Influences of \( \text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5 \) co-doping on structural evolution and dielectric properties of \( \text{Zn}_{0.5}\text{Ti}_{0.5-x}(\text{Al}_{0.75}\text{Nb}_{0.35})_x\text{NbO}_4 \) (0 \( \leq x \leq 0.3 \)) ceramics

H Y Yang\(^1, 2\), S R Zhang\(^1, 2, 4\), H C Yang\(^1, 2\), Y Yuan\(^1, 2, 3\) and E Z Li\(^1, 2\)

\(^1\) National Engineering Research Center of Electromagnetic Radiation Control Materials, University of Electronic Science and Technology of China, Chengdu, China;
\(^2\) Key Laboratory of Multi-Spectral Absorbing Materials and Structures of Ministry of Education, University of Electronic Science and Technology of China, Chengdu, China;
\(^3\) Institute of Electronic and Information Engineering of UESTC in Guangdong, Dongguan 523808, People's Republic of China, China.
\(^4\) E-mail: zsr@uestc.edu.cn

Abstract. In present study, the influences of \( \text{Al}_2\text{O}_3 \) and \( \text{Nb}_2\text{O}_5 \) co-doping for Ti site on structure and microwave dielectric performances of \( \text{Zn}_{0.5}\text{Ti}_{0.5-x}(\text{Al}_{0.75}\text{Nb}_{0.35})_x\text{NbO}_4 \) ceramics were discussed. Pure ixiolite-structured \( \text{Zn}_{0.5}\text{Ti}_{0.5-x}(\text{Al}_{0.75}\text{Nb}_{0.35})_x\text{NbO}_4 \) solid solution is prepared when \( x \leq 0.15 \). Phase transformation takes place at \( 0.2 \leq x \leq 0.3 \), where columbite \( \text{ZnNb}_2\text{O}_6 \) phase exists. The dielectric constant (\( \varepsilon_r \)) of ceramics presents a decline trend, which is attributed to the decrease of dielectric polarizability (0 \( \leq x \leq 0.15 \)) and the formation of \( \text{ZnNb}_2\text{O}_6 \) phase (0.2 \( \leq x \leq 0.3 \)). The quality factor (\( Q\times f \)) , however, decrease till \( x = 0.15 \) and increase after that. The temperature coefficient of resonant frequency (\( \tau_f \)) value varies consistently with the densification. Typical dielectric ceramics (\( x = 0.3 \)) was synthesized at 1150\(^\circ\)C: a \( \varepsilon_r \) of 25.79, a \( Q\times f \) about 56114 GHz and a \( \tau_f \) of -78.18 ppm/\(^\circ\)C, were obtained.

1. Introduction

Microwave dielectric materials are generally applied in modern electronic communication, namely at radars, antennas, filters, resonators, etc. Their importance cannot be emphasized too much. It is crucial to synthesize dielectric materials with excellent properties, such as high quality factor (with \( Q\times f > 1000 \) GHz) value, a near-zero temperature coefficient of resonant frequency (\( \tau_f \)) value and relative permittivity (\( \varepsilon_r \), in the range 5-70) [1, 2].

\( \text{Zn}_{0.5}\text{Ti}_{0.5}\text{NbO}_4 \) material owns an orthorhombic structure, which has received many concerns due to its considerable dielectric properties and suitable sintering temperature (1250\(^\circ\)C, \( \varepsilon_r = 34 \), \( Q\times f = 42500 \) GHz) [3]. Up to now, many studies have been implemented to improve its properties. For instance, divalent cations \( R^{2+} \) (\( R=\text{Mg, Ni, Ca, Co} \)) are usually used to substituted for Zn site [4-7]. For Ti and Nb sites, \( \text{Sn}^{4+}, \text{Zr}^{4+} \) and \( \text{Ta}^{5+} \) are more likely used as substitute sources [3, 8, 9]. It is interesting that there are few reports about the effects of ionic co-substitution on evolution of crystalline phase and dielectric properties of \( \text{Zn}_{0.5}\text{Ti}_{0.5}\text{NbO}_4 \) ceramic. \( \text{Ta}^{5+}/\text{Co}^{2+} \) co-doped \( \text{Nb}^{5+} \) and \( \text{Zn}^{2+} \) ions promote the formation of a tetragonal phase and improve dielectric properties (1175\(^\circ\)C, \( \varepsilon_r = 38.02 \), \( Q\times f = 23550 \) GHz, \( \tau_f = 4.62 \) ppm/\(^\circ\)C) [6].
In previous literatures, co-substitution of Al\(^{3+}/\)Nb\(^{5+}\) ions for Ti site in cubic SrTiO\(_3\) system reduces the Ti\(^{4+}\) ions reduction and improves its dielectric properties [10]. The microwave dielectric properties of orthorhombic-structured Ba\(_{3.75}\)Nd\(_{0.25}\)Ti\(_{18}\)(Al\(_{12}\)Nb\(_{12}\))O\(_{34}\) system are also enhanced because of the substitutions of Al\(^{3+}/\)Nb\(^{5+}\) ions [11]. Therefore, Ti site partial replaced by Al\(^{3+}/\)Nb\(^{5+}\) ions in Zn\(_{0.5}\)Ti\(_{0.5}\).\(_{(Al_{0.75}Nb_{0.35})_{0.5}}\)NbO\(_4\) (0 ≤ x ≤ 0.3) ceramics are considered to study the correlations between microwave dielectric properties and crystal structural evolution.

