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# Crystal structure and microwave dielectric properties of novel $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics

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ABSTRACT

The crystal structural variations of $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics sintered at 1150 °C for 4 h were investigated, and the relationship of these changes and the microwave dielectric properties were studied. Three types of crystal structures were identified with increasing $x$: wolframite, ixiolite, and rutile. While $x \leq 0.4$, the single-phase solid solution of wolframite structure was found. For $0.6 \leq x \leq 0.7$, the ceramics formed a single-phase solid solution of ixiolite structure. And when $x=0.8$, the mixture of two solid solution phases based on the ixiolite and rutile structures was obtained. The microwave dielectric properties of specimens were changed with the crystal structural transitions. Moreover, with the help of $TiO_2$, $\tau_f$ value of the $0.3ZnZrNb_2O_8-0.7TiO_2$ ceramic was adjusted to near zero of $-2.4$ ppm/°C, accompanied with excellent microwave dielectric properties of $\varepsilon_r \sim 41.4$, $Q \times f \sim 38{,}500$ GHz. This constitutes a very promising material for microwave applications.



## 1. Introduction

With the development of high frequency wireless communication technology, microwave dielectric ceramics, which can be used as dielectric resonators, filters, waveguides, substrates, and antennas, have attracted much scientific and commercial attention. In general, it is required that the microwave dielectric ceramic should have a high permittivity ($\varepsilon_r$), a high quality factor ($Q \times f$), and a stable temperature coefficient of the resonant frequency ($\tau_f$) of around 0 ppm/°C [1–5].

Recently, $AZrNb_2O_8$ (A=Zn, Mg, Mn, Co) compounds with monoclinic wolframite crystal structure have attracted increasing attention due to their good dielectric properties [6–13]. Among such compounds, Ramarao et al. [10] reported the microwave dielectric properties of $CoZrNb_2O_8$ ceramics ($\varepsilon_r \sim 12.3$, $Q \times f \sim 26{,}950$ GHz, and $\tau_f \sim -28.2$ ppm/°C). Wu et al. [11] reported $MnZrNb_2O_8$ ceramics exhibiting dielectric properties of $\varepsilon_r \sim 24.6$, $Q \times f \sim 27{,}936$ GHz, and $\tau_f \sim -55.1$ ppm/°C. Zuo et al. [12] investigated the microwave dielectric properties of $MgZrNb_2O_8$ ceramics ($\varepsilon_r \sim 26$, $Q \times f \sim 120{,}816$ GHz, and $\tau_f \sim -50.2$ ppm/°C). In our previous work, the wolframite-structured $ZnZrNb_2O_8$ had a relative permittivity of 29.4, $Q \times f$ value of 61,130 GHz, and a $\tau_f$ value of $-52.6$ ppm/°C [8,9]. However, most of them exhibited relatively low dielectric constant and large negative $\tau_f$ values, which often limited their practical applications. In order to achieve a temperature stable material, the tuning of $\tau_f$ to near-zero value may be achieved by adding other compounds having $\tau_f$ of opposite sign. Rutile $TiO_2$ with the large permittivity ($\sim 105$) and large positive $\tau_f$ value ($\sim +460$ ppm/°C) was often been utilized to improve the dielectric constant and compensate the negative $\tau_f$ value of dielectric [14].

In this present work, $TiO_2$ was combined with $ZnZrNb_2O_8$ to achieve a temperature stable material system. The phase evolution and microwave dielectric properties of $(1-x)ZnZrNb_2O_8-xTiO_2$ system were firstly investigated as a function of $TiO_2$ content ($x=0 \sim 0.8$). The relationship between crystal structure and microwave dielectric properties in the ceramics was also studied.

## 2. Experimental

The starting materials used in this study were high-purity oxide powders (99.9%) of ZnO, $ZrO_2$, $Nb_2O_5$ and $TiO_2$ (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China). Firstly, the powder of the $ZnZrNb_2O_8$ composition was prepared using a conventional solid-state mixed-oxide method, and was calcined at 850 °C for 2 h. For the $(1-x)ZnZrNb_2O_8-xTiO_2$ system, the $ZnZrNb_2O_8$ and $TiO_2$ powders were weighed in appropriate proportions and ball milled for 12 h with ethanol as media. After drying, the powders

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with polyvinyl alcohol as a binder were pressed into pellets 10 mm in diameter and 5 mm in thickness. The compacts were sintered from 1100 °C to 1175 °C for 4 h.

