

Structure and microwave dielectric properties of $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ceramics

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Abstract Low-loss ceramics $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ (ZCTS) ($x = 0, 0.02, 0.05, 0.09, 0.14$) were prepared by the conventional solid-state route. The effects of Sn ratio on phase composition, microstructure, and the microwave dielectric properties of $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ materials were investigated using X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy (EDS). The results revealed that the ZCTS ($x = 0.02, 0.05, 0.09, 0.14$) composites consisted of three crystalline phases: ZnTiO_3 -type phase, Zn_2TiO_4 -type phase, and TiO_2 phase. Due to the compensating effect of rutile TiO_2 , the temperature coefficient of resonant frequency (τ_f) for $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0.02$) ceramic was tuned to near zero value. It was found in our experiment that with the increase of Sn ratio, the microwave dielectrics showed a great promotion in $Q \times f$ when Ti^{4+} was partially substituted by Sn^{4+} . Typically, the $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0.02$) ceramic sintered at 1,220 °C for 4 h exhibited good microwave dielectric properties of $\epsilon_r = 24$, $Q \times f = 66,700$ GHz and $\tau_f = -5.43$ ppm/°C.

1 Introduction

In recent years, with the rapid development of advanced communication systems, the microwave dielectric materials have been widely used for microwave device applications, such as resonators, filters, and oscillators [1–4]. To

meet the demands of microwave circuit designs, microwave dielectric resonator ceramics with a high dielectric constant ($\epsilon_r > 20$) for miniaturization, a high-quality factor ($Q > 2,000$) for better selectivity, and a near zero temperature coefficient of the resonant frequency (τ_f) for stable frequency stability are required [5–7]. Research of new dielectric materials that satisfy such a requirement has been ongoing, while the study for promoting the dielectric properties of currently available materials through appropriate modifications has been also needed.

In the ZnO-TiO_2 system, there are three compounds existing: Zn_2TiO_4 with a face-centered cubic crystal structure, $\text{Zn}_2\text{Ti}_3\text{O}_8$ with a simple cubic structure, and ZnTiO_3 with a rhombohedral structure [8–13]. ZnTiO_3 is an attractive material for applications owing to its low loss at high frequency. However, ZnTiO_3 is unstable at high temperature and decomposes into Zn_2TiO_4 and TiO_2 at temperatures above 945 °C [10, 14–16]. Therefore, many efforts have been made to prepare ZnTiO_3 with improved stability and microwave dielectric properties. The recent studies for A-sites substitutions on the microwave dielectric properties of $\text{Zn}_{1-x}\text{A}_x\text{TiO}_3$ ($A = \text{Ni, Mg, Co, Mn}$) ceramics were studied by researchers [10, 11, 17]. For instance, the microwave dielectric properties of the $\text{Zn}_{0.3}\text{Co}_{0.7}\text{TiO}_3$ specimen with $\epsilon_r \approx 23$, $Q \times f \approx 80,000$ GHz and $\tau_f \approx -50$ ppm/°C was reported by Kim and Lanagan [10]. Although the high-quality factor of the ceramics were obtained, the large τ_f values limited the use for practical applications. A near zero τ_f remains as one of the primary requirements for microwave materials and becomes more and more critical as the operating frequency going higher. Therefore, the further studies of the $\text{Zn}_{1-x}\text{A}_x\text{TiO}_3$ ($A = \text{Ni, Mg, Co, Mn}$) ceramics to achieve a zero τ_f are necessary. Since the ionic radius of Ti^{4+} (0.605 Å, CN = 6) is similar to that of Sn^{4+} (0.69 Å, CN = 6) [18–

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20], the Ti^{4+} ion can be partially substituted by Sn^{4+} ion to form a new solid solutions, which may enhance the thermal stability and dielectric properties [19, 20]. In this work, the effects of Sn^{4+} substitution on the microwave dielectric properties of the $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0-0.14$) ceramics due to the changes in chemical composition, density, and microstructure have been investigated.

