



## New high- $\epsilon$ and high-Q microwave dielectric ceramics: (1-x)Ca<sub>0.61</sub>Nd<sub>0.26</sub>TiO<sub>3</sub> - xNd(Zn<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub>

Bing-Liang Liang, Xing-Hua Zheng\*, De-Ping Tang

College of Materials Science and Engineering, Fuzhou University, Fuzhou 350108, China

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### ABSTRACT

New high- $\epsilon$  and high-Q microwave dielectric ceramics (1-x)Ca<sub>0.61</sub>Nd<sub>0.26</sub>TiO<sub>3</sub> - xNd(Zn<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> (x=0.00–0.40, referred to as (1-x)CNT - xNNT) were prepared by conventional solid-state preparation route. Single orthorhombic perovskite phase was formed when x was not beyond 0.15. And a secondary phase Zn<sub>2</sub>TiO<sub>4</sub> appeared for x=0.20, while ZnO was the secondary phase for the ceramics with x above 0.20. The dielectric constant and temperature coefficient of resonant frequency decreased steadily with increasing x-value. High Q<sub>f</sub>-value of above 10,000 GHz was achieved as x varied from 0.00 to 0.20. However, Q<sub>f</sub>-value decreased rapidly when x was beyond 0.20. Some (1-x)CNT - xNNT ceramics with high  $\epsilon$  and high Q<sub>f</sub> value were obtained:  $\epsilon$  = 78.8, Q<sub>f</sub> = 19,200 GHz,  $\tau_f$  = +135 ppm/°C for x=0.15;  $\epsilon$  = 71.8, Q<sub>f</sub> = 17,300 GHz,  $\tau_f$  = +94 ppm/°C for x=0.20.

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### 1. Introduction

With the tremendous development of modern communication technology such as mobile communication, satellite broadcasting and ultra-high speed wireless LAN, the demands for microwave dielectric resonators, filters and antennas increase rapidly. As a result, microwave dielectric ceramics, the key materials for manufacturing these components, are investigated widely in recent years. A combination of high dielectric constant ( $\epsilon$ ), low dielectric loss (i.e. high Q<sub>f</sub>-value) and near zero temperature coefficient of resonant frequency ( $\tau_f$ ) in microwave dielectric ceramics is necessary to reduce the size of devices, ensure spectral purity at microwave frequencies and high stability of devices, respectively [1]. Nevertheless, it is difficult to achieve in single compound simultaneously. Therefore, to satisfy the three demands mentioned above, the most convenient and promising method is to form a solid solution or mixed phases through combining two or more compounds with similar crystal structure and different microwave dielectric properties [2–4].

Recently, some complex perovskites such as Ln(B<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> (Ln=La, Sm, Nd, Dy, Y; B=Mg, Zn, Co) [5–8] have been extensively investigated due to their excellent microwave dielectric properties, especially their ultrahigh quality factor. In such complex perovskites, the B-site cations and their order determine the crystal symmetry and subsequently the microwave dielectric properties. For example, Nd(Zn<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> (referred to as NNT) possesses

ultrahigh Q<sub>f</sub>-value (170,000 GHz), moderate  $\epsilon$  (31.6) but relative large negative  $\tau_f$  (-42 ppm/°C) [6]. However, the relative large negative  $\tau_f$  limits the practical applications of these compounds. Therefore, to tune the  $\tau_f$  to zero, some compounds such as CaTiO<sub>3</sub> and SrTiO<sub>3</sub>, with high  $\epsilon$ , high Q<sub>f</sub>-value and large positive  $\tau_f$ , have been introduced to Ln(B<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> [9–12]. These investigations show that moderate  $\epsilon$ , high Q<sub>f</sub>-value and near zero  $\tau_f$  have been obtained in these systems such as Nd(Mg<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub>-CaTiO<sub>3</sub> [9], NNT-SrTiO<sub>3</sub> [10] and NNT-CaTiO<sub>3</sub> [11]. In addition, Ca<sub>0.61</sub>Ln<sub>0.26</sub>TiO<sub>3</sub> (Ln=La, Nd, Sm) [13–14], the product of Ca partially substituted by Ln of CaTiO<sub>3</sub>, displays high  $\epsilon$  (~100), high Q<sub>f</sub>-value (>10,000 GHz) and much lower positive  $\tau_f$  than that of CaTiO<sub>3</sub>. In the previous report [15], Ca<sub>0.6</sub>La<sub>0.8/3</sub>TiO<sub>3</sub> combined with La(Mg<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> possesses the excellent microwave dielectric properties as follows:  $\epsilon$  = 43.6, Q<sub>f</sub> = 48,000 GHz,  $\tau_f$  = 1.2 ppm/°C. Moreover, compared to La(Mg<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub>, the sintering temperatures of NNT has lower sintering temperature around 1300 °C, which is in the same temperature range of Ca<sub>0.61</sub>Nd<sub>0.26</sub>TiO<sub>3</sub> (referred to as CNT).