The bulk density of the sintered samples was measured by the Archimedes method. The crystal structures of samples were identified by X-ray diffraction method (Rigaku, D/MAX-2500, Tokyo, Japan) using Cu-Kα radiation with a 5°/min scanning speed. The microstructure of as-fired surfaces of samples was characterized using the scanning electron microscopy (SEM, Philips XL30 ESEM, Netherland). Microwave dielectric properties of samples were measured on a network analyzer (8720ES, Agilent, Santa Clara, CA). The permittivity was measured by the Hakki-Coleman method, and the unloaded $Q$ value was measured by the shielded cavity method [15,16]. The temperature coefficient of resonant frequency was obtained from 25 °C to 85 °C and calculated using Eq. (1):

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

where $f_1$ and $f_2$ are the $TE_{01\sigma}$ resonant frequency of the samples at 25 °C and 85 °C, respectively.

## 3. Results and discussion

Fig. 1 shows the bulk densities of the sintered $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics as a function of sintering temperature. The bulk densities of the samples increased with the increasing sintering temperature and then slightly decreased at higher temperatures of 1150–1175 °C, which could be attributed to over-firing. Moreover, the bulk densities decreased obviously with increasing the $TiO_2$ content. Therefore, the samples sintered at 1150 °C for 4 h were selected to examine the structural and dielectric behaviors of the system in detail.

Fig. 2 illustrates the X-ray diffraction patterns of $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics sintered 1150 °C for 4 h. By indexing the patterns, three structural types were observed with increasing $TiO_2$ content: wolframite, ixiolite and rutile. The interrelation among them led to various structural transitions and a broad range of solid solutions as a function of composition $x$. The upper limit of the first region, a solid solution based on the wolframite structure, was observed up to 40 mol% $TiO_2$. This phenomenon revealed that the sufficient amount of $Ti^{4+}$ could solute into the wolframite-structured $ZnZrNb_2O_8$ (JCPDS no. 48-0324) crystal

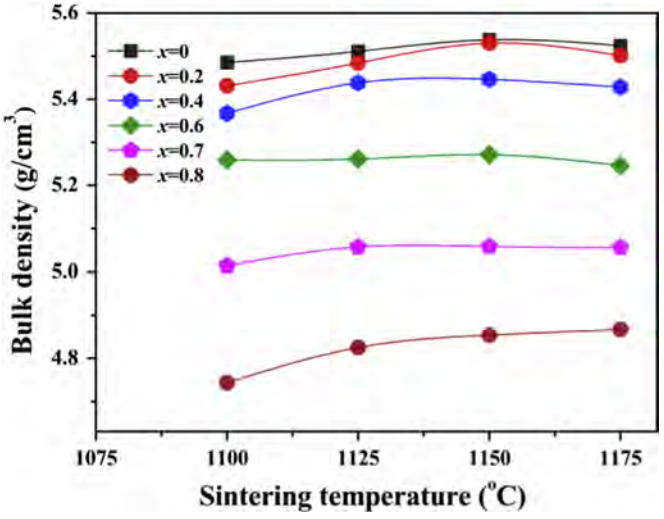


**Fig. 1.** Bulk density of $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics sintered at various temperatures for 4 h.