2 Experimental

The $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics were synthesized by the solid-state ceramic route. High-purity powders of ZnO (99.7 %), Co_2O_3 (99.8 %), SnO_2 (99.9 %) and TiO_2 (99.9 %) were used as the starting materials. The raw oxide materials were weighted according to the stoichiometry proportions and ball milled in an alcohol medium for 6 h in a plastic bottle using zirconia balls. The mixture was dried and calcined at 1,000 °C for 4 h, then re-milled again for 3 h. After drying, the dried powder was mixed with a 6 wt% PVA as a binder, then again dried and ground well. The resultant fine powder was axially pressed into cylindrical disks with different thickness of 4 and 11 mm in a diameter under a pressure of 25 MPa. These pellets were sintered at different sintering temperatures from 1,190 to 1,320 °C for 4 h in air.

After sintering, the bulk densities of the samples were measured using the Archimedes method. The phase composition and crystal structure of the ceramics were examined by X-ray diffraction technique using CuK α radiation (DX-1000 CSC, Japan). Scanning electron microscopy (SEM) (JSM-6460LV, Jeol, Tokyo, Japan) coupled with energy dispersive X-ray spectroscopy (EDS) was employed to study the surface morphology of the specimens. The microwave dielectric properties were measured by a Vector Network Analyzer (E5071C, Agilent Technologies) and a temperature chamber (DELTA 9023, Delta Design, USA). In addition, the temperature coefficients of resonant frequency τ_f values were calculated by the equation: $\tau_f = (f_2 - f_1)/(f_1 \times (t_2 - t_1))$, where f_1 and f_2 were the resonant frequencies at the measuring temperature t_1 (25 °C) and t_2 (85 °C), respectively.

3 Results and discussion

The XRD patterns of $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics sintered at 1,220 °C for 4 h are shown in Fig. 1. For $x = 0$, all the diffraction peaks were identified as $(\text{Zn},\text{Co})\text{TiO}_3$ phase and $(\text{Zn},\text{Co})_2\text{TiO}_4$ phase. Cubic spinel phase with $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$ and rutile phase TiO_2 were observed at $x = 0.02-0.05$, besides the

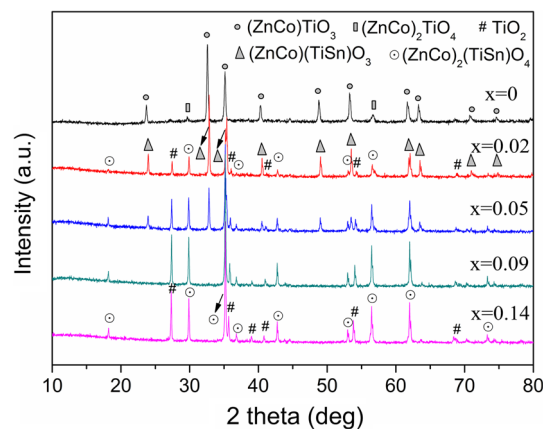


Fig. 1 The XRD patterns of $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics sintered at 1,220 °C for 4 h

hexagonal form of ilmenite $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3$. An ilmenite phase disappeared at $x = 0.09$, only cubic spinel phase $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$ and rutile phase TiO_2 were obtained at $x = 0.09-0.14$. This result indicated that the transformation of hexagonal $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3$ phase to cubic $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$ and TiO_2 was possible at high temperature and the TiO_2 phase increased with the increase of Sn content.

Figure 2 depicts the SEM micrographs of the $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics sintered at 1,220 °C for 4 h. Almost no porosity in compact microstructure was observed in the ceramics. When the content of Sn exceeded 0.05, a significant change was observed in the microstructure, as shown in Fig. 2b–e. This was because the hexagonal $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3$ phase was completely transformed to the cubic $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$. To examine the phase compositions, EDS was employed, as shown in Fig. 2a, b, e and Table 1. According to the ratio of the elements, we can deduce that point A and point C represented ZnTiO_3 -type phase, points B, D and E represented Zn_2TiO_4 -type phase in the ceramic, which were in accord with the XRD result.

