_f\) of MgTiO_3, a small amount of the preovskite phase Sr(Ca)TiO_3, characterized by a high, positive \(\tau_f\) is generally introduced into the main composition.3,4 It should be noted that, in contrast to un-doped MgTiO_3, the composite materials based on MgTiO_3 always display much lower Q values (Q = 55000-7000 at 10 GHz), which can be ascribed to the presence of low-Q Sr(Ca)TiO_3, as well as to the formation of undesirable crystal phases like MgTi_2O_5. When partially substituting magnesium with cobalt in MgTiO_3, materials with high MW parameters have recently been obtained. For instance, in the system (1 - x)Mg_0.95Co_{0.05}Ti_{2.02}O_{10}\), the materials with \(\varepsilon_f = 20.3\), Qxf = 107,000 GHz at 7 GHz, and \(\tau_f = 22.8\) ppm/°C were produced at x = 0.05. However, Mg_0.02Ti_{0.02}O_{10}\ has the better quality factor in microwave rang (Qxf = 357600), the dielectric constant of 18.3, and temperature coefficient of resonant frequency is -50 ppm/°C. However, the sintering temperature is high as 1400°C. [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]_{1+\delta}(Ti_{1-x}Sn_x)O_3+\delta (\delta = 0.02) have the excellent microwave properties, the materials with \(\varepsilon_f = 16.9\), Qxf = 260,000 GHz at 7 GHz, and \(\tau_f = -51\) ppm/°C sintering at 1150°C in the article. The Sn^{4+} substitution for Ti^{4+} improves the Qxf value up to 300,000 GHz sintering at lower temperature.

Magnesium titanate ceramics (MgO-TiO_2) are popular dielectric materials for microwave frequency applications. Among them, the MgTiO_3 ceramic has an ilmenitetype structure, belonging to the trigonal space group \(\bar{R}3\) and possesses a high dielectric constant (\(\varepsilon_f \sim 17\)), a high quality factor (Q x f \sim 160,000 GHz), and a negative \(\varepsilon_f\) value (-30 ppm/°C). Its low cost makes them especially attractive. With the partial replacement of
Mg by Zn or Co, the dielectrics (Mg_{0.95}Co_{0.05})TiO_{3} (ε_r ~ 16.8, Q × f ~ 230,000 GHz, ρ_f ~ -54 ppm/°C) and (Mg_{0.95}Zn_{0.05})TiO_{3} (ε_r ~ 17.1, Q × f ~ 264,000 GHz, and ρ_f ~ -40.3 ppm/°C), also having an ilmenite-type structure, have been reported to possess excellent dielectric properties in particular high Q × f value. However, they suffered from the formation of secondary phases, such as (Mg_{0.95}Zn_{0.05})Ti_{2}O_{5}, which would degrade their dielectric properties. Still, preparation of MgTiO_{3} is quiet critical since Mg-decient compound would lead to a MgTi_{2}O_{5} phase while Mg-rich causes the formation of Mg_{2}TiO_{4} phase. Non-stoichiometric effect for other compounds had been shown by Huang and Belous et al.10,11) However, the variance tolerance of the Mg content to obtain a single MgTiO_{3} phase was not studied ever.

In this paper, the non-stoichiometric [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]^{+}(Ti_{1-x}Sn_x)O_{3}^{+} (δ = 0.02) ceramic system were prepared via the conventional solid-state route to investigate the effect of slight change in (Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05} content on the microwave dielectric properties, phase composition and microstructure of ilmenite-type ceramic.

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×f value was also investigated.

2. Experimental procedure

[(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]^{+}(Ti_{1-x}Sn_x)O_{3}^{+} (δ = 0.02) powders were prepared by the solid state reaction method by mixing individual high-purity oxides MgO, ZnO, CoO, TiO_{2} and SnO_{2}. The starting materials were stoichiometrically weighed. MgO was calcined at 800°C for 6 h to remove moisture content and carbonates. The powders were then dry mixed with an agate mortar and pestle and subsequently wet-mixed by using distilled water. The calcination temperature was 1100°C. The calcined powders with organic binder polyvinyl alcohol were pressed into pellets using a uniaxial press. The binder was evaporated at 650°C for 2 h. [(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]^{+}(Ti_{1-x}Sn_x)O_{3}^{+} (δ = 0.02) were carried out sintering at 1075~1200°C for 4 h. The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) patterns were collected using Cu Kα radiation (at 30 KV and 20 mA) and a graphite monochrometer in the 2θ range of 20 to 60°. The microstructural observations and analysis of sintered surface were performed by 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 dielectric constant and unloaded Q, were measured at 6–12 GHz by the post-resonant method, as suggested by Hakki and Coleman.\textsuperscript{12} This method consisted of parallel conducting plates and coaxial probes on the TE\textsubscript{011} mode, while the third integer denotes the order of the wave guide mode, while the third integer denotes the order of the 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.

