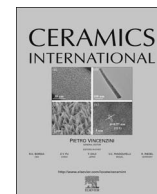




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Effect of TiO_2 on phase composition and microwave dielectric properties of $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ ceramics

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ABSTRACT

Nonstoichiometry has been playing an important role in the microwave dielectric performance of columbites $\text{A}^{2+}\text{Nb}_2\text{O}_6$ ($\text{A}^{2+} = \text{Ca}, \text{Mg}, \text{or a transition metal}$). Herein, with an excess of 0.01 mol Zn, the $Q \times f$ values of ZnNb_2O_6 ceramics could be effectively improved from 121,000 GHz to 138,000 GHz. On the basis of high- Q $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ ceramics, TiO_2 was chosen to further tune the τ_f values for the matrix materials prepared by the conventional solid-state reaction method. The results showed that, with the increase of TiO_2 content, the ZnNb_2O_6 -based ceramics underwent four phase regions: columbite (ZnNb_2O_6) solid solution, ixiolite ($\text{ZnTiNb}_2\text{O}_8$) solid solution, mixture of $\text{ZnTiNb}_2\text{O}_8$ and rutile ($\text{Zn}_{1/3}\text{Nb}_{2/3}\text{O}_{0.5}\text{Ti}_{0.5}\text{O}_2$), and ($\text{Zn}_{1/3}\text{Nb}_{2/3}\text{O}_{0.5}\text{Ti}_{0.5}\text{O}_2$) solid solution. Such changes in phase formation had an important influence on the microwave dielectric behavior of $(1-x)\text{Zn}_{1.01}\text{Nb}_2\text{O}_6-x\text{TiO}_2$ ceramics. Importantly, τ_f could be tuned from $-15.3 \text{ ppm}/^\circ\text{C}$ to $+13.9 \text{ ppm}/^\circ\text{C}$ along with x increased from 0.58 to 0.6. Accompanied with $\epsilon_r \approx 44.64 \sim 47.43$ and $Q \times f \geq 12,300 \text{ GHz}$, these materials are promising candidates for applications in microwave components and devices.

1. Introduction

During the past few decades, microwave dielectric ceramics (MWDCs) has been increasingly developed for microwave components, such as antennas, filters, and resonators, in systems for commercial wireless communication technologies [1,2]. Generally, these MWDCs are required to have a relatively high dielectric constant ($\epsilon_r > 20$) to allow miniaturization of devices, a high quality factor ($Q \times f$, $Q = 1/\tan\delta$) to improve selectivity, and a low temperature coefficient of resonant frequency (τ_f) to enable good temperature stability [3]. Among various MWDC species, the Ta-based complex perovskites like $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT) and $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT) possess excellent microwave dielectric performance [4–6]. However, these ceramics usually need high temperature sintering process ($> 1500^\circ\text{C}$). Besides, the high cost and limited resources of Ta lead to the search for alternative materials based on Nb-analog. There arises a growing interest in the binary niobates $\text{A}^{2+}\text{Nb}_2\text{O}_6$ ($\text{A}^{2+} = \text{Ca}, \text{Mg}, \text{or a transition metal}$) with columbite structure because of their lower sintering temperature and less complicated processing compared with complex perovskites, such as $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BMN) and $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BZN) [7–10]. With a comparably low sintering temperature, $\text{A}^{2+}\text{Nb}_2\text{O}_6$ can be

promising candidates for low-temperature co-fired ceramics (LTCC) integrated to multi-chip modules in the electronic packaging [11,12]. Meanwhile, $\text{A}^{2+}\text{Nb}_2\text{O}_6$ columbites have received much attention for applications in other fields, such as optics, photocatalysts, magnetics and memristors [13–16].

In particular, ZnNb_2O_6 offers superior microwave dielectric properties among the columbite-structured compounds, and has been investigated extensively [7–11,17–22]. Lee et al. [8] reported that pure ZnNb_2O_6 ceramics sintered at 1150°C possess a $\epsilon_r \sim 25$, a high $Q \times f \sim 83,700 \text{ GHz}$ and a $\tau_f \sim -56 \text{ ppm}/^\circ\text{C}$. With low-melting point compounds, such as oxides (B_2O_3 , CuO and V_2O_5) and glasses $\{\text{BaCu}(\text{B}_2\text{O}_5)\}$, the sintering temperature can be further lowered to fit the temperature requirement of LTCC technology; meanwhile, some temperature compensators like ZrTiO_4 and TiO_2 have been used to tune τ_f [17–21]. Additionally, as is reported, nonstoichiometric effect has been playing an important role in the microwave dielectric properties (especially $Q \times f$ values) of MWDCs [4,5]. For instance, small Mg deficiency in BMN could enhance the 1:2 ordering, and increase the Q values from 8 000–12 000 at 8 GHz [23]. In the case of $\text{Zn}_{1+x}\text{Nb}_2\text{O}_6$ ceramics, the $Q \times f$ product can be effectively improved to 120,000 GHz when $x = 0.01$, despite the appearance of Zn-rich secondary phases [22]. Here we chose the underlying high- Q $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ ceramics as

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the matrix, and then used TiO_2 as the temperature compensator to further tune τ_f . The effects of TiO_2 on the phase composition and microwave dielectric properties of $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ ceramics were investigated.

