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Temperature compensating $ZnAl_2O_4$–Co_2TiO_4 spinel-based low-permittivity microwave dielectric ceramics

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Abstract

TiO_2, $CaTiO_3$ and $SrTiO_3$ were added to the $0.79ZnAl_2O_4$–$0.21Co_2TiO_4$ (ZACT in abbreviation) system to control its temperature coefficient of resonant frequency (τ_f). The effects of these additions on sinterability, phase compositions and microwave dielectric properties of the ceramics synthesized by the solid-state reaction were investigated. The results show that TiO_2, $CaTiO_3$ and $SrTiO_3$ can all reduce the densification temperature of the ZACT ceramics within the scope from 75 to 150 °C. $CoTi_2O_5$ second-phase with negative τ_f value appears in the TiO_2 doped ZACT system, which inhibits TiO_2 addition's function for adjusting τ_f value of ZACT ceramics. While, $CaTiO_3$ and $SrTiO_3$ can both tune effectively τ_f value to obtain temperature-stable materials.

Keywords: C. Dielectric properties; Solid state reaction; Temperature compensating; $ZnAl_2O_4$-based ceramics

1. Introduction

As the operating frequency ranges of microwave wireless communications expand, high performance microwave dielectric ceramics with a low permittivity ($\varepsilon_r < 15$) for microwave substrate and antenna application have attracted much scientific and commercial attention. Low permittivity can not only minimize cross coupling with conductors but also shorten the time for the electronic signal transition. In addition, a high quality factor ($Q{\cdot}f$) to increase selectivity and a near zero temperature coefficient of resonator frequency (τ_f) to ensure stability of the frequency against temperature changes are also required [1,2].

Recently, low-permittivity spinel-based materials such as M_2TiO_4 (M = Mg and Co) [3] and MAl_2O_4 (M = Zn and Mg) [4–7] can be proposed as excellent microwave substrate and antenna materials. Then, Lei et al. [8] found that ZACT ceramics sintered at 1500 °C for 3 h exhibits a low ε_r value of 9.9 and a high $Q{\cdot}f$ value of 94,000 GHz, however, its τ_f value has relative high magnitude ($\tau_f = -66.4$ ppm/°C). In principle, the tuning of τ_f to near-zero value could be achieved by adding other compounds having τ_f of opposite sign. TiO_2, $CaTiO_3$ and $SrTiO_3$ additions, have often been utilized and can succeed in controlling τ_f value and improving the sinterability and bulk density of ceramics [7,9,10]. In the present study, the effects of TiO_2, $CaTiO_3$ and $SrTiO_3$ additions on the sinterability, phase compositions and microwave dielectric properties of $0.79ZnAl_2O_4$–$0.21Co_2TiO_4$ ceramics were investigated.

2. Experimental procedure

Reagent grade ceramic powders ZnO, Al_2O_3, TiO_2, CoO, $CaCO_3$, and $SrCO_3$ were used as raw materials. $CaTiO_3$ and $SrTiO_3$ precursors were prepared by $CaCO_3$, $SrCO_3$ and TiO_2, respectively. Stoichiometric starting powders according to the composition of $(1-x)$ZACT$-xTiO_2$ (or $CaTiO_3$, $SrTiO_3$) were milled with agate balls in ethanol for 3 h at a speed of 360 rpm (rotation per minute). The slurry was dried at 80 °C in an infrared stove, and then calcined in air at 1150 °C for 3 h. After milling and drying again, the calcined powders added with 7 wt.% polyvinyl alcohol whose concentration of the aqueous solution is 5 wt.% as a binder were uniaxially pressed into the samples with dimensions of 25 mm in diameter and about 13 mm in height under a pressure of 150 MPa. After sintered at 1300–1500 °C for 3 h at a heating rate of 5 °C/min in air, these

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samples were cooled at a rate of 2 °C/min up to 1000 °C and then they were furnace cooled.

The crystalline phases were analyzed by means of the X-ray diffraction method using CuKα radiation (X'Pert PRO). The microstructure observation and quantitative analysis were performed by field scanning electron microscope (FSEM; FEI-Sirion 200) and energy dispersive X-ray spectroscopy (EDX; Genesis 7000) respectively. The dielectric constant (ε_r) and the unloaded $Q{\cdot}f$ value were measured in the TE_{011} mode by Hakki and Coleman method [11] using an Advantest R3767C network analyzer and parallel silver boards. The temperature coefficient of resonant frequency (τ_f) in the temperature range of 20–80 °C was calculated by formula (1):

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

where f_1 and f_2 represent the resonant frequency at T_1 and T_2, respectively.

