

Influence of sintering process on the microwave dielectric properties of $\text{Bi}(\text{V}_{0.008}\text{Nb}_{0.992})\text{O}_4$ ceramics

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ABSTRACT

Relationship between sintering process, relative density (shrinkage), grain morphological parameters and microwave dielectric properties of $\text{Bi}(\text{V}_{0.008}\text{Nb}_{0.992})\text{O}_4$ ceramics was studied. Influence of incubation time and sintering temperature on the microwave dielectric properties was discussed. The experiential logarithmic relationship and the parabola relationship were used to simulate the relationship between microwave permittivity, different incubation time and different sintering temperatures, respectively. Modification of Bosman and Havinga's correction was used to eliminate the influence of pores on the permittivity of ceramics. The experimental, calculated and modified results corresponded well with each other. Morphological parameters of grains and pores were found to have dominant influence on microwave dielectric loss and the qualitative relationship was given. The best microwave dielectric properties were obtained in ceramics sintered at 830 °C for 2 h with heating ratio of 3 °C min⁻¹ with permittivity about 40 and Qf reaching 18,500 GHz while relative density was only about 93.5%.

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1. Introduction

The microwave dielectrics with high permittivity (>20), low dielectric loss (<10⁻³) and low sintering temperature have played a more and more important role in LTCC (low temperature co-firing ceramic) technology. Both the permittivity and the dielectric loss are often affected by many factors during the sintering process. It is necessary to make sure about the influence of the sintering process on microwave dielectric properties.

The sintering process could be thought as the transformations of a huge number of particles to dense ceramics. Sintering is a phenomenon of particle bonding with the activation of heat. The common interface between particles increases with time by viscous flow or atomic diffusion [1–4]. Microscopically, the sintering process is a result of both surface motion and grain boundary motion to minimize the total sum of surface energy and grain boundary energy. Macroscopically, sintering is simply described as a densification, that is, an increase in bulk density with a decrease in pore volume [5,6].

BiNbO_4 ceramic has attracted much attention since its microwave properties were reported by Kagata et al. [7]. Some modifications of the composition by the addition of oxides [8–11], substituting for A or B site [12–17] have been studied broadly. BiNbO_4 was found to be easy densified with a little amount of V_2O_5

addition or substitution and microwave dielectric properties as a function of V_2O_5 amount has been studied in detail [7,17]. But there are also many equivocal extrinsic contributions to the Qf values at microwave region and it is difficult to distinguish each one from the others. The origin of microwave dielectric loss could only be explained by the complex effect of various influence factors in most cases.

In order to study the influences of the extrinsic contributions on Qf values, $\text{Bi}(\text{V}_{0.008}\text{Nb}_{0.992})\text{O}_4$ ceramic was chosen as an example and two kinds of sintering processes were proposed in this work. To investigate the microwave dielectric properties, the equations for shrinkage have to be established first. Many ideal models have been designed but most of them corresponded poorly to the real results. The so-called phenomenological theory was used in this work. Some experimental formulas were well proposed. The calculated and measured results correspond well with each other. Considering the residual porosity of ceramics, Bosman and Havinga's correction [18,19] was modified a little and the corrected calculated results correspond well with the measured results. The contributions to dielectric loss at microwave regions could be mostly attributed to the microstructure of pores and grain under the two given sintering processes in this work and were discussed in detail.

2. Experimental

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., China), Nb_2O_5 and V_2O_5 (>99%, Zhu-Zhou Harden Alloys Co., Ltd., China) were mixed according to the composition $\text{Bi}(\text{V}_{0.008}\text{Nb}_{0.992})\text{O}_4$ and ball-milled for 4 h with alcohol in a nylon container with ZrO_2 balls. The mixtures were dried and calcined at 700 °C for 4 h. Then the mixtures were re-milled, and after

