Synthesis, characterization and dielectric properties of a novel temperature stable $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramic

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Abstract: $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ microwave dielectric ceramics were prepared via the conventional solid-state reaction route with the aim of reducing the τ_f value and improving the thermal stability. The phase composition and the microstructure were investigated using X-ray diffraction, Raman spectra, and scanning electron microscopy. A set of phase transitions which were induced by composition had been confirmed via the sequence: rutile structure→coexistence of rutile and columbite phase→columbite phase. For $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ microwave dielectric ceramics, the addition of ZnNb_2O_6 content ($x = 0-1$) led to the decrease of ε_r from 62.98 to 23.94. As a result of the high $Q \times f$ of ZnNb_2O_6 ceramics, the increase of ZnNb_2O_6 content also led to the lower sintering temperatures and the higher $Q \times f$ values. The τ_f value was reduced from +108.04 ($x = 0$) to -49.31 ppm/°C ($x = 1$). Among them, high density $0.5\text{CoTiNb}_2\text{O}_8-0.5\text{ZnNb}_2\text{O}_6$ ceramics were obtained at 1175 °C with excellent microwave dielectric properties of ε_r 39.2, $Q \times f$ 40013 GHz, and $\tau_f + 3.57$ ppm/°C.

Keywords: solid-state reaction; $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics; crystal structure; microwave dielectric property

1 Introduction

In recent years, with the rapid development of modern communication technology, dielectric antenna and microwave integrated circuit substrate, microwave dielectric ceramics which are used as the key material of these electronic components have been developed widely [1,2]. For application in microwave frequency field, the dielectric material needs to meet the following three requirements: a large dielectric constant, an excellent quality factor, and a temperature frequency

coefficient that close to zero. However, it is difficult to meet the above three characteristics at the same time in one material system. Therefore, the adjustment of dielectric properties is very important for practical materials. Baumgarte and Blachnik [3] investigated the compositions of $\text{M}^{2+}\text{M}^{4+}\text{Nb}_2\text{O}_8$ ($\text{M}^{2+} = \text{Be, Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd}$; $\text{M}^{4+} = \text{Ti, Zr, Ge, Sn}$), and among the system, $\text{CoTiNb}_2\text{O}_8$ ceramics showed excellent microwave dielectric properties: $\varepsilon_r \sim 65.4$, $Q \times f \sim 65300$ GHz, and $\tau_f \sim 223.2$ ppm/°C [4]. However, the large τ_f value (223.2 ppm/°C) is not conducive to its practical application, and needs to be adjusted. Using two kinds of materials with opposite temperature coefficients is a common way to regulate the temperature coefficient of

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the resonant frequency of the material. Many researchers have made attempts in this area, which have obtained good results [5,6]. Nenasheva *et al.* [7] reported that τ_f was adjusted to 0 ppm/°C when $x = 0.66$ in the $(1-x)\text{ZnNb}_2\text{O}_6-x\text{Zn}_{0.17}\text{Nb}_{0.33}\text{Ti}_{0.5}\text{O}_2$ composite. Li *et al.* [8] reported that τ_f was adjusted to 0.28 ppm/°C in the $(1-x)(\text{Na}_{0.5}\text{La}_{0.5})\text{MoO}_4-x(\text{Na}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$ composite. These studies have proved that the method is effective. For the complex phase ceramics with different crystal structures, it has been proved that the formation of solid solution and secondary phase could also be inhibited effectively and could maintain good microwave dielectric properties [9,10]. Different from the positive τ_f values of $\text{CoTiNb}_2\text{O}_8$ ceramics, ZnNb_2O_6 ceramics with columbite structure have the negative τ_f values and are in the same niobate system as $\text{CoTiNb}_2\text{O}_8$ ceramics. Lee *et al.* [11] reported that the microwave dielectric properties of ZnNb_2O_6 reached $\epsilon_r \sim 25$, $Q \times f \sim 83700$ GHz, and $\tau_f \sim -56$ ppm/°C. Therefore, it is estimated that composite ceramics with near zero τ_f values would be obtained by combining $\text{CoTiNb}_2\text{O}_8$ ceramics and ZnNb_2O_6 ceramics.

In this work, $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ($x = 0-1$) composite ceramics with different structures were prepared via the traditional solid-state reaction method with the aim of reducing the τ_f value and improving the thermal stability. The phase constitution, microstructure, sintering reaction, and microwave dielectric properties of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ($x = 0-1$) composite were studied in detail.