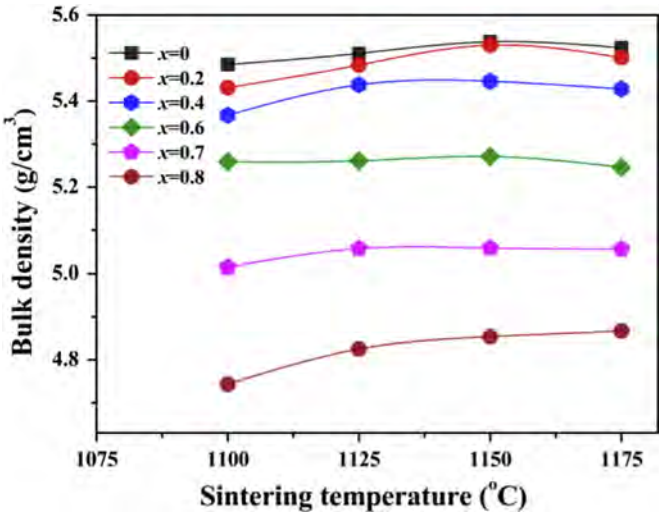


**Fig. 2.** XRD patterns of $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics sintered at 1150 °C for 4 h.

lattice, but did not change the structure. With increasing $TiO_2$ content, only the ixiolite phase appeared, indicating that there is a morphotropic phase transition for this solid solution region between 40 and 60 mol% $TiO_2$. The diffraction peaks of ixiolite phase could be well indexed as crystal structure of $ZnTiNb_2O_8$ (JCPDS no. 48-0323). However, the diffraction peaks were shifted to lower angles with increasing $x$ value. This peak shift, indicating a decrease in unit-cell parameters, is due to the smaller ionic size of $Ti^{4+}$. As $TiO_2$ content exceeded 80 mol%, the X-ray diffraction pattern confirmed that the ixiolite phase decreased and rutile $TiO_2$ (JCPDS no. 21-1276) phase appeared, due to the limited solubility of $Ti^{4+}$ in the previous ixiolite solid solution. This result might be attributed to four $Ti^{4+}$ substituted for one $Zn^{2+}$, one $Zr^{4+}$ and two $Nb^{5+}$, which was balanced in charge and required no lattice defects.

The SEM micrographs of the $(1-x)ZnZrNb_2O_8$–$xTiO_2$ ceramics sintered 1150 °C for 4 h are presented in Fig. 3. With increasing the $TiO_2$ content from 0 to 80 mol%, a remarkable change of grain size for the samples was observed. From Fig. 3(a), the pure $ZnZrNb_2O_8$ ceramic had a dense microstructure with the average grain size of 3 μm. As $x$ increased to 0.4, the denser and more homogeneous distributed grains were obtained with much bigger grain size of 4–5 μm. For $0.6 \le x \le 0.7$, the average grain size of samples reached a maximum value 6 μm and then slightly decreased. However, the rod-like $TiO_2$ grains identified by EDS analysis with a width size of 1 μm and square grains with a size of about more than 4 μm were firstly observed in Fig. 3(f) ($x=0.8$).

The microwave dielectric properties of $ZnZrNb_2O_8$-$TiO_2$ samples sintered at 1150 °C for 4 h are demonstrated in Fig. 4. From Fig. 4(a), the $\varepsilon_r$ showed a monotonic increase along with $x$ in the entire composition range, which lay between the value of individual components. When $x$ value went up from 0 to 0.4, the measured permittivity increased from 27.7 to 55.4. Meanwhile, the $Q \times f$ began with a slow downward from 63,110 to 60,310 GHz then decreased sharply within $0.6 \le x \le 0.7$. With further increasing $x$ to 0.8, a sudden drop of $Q \times f$ value was mainly resulted from the produce of the $TiO_2$ phase. Therefore, one can believe that the decrease of $Q \times f$ value in the range of $x=0 \sim 0.8$ should be ascribed to the difference of crystal structures, accompanied by the wolframite to rutile phase transition [17]. As shown in Fig. 4(b), it could be seen that the $\tau_f$ gradually increased from −58.9 ppm/°C to +17.9 ppm/°C with the increase of $TiO_2$ content. This behavior mainly attributed to the rutile $TiO_2$ with very high $\tau_f$ value. Moreover, the $0.3ZnZrNb_2O_8-0.7TiO_2$ ceramic had a near-zero $\tau_f$

