TiO_2-(Zn_{1/3}Nb_{2/3})O_2-ZrO_2 microwave dielectric ceramics with near-zero temperature coefficient of resonant frequency

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Abstract. (56.33-x)TiO_2-x(Zn_{1/3}Nb_{2/3})O_2-43.67ZrO_2 (x = 2.60-37.66) ceramics with 0.5%wt CuO addition were prepared by the mixed metal oxide route. Effects of sintering temperature were investigated on the sintering behavior and microwave dielectric properties of ceramics. For all ceramics with x = 2.60-37.66, the optimal sintering temperature range was determined to be around 1280 °C. XRD analysis showed that the main crystal line phase of ceramics sintered at 1280 °C changed from ZrTiO_4 type at x = 2.60-30.20 to ZrTi_2O_6 type at x = 30.20-37.66. In addition to the main crystalline phase, trace amounts of secondary phases ZrO_2 and ZnCuTiO_4 were also observed from SEM and EDS analysis for all ceramics. The permittivity decreased with the increasing x in the range of x = 2.60-30.20 and then remained stable at x = 30.20-37.66, corresponding to the density and covalency bond due to the substitution of (Zn_{1/3}Nb_{2/3})^{4+} for Ti^{4+} and phase transition at x = 30.20. Furthermore, it was surprisingly found that the temperature coefficient of resonant frequency was near-zero (τ_f = -9.2 to +9.9 ppm/°C) in a very wide range of x = 10.80-30.20.

1. Introduction

With rapid development of modern wireless communication, microwave components including microwave resonators, filters, substrates, and antenna have been drew a higher demand for the microwave dielectric materials they used. Microwave dielectric ceramics applied for dielectric resonator must satisfy the following three properties: (1) high relative permittivity (ε_r) to minify the size of resonator (D ≈ ε_r^{-1/2}, D is the diameter of resonator). (2) high quality factor (Q or Q×f) value to reduce the dielectric loss (tanδ). (3) near-zero temperature coefficient of resonant frequency (τ_f) to maintain the resonant frequency with the temperature drift. The value of ε_r and Q always shows an opposite tendency. However, the value of τ_f is always preferred to be near zero. There are two ways to adjust τ_f to 0. One way is to add a compound with an opposite τ_f to compensate excessive τ_f, the other way is to drop other elements to form solid solution [1-4].

Zirconium titanate-based ceramics have drawn extensive attention due to its excellent microwave dielectric properties: moderate dielectric constant, high Q×f, and the τ_f can be adjusted to zero by dropping different elements. There are two forms for Zirconium titanate, one is the so-called high temperature phase with α-PbO_2 structure, and the other is the low temperature phase, with that the unit cell have a slight difference in c-axis [5]. The τ_f of pure ZrTiO_4 is +56 ppm/°C, which is too high for
practical application [6]. A lot of study have been done on adding (Zn1/3Nb2/3)O2 into ZrTiO4 in order to get τf near zero ceramics [7,8]. Kim et al. have done research on Zr1−x(Zn1/3Nb2/3)xTiO4 ceramics, they get good microwave dielectric properties when x=0.35: εr = 44, Q×f = 41000 GHz, and τf = -3 ppm /°C [9]. RiaziKhoei et al. have discussed the influence of (Zn1/3Nb2/3)O2 on the microwave dielectric properties of ZrTi2O6 ceramics. By dropping different amount of (Zn1/3Nb2/3)O2, they find that the composition 0.76ZrTi2O6-0.24(Zn1/3Nb2/3)O2 can obtain good microwave dielectric properties: εr = 47, Q×f = 34000 GHz, and τf = 0 ppm /°C [10]. But above all the reports, each scientist could only find a specific composition which can meet the near zero τf [11].

In this work, (56.33-x)TiO2-x(Zn1/3Nb2/3)O2-43.67ZrO2 (x=2.6, 6.7, 10.8, 14.9, 19, 22.7, 26.5, 30.2, 37.7) were prepared by standard solid phase method. In a wide range of the composition, ZrTiO4 or ZrTi2O6 single phase was formed and the ceramics presented near-zero τf, and other microwave dielectric properties were good as well.