2. Experimental

Solid-state reaction was applied to prepare the Zn\(_{0.5}\)Ti\(_{0.5}\).\(_{(Al_{0.75}Nb_{0.35})_{0.5}}\)NbO\(_4\) (0 ≤ x ≤ 0.3) ceramics. Raw materials of ZnO, TiO\(_2\), Al\(_2\)O\(_3\), Nb\(_2\)O\(_5\) with high purity (>99.9%) were proportionately quantified by following its formula. The starting powders were ball milled for 6 h. Next, they were calcined at 950 °C for 3 h and re-milled for 4 h. After that, polyvinyl alcohol (PVA) was added to the obtained powders, that were pressed into cylinders, and then sintered at 1050 °C–1175 °C for 4 h.

The apparent density of specimen was tested by Archimedes method by measuring the weight of ceramic samples in air and water. X-ray diffraction measurements were performed in a Philips X’Pert ProMPD model, in a 2θ angle range of 10°–120°, using Cu Kα radiation. Room temperature Raman spectra were performed using a Raman microscope (LabRAM HR Evolution); the 532 nm line of an Ar laser source with constant power acted as the exciting wavelength. The micrographs of sintered samples were provided by a scanning electron microscope (SEM, FEI Inspect F, United Kingdom). The microwave dielectric properties of the sintered samples were measured, at 5–8 GHz using the Hakki-Coleman dielectric resonator method in TE\(_{011}\) mode by means of a network analyzer (Agilent Technologies HP83752A) and a temperature chamber (Delta 9023, Delta Design, USA). The selection of TE\(_{011}\) mode is based on that this mode propagates inside the sample but is evanescent outside. As a result, electrical energy could be stored in high-Q dielectric resonator[1]. The τ value was estimated from the variation of resonant frequency at certain temperature:

\[
τ = \frac{(f_6 - f_5)}{f_{35} \times 60} \times 10^6 (\text{ppm/}°\text{C})
\]

3. Results and discussion

3.1. Structural characterization from X-ray diffraction and Raman analysis

Figure 1 displays the X-ray diffractions of Zn\(_{0.5}\)Ti\(_{0.5}\).\(_{(Al_{0.75}Nb_{0.35})_{0.5}}\)NbO\(_4\) (0 ≤ x ≤ 0.3) ceramics. Pure orthorhombic Zn\(_{0.5}\)Ti\(_{0.5}\).\(_{(Al_{0.75}Nb_{0.35})_{0.5}}\)NbO\(_4\) phase with Pbcn(60) space group is well-matched with JCPDS card No. 48-0323 at 0 ≤ x ≤ 0.15. This phenomenon illustrates that Al\(^{3+}/\)Nb\(^{5+}\) ions diffuse into Ti site and solid solution is synthesized. According to Shannon’s report [12], radii of (Al\(_{0.75}!Nb_{0.35}!\))\(^{4+}\) cation is 0.625 Å (CN=6), that is to say, the radii of Ti site after substitution is smaller than Ti\(^{4+}\) ion and this would cause a decrease trend of cell volume. However, characteristic peaks of ZnNb\(_2\)O\(_4\) phase, (020) plane at 12° and (040) plane at 24° (marked by arrow), appears when x exceeds 0.15, indicating that excessive amount of Al\(^{3+}/\)Nb\(^{5+}\) ions could bring in a phase transformation between ixiolite and columbite structures.