3. Results and discussion

3.1. TiO_2 addition

Fig. 1 shows XRD patterns of $(1-x)$ZACT$-x\mathrm{TiO_2}$ ceramics sintered at different temperatures. In the ZACT sintered body, $ZnAl_2O_4$ can form a spinel solid-solution with Co_2TiO_4 [8], however, it is observed that second-phase $CoTi_2O_5$ besides spinel phase exist when TiO_2 is added to the ZACT system. Moreover, the X-ray diffraction intensity of $CoTi_2O_5$ phase enhances with the increasement of TiO_2, as shown in Fig. 1(a) and (c), which indicates that TiO_2 addition induces the formation of $CoTi_2O_5$ second phase.

Table 1
Density and microwave dielectric properties of $(1-x)$ZACT$-x\mathrm{TiO_2}$ ceramics sintered at densification temperature.

x value	T_{sint} (°C)	ρ (g/cm^3)	ε_r	$Q{\cdot}f$ (GHz)	τ_f (ppm/°C)
0	1500	4.48	9.90	94,000	−66.40
0.13	1350	4.44	10.67	86,716	−62.16
0.20	1350	4.43	11.13	98,723	−63.31

Density and microwave dielectric properties of $(1-x)$ZACT$-x\mathrm{TiO_2}$ ceramics sintered at densification temperature are shown in Table 1. Density of $(1-x)$ZACT$-x\mathrm{TiO_2}$ ($x = 0.13$ and 0.20) ceramics is nearly equal to that of ZACT ceramics sintered at 1500 °C, which suggests that TiO_2 can lower the densification temperature of ZACT system by 150 °C. As the amount of TiO_2 increases, ε_r value of the $(1-x)$ZACT$-x\mathrm{TiO_2}$ ceramics rises gradually, however the variational rule of $Q{\cdot}f$ value cannot still be understood clearly, while τ_f value does not change obviously (see Table 1). The ε_r value of the second-phase $CoTi_2O_5$ with 18.95 is more than that of the ZACT spinel phase, and the τ_f value of the former with −42.20 ppm/°C is comparable with that of the latter, therefore, it is convinced that the above phenomena appear according to the logarithmic mixing rule [7].

3.2. $MTiO_3$ (M = Ca and Sr) addition

XRD patterns of $(1-x)$ZACT$-x\mathrm{CaTiO_3}$ ceramics sintered at different temperatures are shown in Fig. 2. $(1-x)$ ZACT$-x$-

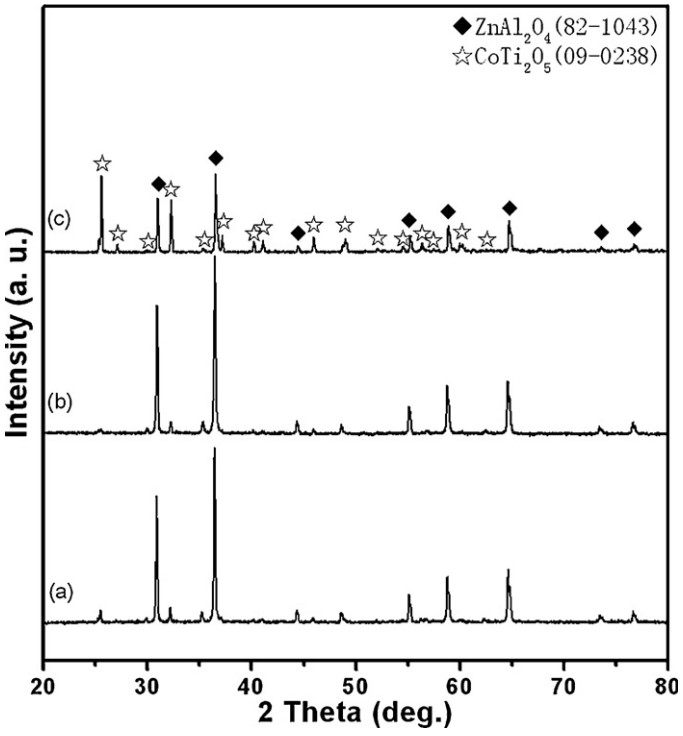

Fig. 1. XRD patterns of $(1-x)$ZACT$-x\mathrm{TiO_2}$ ceramics sintered at different temperatures: (a) $x = 0.13$, 1350 °C; (b) $x = 0.13$, 1450 °C and (c) $x = 0.2$, 1350 °C.