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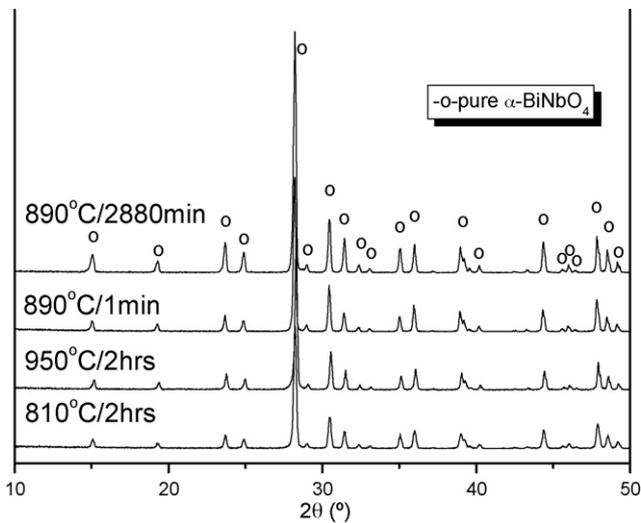


Fig. 1. XRD patterns of BiNbO₄ samples under various sintering conditions.

drying, the powder with 5 wt.% PVA binder was uniaxially pressed into pellets and cylinders in a steel die.

Then the green samples were sintered according to the two kinds sintering courses: various incubation times at a fixed temperature, various sintering temperatures with the same incubation time. According to the two sintering courses, one kind of samples was sintered in the temperature range from 810 °C to 950 °C for 2 h and another kind was sintered at 890 °C from 1 min to 48 h. The heating ratio was always 3 °C min⁻¹.

The bulk densities of the sintered ceramics were measured using the Archimedes method. After surface being polished, the crystalline structures of the Bi(V_{0.008}Nb_{0.992})O₄ ceramics were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). To investigate the morphology of the samples, the surface of the samples were observed by scanning electron microscopy (SEM) (JEOL JSM-6460, Japan). The dielectric constants ϵ_r and the quality values Q at microwave frequency region were measured using the TE₀₁₈ mode resonator method [20]. A network analyzer (8720ES, Agilent, U.S.A.) and a TE₀₁₈ mode dielectric resonator were employed in the measurements.

The morphological parameters of the grains of ceramics were determined using SEM micrographs, using at least 50–400 grains in each case. The average grain sizes were calculated by the line intercept method (length, width and two diagonals were used). In order to consider influence of shape on the grains, the aspect ratio was defined as the ratio between the maximum length and the minimum width taken perpendicular to the length in the planar section of the grains. For a certain ceramic sample, the aspect ratios of grains were measured using about 50 relative intact grains observed in the SEM photos.

3. Results and discussion

XRD patterns of samples sintered at different temperatures for different time are shown in Fig. 1. As known to all, BiNbO₄ has two kinds of structures, orthorhombic (α) phase and triclinic (β) phase, and the former one changes to the later at above 1020 °C [21,22]. Only the pure orthorhombic phase is revealed from XRD results of all kinds of ceramics. In fact, all the ceramics used here belong to orthorhombic structure and only several typical results were listed in Fig. 1. Thus the influence of the second phase on microwave dielectric properties is not considered here in the following.

The pore's shrinkage and grain growth were the major phenomena occurring simultaneously during the sintering process. The dielectric properties of ceramics are strongly dependent on the microstructural features such as grain size, shape and size distribution, total porosity and pore size distribution. In order to analyze the influence of the microstructural features, the model and equation of shrinkage have to be established firstly. Although the simulations using computer have been developed quickly and used to explain some simple example successfully since 1970s, it is still difficult to simulate the real sintering process by a computational model. On the other hand, the so-called phenomenological theory