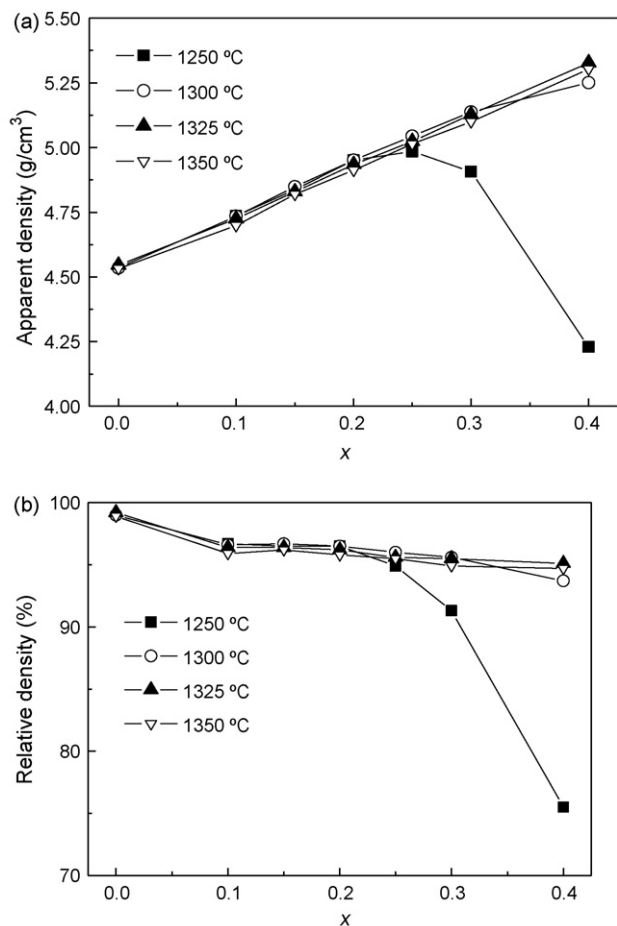
Therefore, it is an interesting issue to investigate the new dielectric system of CNT-NNT. In the present work, (1-x)Ca<sub>0.61</sub>Nd<sub>0.26</sub>TiO<sub>3</sub> - xNd(Zn<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> (hereinafter referred to as (1-x)CNT - xNNT) ceramics were prepared. And microwave dielectric properties were investigated as the functions of composition. The relationships among the microwave dielectric properties and crystal structure, microstructure were also discussed.

### 2. Experimental procedures

The conventional solid-state preparation route was used to synthesize (1-x)CNT - xNNT (x=0.00–0.40) specimens from CaCO<sub>3</sub> (99.8%), Nd<sub>2</sub>O<sub>3</sub> (99.9%), TiO<sub>2</sub> (99.5%) and ZnO (99.99%). According to the composition of (1-x)CNT - xNNT,

\* Corresponding author. Fax: +86 591 22866531.

E-mail address: [brook76@163.com](mailto:brook76@163.com) (X.-H. Zheng).



**Fig. 1.** Apparent density (a) and relative density (b) of the  $(1-x)\text{CNT}-x\text{NNT}$  ceramics as a function of composition.