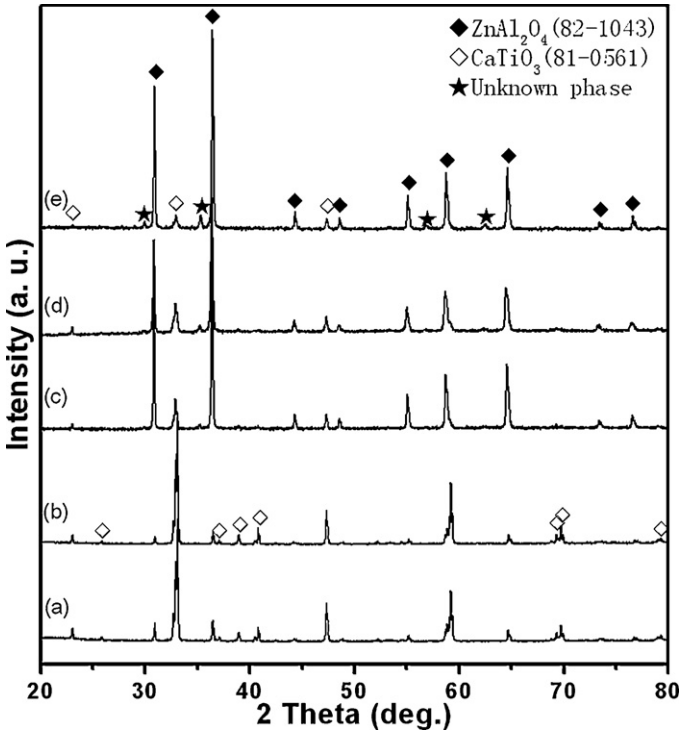

Fig. 2. XRD patterns of $(1-x)$ZACT$-x\mathrm{CaTiO_3}$ ceramics sintered at different temperatures: (a) $x = 0.06$, 1400 °C; (b) $x = 0.07$, 1400 °C; (c) $x = 0.08$, 1350 °C; (d) $x = 0.08$, 1400 °C and (e) $x = 0.08$, 1450 °C.

$CaTiO_3$ ($x = 0.06$ and 0.07) ceramics include $ZnAl_2O_4$-based spinel and $CaTiO_3$ phases (see Fig. 2(a) and (b)). When x value is equal to 0.08, a novel second phase appears in the sintered ceramics, and the X-ray diffraction intensity of $CaTiO_3$ phase reduces quickly. According to JCPDS card, the unknown phase may be $Zn_2Ti_3O_8$, Co_2TiO_4 or Zn_2TiO_4. As sintering temperature increases, the X-ray diffraction intensity of unknown phase enhances gradually while that of $CaTiO_3$ phase weakens (see Fig. 2(c)–(e)), which indicates that the amount of unknown phase increases while that of $CaTiO_3$ phase reduces.

Fig. 3 shows that SEM micrographs of $(1-x)$ZACT$-x$$CaTiO_3$ ceramics sintered at different temperatures. The $(1-x)$ZACT$-x$$CaTiO_3$ system sintered at 1400 °C for 3 h can form dense sintered body, in which cubic grains can be observed, moreover, the cubic grain size reduces when the sintering temperature rises, as shown in Fig. 3(a) and (b). From Fig. 3(b) and (c), it can be found a tendency that cubic grains turn to equiaxial grains with the increasing of sintering temperature from 1400 to 1450 °C, and plate grain (see Fig. 3(c) and (d)) also appear in the $(1-x)$ZACT$-x$$CaTiO_3$ ($x = 0.08$) ceramics sintered at 1450 °C. This observation is reasonable when considering $CaTiO_3$ reaction with base materials to form the unknown phase under special condition such as enough $CaTiO_3$ and sintering temperature.