[23] is mostly practical to simulate experimental results although it lacks some theoretical explanation and support. For samples sintered for different time, the experiential logarithmic relationship is considered as the following:

$$\rho - \rho_0 = k \ln \left(\frac{t}{t_0} \right) \quad (1)$$

where ρ is the relative density while the ρ_0 is the initial value of density, t is the sintering time, k and t_0 are the physical parameters related with the materials, sintering process and grain growing process. For samples sintered at different temperatures, the parabola relationship is assumed as following considering the sintering curve:

$$\rho - \rho_0 = a + bT + cT^2 \quad (2)$$

where T is the sintering temperature, a , b and c are mathematical parameters to be solved, whose physical meanings are not very clear. The effect of porosity dominates the changing trend of permittivity at microwave regions. BiNbO₄ ceramics can be thought as a mixture of BiNbO₄ grains and pores. The large difference of permittivity between them deteriorates dielectric constants of samples ($\epsilon_{\text{BiNbO}_4} \approx 43$, $\epsilon_{\text{air}} \approx 1$). This influence could be eliminated by applying Bosman and Havinga's correction [18,19] as shown in Eq. (1) with some modification considering the real case of ceramics. This correction could be used for very dense ceramics with porosity lower than 5%:

$$\epsilon_{\text{Bosman}} = \epsilon_m [1 + \gamma(P - P_0)] = \epsilon_m [1 + \gamma(1 - \rho - 0.035)] \quad (3)$$

where ϵ_{Bosman} and ϵ_m are corrected and measured dielectric constants, respectively. P is fractional porosity and γ equals to 2, which is the correction coefficient. Considering the remnant pores that could not be expelled from ceramics, the remnant fractional porosity P_0 is introduced and its value is 0.035 according to the percentage density in this work.

Microwave dielectric loss includes two parts: intrinsic loss and extrinsic loss. Intrinsic losses are caused by absorptions of phonon oscillation and extrinsic losses are caused by lattice defect (impurity, cavity, substitution, grain boundaries, size and shapes of grains, second phase, pores, etc.) [24]. Intrinsic losses could be extrapolated from the absorption of IR and it is thought to be not influenced by the sintering behavior [25,26]. The correlation between infrared and microwave dielectric properties of BiNbO₄ ceramics substituted with V₂O₅ has been studied by Kamba et al. [27]. Extrinsic losses are caused by inharmonic terms in the crystal's potential energy and it dominates microwave dielectric losses of ceramic samples usually. In ceramics, the grain boundaries, related to the sizes and shapes of grains, interrupt the perfect symmetry of the crystal and act as two-dimensional defects, contributing significantly into extrinsic dielectric loss [28]. In this work under the two given sintering courses, all the extrinsic losses are attributed to the sizes, shapes of grains and the pores.

3.1. Effect of various incubation times

Fig. 2 shows SEM micrographs of BiNbO₄ samples sintered at 890 °C for 1 min to 48 h. Ceramic sintered for 1 min is porous and grains are all in bar shape with length lying between 0.5 μm and 3 μm as shown in Fig. 2. As incubation time is increasing, bar shape grains grow bigger and bigger, then number of pores is reduced and pores are compressed to be smaller and smaller but could not be eliminated from ceramics absolutely. For ceramics sintered for 48 h, sizes of some bar shape grains reach about 10 μm in width and more than 100 μm in length. The pores, grains shape and size will influence microwave dielectric properties seriously. Table 1 shows the morphological parameters of grains. The average equivalent grain size increases from 0.78 μm to 3.06 μm and aspect ratio increases