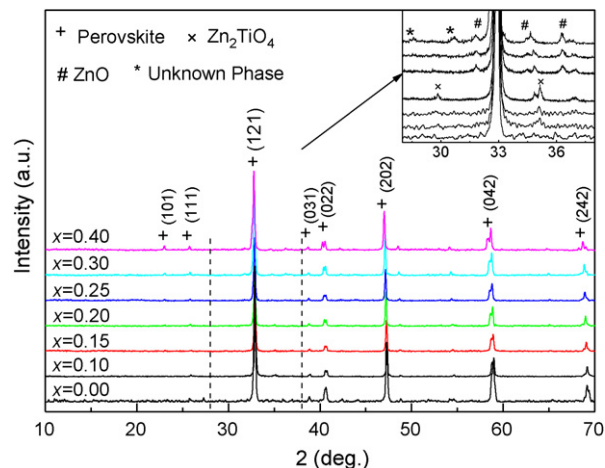
stoichiometric starting powders were ball milled together in polyethylene jar with  $\text{ZrO}_2$  media for 12 h in distilled water. The mixtures were dried and calcined at  $1200^\circ\text{C}$  for 3 h in air. And then the calcined powders were pressed into disks under a pressure of 98 MPa with suitable amount of 5 wt.% solution of polyvinyl alcohol (PVA) as the binder. Then the disks were sintered at  $1250\text{--}1350^\circ\text{C}$  in air for 3 h.

The densities of the sintered pellets were measured with Archimedes method. The phase identification of the present ceramics was carried out by using X-ray diffractometer (XRD, Rigaku D/max Ultima III) with  $\text{Cu-K}\alpha$  radiation. The microstructure observation and elemental analysis were performed on thermal etched specimens through using environmental scanning electron microscope (ESEM, Philips XL30 ESEM-TMP) and energy dispersed spectroscopy (EDS, EDAX New XL30), respectively. The dielectric properties of the specimens at 1 MHz were measured with a precise LCR meter (Agilent 4284A) in the temperature range of  $25\text{--}85^\circ\text{C}$ . The microwave dielectric properties of the specimens were measured with the cavity method [16] in the  $\text{TE}_{018}$  resonant mode by using a network analyzer (Advantest R3767BH).

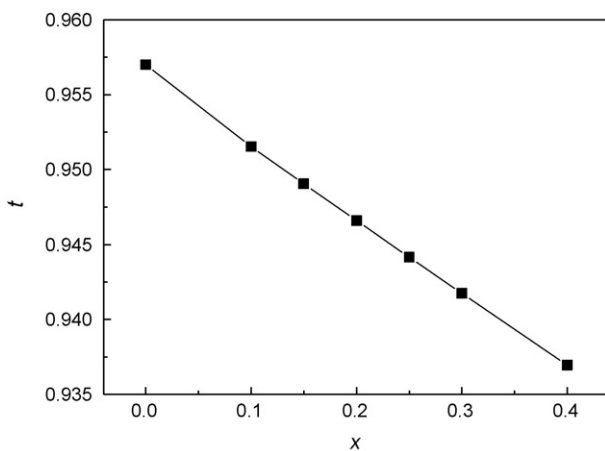
### 3. Results and discussion

Fig. 1 shows the apparent density and relative density of the  $(1-x)\text{CNT}-x\text{NNT}$  ceramics as a function of composition. The dense ceramics, of which the relative densities were all over 94%, were obtained in the sintering temperature range of  $1300\text{--}1350^\circ\text{C}$ . Furthermore, as  $x$  was below 0.30, the high relative density of  $(1-x)\text{CNT}-x\text{NNT}$  ceramics was also obtained at a low sintering temperature of  $1250^\circ\text{C}$ . Moreover, the density of the dense  $(1-x)\text{CNT}-x\text{NNT}$  ceramics increased steadily with  $x$  due to the higher density of NNT than that of CNT [6,14].