In general, different sizes and shapes of grains have different phase compositions [8]. In order to identify the phase compositions of these grains, EDX was performed for the $(1-x)$ZACT$-x$$CaTiO_3$ ($x = 0.08$) ceramics sintered at 1450 °C and the results are shown in Table 2. It is known from Table 2 that grain "a" and "b" are both (Zn, Co)Al_2O_4 spinel phase, and cubic grain "c" is $CaTiO_3$ phase while plate grain "d" is (Zn, Co, Ca)$_2Ti_3O_8$ solid solution. It is shown that the small amount of (Zn, Co)Al_2O_4 exists in the grain "d", possibly because partial electron beams probe other grains around it due to the thickness of the grain "d" lower than the diameter of electron beam.

Table 2
Element content of different grains in $(1-x)$ZACT$-x$$CaTiO_3$ ($x = 0.08$) ceramics sintered at 1450 °C.

Grain	Element content (at.%)					
	Zn	Al	Co	Ca	Ti	O
a	9.46	26.34	5.23	–	1.72	57.25
b	7.76	23.35	3.94	0.84	2.27	61.84
c	1.66	2.95	1.13	17.79	18.25	58.22
d	3.58	7.04	4.21	4.26	12.56	68.35

It is believed that $CaTiO_3$ and sintering temperature can improve ion diffusion, and the more amount of $CaTiO_3$ addition and higher sintering temperature, Ca^{2+} and Ti^{4+} ions diffuse more easily into the ZACT spinel crystal lattice. However, ion solid solubility reduces gradually during cooling, which results in formation of lower temperature phase (Zn, Co, Ca)$_2Ti_3O_8$.

Density and microwave dielectric properties of $(1-x)$ZACT$-x$$CaTiO_3$ as a function of sintering temperature and $CaTiO_3$ content are shown in Fig. 4. As the sintering temperature rises, the density of the $(1-x)$ZACT$-x$$CaTiO_3$

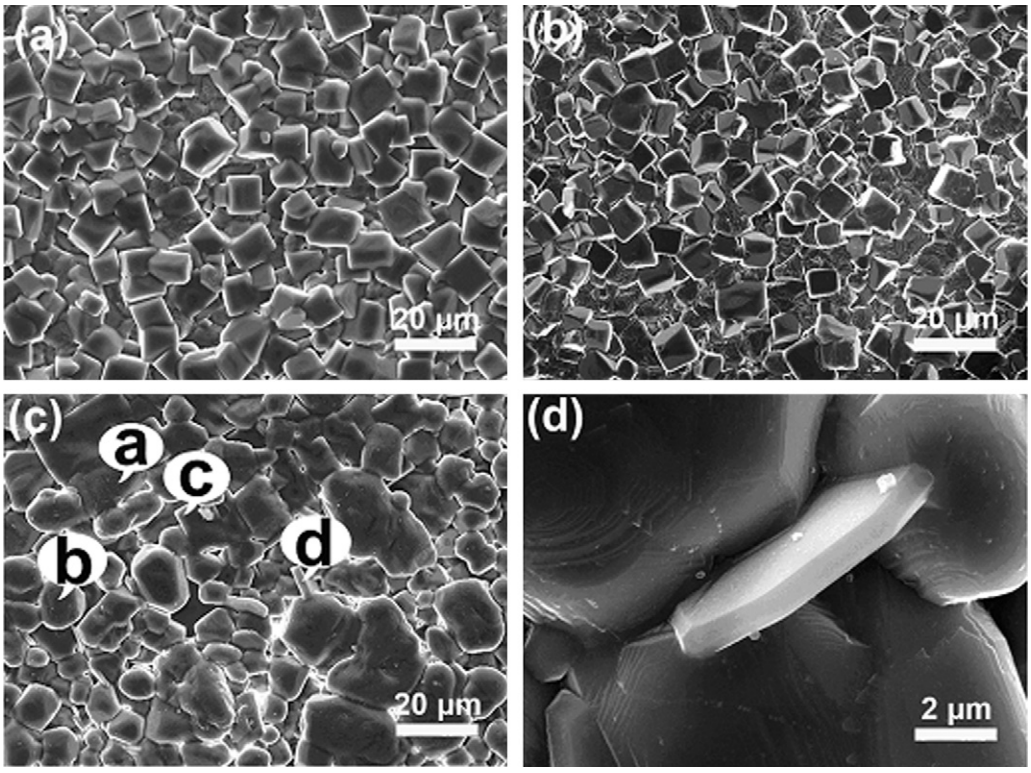

Fig. 3. SEM micrographs of $(1-x)$ZACT$-x$$CaTiO_3$ ceramics sintered at different temperatures: (a) $x = 0.06$, 1400 °C; (b) $x = 0.08$, 1400 °C; (c) $x = 0.08$, 1450 °C and (d) zoom of grain "d".