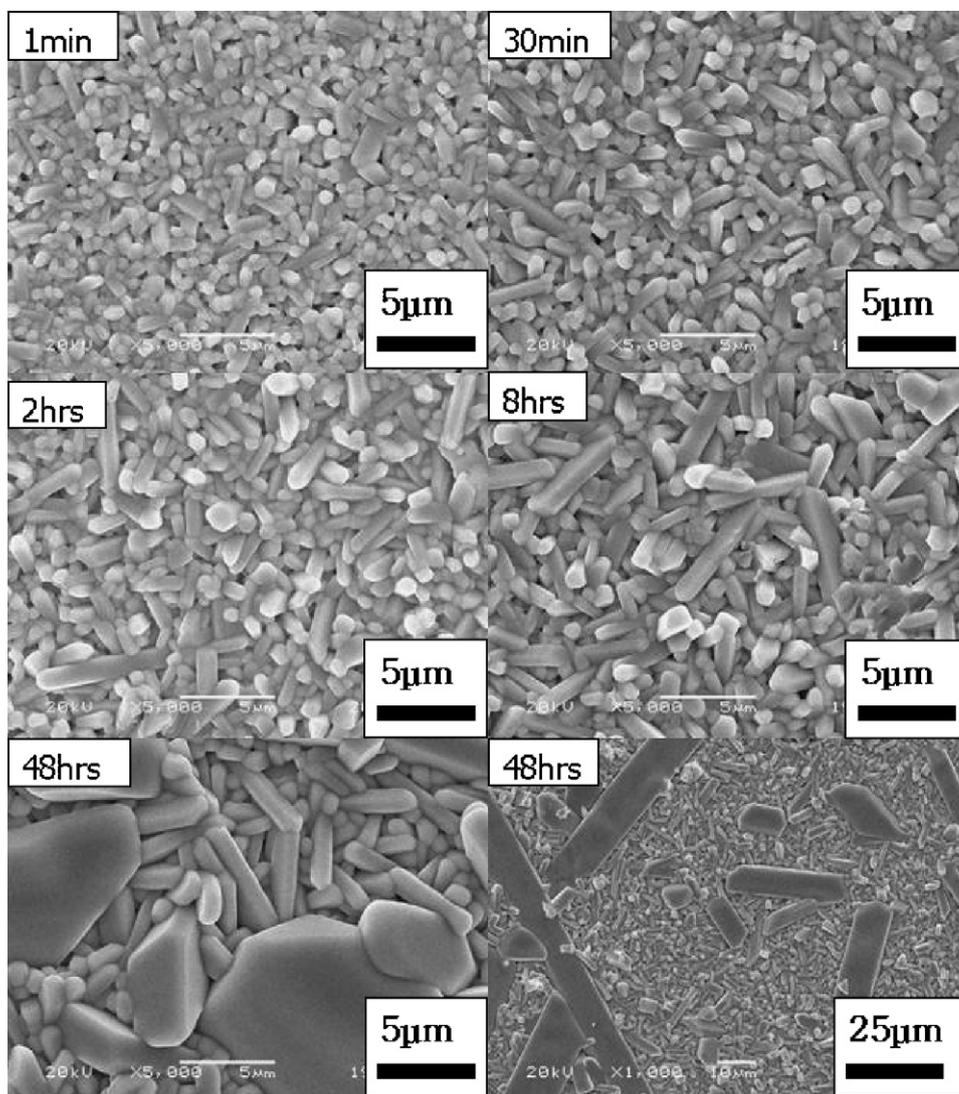


Fig. 2. The SEM micrographs of BiNbO₄ samples sintered at 890 °C for different time.

from 2.97 to 7.37 as the sintering time increased from 1 min to 48 h in average. Grains growth goes with the aspect ratio increase, so the length direction of bar shape grains grows faster than the width direction. In fact the grain size distribution must be bimodal for abnormal grain growth in ceramics in present work, but only the average equivalent values are used considering the convenient discussion for initial work on this field.

Absolute density used to calculate percentage densities is 7.345 g cm⁻³, value of single crystal α -BiNbO₄, and the influence of V₂O₅ substitution was neglected. After parameters of Eq. (1) being well chosen ($k = 0.007$ and $t_0 = 1.5 \times 10^{-5}$), the experiential logarithmic relationship is used to calculate the theoretic values. As shown in Fig. 3, the measured and calculated values correspond well with each other when incubation time is less than 480 min. When incu-

bation time is more than 480 min, calculated relative densities go on to increase as incubation time increased while measured values reaching a saturated value of 0.965. It is because that Eq. (1) is based on an ideal sintering course, in which pores could be abso-