X-ray diffraction patterns of the  $(1-x)\text{CNT}-x\text{NNT}$  ceramics are illustrated in Fig. 2. In the whole investigated composition range, orthorhombic perovskite was observed and the correspond-



**Fig. 2.** X-ray diffraction patterns of the  $(1-x)\text{CNT}-x\text{NNT}$  ceramics.



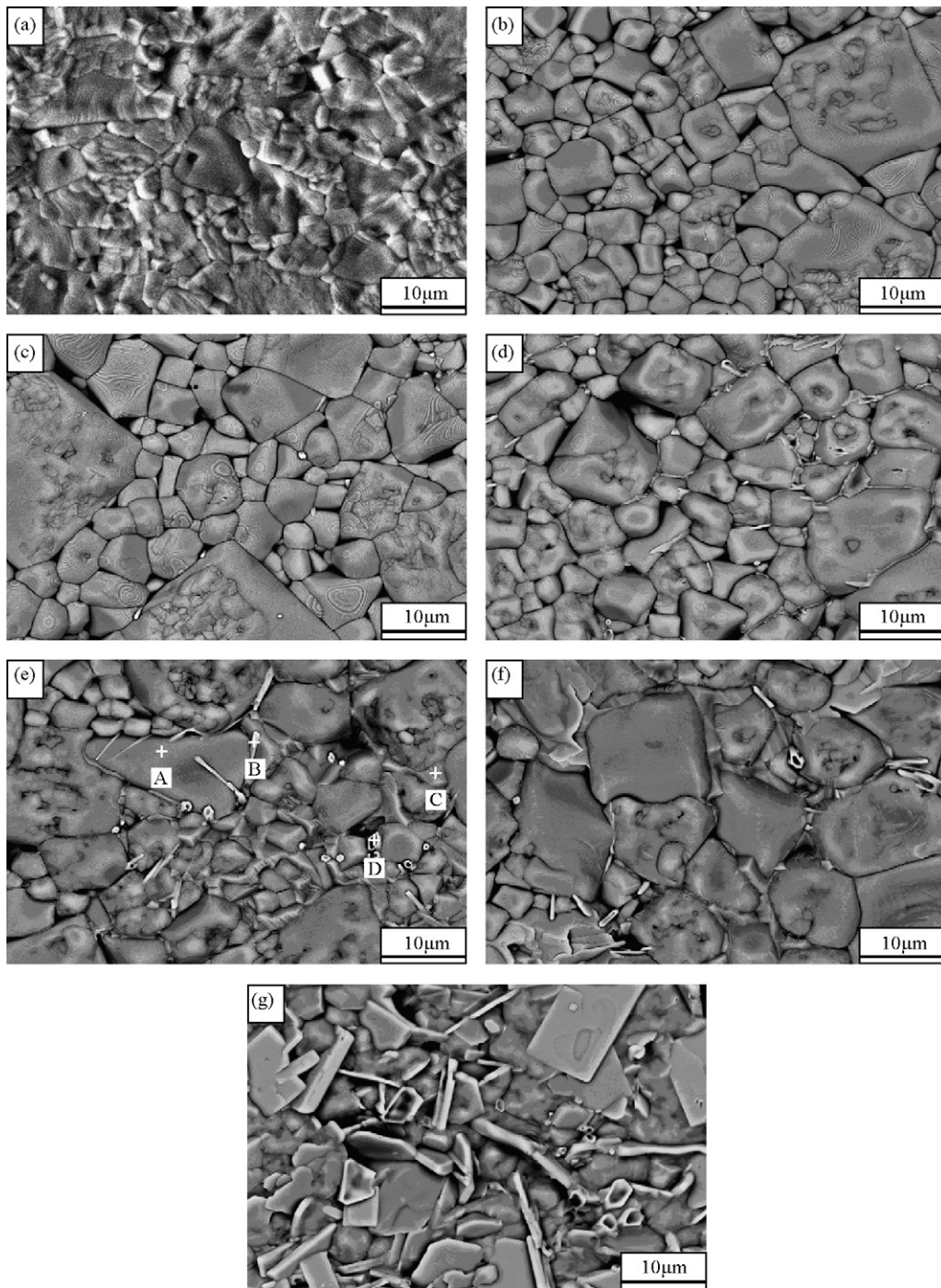
**Fig. 3.** Tolerance factor ( $t$ ) of the perovskite structure in the  $(1-x)\text{CNT}-x\text{NNT}$  ceramics.

ing diffraction peaks shifted to low angle. This implied that the unit cell volume of perovskite phase was enlarged with the increasing NNT content. Only orthorhombic perovskite phase was detected for the  $(1-x)\text{CNT}-x\text{NNT}$  ceramics when  $x$  was not beyond 0.15. A secondary phase  $\text{Zn}_2\text{TiO}_4$  was formed for  $x=0.20$ . As  $x$  exceeded 0.20, however,  $\text{Zn}_2\text{TiO}_4$  phase disappeared and ZnO phase was detected. And the amount of ZnO phase increased with increasing  $x$ . Two extra peaks were present in the specimen of  $x=0.40$ , which were difficult to be identified.