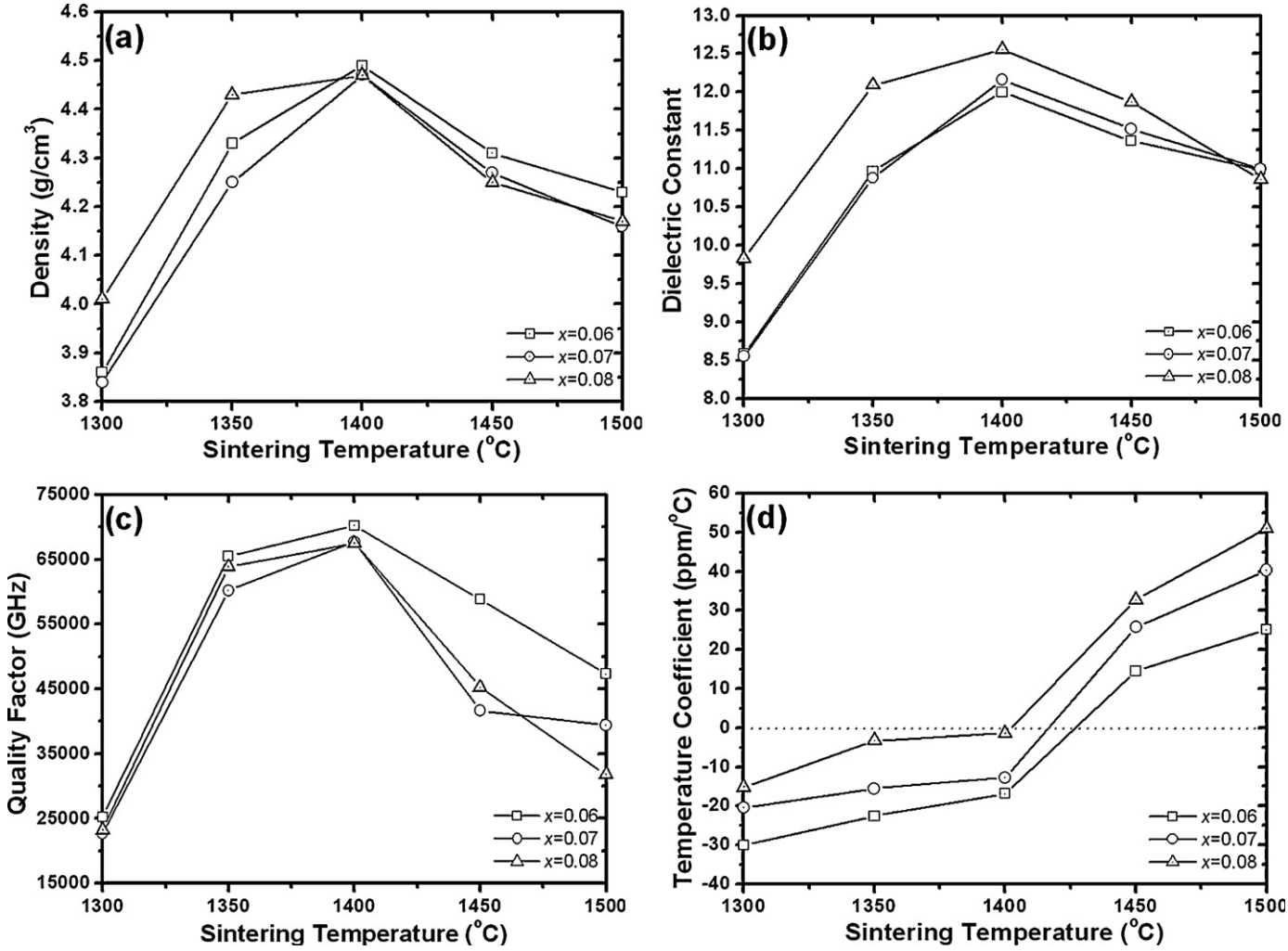

Fig. 4. Density and microwave dielectric properties of $(1-x)$ZACT$-x$CaTiO$_3$ as a function of sintering temperature and CaTiO$_3$ content.

