Effect of SnO₂ substitution on microwave dielectric characteristics of Zn₀.₁₅Nb₀.₃Ti₀.₅₅O₂ ceramics

H C Yang¹,², S R Zhang¹,²,４, Y W Chen¹,², H Y Yang¹,², Y Yuan¹,²,３ and E Z Li¹,²

¹ National Engineering Research Center of Electromagnetic Radiation Control Materials, University of Electronic Science and Technology of China, Chengdu, 610054;
² Key Laboratory of Multi-Spectral Absorbing Materials and Structures of Ministry of Education, University of Electronic Science and Technology of China, Chengdu, 610054;
³ Institute of Electronic and Information Engineering of UESTC in Guangdong Dongguan 523808, People's Republic of China

Abstract. The relevance of Sn⁴⁺ substituted for Ti⁴⁺ of Zn₀.₁₅Nb₀.₃Ti₀.₅₅O₂ ceramics is investigated. X-ray diffraction patterns indicate that the major phase can be matched with Zn₀.₁₅Nb₀.₃Ti₀.₅₅O₂ and a second phase ZnTiNb₂O₈ appears in different composition. The content of ZnTiNb₂O₈ phase gradually increases along with more substitution, which is contributed to the decline of εᵣ. The decrease of grain size and the observed pores have negative influence on Q×f values. And the τᵣ values move towards a lower value, corresponding to the variation of εᵣ. An optimal combination of microwave dielectric properties is: εᵣ=83.2, Q×f=15456 GHz, τᵣ=301.5 ppm/℃ with x=0.03, sintered at 1050 °C.

1. Introduction
Microwave dielectric ceramic is core component of microwave devices in wireless communication area over decades. After the initial report about dielectric properties of BaO-TiO₂ binary system by H. M. O'Bryan in 1974 [1], researchers continuously explore new ceramics with different permittivity and satisfied quality factor.

Compared with the typical high dielectric constant perovskites (ABO₃) ceramics, ZnO-Nb₂O₅-TiO₂ system is a new family with adjustable permittivity and lower sintering temperature [2, 3]. For Zn₁Nb₂O₆ phase with an order super-structure of α-PbO₂, it was demonstrated to be promising materials with excellent properties: εᵣ=21.2, Q×f=79200 GHz, τᵣ=73ppm/℃ [4]. And the columbite ZnNb₂O₆ has been concentrated investigated due to its high Q×f value approach to 83700 GHz [5]. Besides, the temperature coefficient of both Zn₁Nb₂O₆ and ZnNb₂O₆ can be tunable to near zero by adding TiO₂ [6,7]. More recently, the investigations about the structure-properties relationship of ZnTiNb₂O₈ ceramics are reports systematically [8], i.e. ZnTi(Nb₁₋ₓTaₓ)₂O₈ [9], MgₓZn₉₋ₓTiNb₂O₈ [10], (Zn₁₋ₓCoₓ)TiNb²O₈ [11], Zn(Ti₁₋ₓSnₓ)NbO₆ [12] and so on. Furthermore, Zn₁₀.₁₅Nb₅.₀₅Ti₀.₅₅O₂ in rutile structure was reported in (Zn₁₋ₓB₂₋ₓ)₃Ti₁₋ₓO₂ (B²⁺=Nb, Ta) ceramics when x=0.45 [13]. And then, it is a second phase when Ca²⁺ and Sn⁴⁺ co-substituted in ZnTiNb₂O₁₀ [14]. Zn₁₀.₁₅Nb₅.₀₅Ti₀.₅₅O₂ also appeared when Co²⁺ occupied in Zn-site [11], Sb⁵⁺ substituted for Nb-site [15] and Co together with Ta co-doped in Zn₀.₅Ti₀.₅NbO₄ [16], in which favourable effect on the microwave dielectric properties...
was verified: $\varepsilon_\infty=35.93$, $Q\times f=23515$ GHz; $\varepsilon_r=0$, $Q\times f=31000$ GHz, $\varepsilon_r=-67.91$ ppm/°C and $\varepsilon_r=38.02$. $Q\times f=23550$ GHz, $\varepsilon_r=4.62$ ppm/°C, respectively. Meanwhile, Li et al demonstrated that Li$_2$O-B$_2$O$_3$-SiO$_2$ glass can enhance the sintering process of Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ [17] and ZnO-B$_2$O$_3$-SiO$_2$ glass was a satisfied sintering aid for Zn$_{0.3}$Mg$_{0.7}$TiO$_3$-Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ ceramics [18]. Besides, $x$ Zn$_{0.3}$Ti$_{0.5}$Nb$_{0.2}$O$_{2+x}(1-x)$ Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ ceramics possessed a near zero temperature coefficient when $x=0.516$ [19]. However, the research about structure modification for Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ ceramics by ions substitution and the dependence of phase composition upon microwave dielectric properties has been hardly reported.