The τ_f values of the $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics sintered at 1,220 °C for 4 h are shown in Fig. 3. The τ_f values of the ceramics changed considerably with Sn addition, which increased remarkably from -46.3 to $+95.58$ ppm/°C. As we know, the temperature coefficient of resonant frequency was related to the composition, additives and second phase of the ceramics [21, 22]. From the XRD result, it was obvious that the TiO_2 phase increased with the increase of Sn content ($x < 0.09$). Therefore, the increase in τ_f value in the composition was attributed to the increased amount of TiO_2 phase which possessed a τ_f value of about $+400$ ppm/°C [7], compared with the negative τ_f phases (spinel and ilmenite: -60 ppm/°C [10]). However, the τ_f value stopped increasing at $x = 0.09$, because the ilmenite $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3$ phase was

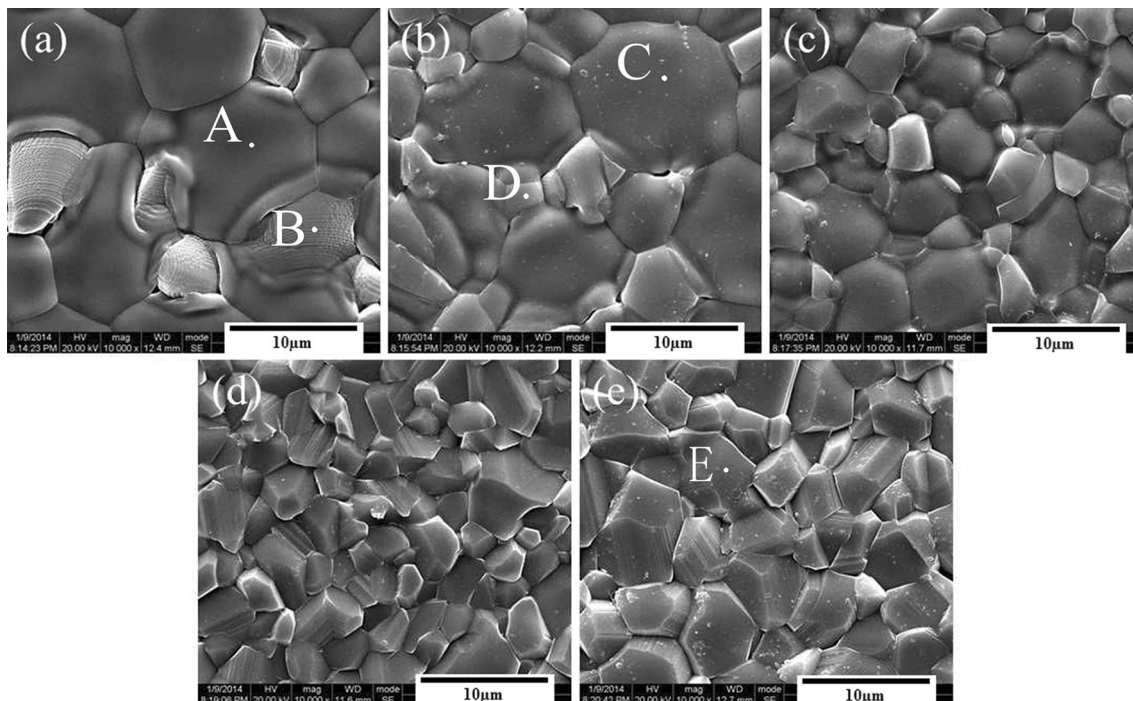


Fig. 2 The SEM micrographs of $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ (a $x = 0$, b $x = 0.02$, c $x = 0.05$, d $x = 0.09$, e $x = 0.14$) ceramics sintered at 1,220 °C for 4 h

Table 1 EDS data of the $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.14$) ceramic corresponding to Fig. 2a, b, e