3. Results and discussion

Figure 1 shows the X-ray powder diffraction patterns of [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) ceramics sintered at various temperatures (x = 0.05) specimens structure with the single phase (ICDD#00-066-0494), with no secondary phase detected sintering at various temperatures. In Fig. 2, only the rhombohedral structure was observed with XRD sintered at 1250°C. X-ray diffraction (XRD) patterns recorded from the [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) ceramics sintered at various temperatures for 4 h are shown in Fig. 1. The rhombohedral structure (ICDD-PDF 001-073-7752) [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) (which can be indexed as MgTiO\textsubscript{3}), ICDD-PDF#00-025-1157, was identified as the main phase, implying the forming of a solid solution. In addition to [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02), without any secondary phase was observed. Moreover, significant variation was not detected from the XRD patterns of the specimens at different x values (x = 0–0.2) in our experiment.

In order to confirm the formation of the solid solution, the lattice parameters of [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) ceramics sintered at 1150°C were measured and are demonstrated in Table 1. An increase in the lattice parameters was found for [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) ceramics in comparison with that of ilmenite-type structure (MgTiO\textsubscript{3}). The results indicated that with the partial replacement of Ti\textsuperscript{4+} by Sn\textsuperscript{4+}, [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) ceramics would form solid solutions. Moreover, formation of [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) would lead to an increase in the lattice parameters from a = b = 5.0641 Å, c = 13.915 Å in [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) to a = b = c = 5.1842 Å, c = 13.871 Å. The cell volumes increased as more Sn\textsuperscript{4+} replace of Ti\textsuperscript{4+}. This is because the ionic radii of Sn\textsuperscript{4+} (0.69 Å) are larger than that of Ti\textsuperscript{4+} (0.605 Å).

In Fig. 3 shown SEM photographs of [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) ceramics sintered at various temperatures for 4 h. The grain size increased with increasing sintering temperatures. However, rapid grain growth was observed at 1175°C and the pores were almost eliminated for the specimen sintered at 1125°C. The relative density and dielectric constant of the [(Mg\textsubscript{0.7}Zn\textsubscript{0.3})\textsubscript{0.95}Co\textsubscript{0.05}]\textsubscript{1}+(Ti\textsubscript{1}+Sn\textsubscript{0.2})O\textsubscript{3+\delta} (δ = 0.02) (x = 0–0.2) solid solutions as a function of the sintering temperature for 4 h are shown in Fig. 5. Notice that the relative

| x   | 0    | 0.03 | 0.05 | 0.07 | 0.09 | 0.1  | 0.2  |
|-----|------|------|------|------|------|------|------|
| a   | 5.0641 | 5.07065 | 5.0772 | 5.08375 | 5.0903 | 5.09685 | 5.1842 |
| b   | 5.0641 | 5.07065 | 5.0772 | 5.08375 | 5.0903 | 5.09685 | 5.1842 |
| c   | 13.915 | 13.90767 | 13.90032 | 13.89303 | 13.88565 | 13.8737 | 13.871 |
| Vm  | 309.0426 | 309.6793 | 310.315 | 310.9538 | 311.59 | 312.2286 | 322.8508 |
| Om (theory) | 63.4206 | 63.4026 | 63.3906 | 63.3786 | 63.3666 | 63.3606 | 63.3006 |
| Om (exp) | 62.1 | 61.9741 | 61.8359 | 61.7555 | 60.8936 | 60.0499 | 60.4836 |
| dielectric (cal.) | 18.914 | 18.6206 | 18.348 | 18.0829 | 17.8264 | 17.587 | 14.4557 |
| dielectric (measured) | 16.9 | 16.5 | 16.1 | 15.8 | 14.5 | 13.4 | 11.91 |
densities apparently increased with increasing sintering temperature to a maximum at 1150°C and slightly decreased thereafter. Based on EDS, large grains (Fig. 4(a), spot A) were identified as [(Mg0.7Zn0.3)0.95Co0.05]1-xSnxO3+δ (x = 0.05) ceramics sintered at 1250°C and (b) EDX data of [(Mg0.7Zn0.3)0.95Co0.05]1-xSnxO3+δ (x = 0.05) ceramics for spot A. Spot A (atom %): Mg K: 18.31, Co K: 2.56, Zn-L: 9.11, Ti K: 24.61, Sn L: 1.23, O K: 45.69.

The relative bulk density and dielectric constant of the [(Mg0.7Zn0.3)0.95Co0.05]1-xSnxO3+δ ceramics for spot A. Spot A (atom %): Mg K: 20.12, Co K: 2.56, Zn-L: 16.41, Sn L: 2.02, O K: 48.8.

The relative bulk density and dielectric constant of the [(Mg0.7Zn0.3)0.95Co0.05]1-xSnxO3+δ ceramics sintered at different temperatures addition. The relative bulk density and dielectric constant of the [(Mg0.7Zn0.3)0.95Co0.05]1-xSnxO3+δ ceramics for spot A. Spot A (atom %): Mg K: 18.31, Co K: 2.56, Zn-L: 9.11, Ti K: 24.61, Sn L: 1.23, O K: 45.69.