2. Experimental methods
TiO2-(Zn1/3Nb2/3)O2-ZrO2 was prepared by conventional solid-state method. The raw material was all reagent-grade rutileTiO2, ZnO, Nb2O5 (>99.99%, Guo-Yao Co., Ltd., Shanghai, China) and ZrO2. After weighing according to the stoichiometry (56.33-x)TiO2-x(Zn1/3Nb2/3)O2-43.67ZrO2, the material was mixed and milled in nylon jar with zirconium ball as a milling medium for 2 hours. The mixture was then dried in the oven at 110°C for 24 hours and presintering at 950°C for 4 hours. After milling and dried the products above again, 8%wt Polyvinyl Alcohol was added to the obtained powder and then pressed into the mould with 15mm in diameter and 7.5mm in height. At last the green pellet was dwel led at 550°C for 0.5 hour and then sintering in the muffle furnace at 1220°C, 1260°C, 1280°C, 1300°C and 1340°C for 4 hours.

The phase structure of the ceramics was investigated by X-ray diffraction using Cu Kα1 radiation (40.0KV, 30mA, XRD-7000S/L, SHIMADZU, Tokyo, Japan). The morphology of grain surface was analyzed by scanning electron microscope (SEM, VEGA3, TESCAN, Czekh) and energy-dispersive spectrometry (EDS, X-MAX, Oxford) was carried out at the same time. All the samples used for SEM and EDS were polished and then thermal etching at 1150°C for 15min. Archimedes method was applied to the bulk density measurement. Dielectric constant εr and quality factor Q were tested by TE01δ dielectric resonator method using network analyzer (E5071C, Agilent). Because Q is varied with center frequency f, so Q×f is employed to characterize the quality factor Q of the samples. Temperature coefficient of resonant frequency was determined between 20°C to 80 °C by the method above.

3. Results and discussion
Figure 1 shows the XRD patterns of the (56.33-x)TiO2-x(Zn1/3Nb2/3)O2-43.67ZrO2 samples at the optimal sintering temperature 1280°C. Crystal indices have been labeled referring to ZrTiO4 (JCPDS#340415) or ZrTi2O6 (JCPDS#751739) standard cards. When the mole content of (Zn1/3Nb2/3)O2 is relatively low (x≤26.5), the ceramics presents a ZrTiO4 single phase. The most distinctive difference appears at 37°. An apparent new peak formed near the 200 peak when x>26.5, which is determined to be the ZrTi2O6 120 peak. In ZrTiO4 region, (Zn1/3Nb2/3)4+ takes prior position in Ti4+ sites [10]. In ZrTi2O6 region, (Zn 1/3Nb2/3)4+ ions randomly substituted both the Zr 4+ site and Ti 4+ site [12]. This phase transition derived from the covert between order to disorder in atom occupation. As the content of (Zn1/3Nb2/3)O2 increasing, all the peaks shift to the left, which indicates the enlargement of the lattice parameter. The reason for the this transition lies on the replacement of (Zn1/3Nb2/3)4+ (mean ion radius 0.673 Å ) ion to Zr4+ or Ti4+ ion (mean ion radius 0.663 Å) [13].

Figure 2 illustrates the typical backscattered SEM image of the polished surfaces of (56.33-x)TiO2-x(Zn1/3Nb2/3)O2-43.67ZrO2 sintered at 1280°C. All the samples have been thermal etched at 1150°C for 15min. As (Zn1/3Nb2/3)O2 increasing, the average grain size grows from 5μm to 15μm. The lower sintering temperature of (Zn1/3Nb2/3)O2 (1150°C) may be responsible for this growth. As is shown in SEM image, there are three different regions which stands for three different phase compositions in the ceramics. Table 1 shows the element composition and content of the main phase according to
energy-dispersive spectrometry (EDS). For the main phase, the element content of Zn and Nb raises along with the increasing of $x$, which means the added Zn$^{2+}$ and Nb$^{5+}$ have mostly dissolved in ZrTiO$_4$ or ZrTi$_2$O$_6$ crystal lattice and take the place of Ti$^{4+}$ or Zr$^{4+}$ ion. The lighter color region is determined to be ZrO$_2$ and the element of darker region was Zn, Cu and Ti (most likely to be ZnCuTiO$_4$). ZrO$_2$ lays in the main phase and ZnCuTiO$_4$ exists in the grain boundary. The location of secondary phase result from their sintering temperature of ZrO$_2$ (more than 1450°C) and ZnCuTiO$_4$ (1150°C). CuO is benefit for liquid phase sintering and exist in grain boundary, so it may be easier for CuO to combine ZnO and TiO$_2$ and then form ZnCuTiO$_4$ phase between the boundary.

Figure 1. XRD patterns of (56.33-$x$)TiO$_2$-$x$(Zn$_{1/3}$Nb$_{2/3}$)O$_2$-$43.67$ZrO$_2$ ($x$ = 2.60-37.66) ceramics sintering at 1280°C with 0.5%wt CuO for 4h.