Atom (%)					
Spot	Co	Zn	Ti	Sn	O
A	19.01	8.98	27.14		44.87
B	19.82	12.64	17.44		50.09
C	18.29	6.36	23.29	0.51	51.55
D	20.10	13.19	17.68	1.24	47.79
E	30.22	12.69	19.35	1.90	35.84

completely transformed to the cubic $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$ and rutile phase TiO_2 , as shown in Fig. 1 ($x = 0.09, x = 0.14$). The content of $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$ and TiO_2 phases stopped increasing at $x = 0.09$ and 0.14. Therefore, the τ_f value kept almost constant at last. Typically, The τ_f value of $-5.4 \text{ ppm}/^\circ\text{C}$ was obtained when $x = 0.02$.

The (a) bulk density, (b) dielectric constant (ϵ_r) and (c) quality factor ($Q \times f$) of the $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics as a function of the sintering temperature are illustrated in Fig. 4. It was observed that the bulk densities increased at the beginning of the sintering because of the elimination of pores, then followed by a decrease, which was attributed to the abnormal grain growth. The bulk densities achieved a relative high densities at 1,220 °C when x value varied from 0 to 0.05. However, as the amount of Sn increased above 0.05,

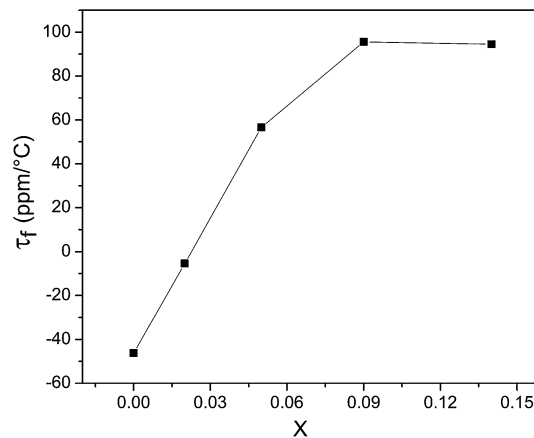


Fig. 3 The temperature coefficients of resonant frequency of $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics sintered at 1,220 °C for 4 h

the relative high densities of the ceramics were obtained at 1,280 °C, which was related to the composition of the ceramics, as shown in Fig. 1. The variation of the dielectric constant as a function of the sintering temperature showed a similar tendency as the bulk densities, as shown in Fig. 4b. As the amount of Sn increased, the dielectric constant of the samples initially increased, then reached a saturated value at the point $x = 0.09$, and finally decreased with further increasing the Sn content. From the XRD result, it was obvious that as the content of Sn changed from

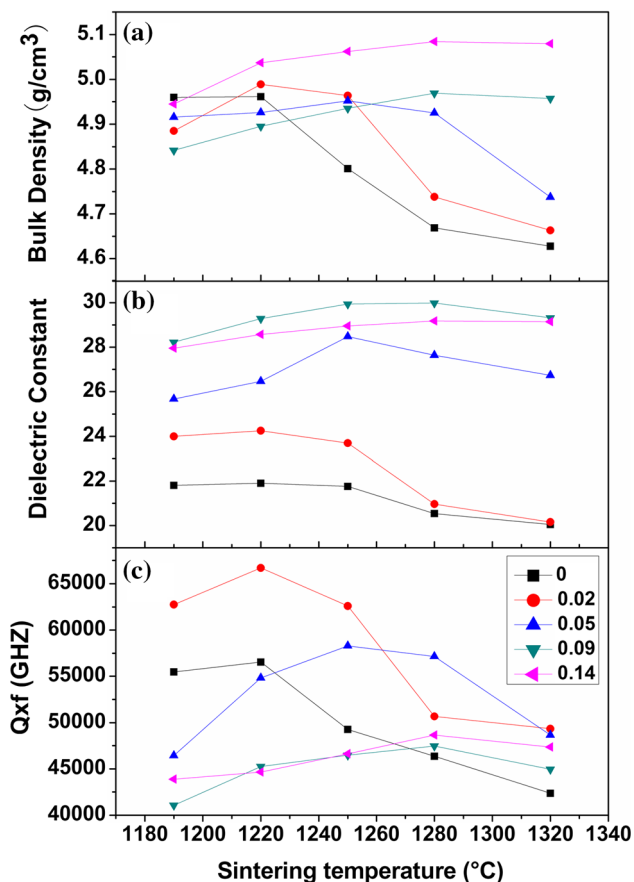


Fig. 4 **a** Bulk density, **b** dielectric constant and **c** quality factor of $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics as a function of the sintering temperature

