



Letter

Low-loss microwave dielectric ceramics in the $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x = 0-0.1$) system

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ABSTRACT

$(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x = 0-0.1$) ceramics with high relative density were prepared by the conventional solid-state reaction, followed by sintering at 1290–1380 °C. X-ray diffraction patterns illustrated that a single rhombohedral crystal structure solid solution could be formed between the two end members with $0 \leq x \leq 0.1$. The unit cell volume slightly increased with increasing Zn content (x). The microwave dielectric properties of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ceramics showed a significant dependence on the Zn content, the density of the specimen, and to some extent on the morphology of the grains. Specimen using $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ sintered at 1350 °C for 3 h could obtain the microwave dielectric properties as follows; an ϵ_r value of ~ 20 , a $Q \times f$ value of $\sim 107,000$ GHz (measured at $f = 9.27$ GHz), and a τ_f value of -60 ppm/°C.

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1. Introduction

Demand for low loss microwave ceramic components has been dramatically increasing in recent years and the rapid growth of wireless communication industry has further led to extensive research and development in the area of microwave dielectrics [1–6]. In addition to the need for new dielectric materials, it is also desirable to promote the dielectric properties of currently available materials through appropriate modifications [7–9]. A recent study on the microwave dielectric properties of ATiO_3 ($A = \text{Ni}, \text{Mg}, \text{Co}, \text{Mn}$) ceramics was reported by Kim et al. [10,11]. To lower the dielectric loss, the manner of equivalent-charge trace substitutions for A-sites of the microwave dielectric ceramics had been reported [12–14]. In this family, the low loss dielectric ceramic materials such as the series of $(\text{Mg}_{1-x}\text{M}_x)\text{TiO}_3$ ($M = \text{Mg}, \text{Zn}, \text{Co}, \text{Ni}, \text{Mn}$) [11–13] systems have been investigated due to their good dielectric properties for microwave applications.

Cobalt titanate (CoTiO_3) ceramic is a dielectric material applied at microwave frequencies. It has an ilmenite-type structure and exhibits a dielectric constant (ϵ_r) of ~ 22 , a quality factor ($Q \times f$) value of $\sim 50,000$ GHz, and a temperature coefficient of resonant frequency (τ_f) of ~ 55 ppm/°C in the microwave frequency range [10]. For high frequency microwave devices applications, the dielectric loss of the ceramics should be further lowered to increase the frequency selectivity. Since the ionic radius of Zn^{2+} (0.74 Å, CN = 6) is similar to that of Co^{2+} (0.65 Å, CN = 6) [15], the Co^{2+} ion can be partially substituted by Zn^{2+} ion to form $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ solid

solutions, and from previous experiences, it is possible to obtain a new low-loss dielectric.

In this work, the effects of progressive Zn substitution on the microwave dielectric properties of the sintered $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x = 0-0.1$) ceramics due to the changes in chemical composition, lattice volume, density, and microstructure have been determined.

2. Experimental procedure

The microwave dielectric ceramics of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x = 0-0.1$) system were prepared using conventional solid-state from individual high-purity powders: CoO (95%), ZnO (99%), and TiO_2 . The starting powders were mixed according to a stoichiometry ratio to synthesize $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ceramics. The mixed powders were ground with zirconium ball in distilled water for 12 h and then dried the wet mixtures at 100 °C in air until the moisture were took out of it. The dry mixtures were calcined at 1100 °C for 5 h after they were milled and sieved through 100-mesh screen. The calcined powders $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ were re-milled for 12 h and dried it again. The prepared powders added 30 wt% solution of PVA (Polyvinyl alcohol 500, Showa) as a binder and then granulated by sieving through 100-mesh. The milled powders were pressed into disk 11 mm in diameter and 5 mm in thickness under the pressure of 200 MPa. The pellets were sintered at temperatures 1290–1380 °C for 3 h in the air. The heating rate and the cooling rate were both controlled at 10 °C/min.

The crystalline phases of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ were identified by XRD (Siemens D5000, Germany) using $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation which operated at 40 kV and 40 mA. The microstructural observations and analysis of sintered surface were performed using a scanning electron microscope (SEM, FEI Quanta 400F) and an energy dispersive X-ray spectrometer (EDS). The lattice parameters of the samples were evaluated according to the GSAS software with Rietveld analysis and the least squares method to fit the XRD patterns [16–18]. The apparent densities of the sintered specimens were measured by the Archimedes method using distilled water as the liquid. The dielectric constant (ϵ_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [19–21]. The dielectric resonator was placed between two brass plates just like a cavity. The Microwave dielectric properties were measured by HP8757D network analyzer and HP83630A sweep oscillator. For temperature coefficient of resonant frequency (τ_f), the technique is the same as that of quality factor measurement. The test cavity is placed over a thermostat and noted