2 Experimental

CoO (99%), TiO_2 (99.9%), ZnO (99%), and Nb_2O_5 (99.99%) were used as raw materials and purchased from Sinopharm Chemical Reagent Co., Ltd. The raw materials were mixed by a stoichiometric ratio using alcohol as a milling medium for 24 h. The dried powders were calcined at 1200 and 1100 °C for 4 h to synthesize $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 . The calcined powders were mixed according to the ratio of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ and then ball-milled for 6 h. The slurries were dried at 80 °C for 1 h and sieved with 200# mesh. Polyvinyl alcohol (PVA) was added into the sifted powders and the powders were pressed together into pellets with 10 mm in diameter and 5 mm in thickness at a pressure of 150 MPa. The pellets were then heated at 500 °C for 2 h to discharge

the PVA and later sintered in the range of 1150 to 1300 °C for 4 h.

The crystal structures were characterized by X-ray diffraction (XRD, Rigaku, DMAX-RB, Japan) with Cu K α radiation. The microstructure of the sintered ceramics was observed by a scanning electron microscopy (SEM, JSM-6710F, JEOL, Japan) and the composition of the ceramics was analyzed by energy dispersive spectrometer (EDS, NS7, Thermo, USA). The structure parameters were obtained from the Rietveld refinement results of the XRD data using GSAS-EXPGUI software [12]. Raman spectroscopy was performed using a LabRam HR (Jobin-Yvon, France). The density was confirmed by Archimedes methods. Microwave dielectric properties of the ceramics were measured by a network analyzer (8720ES, Agilent, USA) using Hakki–Coleman's dielectric resonator method, modified and improved by Hakki *et al.* [13–15]. All measurements were obtained in the frequency of 4–12 GHz at room temperature. The temperature coefficients of the resonant frequency were measured in the temperature range from 20 to 80 °C. The τ_f value was calculated using the formula below:

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

where f_1 and f_2 are the resonant frequencies at T_1 and T_2 .

3 Results and discussion

3.1 Phase and structure analysis

Figure 1 shows the XRD patterns of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics sintered at the optimum sintering temperature for 4 h. All the diffraction peaks could be a good index of $\text{CoTiNb}_2\text{O}_8$ (JCPDS #52-1875) and ZnNb_2O_6 (JCPDS #37-1371) stage. The composite ceramic samples showed single rutile phase structure of $\text{CoTiNb}_2\text{O}_8$ ceramics when $x < 0.3$. With the increase of x , the columbite phase structure of ZnNb_2O_6 ceramics appeared gradually. When $x > 0.6$, the $\text{CoTiNb}_2\text{O}_8$ phase disappeared completely. The results indicated that the serious ionic diffusion and solid solution reaction had occurred in the system. When $0 < x < 0.3$, the ceramics were the solid solution based on $\text{CoTiNb}_2\text{O}_8$ phase. With the increasing ZnNb_2O_6 content, the ZnNb_2O_6 phase appeared. When $x > 0.6$, the ceramics were the solid solution based on ZnNb_2O_6 phase. Rietveld refinement was used to analyze the structure evolution in the $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ system.

Fig. 3 (a) The rutile octahedral structure of $\text{CoTiNb}_2\text{O}_8$ ceramics, and (b) the columbite octahedral structure of ZnNb_2O_6 ceramics.