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

Here \(\varepsilon_r\), \(V_m\), and \(\alpha_m\) are the relative permittivity, molar volume, and macroscopic polarizability, respectively. Using the experimental relative permittivity data and unit-cell volume data, the macroscopic polarizability, \(\alpha_m\), was calculated. The theory polarizability data show in Table 1 an almost sigmodal increase with increasing Zn2+ content, while the unit-cell volume increased with x. The relative permittivity increased with \(\alpha_m\), when the value of \(\alpha_m\) 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,

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

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 [(Mg0.7Zn0.3)0.95Co0.05]1-xSnxO3+δ (x = 0.02) end member is large than the \(\alpha_m(\text{theory})\) value, the \(\alpha_m(\text{exp})\) values are larger than \(\alpha_m(\text{theory})\). Shannon\textsuperscript{[13]} 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 \(\alpha_m(\text{exp})\) value for [(Mg0.7Zn0.3)0.95Co0.05]1-xSnxO3+δ (x = 0.02) may thus be due to compression effects caused by the large difference.
between the ionic polarizabilities of Sn⁴⁺ and Ti⁴⁺. This agrees with the harmonic-oscillator model.¹⁵

Figure 7 shows the $Qxf$ values of $[(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}]_{1-x}(Ti_{1-x}Sn_x)O_{3+δ}$ ($δ = 0.02$) ceramics system sintered at different temperatures as a functions of the $x$ value. The maximum $Qxf$ value sintered at 1150°C with $x$ form 0.03 to 0.07, maximum $Qxf$ value is 300,000 GHz sintered at 1150°C with $x$ value is 0.05.

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 0.03 to 0.05, the \(Q_{\text{xf}}\) value of \([(\text{Mg}_{0.7}\text{Zn}_{0.3})_{0.95}\text{Co}_{0.05}]_1\beta \\text{(Ti}_1\text{Sn})_\beta \text{O}_{3+\delta} (\delta = 0.02)\) increased dramatically from 280,000 to 300,000 GHz, which is due to the relative density increased. Thus, \([(\text{Mg}_{0.7}\text{Zn}_{0.3})_{0.95}\text{Co}_{0.05}]_1\beta \\text{(Ti}_1\text{Sn})_\beta \text{O}_{3+\delta} (\delta = 0.02)\) is a suitable material for the application in microwave devices.

Figure 8 shows the \(\tau_\varepsilon\) values of \([(\text{Mg}_{0.7}\text{Zn}_{0.3})_{0.95}\text{Co}_{0.05}]_1\beta \\text{(Ti}_1\text{Sn})_\beta \text{O}_{3+\delta} (\delta = 0.02)\) ceramics sintered at various temperatures as a function of the \(\text{Zn}^{2+}\) content. The remarkable variations in the \(\tau_\varepsilon\) values of \([(\text{Mg}_{0.7}\text{Zn}_{0.3})_{0.95}\text{Co}_{0.05}]_1\beta \\text{(Ti}_1\text{Sn})_\beta \text{O}_{3+\delta} (\delta = 0.02)\) were recognized by the \(\text{Sn}^{4+}\) substitution for \(\text{Ti}^{4+}\) and these values ranged from \(-52\) to \(-59\) ppm/°C. Thus, it is considered that the additional improvement in the \(\tau_\varepsilon\) value is required for the dielectric resonator applications at high frequency.

4. Conclusion

The microwave dielectric properties of \([(\text{Mg}_{0.7}\text{Zn}_{0.3})_{0.95}\text{Co}_{0.05}]_1\beta \\text{(Ti}_1\text{Sn})_\beta \text{O}_{3+\delta} (\delta = 0.02)\) solid solutions were investigated. The quality factor of \([(\text{Mg}_{0.7}\text{Zn}_{0.3})_{0.95}\text{Co}_{0.05}]_1\beta \\text{(Ti}_1\text{Sn})_\beta \text{O}_{3+\delta} (\delta = 0.02)\) solid solutions increased with increasing \(\text{Sn}^{4+}\) content \((x\) below 0.05), whereas that of \([(\text{Mg}_{0.7}\text{Zn}_{0.3})_{0.95}\text{Co}_{0.05}]_1\beta \\text{(Ti}_1\text{Sn})_\beta \text{O}_{3+\delta} (\delta = 0.02)\) solid solutions remarkably increased from 280,000 to 300,000 GHz. It was found that the increase in the \(Q_{\text{xf}}\) value of the \([(\text{Mg}_{0.7}\text{Zn}_{0.3})_{0.95}\text{Co}_{0.05}]_1\beta \\text{(Ti}_1\text{Sn})_\beta \text{O}_{3+\delta} (\delta = 0.02)\) solid solutions may be related to the grain size decrease which is opposite to general results and this relation is consistent with that of \(\text{Al}_2\text{O}_3\). The \(\text{Sn}^{4+}\) and substitution for \(\text{Ti}^{4+}\) improves the \(Q_{\text{xf}}\) value sintering at lower temperature compare with pure \(\text{MgTiO}_3\). 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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