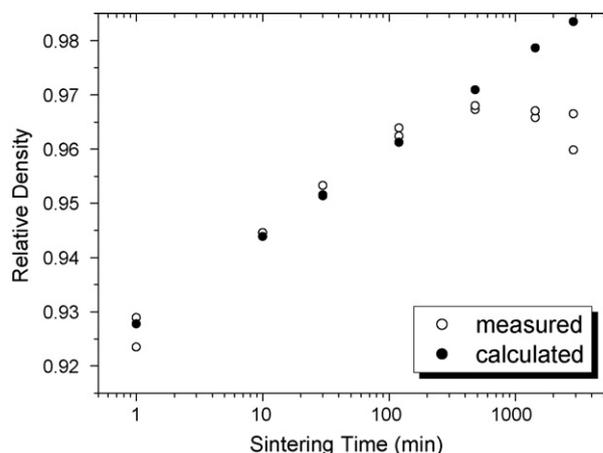


Fig. 3. Measured and calculated relative densities as a function of sintering time for BiNbO₄ ceramics sintered at 890 °C.

Table 1
Morphological parameters of grains for ceramics sintered for various time.

Sintering time (min)	Average size (μm)	Aspect ratio
1	0.78	2.97
30	0.91	3.00
120	1.00	3.83
480	1.16	4.87
2880	3.06	7.37

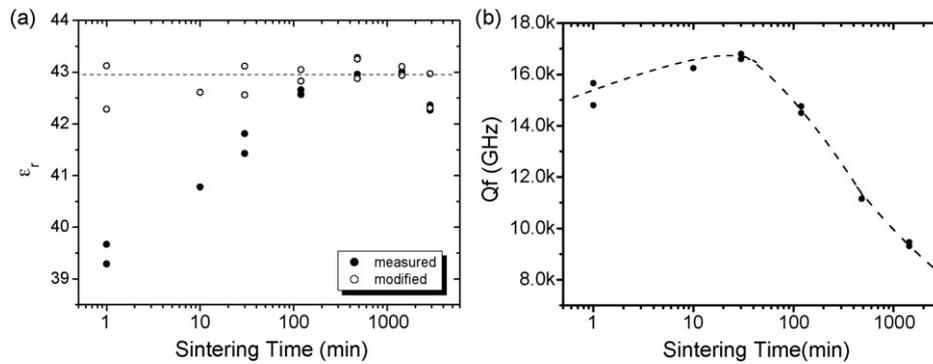


Fig. 4. Microwave dielectric properties of BiNbO₄ samples sintered at 890 °C for various time.

lutely eliminated from ceramics gradually and ideal relative density could reach to theoretic maximum value 1 when incubation time is long enough. But in actual ceramics, pores are sealed and shrunk as incubation time is increased. Consequently, internal pressure of pores will prevent their further shrinkage and the balance of internal and external pressure is established. The different sizes of bar shape grains also offer the feasibility for pores preservation. Finally pores could not be absolutely eliminated from ceramics.

Microwave permittivity of ceramics sintered at 890 °C for various sintering time is shown in Fig. 4(a). It has similar trend with that of relative density shown in Fig. 3. Modified values are calculated using Eq. (3). Real permittivity ϵ_r of BiNbO₄ is about 43 after eliminating the influence of pores. The ϵ_r no longer appears sensitive to sintering time while it reaching 120 min although grains go on growing macroscopically. It seems that there is no clear correlation between ϵ_r and grain size here.

Qf values firstly increase from 15,000 GHz to 16,500 GHz as sintering time increased from 1 min to 30 min as shown in Fig. 4(b). Then it decreases to 8100 GHz when sintering time reaches 2880 min. The microwave permittivity is influenced mostly by pores in ceramics while dielectric loss being influenced by pores and morphological parameters of grains. When sintering time is less than 30 min, Qf values increase slowly having similar trend with that of relative density. It implies that porosity brings negative influence on Qf values of ceramics. To study additional loss terms in a simple manner, we discuss $\tan \delta$ rather than Qf in the following.