ceramics are shown in Fig. 4. For ZnNb_2O_6 which belongs to the columbite structure, the theoretical analysis revealed that there are 108 fundamental modes belonging to the following irreducible representations: $13A_g + 14B_{1g} + 13B_{2g} + 14B_{3g} + 13A_u + 14B_{1u} + 13B_{2u} + 14B_{3u}$ in which 54 modes ($13A_g + 14B_{1g} + 13B_{2g} + 14B_{3g}$) are Raman active and the other ($13A_u + 14B_{1u} + 13B_{2u} + 14B_{3u}$) are infrared active. Table 1 reveals that the positions correspond to the peaks in the ZnNb_2O_6 crystal [17,18]. Table 2 illustrates that the Raman vibrational mode assignments of ZnNb_2O_6 [18–20]. For $\text{CoTiNb}_2\text{O}_8$ that belongs to the rutile structure, theoretical analysis [21] shows that there are 15 fundamental modes belonging to the following irreducible representations: $A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + 2B_{1u} + E_g + 3E_u$ in which 4 modes ($A_{1g} + B_{1g} + B_{2g} + E_g$) are Raman active and other 4 modes ($A_{2u} + 3E_u$) are infrared active. The other 3 modes ($A_{2g} + 2B_{1u}$) are neither Raman active nor infrared active. There are mainly three basic modes that attribute to $\text{CoTiNb}_2\text{O}_8$: lattice vibration for 122 cm^{-1} ; CoO_6 octahedra stretching deformation for 278 cm^{-1} and Nb–O symmetric vibration for 684 cm^{-1} [22,23]. When the transition from rutile to columbite took place, the E_g vibration mode caused by Ti–O stretching vibration disappeared at 455 cm^{-1} . Simultaneously, the vibration mode from NbO_6 octahedron-symmetrical stretching vibration (located at 887 cm^{-1}) belonging to ZnNb_2O_6 enhanced gradually and appeared as the main peak. In addition, three extra vibration modes started to appear obviously, where the A_g mode at 250 cm^{-1} assigned to Zn–O stretching, O–Nb–O bending vibrations, the A_g mode at 405 cm^{-1} assigned to O–Nb–O bending vibrations and the A_g mode at 532 cm^{-1} assigned to Nb–O stretching vibration. The ZnO_6 was defined by the Zn–O bonds because of the serious distortion of the ZnO_6 octahedron [24]. With the increase of ZnNb_2O_6 content, the Zn–O stretching vibration peaks ($250, 272,$

Fig. 4 Raman spectra of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics. $A_{g(1)}$, $B_{1g(1)}$, $B_{2g(1)}$, and $E_{g(1)}$ were the modes of $\text{CoTiNb}_2\text{O}_8$ ceramics, $A_{g(2)}$, $B_{1g(2)}$, $B_{2g(2)}$, and $B_{3g(2)}$ were the modes of ZnNb_2O_6 ceramics.

$280, 293, 309,$ and 329 cm^{-1}) became stronger gradually. Besides, with the increase of x , it can be found that the A_g vibration mode at 887 cm^{-1} shifted slightly towards higher wavenumber and then reached 895 cm^{-1} , the A_g vibration mode shifted to lower wavenumber and finally reached 241 cm^{-1} . The cell volume increased while the content of ZnNb_2O_6 increased as shown in Fig. 2, which led to the increase of the atomic distances in the ZnO_6 octahedron and this also weakened the covalent bond strength between Zn–O bonds [25]. Therefore, the A_g vibration mode located at 250 cm^{-1} shifted to the lower wavenumber.

Table 1 Complied polarized Raman modes for the ZnNb_2O_6 single crystal and theoretical date. Reproduced with permission from Ref. [18], © AIP Publishing LLC 1977 (Unit: cm^{-1})

13A _g		14B _{1g}		13B _{2g}		14B _{3g}	
Theo.	Meas.	Theo.	Meas.	Theo.	Meas.	Theo.	Meas.
895	895	833	832	833	832	835	832
650	659	702	705	639	648	712	705
533	532	571	567	486	481	598	605
480	481	496	491	454	455	461	455
399	405	442	445	390	393	440	445
320	329	389	393	321	329	352	363
284	293	351	363	273	272	337	330
251	241	305	309	239	241	278	280
223	211	266	271	219	211	220	213
155	194	213	213	200	194	150	145
145	145	168	169	134	132	135	132
73	n.o.	155	146	100	n.o.	84	n.o.
51	n.o.	123	122	53	n.o.	57	n.o.
—	—	26	n.o.	—	—	25	n.o.