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Table 1
Lattice parameters of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x=0-0.1$) ceramic systems sintered at 1350°C for 3 h.

x-Value	Lattice parameters of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ceramics			
	a (Å)	c (Å)	Theoretical density (g/cm^3)	Cell volume (Å^3)
0	5.0653 (± 0.0009)	13.9199 (± 0.0014)	4.985	309.297
0.02	5.0656 (± 0.0007)	13.9204 (± 0.0017)	4.988	309.345
0.04	5.0666 (± 0.0008)	13.9243 (± 0.0019)	4.989	309.554
0.05	5.0672 (± 0.0011)	13.9259 (± 0.0027)	4.9896	309.663
0.06	5.0675 (± 0.0009)	13.9278 (± 0.0022)	4.9904	309.742
0.08	5.0684 (± 0.0008)	13.9279 (± 0.0019)	4.993	309.854
0.1	5.0688 (± 0.0010)	13.9298 (± 0.0027)	4.995	309.944

Table 2
The microwave dielectric properties of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ceramic systems sintered at 1350°C for 3 h.

x-Value	Apparent density (g/cm^3)	Relative density (%)	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/ $^\circ\text{C}$)	Ref.
0	Unknown	Unknown	~ 22	$\sim 50,000$	~ -55	[3]
0	4.5	90.26	19.45	48,800	-58.9	This work
0.02	4.52	90.6	19.6	51,200	-59.7	This work
0.04	4.62	92.59	19.74	69,200	-59.7	This work
0.05	4.69	93.99	20.04	107,000	-59.1	This work
0.06	4.65	93.1	19.92	74,200	-60.1	This work
0.08	4.59	91.93	19.8	61,900	-62.3	This work
0.10	4.56	91.28	19.5	49,000	-62.6	This work

the variations in resonant frequency per 10°C (Δf) during the temperature changed from $+30$ to $+80^\circ\text{C}$. The τ_f (ppm/ $^\circ\text{C}$) can be calculated by

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is resonant frequency at T_1 and f_2 is the resonant frequency at T_2 .

3. Results and discussion

Fig. 1 shows the room temperature X-ray diffraction patterns recorded from the $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x=0-0.1$) ceramics sintered at 1350°C for 3 h. No second phase was detected and the XRD patterns showed an ilmenite-structured CoTiO_3 phase (ICDD PDF#77-1373) for the entire compositional range ($x=0-0.1$), which is expected to be single phase as the two extreme compositions CoTiO_3 and ZnTiO_3 have the same structure and there is little difference in the ionic radii of Co^{2+} (0.65 Å , CN=6) and Zn^{2+} (0.74 Å , CN=6). As illustrated, the diffraction peaks of (104) and (110) slightly shift to a lower angle as x increases due to the incorporation of larger

Zn^{2+} in place of Co^{2+} . It indicates the formation of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x=0-0.1$) solid solutions.

The measured theoretical density (TD), lattice parameters, and cell volume of the various sintered compacts are presented in Table 1. The lattice parameters of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ solid solutions calculated from XRD patterns increase from $a = 5.0653 \pm 0.0009 \text{ Å}$ and $c = 13.9199 \pm 0.0014 \text{ Å}$ in CoTiO_3 to $a = 5.0688 \pm 0.0010 \text{ Å}$ and $c = 13.9298 \pm 0.0027 \text{ Å}$ in $(\text{Co}_{0.9}\text{Zn}_{0.1})\text{TiO}_3$ as expected. As mentioned previously, it is a result from the incorporation of larger Zn^{2+} in place of Co^{2+} . The cell volume also slightly increases with the increase of Zn content. In addition, the theoretical density varies in a consistent trend and increases as the x value increases. It linearly increases from $4.985 \text{ g}/\text{cm}^3$ at $x=0$ – $4.995 \text{ g}/\text{cm}^3$ at $x=0.1$ showing a small variance.

Table 2 illustrates the microwave dielectric properties of the $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x=0-0.1$) ceramic system sintered at 1350°C for 3 h. The slight variation in the τ_f value was mainly related to the small cell volume change. With the increase of x in the compound, the relative density increased to a maximum of 93.99% at $x=0.05$ and decreased thereafter. In addition, the variation of ϵ_r and $Q \times f$ was consistent with that of relative density. It shows that the $Q \times f$ value can be improved from 48,800 GHz at $x=0$ to 107,000 GHz (at 9.27 GHz) at $x=0.05$ indicating the initial increase of ZnO has a more prominent effect on the $Q \times f$ values than the subsequent additions. Also, it suggests that $x=0.05$ is an appropriate value for the compound to achieve low dielectric loss.