Rietveld refinement analysis performed by GSAS-EXPGUI software[13, 14] is used to obtain crystal structural information, such as cell volume and volume fraction of each phase. Detailed refined steps include background, profile parameters and constraints. The X-ray diffraction profile (x = 0.20), refined using two different approaches, is shown in Figure 2. One is using single Zn\(_{0.5}\)Ti\(_{0.5}\)NbO\(_4\) phase, and the other is considering Zn\(_{0.5}\)Ti\(_{0.5}\)NbO\(_4\) and ZnNb\(_2\)O\(_4\) phases as initial models. As can see from Figure 2 (a), the discrepancy is significant when single Zn\(_{0.5}\)Ti\(_{0.5}\)NbO\(_4\) phase is used, especially in the range of 20–30°, and the evaluating indexes are also less-credible (R\(_{wp}\) = 0.0773, R\(_p\) = 0.0574, \(χ^2\) = 3.025), which suggests additional diffraction patterns are required in the fitting process. Figure 2 (b) displays two phases fitting results. All the diffraction peaks are well-fitted, and the R\(_{wp}\) = 0.0611, R\(_p\) = 0.0472, \(χ^2\) = 1.890 are acceptable, confirming that Zn\(_{0.5}\)Ti\(_{0.5}\)NbO\(_4\) and ZnNb\(_2\)O\(_4\) composites are present (volume fractions of Zn\(_{0.5}\)Ti\(_{0.5}\)NbO\(_4\) phase at x = 0.20–0.30 are 79.02%, 75.69% and 58.92%, respectively).
In order to confirm the formation of ZnNb$_2$O$_6$ phase at $x>0.15$, the Raman spectra of Zn$_{0.5}$Ti$_{0.5}$
$(Al_{0.75}Nb_{0.35})_x$NbO$_4$ ($x = 0.0, 0.15, 0.20$) ceramics were obtained, as shown in Figure 3. According to the
Rietveld refinement results, two phases coexist at $x>0.15$, and Zn$_{0.5}$Ti$_{0.5}$NbO$_4$ phase is the main
crystalline phase. That is to say, the vibrational contributions are still dominated by this phase. At $x = 0$, the vibrational spectrum is similar with Liao’s work[15], suggesting pure ixiolite Zn$_{0.5}$Ti$_{0.5}$NbO$_4$
phase is synthesized. With $x$ increasing to 0.15, no additional band is observed, which implies that a solid solution is formed. However, as we can see from the vertical dotted line at 300 cm$^{-1}$ and 680 cm$^{-1}$,
the peak intensities of $B_{1g(3)}$, $B_{2g(1)}$ and $A_{g(1)}$ modes of Zn$_{0.5}$Ti$_{0.5}$NbO$_4$ phase are gradually decreasing
and a new band at about 470 cm$^{-1}$, corresponding to the $A_g$ mode of ZnNb$_2$O$_6$ phase, emerges at $x = 0.20$ [16]. These results corroborate the refinement data, that ZnNb$_2$O$_6$ phase appears at $x = 0.20$ and
volume fraction of Zn$_{0.5}$Ti$_{0.5}$NbO$_4$ phase decreases as $x$ increases.

Figure 1. (a) X-ray diffraction patterns of sintered samples and (b) enlargement of X-ray diffractive profile in the range of 20 degrees (arrows represent the (020) and (040) planes of ZnNb$_2$O$_6$ phase).

Figure 2. X-ray diffraction profile ($x = 0.20$) after refinement, where (a) single Zn$_{0.5}$Ti$_{0.5}$NbO$_4$
phase and (b) Zn$_{0.5}$Ti$_{0.5}$NbO$_4$ and ZnNb$_2$O$_6$ phases are used as initial models (red circle is the observed value, black line is the calculated value, the vertical line presents the bragg position, the blue line at the bottom is the error line that indicates the discrepancy between theoretical and experimental data).
3.2. Microstructure analysis

Figure 4 depicts the micrographs of as-sintered samples when sintered at optimum temperature (1050°C). The grain boundary is clearly observed. Pure Zn$_{0.5}$Ti$_{0.5}$NbO$_4$ ceramic has a smaller average grain size about 2.24 μm. In this study, average grain size shows an increase trend from 4.16 μm to 6.78 μm. At $x = 0$–0.1, the substitution of Al$^{3+}$/Nb$^{5+}$ ions could enhance the grain size. However, when $x \geq 0.2$, ZnNb$_2$O$_6$ phase is formed, which promotes the growth of the grains. A similar conclusion could be retrieved in ZnNb$_2$O$_6$ modified ZrTi$_2$O$_6$ ceramics, where the increase in the amount of ZnNb$_2$O$_6$ phase promoted the increase of the grain size from 3.1 to 26.2 μm. Therefore, the growth of grain for $x \geq 0.2$ should be attributed to the formation of ZnNb$_2$O$_6$ phase [17].