Table 2 Raman vibrational mode assignments for ZnNb_2O_6

Wavenumber (cm^{-1})	Symmetry	Mode vibration
213	$\nu_{10}(\text{B}_{1g})$	O–Nb–O bending, Nb–O stretching, and Zn–O stretching
241	$\nu_8(\text{A}_g)$	Zn–O stretching, O–Nb–O bending
272	$\nu_7(\text{B}_{2g})$	Zn–O stretching, O–Nb–O bending
280	$\nu_8(\text{B}_{3g})$	Zn–O stretching, O–Nb–O bending
293	$\nu_7(\text{A}_g)$	Zn–O stretching, O–Nb–O bending
309	$\nu_8(\text{B}_{1g})$	Zn–O stretching, O–Nb–O bending
329	$\nu_6(\text{A}_g)$	Nb–O stretching, Zn–O stretching, and O–Nb–O bending
363	$\nu_6(\text{B}_{3g})$	O–Nb–O bending, Zn–O stretching
393	$\nu_4(\text{B}_{2g})$	O–Nb–O bending
405	$\nu_5(\text{A}_g)$	O–Nb–O bending
445	$\nu_5(\text{B}_{1g})$	Nb–O stretching
481	$\nu_3(\text{B}_{2g})$	Nb–O stretching, Zn–O stretching
532	$\nu_3(\text{A}_g)$	Nb–O stretching vibration
567	$\nu_3(\text{B}_{1g})$	Nb–O stretching, Zn–O stretching
605	$\nu_3(\text{B}_{3g})$	Nb–O stretching, Zn–O stretching
648	$\nu_2(\text{B}_{2g})$	Nb–O stretching
705	$\nu_2(\text{B}_{1g})$	Nb–O stretching
832	$\nu_1(\text{B}_{1g})$	Nb–O anti-symmetric stretching
895	$\nu_1(\text{A}_g)$	Nb–O symmetric stretching

Similarly, the A_g vibration mode located at 887 cm^{-1} should shift to the higher wavenumber instead of the lower one. The reason for this phenomenon could be

the increase of the symmetry of the crystal because of the sample transition from the disordered phase structure for $x = 0.3$ to single columbite phase structure for $x = 1$.

3.3 Morphological analysis

Figure 5 illustrates the SEM images of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics. Table 3 shows the EDS results of composite ceramics. With the optimized sintering temperature, each component on the ceramic surface was arranged closely. The microstructure shows that the ceramics appear different characteristics on the shape and size of grains with the increase of ZnNb_2O_6 content. For samples with $x < 0.2$ (Figs. 5(a) and 5(b)), the grain mainly appeared equiaxed structure with large grain size ($> 20 \text{ mm}$), and each larger grain seems to merge with many small grains. For $x = 0.2$ in Fig. 5(c), the microstructure presents two groups of grains with different grain sizes. The large ones with grain size of 5 mm distributed very uniformly, and many staircase crystal growth stripes appeared on the surface of the grain. The small ones were very tiny grains with grain sizes of $1\text{--}2 \text{ mm}$. As listed in Table 3, the two smaller ones (denoted as A and C) were identified as $\text{CoTiNb}_2\text{O}_8$ phase, the bigger ones (denoted as B) were identified as the solid solution based on $\text{CoTiNb}_2\text{O}_8$ phase. For $x = 0.3$ and 0.4 in Figs. 5(d) and 5(e), the grain sizes reduce to $0.5\text{--}2.5 \text{ mm}$. The small grains were identified as ZnNb_2O_6 phase and the large polygon-like grains were identified as the solid solution based on $\text{CoTiNb}_2\text{O}_8$ phase. For those grain boundary system with two phases, there would be pinning effect on the movement of the grain boundary while there were second phase inclusions on the grain boundary. In order to pass through the inclusions in the second phase, the interfacial energy of the system needed to be reduced, resulting in the decrease of the interface continuous progress, which also made the interface become straight. When the driving force of the grain boundary was the same as the resistance force caused by the second phase material, the grain boundary stopped moving and the grain size reached stable. This effect led to the decrease of the grain sizes. When $0.5 \leq x < 1$ (Figs. 5(f)–5(j)), the energy spectrum results showed that all the grains contain five elements with certain content: Zn, Ti, Co, Nb, and O, which indicated that there will be the diffusion of ions and formation of solid solutions in composite ceramics. The $\text{CoTiNb}_2\text{O}_8$ phase revealed in Fig. 1 was not

Fig. 5 SEM images of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics with $x =$ (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5, (g) 0.6, (h) 0.7, (i) 0.8, (j) 0.9, and (k) 1 sintered at 1175 °C for 4 h.

Table 3 EDS analysis of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics marked in Fig. 5

(Unit: at%)

Spot	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Co	13.58	10.55	13.43	0.89	7.46	6.54	1.27	1.78	5.69	5.97	4.80	2.85	1.96	1.71
Ti	14.99	13.19	6.09	0.73	9.81	8.82	1.84	2.01	9.90	4.36	4.67	3.21	2.63	2.30
Zn	0	3.23	0	12.49	3.34	4.72	9.66	8.13	5.18	7.79	9.25	7.69	8.67	7.60
Nb	42.81	44.62	44.25	38.55	32.56	34.68	30.71	26.82	30.63	31.97	39.43	32.00	32.30	30.29
O	28.61	28.41	36.22	47.34	46.83	45.24	56.52	54.67	48.60	49.91	41.84	54.25	54.43	58.11

shown in Fig. 5, this phenomenon could be caused by the low content of $\text{CoTiNb}_2\text{O}_8$ phase and it is not obvious in SEM images.