Indeed, it is verified that the replacement of Sn for Ti could optimize the microwave dielectric properties of Sr$_3$TiO$_4$ [20], and it crystallized in a structure of tetragonal phase (I4/mmm) firstly and then transform into orthorhombic type (Pccn). Adding SnO$_2$ into initial composition of BaTi$_6$O$_9$ [21], the dielectric constant linearly decreased from 38.9 to 37.5, $Q\times f$ values distinctly changed from 45600 to 33100 GHz, and $\tau_f$ values shifted in a narrow region. Specially, Sn$^{4+}$ has a limited solubility around $x=0.15$ in Zn(Ti$_{1-x}$Sn)$_2$O$_{2+x}$ [12]. Although secondary phase of BaSm$_2$O$_5$ and Sn$_4$(Sn,Ti)$_2$O$_7$ were observed in the co-substituted Ba$_{8.38}$(Sm$_{1.9}$Nd$_{0.02}$)$_3$(Ti$_{1-x}$Sn)$_{18}$O$_{54}$ ceramics, excellent microwave dielectric characteristics were achieved with $\tau_\infty=0.8$ and $\tau_f=0.05$ [22]. Specially, Sn$^{4+}$ has been applied to ZnO-Nb$_2$O$_5$-TiO$_2$ system by Li et al [23] and Wang et al [24] to modify the microwave dielectric properties.

Hence, referring to the rare reports of Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$-based ceramics, the approximate radii of Sn$^{4+}$ and Ti$^{4+}$ as well as the positive impact of substitution Sn for Ti on microwave dielectric properties in parallel investigations, the introduction of SnO$_2$ into Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ may generate improvement of dielectric characteristics integrally. In this work, the effect of phase composition on the evolution of microstructure, density and microwave dielectric properties was investigated in detail after doping SnO$_2$ in Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ ceramics.

2. Experimental methods

ZnO, Nb$_2$O$_5$, TiO$_2$ and SnO$_2$ powders with a reagent-grade were used to prepare Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$-$x$SnO$_2$ ($x=0$–0.05) ceramics via solid state method. All the oxide powders were weighed and then mixed for 6 h, where zirconia balls and deionized water were medium. After putting into the drying oven, the powders were calcined at 950 °C for 4 h. Subsequently, the calcined compositions were milled again to obtain more uniform powder. Adding 3 wt. % PVA into the dried powders, the mixture was pressed into disks (Φ15mmx7mm). The formed cylindrical samples were sintered in the temperature range of 1025 °C–1075 °C for 4 h to measure relevant properties.

The X-ray diffraction patterns (Philips X’Pert ProMPD, Amsterdam, The Netherlands) were obtained in the region of 10° ~ 120° with a minimal step of 0.013° using Cu Kα radiation. The micrographic images of the ceramics with highest density were recorded through scanning electron microscopy (SEM, FEI Inspect F, the United Kingdom). Hakki-Coleman dielectric resonator method was a widespread tool to collect the microwave dielectric properties equipped with a network analyzer (HP83752A, the United States) in TE011 mode. The $\tau_f$ values was calculated according to the measured resonant frequency at 25 °C and 85 °C as follow:

$$
\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)}
$$

Where $f_{85}$ and $f_{25}$ represent the resonant frequencies at temperature 85 °C and 25 °C in the TE01δ mode, respectively.

3. Results and discussion

3.1. Crystal structure analysis

The stacked XRD patterns of Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$-based well sintered ceramics are displayed in Figure 1 (a), and the enlarged patterns with 2θ ranging from 25°–32° are presented in Figure 1 (b). The
reflection peaks of different composition can be allocated to Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ (JCPDS #79-1186) and ZnTiNb$_2$O$_8$ (JCPDS #88-1973), corresponding to a space group P42/mnm (136) and Pbcn (60), respectively. As shown, along with the increasing addition of SnO$_2$, the strongest peak of ZnTiNb$_2$O$_8$ which is indexed as the crystallographic plane (111) become more and more apparent. It is indicating that the content of orthorhombic ZnTiNb$_2$O$_8$ phase continuously goes up.

![Figure 1](image1.png)

**Figure 1.** (a) The XRD patterns of different Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$-based ceramics; (b) The enlarged XRD patterns of 2θ=25~32°.