Figure 2. SEM micrographs of the thermal etched surfaces of (56.33-$x$)TiO$_2$-$x$(Zn$_{1/3}$Nb$_{2/3}$)O$_2$-$43.67$ZrO$_2$ ceramics sintering at 1280°C: (a) $x$=6.7; (b) $x$=14.9; (c) $x$=22.7; (d) $x$=30.2.
Table 1. A table with headings spanning two columns and containing notes.

| Point | Ti    | Zr    | Zn    | Nb    | O     | Cu    | Total |
|-------|-------|-------|-------|-------|-------|-------|-------|
| A     | 13.84 | 13.92 | 0.59  | 2.20  | 69.44 | 0     | 100   |
| B     | 11.97 | 14.72 | 1.57  | 4.19  | 67.56 | -0.02 | 100   |
| C     | 10.15 | 14.27 | 2.55  | 6.63  | 66.37 | 0.03  | 100   |
| D     | 5.98  | 14.06 | 3.64  | 8.22  | 67.54 | 0.56  | 100   |
| E     | 9.4   | 0.11  | 17.75 | 0.54  | 59.87 | 11.58 | 100   |

Figure 3 shows the bulk density of the ceramics sintered at different temperatures for 4h. With the temperature increased from 1220 to 1340°C, the bulk density of most samples first increased from 1220 to 1280°C and then decreased when sintering temperature is more than 1280°C, which indicates the optimal sintering temperature is near 1280°C. For the temperatures at 1280°C, when the x value increased from 2.6 to 26.5, the density increased gradually from 4.95 to 5.09 g/cm³, and this densification may root in the heavier atom replacement in ZrTiO₄ crystal. The slight decrease at x = 30.2 derived from the ZrTiO₄ to ZrTi₂O₆ phase transition and the relatively low theoretical density of ZrTi₂O₆. With the dropping (Zn₁/₃Nb₂/₃)O₂ content continues to increase, the density increased from 5.04 to 5.10 g/cm³, which due to the heavier atom replacement as well.

Figure 3. Bulk density of the (56.33-x)TiO₂-x(Zn₁/₃Nb₂/₃)O₂-43.67ZrO₂ ceramics sintered at 1220 to 1340°C for 4h.

Figure 4 shows the relative permittivity εᵣ of (56.33-x)TiO₂-x(Zn₁/₃Nb₂/₃)O₂-43.67ZrO₂ ceramics at different sintering temperature for 4h. With the temperature increased from 1220 to 1340°C, there is no obvious fluctuation on εᵣ. There are two important factors which have the most influence on relative permittivity: density and covalency bond. In ZrTiO₄ phase region x=2.7 to 26.5, εᵣ decreased with the increase of (Zn₁/₃Nb₂/₃)O₂ content which is on the opposite tendency of the density. Zhang et al. [14] had suggested that (Zn₁/₃Nb₂/₃)⁴⁺ substituted for Ti⁴⁺ ions in Ba₃Ti₄-x(Zn₁/₃Nb₂/₃)ₓNb₂O₂₁ ceramics caused the decrease of dielectric constant because the covalency of Zn–O and Nb–O has more stronger covalency bond than that of Ti–O bonds in the AO₆ octahedra. A platform appeared at x=26.5 to 30.2 for the temperatures from 1220 to 1300°C, which is in ZrTi₂O₆ phase region. The reason for this abnormal situation lies on the higher εᵣ for ZrTi₂O₆. As the x continued to increase, εᵣ decreased at x>30.2, which was derived from covalency bond.
Figure 4. $\varepsilon_r$ of (56.33-x)TiO$_2$-x(Zn$_{1/3}$Nb$_{2/3}$)O$_2$-43.67ZrO$_2$ ceramics sintered at 1220 to 1340°C for 4h.