2. Experimental procedure

The $(1-x)\text{Zn}_{1.01}\text{Nb}_2\text{O}_6-x\text{TiO}_2$ ceramics were prepared through the conventional solid-state reaction method. High-purity grade ZnO (99.99%), Nb_2O_5 (99.99%) and TiO_2 (99.99%) were used as the starting materials. Firstly, ZnO and Nb_2O_5 were weighed based on the nominal composition of $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$, and ball-mixed in ethanol for 4 h with zirconia balls. The slurry was dried and calcined at 1100 °C for 4 h in air. The as-prepared $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ powder was then ball-milled with TiO_2 to form the $(1-x)\text{Zn}_{1.01}\text{Nb}_2\text{O}_6-x\text{TiO}_2$ mixture. Together with the organic binder (5 wt% polyvinyl alcohol), they were uniaxially pressed under 200 MPa into cylinders and pellets with proper specification. The samples were sintered in a temperature range of 1100–1250 °C for 4 h in air at a heating rate of 5 °C/min.

The crystal phases of the as-prepared ceramics were characterized by X-ray diffraction (XRD) analysis with $\text{Cu K}\alpha$ radiation (D8 Advance; Bruker, Karlsruhe, Germany). The bulk densities of the ceramics were measured by the Archimedes method. The microstructures were observed by scanning electron microscopy (SEM; MERLIN VP Compact, Carl Zeiss, Germany). A network analyzer (HP8720ES, Hewlett-Packard, Santa Rosa, CA) was used to measure the microwave dielectric properties. The dielectric constants were measured using the Hakki-Coleman [24] post-resonator method by exciting the TE_{011} resonant mode of the dielectric resonators as suggested by Courtney [25]. The unloaded quality factors were measured using the TE_{018} mode in a cavity method [26]. The temperature coefficients of the resonant frequencies of the TE_{011} mode were measured in a temperature range of 25–80 °C. The τ_f values were calculated by the following relationship:

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

where f_1 and f_2 are the resonant frequency at T_1 and T_2 , respectively.

3. Results and discussion

As is reported, the structure of columbite ANb_2O_6 is a cationic ordered structure of $\alpha\text{-PbO}_2$, where AO_6 and NbO_6 octahedra form independent zig-zag chains by sharing edges along the c -axis; while TiO_2 with rutile structure can be interpreted from the disordered hexagonal close packed $\alpha\text{-PbO}_2$ structure [11,13,14]. Hence, with such similarity in crystal structure, it seems easy to form solid solution for

$(1-x)\text{Zn}_{1.01}\text{Nb}_2\text{O}_6-x\text{TiO}_2$ ceramics. To verify that, the XRD experiments were performed on these samples, and the results are shown in Fig. 1, from which four phase regions (labelled I, II, III and IV) can be readily seen with the increase of TiO_2 content. As $0 \leq x \leq 0.3$, the samples are identified as an ordered structure of columbite similar to ZnNb_2O_6 compound (JCPDS 37–1371). In this phase region I, all the samples show the detections of superlattice peak at $2\theta \sim 25^\circ$, and the intensity decreases with increasing x . Meanwhile, the reflection peaks shift to higher angles, indicating that Ti^{4+} enters the lattices of matrix to form solid solution, in terms of the smaller ionic radius of Ti^{4+} than that of Zn^{2+} and Nb^{5+} with the same coordination number [27]. When TiO_2 content is 0.5 ~ 0.56 (region II), the superlattice reflection ($2\theta \sim 25^\circ$) become undetectable; the samples transform into an ixiolite structure corresponding to $\text{ZnTiNb}_2\text{O}_8$ compound (JCPDS 48-0323). Basically, the XRD patterns of ixiolite and columbite are quite similar despite the superlattice reflections, and $\text{ZnTiNb}_2\text{O}_8$ is considered to be a structural modification of ZnNb_2O_6 . With the further increase of TiO_2 content ($0.58 \leq x \leq 0.6$, region III), the ixiolite phase accompanied with a secondary rutile phase of $(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.5}\text{Ti}_{0.5}\text{O}_2$ (JCPDS 39–0291) can be observed. The intensities of secondary phase show an increase with x . When TiO_2 content increases to 0.7 (region IV), the samples nearly exhibit a single-phase rutile structure of $(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.5}\text{Ti}_{0.5}\text{O}_2$.