Table 1 shows the crystal constants of orthorhombic perovskite phase in the  $(1-x)\text{CNT}-x\text{NNT}$  ceramics. With  $x$  increasing, unit cell volume increased almost linearly though lattice constants  $a$ ,  $b$  and  $c$  varied in different ways. As for perovskite structure  $\text{ABO}_3$ , CNT and NNT could be represented as  $\text{A}_{0.87}\text{BO}_3$  and  $\text{ABO}_3$ , respectively. Subsequently,  $(1-x)\text{CNT}-x\text{NNT}$  could be represented as

**Table 1**  
Lattice parameters and volume of unit cell ( $V_u$ ) of orthorhombic perovskite phase in  $(1-x)\text{CNT}-x\text{NNT}$  ceramics.

$x$	$a$ ( $\times 10^{10}/\text{m}$ )	$b$ ( $\times 10^{10}/\text{m}$ )	$c$ ( $\times 10^{10}/\text{m}$ )	$V_u$ ( $\times 10^{30}/\text{m}^3$ )
0.10	5.4402	7.6769	5.4195	226.3393
0.15	5.4501	7.6860	5.4256	227.2755
0.20	5.4602	7.6953	5.4246	227.9302
0.25	5.4586	7.7028	5.4312	228.3630
0.30	5.4745	7.7053	5.4271	228.9295
0.40	5.4861	7.7166	5.4404	230.3141



**Fig. 4.** Backscattered electron images of the  $(1-x)\text{CNT}-x\text{NZT}$  ceramics sintered at  $1350^\circ\text{C}$ : (a)  $x=0.00$ , SEM micrographs; (b)  $x=0.10$ ; (c)  $x=0.15$ ; (d)  $x=0.20$ ; (e)  $x=0.25$ ; (f)  $x=0.30$ ; (g)  $x=0.40$ .

$\text{A}_{0.87+0.13x}\text{BO}_3$ . Apparently, with the increasing content of NZT, more ions of  $\text{Ca}^{2+}$  and  $\text{Nd}^{3+}$  occupied the A-sites, which resulted in the reduction of the A-site vacancies. Meanwhile, the average ionic radii in B-sites also increased since  $\text{Zn}^{2+}$  ion was larger than  $\text{Ti}^{4+}$  ion [17]. As a result, unit cell volume increased with the increasing content of NZT.

In general, the tolerance factor ( $t$ ) is used to evaluate the stability of some crystal structures such as perovskite and tungsten bronze [18,19]. The tolerance factor of perovskite solid solution in  $(1-x)\text{CNT}-x\text{NZT}$  ceramics can be calculated from the equation reported previously [19]. As shown in Fig. 3, the tolerance factor

decreased with increasing  $x$ -value in the present ceramics. Therefore, the perovskite structure became unstable and the secondary phase of  $\text{Zn}_2\text{TiO}_4$  and  $\text{ZnO}$  were formed for the ceramics when  $x$  was beyond 0.20.

SEM images of the  $(1-x)\text{CNT}-x\text{NZT}$  ceramics are shown in Fig. 4. Little amount of pore was observed in these specimens. When  $x$  was below 0.20, granular grains with some abnormal grain growth could be observed in  $(1-x)\text{CNT}-x\text{NZT}$  ceramics and no significant change occurred. The EDS results indicated that the granular grain (spot A) had near nominal cation ion ratios (seen in Table 2). It was consistent with XRD analysis. However, a small amount of

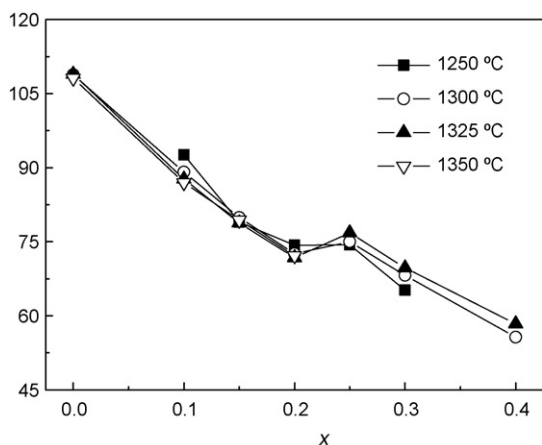


Fig. 5. Dielectric constant of the  $(1-x)\text{CNT}-x\text{NZT}$  ceramics sintered at different temperatures.