Considering volume and surface area of pores with assumed sphericity, the following expression could be obtained [29]:

$$S \propto \left(\frac{P}{1-P} \right)^{2/3} \quad (4)$$

where P is the fractional porosity and S is the surface area of the pores. Considering the two dimension of area affection, the effect of porosity on the dielectric loss $\tan \delta$ could be described as follows [29]:

$$\tan \delta = (1-P)\tan \delta_0 + P(AS) \quad (5)$$

where $\tan \delta$ is the loss tangent of the fully dense material and A is a constant related to materials characteristic. More universal expression could be given as:

$$\tan \delta \propto k_0 + k_1\rho + k_2(1-\rho)\left(\frac{1-\rho}{\rho}\right)^{2/3} \quad (6)$$

k_0 is a constant related to the intrinsic loss, k_1 is related to the loss tangent of the fully dense material, which should depend on the porosity [29], and k_2 is related to the surface area of the pore volume and ρ is the relative density. The $\tan \delta$ should decrease as the ρ increasing due to the complex effect of Eq. (6).

Influence of grains size and shape is difficult to be explained qualitatively for a certain ceramic. Dielectric loss tangent at microwave frequency is mainly caused by anharmonic terms from various kinds of defects. It is known that the grain boundaries act as two-dimensional defects and may contribute significantly into extrinsic dielectric loss. The total number of grain boundaries decreases as increase of average grain size. It is expected that as grain size increases, $\tan \delta$ should decrease because of a reduction in the number of grain boundaries per unit volume. There are some facts supporting this conclusion, such as Kim's work on a study of Ba(Mg_{1/3}Ta_{2/3})O₃ doped with nickel, in which they found that as grain size decreased, $\tan \delta$ increased [30]. Ichinose and Shimada also reported that Qf of Ba(Mg_{1/3}Ta_{2/3})O₃ ceramics gradually increased as grain size increasing and reached a maximum value of 400 THz with average grain size over 9 μ m [28]. In Stuart J. Penn's study, $\tan \delta$ of alumina ceramics with high-density ($98.1 \pm 0.5\%$) remained constant for samples with a grain size less than about 3 μ m and then increased rapidly as the size increasing to more than 6 μ m [29]. But some other researcher's results showed that grain size did not affect $\tan \delta$. It was noted by Iddles that in zirconium tin titanate ceramic grain size did not affect the $\tan \delta$ [31]. Kucheiko et al. found that grain size did not influence $\tan \delta$ in un-doped CaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO₃ ceramics [32]. It is very difficult to make a definite conclusion on the influence of grain size for ceramic samples on dielectric losses.

This problem could be attributed to that the interplay of so many factors (grain size, porosity, ordering, and presence of liquid phases) makes it too difficult to make definitive conclusions only on grain size–dielectric loss relationship. It is undoubted that grain size increasing would decrease the anharmonicity in ceramics and this would diminish $\tan \delta$. Some subsequent effects associating with grain growth will deteriorate dielectric losses. Grain size and pores distributions are deteriorated due to the excess heat activity and unhomogeneity of grains also increased. These factors would increase the anharmonicity of ceramics while the grain growth decreasing it. In another word, ceramics with big and even grain size would have low dielectric loss but this kind of ceramic was difficult to be obtained in most kinds of microwave dielectric ceramics. For the Bi(V_{0.008}Nb_{0.992})O₄ ceramics here, the large bar shape grains were obtained and the aspect ratio of bar shape also increased quickly as the average grain size increased as shown in Fig. 2. These phenomena lead to a complex incremental effect on $\tan \delta$ and Qf values decreased quickly when the sintering time is more than 30 min although relative density and grain size are increased. Considering grain size and shape's effect, the universal expression of dielectric loss $\tan \delta$ could be described as:

$$\tan \delta \propto b_0 + \sum_{i=1}^N b_i(D_i - \bar{D})^n \quad (7)$$

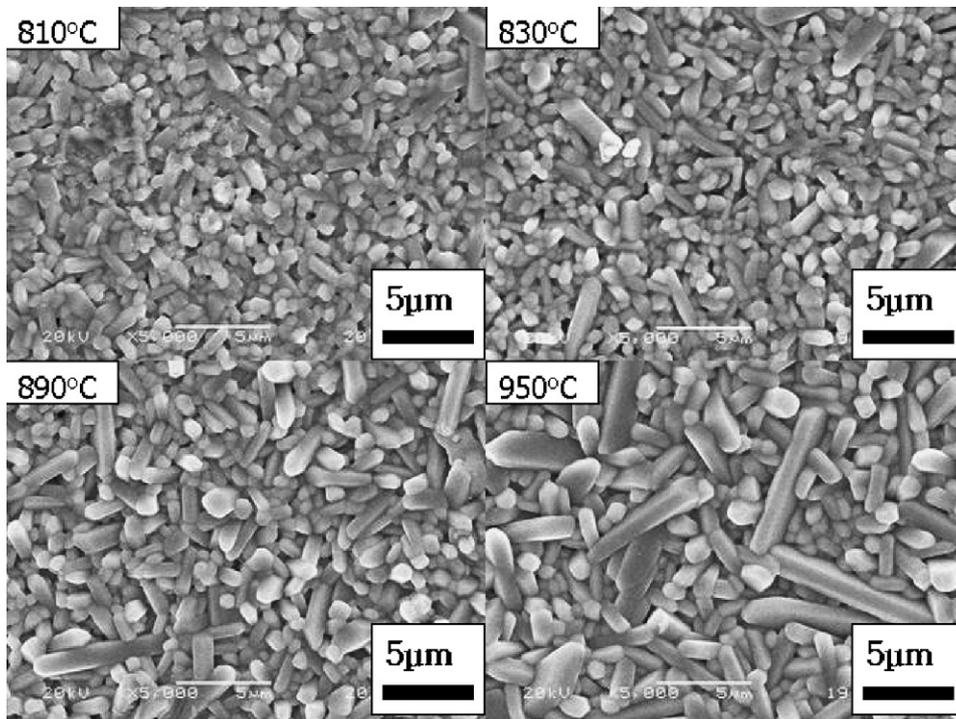


Fig. 5. The SEM micrographs of BiNbO₄ samples sintered at various temperatures for 2 h.

Table 2
Morphological parameters of grains for ceramics sintered at various temperatures.

Sintering temperature (°C)	Average size (μm)	Aspect ratio
810	0.72	2.00
830	0.74	2.28
890	1.00	3.83
950	1.27	5.24

where b_0 a constant related to intrinsic loss of single crystal samples, \bar{D} is the average grain size, N is the number of all the grains, D_i is the effective size of the i th grain, b_i is the parameter related with the shape of the i grain, and n is the error index.

3.2. Effect of various sintering temperatures

As sintering temperature increases, grain sizes increase and number of pores reduces as shown in Fig. 5. Grain growth is similar with that described for Fig. 2. The morphological parameters are shown in Table 2. The average grain size increases from 0.72 μm to 1.27 μm and the aspect ratio increased from 2 to 5.24 as the sintering temperature increased from 810 °C to 950 °C. Both the higher

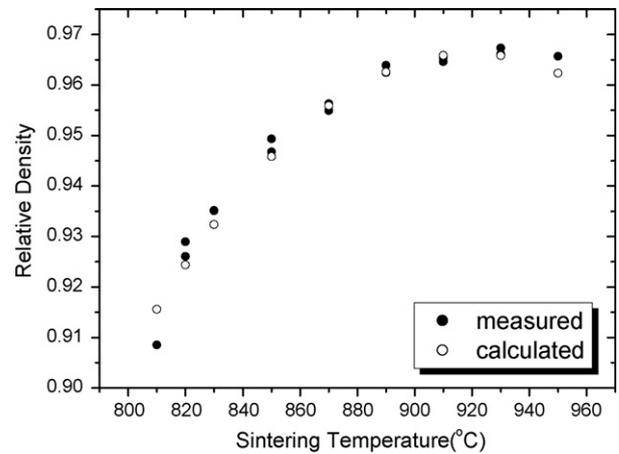


Fig. 6. The relative density of BiNbO₄ ceramics sintered at various temperatures for 2 h.