0 to 0.09, the rutile phase TiO_2 was increased with increasing the Sn content, then the TiO_2 content kept almost constant because the hexagonal $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3$ phase completely decomposed into cubic $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$ and rutile TiO_2 . As we know, the dielectric constant of TiO_2 was high ($\epsilon_r \approx 100$) [23], compared with the spinel and ilmenite phases ($\epsilon_r \approx 20$) [10]. Therefore, the increase in ϵ_r value was attributed to the increase of TiO_2 phase. For the sample $x = 0.14$, the decrease in ϵ_r value might be due to the replacing Ti^{4+} with Sn^{4+} in $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$. From Fig. 4c, it was found that the $Q \times f$ value first increased with increasing the temperature and reached the maximum, then declined with the sintering temperature further increased. As the content of Sn increased from 0 to 0.14, the $Q \times f$ value initially increased from 56,536 to 66,700 GHz, then decreased. It is well known that the microwave dielectric loss is mainly caused not only by the intrinsic factors but also by extrinsic factors such as the pores, the grain morphology, and the second phases [23–26]. And the ilmenite ZnTiO_3 structure has excellent microwave dielectric properties among these phases [15, 27, 28]. Therefore, the increase in $Q \times f$ value was due to the

formation of the $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3$ solid solution when Ti^{4+} was partially substituted by Sn^{4+} in the $(\text{Zn},\text{Co})\text{TiO}_3$ ceramic. The quality factor in $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0.05, 0.09, 0.14$) composition region was determined by the relative amount of phases between the spinel $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$ and ilmenite $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3$ structure [10]. The decrease in $Q \times f$ value was attributed to the formation of Zn_2TiO_4 -type structure, which had lower $Q \times f$ value than ZnTiO_3 -type structure [27, 28]. In general, the $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0.02$) ceramic sintered at 1,220 °C had good microwave dielectric properties of $\epsilon_r = 24$, $Q \times f = 66,700$ GHz and $\tau_f = -5.43$ ppm/°C.

4 Conclusions

The effects of Sn ratio on phase composition, microstructure, and the microwave dielectric properties of $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics were investigated. The results revealed that three crystalline phases were identified in the ZCTS ($x = 0, 0.02, 0.05, 0.09, 0.14$) ceramics: $(\text{Zn},\text{Co})\text{TiO}_3 + (\text{Zn},\text{Co})_2\text{TiO}_4$ phases at $x = 0$, $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3 + (\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4 + \text{TiO}_2$ phases at $x = 0.02$ and 0.05, $(\text{Zn},\text{Co})_2(\text{Ti},\text{Sn})\text{O}_4$ and TiO_2 phases at $x = 0.09$ and 0.14. As the amount of Sn increased, the $Q \times f$ value of the samples initially increased because of the formation of the $(\text{Zn},\text{Co})(\text{Ti},\text{Sn})\text{O}_3$, then reached a saturated value, and finally decreased with further increasing the Sn content. Due to the compensating effect of rutile TiO_2 ($\tau_f \approx +400$ ppm/°C), the temperature coefficient of resonant frequency (τ_f) for $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0.02$) ceramic was tuned to near zero value. Typically, the $(\text{Zn}_{0.3}\text{Co}_{0.7})\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0.02$) ceramic sintered at 1,220 °C for 4 h exhibited good microwave dielectric properties of $\epsilon_r = 24$, $Q \times f = 66,700$ GHz and $\tau_f = -5.43$ ppm/°C.

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