The surface microstructural photographs of $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ ceramics sintered at different temperatures for 3 h are shown in Fig. 2. Small pores existed at the grain boundary for specimen sintered at 1290°C , causing the low relative densities in ceramics, and

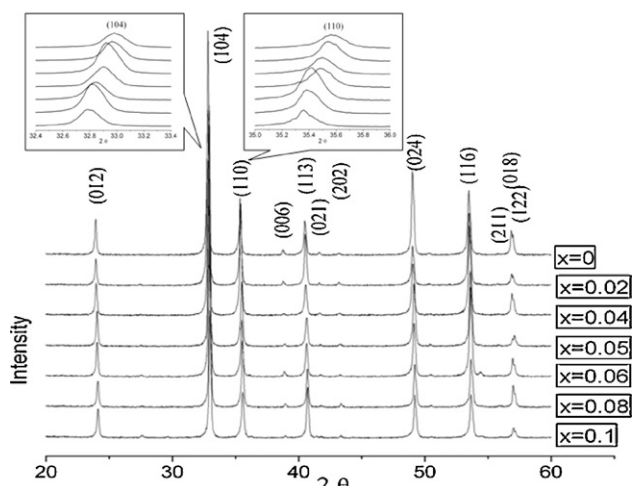


Fig. 1. X-ray diffraction patterns of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x=0-0.1$) ceramics sintered at 1350°C for 3 h.

Table 3
The EDS data of the $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ ceramics.

Sintering temperature	Atom%			
	Co K	Zn K	Ti K	O K
1290°C	24.99	2.17	27.29	45.55
1320°C	24.65	2.13	26.45	46.77
1350°C	24.23	1.93	26.19	47.65
1380°C	25.71	1.80	31.57	40.92

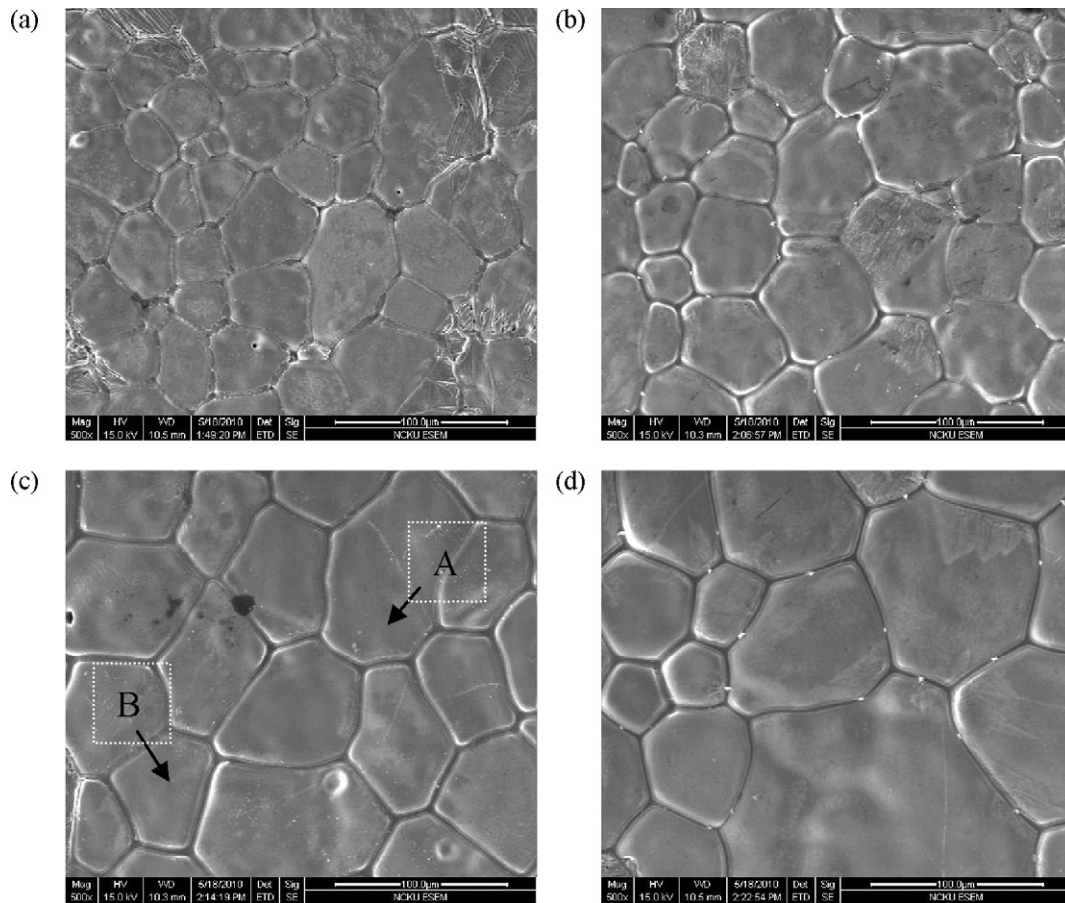


Fig. 2. SEM photographs of $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ ceramics sintered at (a) 1290 °C, (b) 1320 °C, (c) 1350 °C, and (d) 1380 °C for 3 h.

disappeared as the sintering temperature increased. For specimen sintered at 1350 °C, grains are slightly enlarged and the samples have a fairly uniform grain size distribution leading to a lowering of lattice defects and imperfection. However, for 1380 °C-sintered samples, the grain morphology indicates an abnormal grain growth. The compositions from EDS analysis (Table 3) qualitatively matches to the respective compound $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$. However, the result also indicates that the Zn atomic percentage varied from 2.17 to 1.8 atm% when the sintering temperature increased from 1290 to 1380 °C owing to the Zn evaporation at high sintering temperatures.