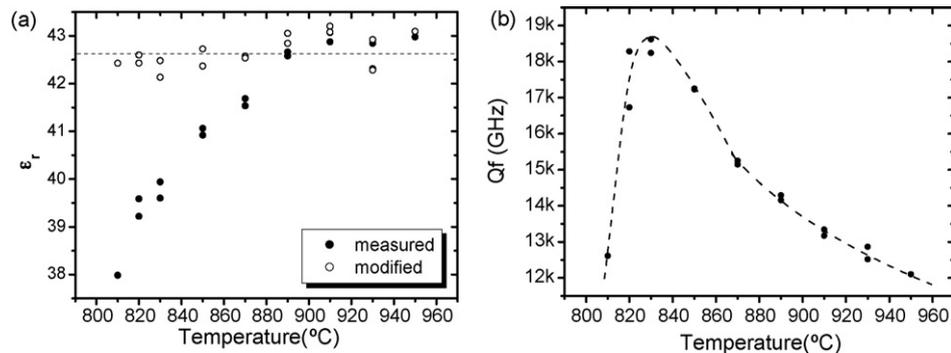


Fig. 7. Microwave dielectric properties of BiNbO₄ samples sintered at various temperatures for 2 h.

temperature and longer incubation time are the impetus for grain growth and aspect ratio increase. From the data in Tables 1 and 2, morphological parameters of samples sintered for a certain time and a certain temperature could be similar with each other. This is the equivalent result and microwave dielectric properties would also be similar with each other.

Fig. 6 shows the relative density of samples sintered at 810–950 °C for 2 h. As sintering temperature increases, relative density increases according to the parabola relationship as shown in Eq. (2). The calculated values are shown in Fig. 6 with parameters given as $a = -2.6$, $b = 7.8 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$, and $c = -4.2 \times 10^{-6} \text{ } ^\circ\text{C}^{-2}$. And they fit well with the measured values.

Microwave permittivity increases from 38 to 42.6 when sintering temperature increases from 810 °C to 890 °C as shown in Fig. 7(a). When above 890 °C, permittivity keeps nearly a constant not changing with sintering temperature because the balance between pores and BiNbO₄ grains is obtained. Using Eq. (3), the modified values are obtained and microwave permittivity of BiNbO₄ is nearly 42.6 which is little smaller than that obtained according to Fig. 4. Qf values increase from 12,500 GHz to 18,500 GHz as sintering temperature increase from 810 °C to 830 °C. Then it decreases to 12,000 GHz for ceramic sintered at 950 °C. As discussed above, when sintering temperature increase number of pores reduces, grain grow bigger and bigger and the aspect ratio also increases, so Qf value would have a maximum at a proper temperature and sharply decreases at higher temperature. As the same heating activation, influences of the two sintering courses on microwave dielectric properties of ceramics are similar.

4. Conclusions

Microwave dielectric properties of Bi(V_{0.008}Nb_{0.992})O₄ ceramics sintered at different conditions have been studied. The experiential logarithmic relationship and the parabola relationship fit the two models (different incubation time and different sintering temperatures) well, respectively before ceramics being well densified. As the amounts of pores decreased, microwave permittivity increases and it reaches saturated with the final remnant pores. Porosity and the unhomogeneity of grains increase the extrinsic microwave dielectric loss while the increase of gains size decrease it. Qualitative conclusions are given by analyzing and summarizing present and some others' work. In this work, the best microwave properties could be obtained in ceramic sintered at 830 °C for 2 h with the permittivity about 40, Qf about 18,500 GHz but the percentage density about 93.5%.

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