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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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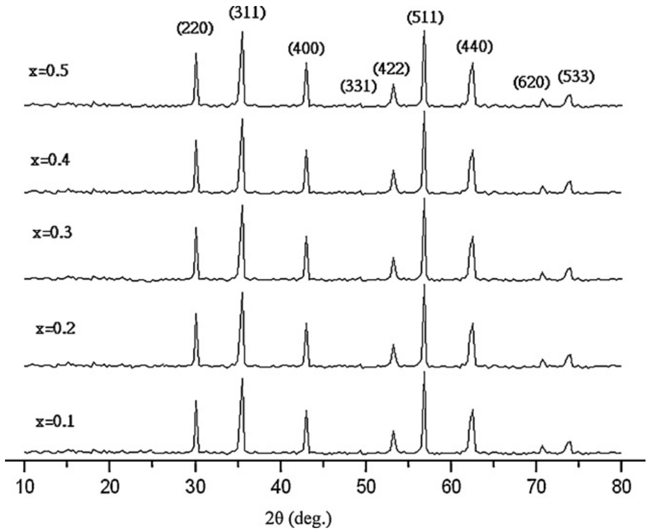

Fig. 1. X-ray diffraction patterns of $[(Mg_{1-x}Zn_x)_{0.95}Co_{0.05}]_2TiO_4$ ceramics sintered at 1225 °C.

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