![Figure 4. Micrograph of as-sintered samples sintered at 1150°C for 4 h, where (a) to (c) represents $x = 0.05$, 0.1 and 0.2.](image)

The growths of density are shown in Figure 5. Theoretical density increases at $x = 0$–0.3. It is worth noting that there is a sharp increase at $x = 0.2$. According to the evolution of diffraction peaks, ZnNb$_2$O$_6$ phase emerges after $x = 0.15$, the increase trend may be resulted from the large theoretical density of ZnNb$_2$O$_6$ phase (5.42 g/cm$^3$) compared with Zn$_{0.5}$Ti$_{0.5}$NbO$_4$ phase (5.34 g/cm$^3$) at $x = 0.2$. Both the apparent density and relative density increase at first, and decrease after that. The densification presents a largest value at $x = 0.15$ and then drops, which could agree with the formation of ZnNb$_2$O$_6$ phase.
3.3. Microwave dielectric properties analysis

The $\varepsilon_r$ value is affected by internal and external factors, such as densification, dielectric polarizability, secondary phase content. In this work, all the samples achieve high densification (> 96%), the influence of densification is negligible. Therefore, dielectric polarizability is vital for the variation of the $\varepsilon_r$ value in solid solution region ($A$ region, $0 \leq x \leq 0.15$). For complex compounds, the total polarizability can be calculated by the sum of the polarizabilities of the ions. In dielectric ceramics fields, this formula is used to evaluate the $\varepsilon_r$ value of materials.

The calculated $\varepsilon_r$ value is obtained from Clausius-Mosotti relationship by using the ionic polarizability [18]:

$$\alpha = \frac{3V_m(e_r - 1)}{4\pi(e_r + 2)}$$

$$\alpha = \alpha_{Zn} + (1 - 2x)\alpha_{Ti} + 1.5 x \alpha_{Al} + (2 + 0.7 x)\alpha_{Nb} + 8 \alpha_{O}$$  \hspace{1cm} (3)

Where $\alpha$ and $V_m$ refers to the theoretical ionic dielectric polarizability and molar volume, respectively. $\alpha_{Zn}=2.04 \text{ Å}^3$, $\alpha_{Ti}=2.93 \text{ Å}^3$, $\alpha_{Al}=0.79 \text{ Å}^3$, $\alpha_{Nb}=3.97 \text{ Å}^3$, $\alpha_{O}=2.01 \text{ Å}^3$ [19]. The theoretical $\varepsilon_r$ value is listed in Table 1. Both the measured and calculated $\varepsilon_r$ value decline in the region of $0 \leq x \leq 0.3$. The discrepancies, however, exist in the sintered samples. As one can expect from the fact that dielectric polarizability of ceramic is not only caused by the ionic polarizability, but also the electronic polarizability. Besides, the experimental technology and densification also results in the differences between the measured and calculated $\varepsilon_r$ value. After $x = 0.15$, secondary ZnNb$_2$O$_6$ phase appears and the measured $\varepsilon_r$ value still decreases. This trend is attributed to the content of each phase. For ZnNb$_2$O$_6$, it has a much smaller $\varepsilon_r \sim 25.1$ and its volume fraction increases, causing a drop of $\varepsilon_r$ value by following the logarithm rule [20]:

$$\ln \varepsilon_r = V_1 \ln \varepsilon_{r1} + V_2 \ln \varepsilon_{r2}$$  \hspace{1cm} (4)
Table 1. Theoretical molecular polarizability, volume fraction and \( \varepsilon_r \) value in Zn\(_{0.5}\)Ti\(_{0.5}\)\(_x\)(Al\(_{0.75}\)Nb\(_{0.35}\))\(_x\)NbO\(_4\) (0 \( \leq x \) \( \leq 0.3 \)) ceramics.