The Q×f value for different (56.33-x)TiO$_2$-x(Zn$_{1/3}$Nb$_{2/3}$)O$_2$-43.67ZrO$_2$ composition sintering at 1220 to 1340°C for 4h are shown in Figure 5. In the range of x=2.7 to 14.9, the Q×f increased with the sintering temperature. As the x continued to increase, the Q×f of low sintering temperature samples began to surpass the Q×f of 1340°C samples. There are many factors to affect the dielectric loss of a certain material. Beside the internal lattice vibration make up the primary microwave dielectric loss, the second phases, the porosity, the lattice defects and the average grain size all have contribution to the dielectric loss [15]. At the region of x= 2.6 to 22.7, the Q×f value increases steadily along with the increasing of (Zn$_{1/3}$Nb$_{2/3}$)O$_2$. (Zn$_{1/3}$Nb$_{2/3}$)O$_2$ have a relative high Q×f, which may somehow indicates the lower dielectric loss of Zn and Nb vibration mode than Zr or Ti vibration mode, making the rapid promotion of Q×f. And at the region of x= 26.5 to 37.7, Q×f value decreased straightforward with the increasing added (Zn$_{1/3}$Nb$_{2/3}$)O$_2$. When observing the outlook of the ceramics, some black spot appeared on the pellet surface, which indicates that some Ti$^{4+}$ ion have transformed into Ti$^{3+}$ by therm reduction reaction. And the area of black region become wider with the increasing (Zn$_{1/3}$Nb$_{2/3}$)O$_2$. The appearance of Ti$^{3+}$ represents the formation of oxygen vacancies, and thus makes for the decaying of quality factor. Besides the therm reduction, the increasing poros observed in SEM also damps the Q×f value.

Figure 6 shows the temperature coefficient of resonant frequency of (56.33-x)TiO$_2$-x(Zn$_{1/3}$Nb$_{2/3}$)O$_2$-43.67ZrO$_2$ ceramics sintered at 1280°C for 4h. All the data was measured from 25 to 80°C and use the formula $\tau_f = \frac{F_{80} - F_{25}}{F_{25}(80 - 25)} \times 10^6$. With the increasing of (Zn$_{1/3}$Nb$_{2/3}$)O$_2$, $\tau_f$ decreased by the negative direction from 24 to -25ppm/°C. To satisfy the practical application, the absolute value of $\tau_f$ need to be as small as possible, usually -10ppm/°C≤$\tau_f$≤10ppm/°C. In a grand range of x from 10.9 to 30.2, the $\tau_f$ values are all near zero, from -9.2 to 9.9ppm/°C. In general, the $\tau_f$ value depends on the phase composition and structure of the ceramic [16, 17]. Single ZrTiO$_4$ phase solid solution can restrain the $\tau_f$ from dramatic change, and dropping (Zn$_{1/3}$Nb$_{2/3}$)O$_2$ makes this reduction on $\tau_f$. The reason for decrease dues to octahedra distortion. Collar et al. have reported the influence of structural change on $\tau_6$, which points out that the octahedra tilting would lead to the $\tau_f$ value decrease when this tilting intensified [18]. As the ratio of being replaced Ti$^{4+}$ for (Zn$_{1/3}$Nb$_{2/3}$)$^{4+}$ increasing, the distortion degree of Ti-O octahedra became deeper, hence the $\tau_f$ of ZrTiO$_4$ decrease. As a result, a series of composition
with high microwave dielectric constant, good quality factor and near-zero temperature coefficient of resonant frequency have been prepared by sintering at 1280°C for 4h.

![Figure 5](image)

**Figure 5.** Bulk density of the $(56.33-x)\text{TiO}_2-x(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_2-43.67\text{ZrO}_2$ ceramics sintered at 1220 to 1340°C for 4h.

![Figure 6](image)

**Figure 6.** Bulk density of the $(56.33-x)\text{TiO}_2-x(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_2-43.67\text{ZrO}_2$ ceramics sintered at 1220 to 1340°C for 4h.

4. Results and discussion

$(56.33-x)\text{TiO}_2-x(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_2-43.67\text{ZrO}_2$ ceramic were prepared using traditional solid method. The phase structure, microstructure, Raman spectra, microwave dielectric properties as a function of $(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_2$ were also characterized in details. All the samples are sintered at 1280°C for 4h. The XRD image shows that ZrTiO$_4$ single phase was formed at $x=2.6$ to 26.5 and ZrTi$_2$O$_6$ single phase was
formed at $x=30.2$ to 37.7. The SEM image and EDS analysis can clearly identify the crystal structure and composition correspond to XRD result. The specimens show good microwave dielectric properties for resonators application when $10.8 \leq x \leq 30.2$: $\varepsilon_r$ from 28.7 to 43.4, $Q\times f$ from 18000 to 24000GHz, $\tau_f$ from -9.2 to 9.9 ppm/°C.

Acknowledgements
This work is supported by the National Key Research and Development Plan (Grant No. 2017YFB0406301) and the Scientific Research Project of Education Department of Hubei Province (Grant No. B2017172).

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