The crystal structure of the Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ and ZnTiNb$_2$O$_8$ phase are plotted in Figure 2 (a) and (b). Since Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ and TiO$_2$ both crystalized in a rutile type, Zn$^{2+}$, Ti$^{4+}$ couple with Nb$^{5+}$ occupy the center of octahedron, named a Wyckoff position of 2a, while all the oxygen atoms distribute in 4f Wyckoff position. For ZnTiNb$_2$O$_8$ phase, three kinds of cations stay the same 4c Wyckoff position, and O scatters in the 8d Wyckoff position. The polyhedron connects with each other through the sharing-edge and the apical oxygen in the two phases.

![Figure 2](image2.png)

**Figure 2.** The structure of Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$ (a) and ZnTiNb$_2$O$_8$ (b).

3.2. *Surface microstructure and density analysis*

The surface micrographs of doped Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$-based ceramics sintered at 1050°C are given in Figure 3 (a: x=0; b: x=0.03; c: x=0.04). The whole images exhibit obvious grain boundary and compact microstructure except x=0.04 with some pores. Due to the small amount of the ZnTiNb$_2$O$_8$ phase, the shape of the grains nearly maintains the same in the observed area. It is clear that the grain size goes through a distinct variation. According to Q. J. Mei et al, the grain is extremely small of ZnTiNb$_2$O$_8$ ceramics [25]. Therefore, with more content of the second phase, the grain size inevitably declines. Subsequently, the small grain will lead to more grain boundary and more pores as we can detect in the photos, which would have a negative influence on the microwave dielectric properties.
3.3. Microwave dielectric properties:

A persistent decline of dielectric constant is plotted in Figure 4 (a), and the values of different sintering temperature are displayed in different color. As shown, dielectric constant values sintered at 1050°C are integrally higher than the corresponding values of other temperature, indicating that the ceramics are more compact sintered at 1050°C. Meanwhile, the decrement of the permittivity ranging from 92.03 to 72.72 is ascribed to the appearance of ZnTiNb$_2$O$_8$ phase. Generally, the dielectric constant of composite ceramics can be predicted by Logarithmic mixing rule:

$$\ln \varepsilon_r = V_1 \ln \varepsilon_1 + V_2 \ln \varepsilon_2$$  \hspace{1cm} (2)

Where the relevant values are selected from the peer’s work, for Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$, the $\varepsilon_1$=93.58, for ZnTiNb$_2$O$_8$, the $\varepsilon_2$=34.3, and $V_i$ means the volume fraction of each phase. According to the formula, the $\varepsilon_r$ of the multiphase ceramics should be linearly dropped with the increasing content of low permittivity phase. Therefore, the variation of the measured values is reasonable. On the other hand, permittivity is closely related to relative density of the ceramics. Figure 4 (b) shows the relative densities of the samples sintered in different conditions. For different composition, the ceramics sintered at 1050°C all reach to the highest density, corresponding to the relatively larger $\varepsilon_r$. And the change tendency of the relative density is similar to the variation of $\varepsilon_r$.

Figure 4. Variation of permittivity (a) and relative density (b) of Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$-based ceramics sintered at different temperature.

Figure 5 presents the fluctuation of the experimental $Q\times f$ values. The values of samples with the highest density increase to 15456 GHz at $x = 0.03$ following a slowly decline to 12791 GHz. As known, the factors that affect the dielectric loss are usually concluded to intrinsic and extrinsic parts. Combining with the analysis above, a second phase is confirmed by XRD and the obvious change of grain size is observed via SEM. The augment of the $Q\times f$ values stems from the growth of grains and a more uniform microstructure. Besides, the composition of ceramic will affect the $Q\times f$ values chiefly.
The lower dielectric loss of ZnTiNb$_2$O$_8$ leads to a more excellent $Q\times f$ values. Nevertheless, the effect of grain boundary is more apparent than the influence of phase content of ZnTiNb$_2$O$_8$ because a lot of small grains appear when $x \geq 0.04$. Up to our knowledge, more grain boundary generated more dielectric loss, and the clear pores with $x=0.04$ both have negative impact on $Q\times f$ values.

![Figure 5](image)

**Figure 5.** Variation of $Q\times f$ values of Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$-based ceramics sintered at different temperature.