The typical microstructures of as-prepared ceramics are shown in Fig. 2. The stoichiometric ZnNb_2O_6 ceramics sintered at 1200 °C is given as a comparison shown in Fig. 2a, where grains distribute uniformly to form a very dense microstructure. With an excess of 0.01 mol Zn, the abnormal grain growth (AGG) can be easily seen from the nonstoichiometric sample $(\text{Zn}_{1.01}\text{Nb}_2\text{O}_6)$ sintered at 1200 °C shown in Fig. 2b. Actually, this AGG phenomenon is very common in $\text{A}^{2+}\text{Nb}_2\text{O}_6$ series ceramics, reported by Pullar [11]. With 0.1 mol TiO_2 additions as shown in Fig. 2c, the AGG seems suppressed for the sample sintered at 1150 °C, giving a dense microstructure with smaller grains. With a higher content of 0.3 mol TiO_2 , AGG reappears in Fig. 2d. Further increasing the TiO_2 content (Fig. 2e–g), the enhanced AGG results in enlarged grains for the samples sintered at an equivalent temperature. Meanwhile, the EDS analyses were also conducted on these samples. To illustrate the variations of compounds in these four phase regions, the element content of the samples with $x = 0, 0.5, 0.6$ and 0.7 were chosen to show in Fig. 2h. With the increase of TiO_2 content, the content of Zn and Nb shows a decrease, while that of Ti increases. Under the detection accuracy of EDS analysis, it indicates that the proportion of each element is close to its nominal composition of the compounds in these four phase regions. The result is consistent with that of XRD characterization.

As is well known, among the key parameters of MWDCs, ϵ_r , $Q \times f$ and τ_f , the origin of microwave dielectric loss ($Q \times f$) is the least understood and is the overall embodiment of intrinsic and extrinsic factors. Intrinsic losses are dependent on crystal structure, which can be described by the nonequilibrium phonon distribution under an ac electric field; while extrinsic losses are associated with the imperfections in crystal structure, including impurity, porosity, grain size, grain boundary, etc. [4,5,28]. In fact, dielectric losses are mainly dominated by extrinsic factors and are not the same in all cases. In general, for a certain composition, the microwave dielectric properties (ϵ_r and $Q \times f$ value) would reach their maximum values under optimized sintering temperatures, hence their variations against sintering temperature almost share a similar trend with that between density and sintering temperature. However, it does not always follow this trend for some compositions of $(1-x)\text{Zn}_{1.01}\text{Nb}_2\text{O}_6-x\text{TiO}_2$. The variations of bulk density, ϵ_r and $Q \times f$ value for $0.9\text{Zn}_{1.01}\text{Nb}_2\text{O}_6-0.1\text{TiO}_2$ ceramics are depicted in Fig. 3. It can be clearly seen that the bulk densities and dielectric constants follow a typical increase-then-decrease variation, and their maximum values occur at an optimized sintering temperature of 1150 °C; while the $Q \times f$ values still increase with the increase of sintering temperature. As the grain size show an increase with increasing sintering temperature, the number of grain boundaries per

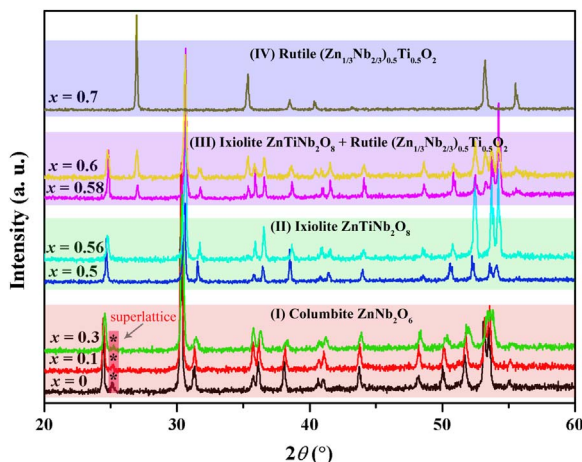


Fig. 1. XRD patterns of $(1-x)\text{Zn}_{1.01}\text{Nb}_2\text{O}_6-x\text{TiO}_2$ ($x = 0, 0.1, 0.3, 0.5, 0.56, 0.58, 0.6$ and 0.7) ceramics sintered at 1200 °C.

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