3.4 Sintering behavior

The relative densities of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics are depicted in Fig. 6. The relative densities of each composition kept increasing with rising temperature and then decreased until it reached its maximum value. For different values of x , the sintering temperatures to obtain the maximum relative densities of the samples decreased with the increase of x . The optimum sintering temperature of $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 ceramics are 1250 and 1175 °C, respectively [4,11]. This phenomenon indicated that the increase of ZnNb_2O_6 content could reduce the sintering temperature

Fig. 6 Bulk densities of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics as a function of sintering temperatures.

of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics which was caused by the lower sintering temperature of ZnNb_2O_6 ceramic.

3.5 Microwave dielectric properties

Figure 7(a) shows the dielectric constants of the $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics sintered at different temperatures. The changing trend of the dielectric constant of the ceramic along with sintering temperature was same as that of the density: reaching its maximum value at a specific temperature and then decreased. The increase of ZnNb_2O_6 content caused the sharp reduction of the dielectric constant values. When $x < 0.5$, the dielectric constant values declined from 61.89 ($x = 0.1$) to 30.7 ($x = 0.5$). The dielectric constants of the composite can be calculated using the mixture rule [26]:

$$\ln \varepsilon_r = v_1 \ln \varepsilon_{r1} + v_2 \ln \varepsilon_{r2} \quad (2)$$

where ε_r is the dielectric constant of the $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics, v_1 and v_2 are the volume fractions of $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 , respectively; ε_{r1} and ε_{r2} are the dielectric constant of $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 , respectively. The values of the calculated dielectric constant and the measured dielectric constant are depicted in Fig. 7(b). The calculated dielectric constant values were lower than the measured values while the content of ZnNb_2O_6 was less than 50%. For

Fig. 7 (a) Dielectric constants of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics as a function of sintering temperatures, and (b) the change of dielectric constants of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics vs. x .

further increasing ZnNb_2O_6 content, the calculated dielectric constant values were higher than the measured values. Apart from these differences, the calculated dielectric constant and measured dielectric constant showed the similar trend. The main reason of the deviation between the measured values and the theoretical values was that the low content of ingredients were dissolved into the high content phase, and partly formed the solid solution while x was either too small or too large, so the dielectric properties were different from the mixture rule of the composite materials. It mainly depended on the crystal structure of the main phase. According to the Raman result, when $0 < x \leq 0.4$, the main phase was $\text{CoTiNb}_2\text{O}_8$, the ε_r values were skewed to the ε_r value of $\text{CoTiNb}_2\text{O}_8$. For $0.5 \leq x < 1$, the main phase was ZnNb_2O_6 , the ε_r values were biased to the ε_r value of ZnNb_2O_6 .

Figure 8(a) demonstrates $Q \times f$ values of the $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics as functions of x and sintering temperatures. With the increase of x , the variation of $Q \times f$ values of the ceramics along with the sintering temperatures was the same as dielectric constants. This phenomenon was mainly ascribed to the low sintering temperature of ZnNb_2O_6 . Figure 8(b) gives the relationship between the $Q \times f$ values of the composite ceramics and the change of x values. For samples of $x = 0.1$, the $Q \times f$ values were 38,220 GHz which matched the theoretical value quite well. For samples of $0.2 < x < 0.4$, the $Q \times f$ values reduced to lower than 38,220 GHz, which deviated from theoretical value seriously. Upon further increasing ZnNb_2O_6 content, the $Q \times f$ values began to increase again. When it comes to $x = 1$, the $Q \times f$ values reached 96,392 GHz. The $Q \times f$ values of the composite can be calculated using the mixture rule [27]:

$$Q^{-1} = v_1 Q_1^{-1} + v_2 Q_2^{-1} \quad (3)$$

where Q^{-1} is the quality factor of the $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics, v_1 and v_2 are the volume fractions of $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 , respectively; Q_1^{-1} and Q_2^{-1} are the quality factors of $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 , respectively. The results calculated by the formula are shown in Fig. 8(b). It can be seen that the measured $Q \times f$ values for intermediate components were significantly lower than the theoretical values. The dielectric loss of materials at microwave frequencies could be divided into two categories: one is the intrinsic loss, which is mainly controlled by the lattice vibration mode; the other one is the external loss,