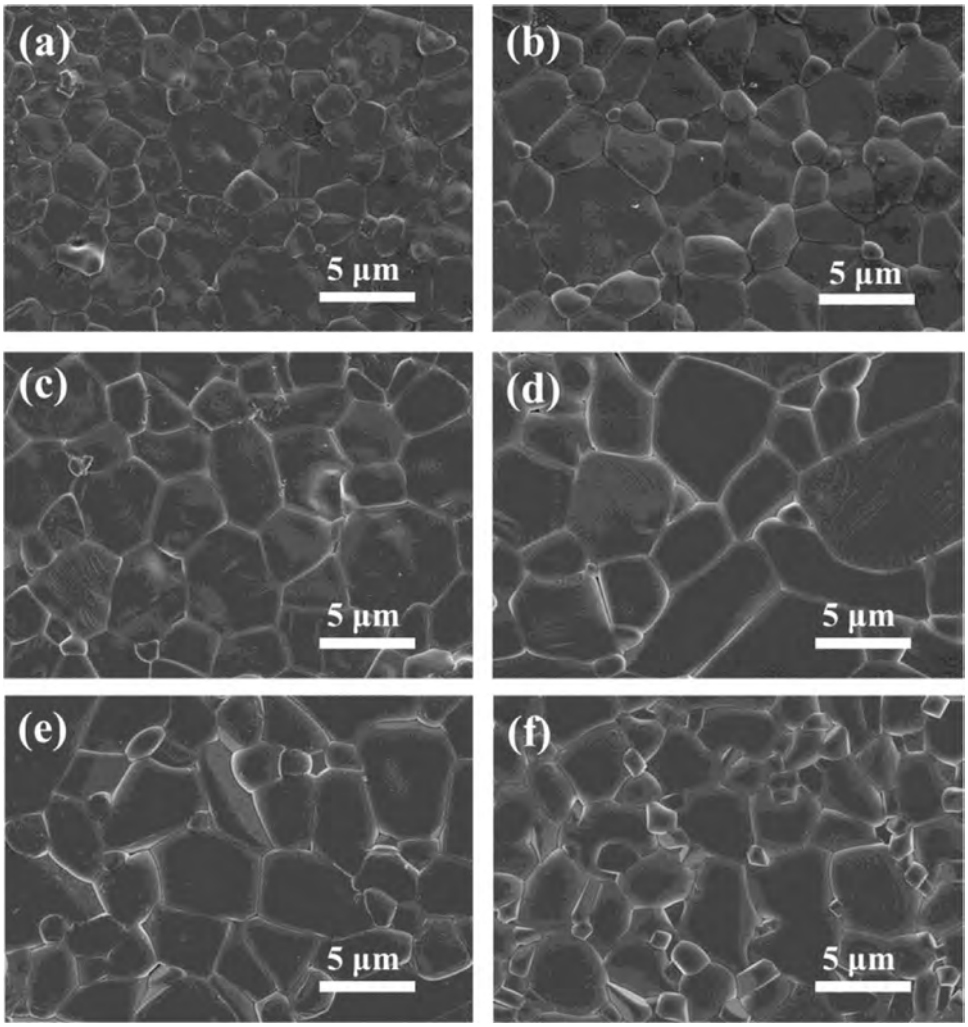


**Fig. 3.** SEM micrographs of $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics sintered at 1150 °C for 4 h: (a) $x=0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.7$, and (f) $x=0.8$.

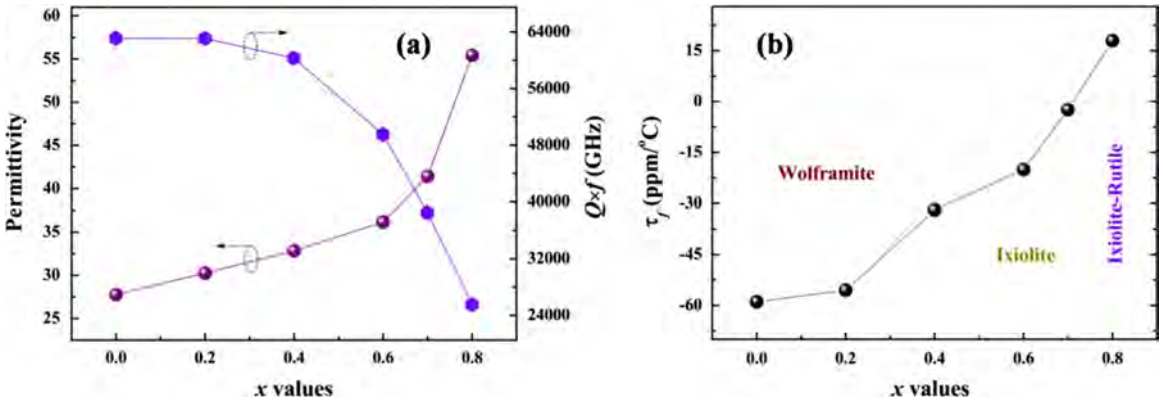


**Fig. 4.** The microwave dielectric properties of the $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics sintered at 1150 °C for 4 h.

value of −2.4 ppm/°C. This would possibly make the $(1-x)ZnZrNb_2O_8-xTiO_2$ ceramics more applicable for microwave devices.

## 4. Conclusion

The phase evolution, microstructure and microwave dielectric properties of $(1-x)ZnZrNb_2O_8-xTiO_2$ ($x=0\sim0.8$) ceramics were investigated. The XRD pattern revealed that three distinct phase regions were observed with mol% ($x$) of $TiO_2$: wolframite, ixiolite, mixture of ixiolite and rutile solid solution region. The permittivity and temperature coefficient of resonant frequency showed the similar variation trend and increased from 27.7 to 55.4 and −58.9 to 17.9 ppm/°C in the entire composition range, respectively. Meanwhile, the quality factor continuously decreased from 63,110 to 26,500 GHz as a result of phase transition. The specimen comprising $0.3ZnZrNb_2O_8-0.7TiO_2$ possesses a middle permittivity of 41.4, an high $Q\times f$ of 38,500 GHz, and a very small $\tau_f$ of −2.4 ppm/°C, demonstrating a unique potential for temperature stable

microwave applications.

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