| \( x \)       | \( \alpha_1 \) (Å\(^3\)) | \( \varepsilon_{r1} \) | \( V_1 \) (%) | \( \varepsilon_{r2} \) | \( \varepsilon_{rCal} \) | \( \varepsilon_{rMea} \) |
|---------------|----------------------|-------------------|----------|-----------------|----------------|----------------|
| 0.00          | 28.99                | 31.90             | 100.00   | 25.01           | 31.90          | 37.21          |
| 0.05          | 28.90                | 30.90             | 100.00   | 25.01           | 30.92          | 34.53          |
| 0.10          | 28.80                | 30.00             | 100.00   | 25.01           | 30.00          | 33.30          |
| 0.15          | 28.71                | 29.24             | 100.00   | 25.01           | 29.24          | 31.32          |
| 0.20          | 28.61                | 28.35             | 79.02    | 25.01           | 27.62          | 29.41          |
| 0.25          | 28.52                | 27.54             | 75.69    | 25.01           | 26.90          | 27.90          |
| 0.30          | 28.42                | 26.02             | 58.92    | 25.01           | 25.60          | 25.79          |

\( \alpha_1 \) and \( \varepsilon_{r1} \) are the molecular polarizability and calculated \( \varepsilon_r \) value of Zn\(_{0.5}\)Ti\(_{0.5}\)NbO\(_4\) phase.

\( \varepsilon_{r2} \) is the \( \varepsilon_r \) value of ZnNb\(_2\)O\(_6\) phase obtained from literature [21].

\( \varepsilon_{rCal} \) and \( \varepsilon_{rMea} \) are the total calculated \( \varepsilon_r \) value and measured \( \varepsilon_r \) value.

The Q\( \times f \) and \( \tau_f \) values are presented in Figure 6. The Q\( \times f \) value firstly decreases till \( x = 0.15 \), and increases after that. It is reported that there are many influences that contribute to the Q\( \times f \) value. Intrinsically, anharmonicity effect of lattice vibration causes energy loss. It is the interaction between microwave electromagnetic field and anharmonic lattice vibration that changes the frequency of phonon vibration and ultimately affects the dielectric loss[22]. Therefore, the increase of anharmonicity of lattice vibration in crystal would reduce the Q\( \times f \) value [23]. Extrinsically, grain growth, densification and phase content will affect its changes [18]. In our present study, the increase of average size of grain decreases the crystal boundary amounts, and this would reduce the dielectric loss and improve the Q\( \times f \) value. Improvement of relative density also devote positive contributions. Moreover, the crystal structure isn’t altered at 0 \( \leq x \leq 0.15 \). Therefore, it could be possibly inferred that Al\(^{3+}\)/Nb\(^{5+}\) ions increase the lattice anharmonicity and this reason decreases the Q\( \times f \) value dramatically [24]. At 0.2 \( \leq x \leq 0.3 \), the enhancement of Q\( \times f \) value is attributed to increase of ZnNb\(_2\)O\(_6\) phase content (see Table 1) [25], which is reported with a Q\( \times f \) about 83700 GHz. The \( \tau_f \) value, however, shows a consistent trend with the relative density. Previous literature indicates that the \( \tau_f \) value is inseparable with the phase constitution, densification, additives and phase content [26, 27]. Therefore, it could be considered that increase of relative density (at 0 \( \leq x \leq 0.15 \)) improves the temperature stability of ceramic and makes the \( \tau_f \) value move to zero. With \( x \) exceeds 0.15, the decrease of relative density causes the opposite trend of \( \tau_f \) value.

Figure 6. Variations of Q\( \times f \) and \( \tau_f \) values as function of \( x \) value.
4. Conclusions

The present work has studied the influences of Al$^{3+}$/Nb$^{5+}$ ionic co-doping on crystal structure, microstructure and microwave dielectric properties of Zn$_{0.5}$Ti$_{0.5-x}$(Al$_{0.75}$Nb$_{0.35}$)$_x$NbO$_4$ ceramics ($0 \leq x \leq 0.3$). The results show that ixiolite solid solution could be prepared in the region of $0 \leq x \leq 0.15$. Excessive doping content ($x \geq 0.2$) brings in a secondary ZnNb$_2$O$_6$ phase. The average grain size and densification of as-sintered ceramic samples are improved as $x$ value increases. The drop of $\varepsilon_r$ value is influenced by the decreased molecular polarizability and phase composition. The $Q \times f$ value firstly declining to $x = 0.15$ is attributed to the increase of intrinsic lattice anharmonicity, and then increasing till $x = 0.3$ is contributed from the higher $Q \times f$ value of ZnNb$_2$O$_6$ phase. The $\tau_f$ value is closely related with the relative density.

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