Fig. 3 illustrates the dependence of apparent density and dielectric constant on the sintering temperature of $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ ceramics. The apparent density increased with increasing sintering temperature to a maximum value of 4.69 g/cm³ corresponding to a relative density of 93.99% at 1350 °C and thereafter it decreased due to the evaporation of ZnO and rapid grain growth of the specimen. The relationship between dielectric constant and sintering temperature of $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ shows a similar trend as between density and sintering temperature. The dielectric constant is also maximum at 1350 °C with $\epsilon_r = 20.04$. Fig. 4 shows the dependence

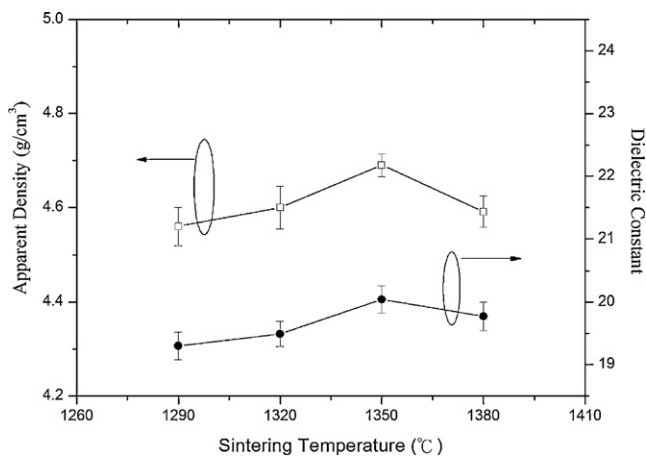


Fig. 3. Dependence of apparent density and dielectric constant on the sintering temperature of $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ ceramics.

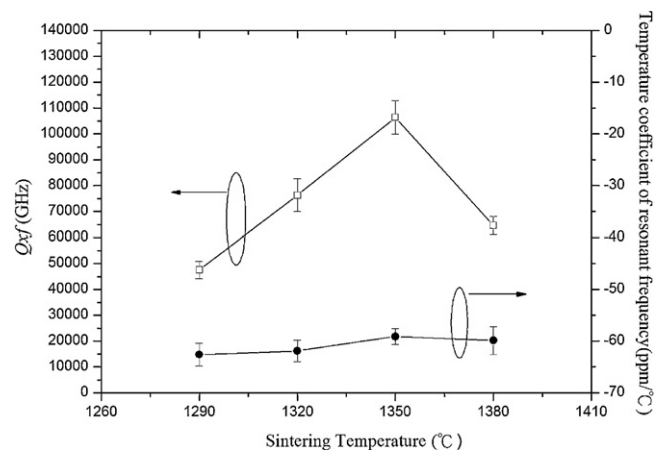


Fig. 4. Dependence of $Q \times f$ and τ_f on the sintering temperature of $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ ceramics.

of $Q \times f$ and τ_f on the sintering temperature of $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ ceramics and these properties also vary substantially with sintering temperature. The maximum value of the $Q \times f$ ($= 107,000$ GHz at 9.27 GHz) is also shown at the sintering temperature corresponding to a maximum density as well as a relatively uniform grain morphology. The measured τ_f values ranged from -59.1 to -62.6 ppm/ $^\circ\text{C}$ as the specimen sintered at 1290 – 1380 $^\circ\text{C}$.

4. Conclusion

The microwave dielectric properties of $(\text{Co}_{1-x}\text{Zn}_x)\text{TiO}_3$ ($x=0$ – 0.1) ceramic systems were presented in this experiment. Samples with 0.05 mol% replacement of Co by Zn exhibits a single CoTiO_3 phase with a rhombohedral crystal structure suggesting a formation of solid solution. The optimal microwave dielectric properties can be achieved for specimen using $(\text{Co}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ sintered at 1350 $^\circ\text{C}$ for 3 h with a dielectric constant (ϵ_r) of ~ 20 , a $Q \times f$ value of $\sim 107,000$ GHz (at $f=9.27$ GHz), and a temperature coefficient of resonant frequency (τ_f) of ~ 60 ppm/ $^\circ\text{C}$.

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