ceramics initially increases and then decreases after reaching the maximum at 1400 °C (see Fig. 4(a)), which is 100 °C lower than that of ZACT. The correlations between ε_r (or $Q{\cdot}f$) value and sintering temperature nearly reveal the same trend as those between density and sintering temperature, as observed in Fig. 4(a)–(c), which suggests that the density is the dominating factor to control ε_r and $Q{\cdot}f$ value. It takes on a tendency that ε_r value increases while $Q{\cdot}f$ value reduces slightly with the increasing of CaTiO$_3$. An increase in CaTiO$_3$ content and sintering temperature is beneficial to the improvement of τ_f value of $(1-x)$ZACT$-x$CaTiO$_3$ ceramics, as shown in Fig. 4(d). τ_f value of CaTiO$_3$ (τ_f = +800 ppm/°C) is higher than that of ZACT (τ_f = −66.40 ppm/°C), therefore, the above variation is reasonable according to the mixing rule for composite materials [7]. However, when x value reaches to 0.08, CaTiO$_3$ reacts with matrix to form (Zn, Co, Ca)$_2$Ti$_3$O$_8$ phase, which indicates that (Zn, Co, Ca)$_2$Ti$_3$O$_8$ could also have a positive τ_f value.

In general, the optimal microwave dielectric properties can be achieved in $(1-x)$ZACT$-x$CaTiO$_3$ (x = 0.08) sintered at 1400 °C for 3 h with an ε_r value of 12.6, a $Q{\cdot}f$ value of 67,480 GHz, and a τ_f value of −1.4 ppm/°C.

When SrTiO$_3$ is added to ZACT system, the densification temperature of $(1-x)$ZACT$-x$SrTiO$_3$ ceramics reduce to 1425 °C, which is lower than that of ZACT ceramics by 75 °C. Furthermore, $(1-x)$ZACT$-x$SrTiO$_3$ ceramics have the same phase composition and microstructure as the $(1-x)$ZACT$-x$CaTiO$_3$ ceramics. $(1-x)$ZACT$-x$SrTiO$_3$ (x = 0.05) ceramics sintered at 1425 °C for 3 h exhibits excellent microwave dielectric properties: ε_r = 11.6, $Q{\cdot}f$ = 49,950 GHz, τ_f = −2.2 ppm/°C.

4. Conclusions

(1) TiO$_2$, CaTiO$_3$ and SrTiO$_3$ can all reduce the densification temperature of the ZACT ceramics within the scope from 75 to 150 °C.

(2) $(1-x)$ZACT$-x$TiO$_2$ ceramics include ZnAl$_2$O$_4$-based spinel and CoTi$_2$O$_5$ phases. When a small amount of MTiO$_3$ is added, ZnAl$_2$O$_4$-based spinel and CaTiO$_3$ phases exist in the $(1-x)$ZACT$-x$MTiO$_3$ (M = Ca and Sr) ceramics, and further doping MTiO$_3$ will promote its reaction with matrix to form (Zn, Co, M)$_2$Ti$_3$O$_8$ phase.

(3) TiO_2 cannot adjust τ_f value of $(1-x)ZACT-xTiO_2$ ceramics to near-zero, while $CaTiO_3$ and $SrTiO_3$ can both tune effectively τ_f value to obtain a temperature-stable material. The excellent microwave dielectric properties can be exhibited as follows: $(1-x)ZACT-xCaTiO_3$ ($x = 0.08$) sintered at 1400 °C with $\varepsilon_r = 12.6$, $Q{\cdot}f = 67{,}480$ GHz and $\tau_f = -1.4$ ppm/°C, and $(1-x)ZACT-xSrTiO_3$ ($x = 0.05$) sintered at 1425 °C with $\varepsilon_r = 11.6$, $Q{\cdot}f = 49{,}950$ GHz and $\tau_f = -2.2$ ppm/°C.

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