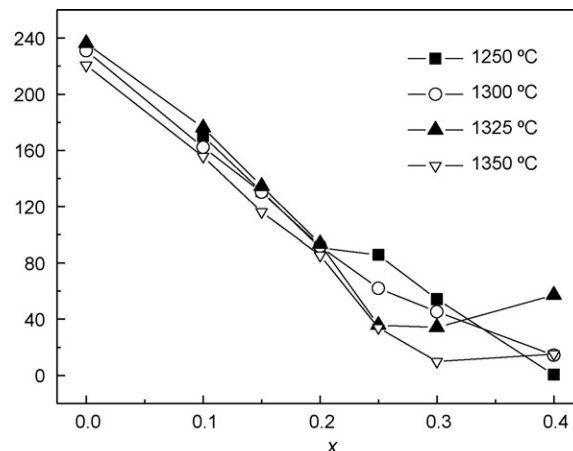


Fig. 7. Temperature coefficient of resonator frequency of the  $(1-x)\text{CNT}-x\text{NZT}$  ceramics sintered at different temperatures.

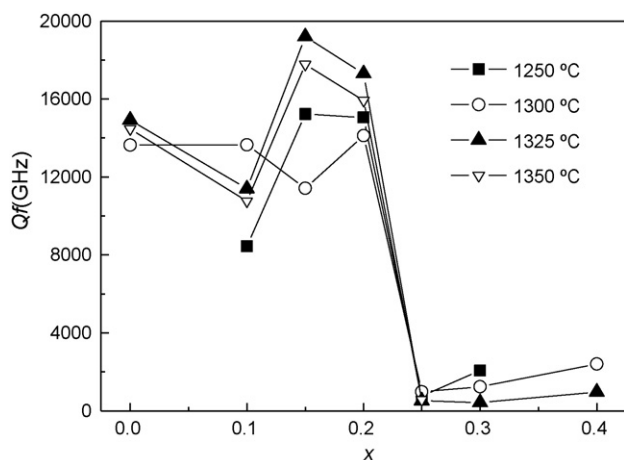


Fig. 6. Qf value of the  $(1-x)\text{CNT}-x\text{NZT}$  ceramics sintered at different temperatures.

white-stick-like grains and grain boundary phase were present in the ceramics with higher  $x$  value. The grain boundary phase (spot C) was rich in Zn and poor in Ca/Nd for  $x=0.25$ . Since the size was too small, in consideration of the measurement error, the grain boundary phase could be identified as  $\text{Zn}_2\text{TiO}_4$ , combining with XRD analysis. With the increasing content of NZT, the grain boundary phase possessed richer Zn, corresponding to the secondary phase ZnO. Meanwhile, some plate-like grains appeared for  $x=0.30$  and were more remarkable for  $x=0.40$ .

Figs. 5–7 show the dielectric constant, Qf-value and the temperature coefficient of resonator frequency of the  $(1-x)\text{CNT}-x\text{NZT}$  ceramics sintered at different temperature, respectively. Qf value and  $\varepsilon$  were measured in the frequency range of 2.9–4.1 GHz and  $\tau_f$  was calculated from temperature coefficient of dielectric constant

( $\tau_\varepsilon$ ) according to the following equations [20]:

$$\tau_f = -\frac{\tau_\varepsilon}{2} - \alpha \quad (1)$$

$$\tau_\varepsilon = \frac{\varepsilon_{85} - \varepsilon_{25}}{60\varepsilon_{25}} \quad (2)$$

where  $\alpha$  is the coefficient of linear expansion and approximately equals to 6–10 ppm/°C for ceramic materials [21];  $\varepsilon_{85}$  and  $\varepsilon_{25}$  are the dielectric constants of 85 °C and 25 °C measured at 1 MHz, respectively.