Temperature coefficient of resonant frequency $\tau_f$ reflects the stability of crystal structure. An approximate zero $\tau_f$ value corresponds to a more stable system. In our work, the $\tau_f$ values vary in an extensive region, decreasing from 346.00 to 257.67 ppm/℃. The prior reports illustrate that the variation of $\tau_f$ values is associated with $\tau_\varepsilon$:

$$\tau_f = -(\tau_\varepsilon + \frac{\alpha_f}{2})$$  \hspace{1cm} (3)

Where the $\tau_\varepsilon$ is reckon as a parameter determined by polarizability and it would go up as the drop of $\varepsilon_r$ values. As for $\alpha_f$, it is a stable values changing in a narrow range in microwave dielectric ceramics. According to the results in Figure 6, the $\tau_f$ values and $\varepsilon_r$ values of the ceramics sintered at 1050 ℃ both linearly declined, suggesting a more stable materials are obtained with increasing $x$ value.

![Figure 6](image)

**Figure 6.** Variation of $\tau_f$ and $\varepsilon_r$ values of Zn$_{0.15}$Nb$_{0.3}$Ti$_{0.55}$O$_2$-based ceramics sintered at 1050 ℃.
4. Conclusions
Multiphase compact \( \text{Zn}_{0.15}\text{Nb}_{0.3}\text{Ti}_{0.55}\text{O}_{2} \)-based ceramics have been prepared in this investigation. The most satisfied microwave dielectric property is described as: \( \varepsilon_r=83.2, \quad Q\times f=15456 \text{ GHz}, \quad \tau_f=301.5 \text{ppm/}^\circ\text{C} \) with \( x=0.03 \) sintered at 1050\(^\circ\text{C} \). The variation of the permittivity is mainly determined by the volume fraction of the second phase and the relative density, while grain size and the phase composition are closely responsible for the change of \( Q\times f \) values. Temperature coefficient move towards to a lower value, corresponding to the decline of \( \varepsilon_r \).

Acknowledgements
This work is partly supported by the Science and Technology Planning Project of Guangdong Province, China (No.2017A010103001) and National Natural Science Foundation of China 51872037.

References
[1] O'Bryan H M, Thomson J 2010 *J Am Ceram Soc* **57** 522
[2] Dell'agli G, Spiridigliozzi L, Marocco A, Accardo G, Frattini D, Kwon Y, Yoon S P 2017 *Ceram Int* **43** 12799
[3] Accardo G, Frattini D, Ham H C, Han J H, Yoon S P 2018 *Ceram Int* **44** 3800
[4] Huang C L, Yang W R, Yu P C 2014 *J Eur Ceram Soc* **34** 277
[5] Baumgarte A, Blachnik R 1992 *Mater Res Bull* **27** 1287
[6] Kim D, Kim D, Hong K S 2000 *J Mater Res* **15** 1331
[7] Park H S, Yoon K H, Kim E S 2010 *J Am Ceram Soc* **84** 99
[8] Liao Q, Li L 2012 *Dalton Trans* **41** 6963
[9] Liao Q, Li L, Zhang P, Cao L, Han Y 2011 *Solid State Sci* **13** 1201
[10] Liao Q, Li L, Ding X, Ren X, Kabos P 2012 *J Am Ceram Soc* **95** 1501
[11] Huan Z, Sun Q, Ma W, Wang L, Xiao F, Chen T 2013 *J Alloys Compd* **551** 630
[12] Liao Q, Li L, Zhang P, Cao L, Han Y 2011 *Mater Sci Eng, B* **176** 41
[13] Kim E S, Kang D H 2008 *Ceram Int* **34** 883
[14] Li L, Cai H, Yu X, Liao Q, Gao Z 2014 *J Alloys Compd* **584** 315
[15] Li L, Cai H, Ren Q, Sun H, Gao Z 2014 *Ceram Int* **40** 12213
[16] Yang H, Li E, Duan S, He H, Zhang S 2017 *Mater Chem Phys* **199** 43
[17] Li E, Yang H, Yang H, Zhang S 2018 *Ceram Int* **44** 8072
[18] Li E, Yang Y, Yang H, Yuan Y, Zhang S 2018 *J Mater Sci: Mater Electron* **29** 11901
[19] Yang H, Zhang S, Yang H, Zhang X, Li E 2018 *Inorganic chemistry* **57** 8264
[20] Liu B, Huang Y H, Song K X, Li L, Chen X M 2018 *J Eur Ceram Soc* **38** 3833
[21] Yang C F, Tzou W C, Chung H H, Diao C C, Huang C J 2009 *J Alloys Compd* **477** 673
[22] Xiang M C, Yi L 2010 *J Am Ceram Soc* **85** 579
[23] Li L, Liao Q, Zhang P 2009 *Ferroelectr* **388** 54
[24] Huanping W, Qilong Z, Hui Y, Jiali Z 2004 *Electronic Components Materials* **23** 4
[25] Mei Q J, Li C Y, Guo J D, Wu H T 2015 *J Alloys Compd* **626** 217