Fig. 8 (a) $Q \times f$ values of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics as a function of sintering temperatures, and (b) the variety of $Q \times f$ values of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics with x values.

which is mainly affected by the combined effects of the second phase, the oxygen vacancy, the grain size, and the compactness [28,29]. For the intermediate components of the composite, the grain size was smaller than that of the single phase (Fig. 5) which led to the increase of the grain boundaries and micro porosities, and the decrease of $Q \times f$ values. For the samples of $0.2 < x < 0.4$, the effect of the increasing amounts of grain boundaries caused by the sharp decrease of grain sizes on the $Q \times f$ values could be greater than that of samples with small x values.

The τ_f values of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ composite ceramics as function of x are revealed in Fig. 9. With the increase of x values, the τ_f values reduced from +108.04 to -49.31 ppm/°C. For samples of $x = 0.5$, the τ_f values reached 3.57 ppm/°C. It is obvious that near zero temperature coefficient of resonant frequency can be obtained between $x = 0.5$ and $x = 0.6$. With the increasing x , the reason for the increase of the τ_f value can be attributed to the positive temperature coefficient of resonant frequency of ZnNb_2O_6 ceramics. The temperature coefficient of resonant frequency of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ can

Fig. 9 Temperature coefficients of resonant frequency of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics sintered at the optimum sintering temperature.

be calculated according to the following formula [27, 30]:

$$\tau_f = v_1 \tau_{f1} + v_2 \tau_{f2} \quad (4)$$

where τ_f is the temperature coefficient of the resonant frequency of the $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics, v_1 and v_2 are the volume fractions of $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 , respectively; τ_{f1} and τ_{f2} are the temperature coefficients of the resonant frequency of $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 , respectively. Figure 9 shows the calculated temperature coefficients of the resonant frequency curve. The variation of the temperature coefficients of resonant frequency with the component was different from the expected calculated values. The calculated zero temperature coefficient of the resonant frequency was obtained when x was around 0.725. When x was between 0.2 and 0.8, the measured values were lower than the expected calculated values and the temperature coefficient point of zero resonance frequency when x was around 0.5. This phenomenon may be attributed to the transition of the crystal structure with different x values in composite ceramics. The peak intensities of $\text{CoTiNb}_2\text{O}_8$ and ZnNb_2O_6 in the Raman spectra should be the same because of the same content of the two phases at $x = 0.5$. But as shown in Fig. 4, the peak located at 684 cm^{-1} in the vibrational mode of $\text{CoTiNb}_2\text{O}_8$ has disappeared at $x = 0.5$. The main phase was the columbite phase of ZnNb_2O_6 . It was revealed that the solid solution in the composite ceramic with $x = 0.5$ was mainly ZnNb_2O_6 based solid solution. Because the τ_f values of ZnNb_2O_6 was negative, the measured values were lower than the calculated values, which led to the early appearance of the near zero temperature coefficient of the resonance frequency. This effect and

the increase in the content of ZnNb_2O_6 led to a rapid decrease in the temperature coefficient of the resonance frequency and the near zero temperature coefficient of the resonance frequency was obtained at a smaller x value.

4 Conclusions

Crystal structure and microwave dielectric properties of $(1-x)\text{CoTiNb}_2\text{O}_8-x\text{ZnNb}_2\text{O}_6$ ceramics with controlled temperature coefficient were studied in this work. The influence of the addition of ZnNb_2O_6 on the crystal structure was analyzed in detail using a combination of X-ray diffraction, Raman spectra, and scanning electron microscopy. The system remained rutile phase structure until $x = 0.2$ and the phase transition occurred between $x = 0.3$ and $x = 0.6$. When $x \geq 0.7$, the system maintained the columbite phase structure. The crystal structure had a significant influence on the dielectric properties of ceramics. Near zero temperature coefficient of the resonance frequency was obtained at $x = 0.5$. The good densification of $0.5\text{CoTiNb}_2\text{O}_8-0.5\text{ZnNb}_2\text{O}_6$ ceramics could be achieved at 1175°C for 4 h with ε_r value of 39.2, $Q \times f$ value of 40013 GHz, and τ_f value of $+3.57 \text{ ppm}/^\circ\text{C}$.

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