As the  $x$ -value increased from 0.00 to 0.40,  $\varepsilon$  almost linearly dropped from near 110 to about 56. Dielectric constant increased slightly for  $x=0.25$  due to the appearance of ZnO. This variation trend of  $\varepsilon$  with composition mainly resulted from the increase of NZT with lower dielectric constant ( $\varepsilon=31.6$ ) and the existence of secondary phases. According to the Clausius–Mossotti equation, dielectric constant varied with the total molecular dielectric polarizability and molar volume. The expansion of the unit cell volume also led to the decline of dielectric polarizability in the unit volume, which also resulted in the reduction of the dielectric constant [22]. As shown in Fig. 7,  $\tau_f$  shifted to zero with the increasing NZT content. And the variation of  $\tau_f$  with  $x$ -value was similar to that of  $\varepsilon$ , which can be attributed mainly to the dilution of dielectric constant.

In summary, the microwave dielectric properties of  $(1-x)\text{CNT}-x\text{NZT}$  ceramics sintered at 1325–1350 °C exhibited high dielectric constant (72–80), high Qf value (>15,000 GHz) and relatively low temperature coefficient ( $\tau_f \sim 100$  ppm/°C) for  $x=0.15$  and 0.20.

But the Qf-value was over 10,000 GHz within the composition range from 0.00 to 0.20. Especially for  $x=0.15$  or 0.20, the Qf-value was near 20,000 GHz. However, the Qf-value decreased rapidly when  $x$  was above 0.20. The loss of dielectric at microwave frequency includes intrinsic loss and extrinsic loss [23]. The former mainly results from the attenuation of anharmonic phonon in the crystal lattice. The latter is related to such factors as crystal defects, secondary phases, grain boundaries and pores. In this work, the amount of A-site vacancies decreased with the introduction of NZT, which could abate the crystal distortion [24]. And the  $(1-x)\text{CNT}-x\text{NZT}$  ceramics with small  $x$ -value exhibited the homogeneous grains. In addition, the small amount of secondary phase  $\text{Zn}_2\text{TiO}_4$  exhibited high Qf-value of 19,000 GHz [25]. Therefore, the high Qf value was achieved when  $x$  was not above 0.20. Nevertheless, the mixed phases and inhomogeneous grains were observed for the ceramics with  $x$  above 0.20. On the

Table 2  
EDS results of the  $(1-x)\text{CNT}-x\text{NZT}$  specimens sintered at 1350 °C.

x	Spots	Atom(%)			
		Ca	Nd	Zn	Ti
0.25	A	24.47	21.89	5.68	47.96
	B	26.12	28.86	5.75	39.27
	C	14.08	14.11	40.56	31.26
	D	24.46	25.17	6.61	43.76

other hand, the appearance of ZnO should lead to the tremendous increment of dielectric loss [8]. Subsequently, Qf-value degraded significantly.

#### 4. Conclusions

Only orthorhombic perovskite solid solution was formed in the  $(1-x)\text{CNT} - x\text{NZT}$  ceramics when  $x$  was below 0.20. A small amount of  $\text{Zn}_2\text{TiO}_4$  and ZnO appeared in the  $(1-x)\text{CNT} - x\text{NZT}$  ceramics for  $x=0.20$  and  $x>0.20$ , respectively. High  $\varepsilon$  ( $>70$ ) and Qf-value ( $>10,000\text{GHz}$ ) were observed for the ceramics when  $x \leq 0.20$ . The  $(1-x)\text{CNT} - x\text{NZT}$  ceramics sintered at  $1325^\circ\text{C}$  possessed excellent microwave dielectric properties as follows:  $\varepsilon = 78.8$ ,  $\text{Qf} = 19,200\text{GHz}$ ,  $\tau_f = +135\text{ppm}/^\circ\text{C}$  and  $\varepsilon = 71.8$ ,  $\text{Qf} = 17,300\text{GHz}$ ,  $\tau_f = +94\text{ppm}/^\circ\text{C}$  for  $x=0.15$  and  $x=0.20$ , respectively. The relationships between the crystal structure, tolerance factor and microwave dielectric properties were also discussed.

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