

Sintering Behavior and Dielectric Properties of Bi_3NbO_7 Ceramics Prepared by Mixed Oxides and High-Energy Ball-Milling Methods

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The sintering behavior and dielectric properties of Bi_3NbO_7 ceramics prepared by the high-energy ball milling (HEM) method and conventional mixed oxides method with V_2O_5 addition were investigated. All the samples were sintered between 840° and 960°C. For the ceramics prepared by the mixed oxides method, the pure tetragonal Bi_3NbO_7 phase formed without any cubic phase. With changing sintering temperature, the dielectric constant ϵ_r lies between 79 and 92, while the $Q \times f$ values are between 300 and 640 GHz. The samples sintered at 870°C have the best microwave dielectric properties with $\epsilon_r = 79$, $Q \times f = 640$ GHz, and the temperature coefficients of resonant frequency τ_f between 0 and -20 ppm/°C. For the ceramics prepared by the HEM, a pure cubic phase was obtained. The ϵ_r changes between 78 and 80 and $Q \times f$ were between 200 and 290 GHz.

I. Introduction

THE Bi_2O_3 - Nb_2O_5 binary system has good microwave dielectric properties and has attracted attention in recent years. Particularly, studies on BiNbO_4 dielectric ceramics were broadly carried out.¹⁻⁵ Although BiNbO_4 ceramics have good properties for microwave application and LTCC (sintering temperature [ST] $\approx 900^\circ\text{C}$, $\epsilon_r \approx 43$, and $Q \times f > 10\,000$ GHz¹), the reaction between the BiNbO_4 and Ag electrode limited its further application.^{6,7} Compared with BiNbO_4 composition, other compounds in the Bi_2O_3 - Nb_2O_5 binary system have been less studied for microwave applications. But some of them such as Bi_3NbO_7 composition having no reaction with an Ag electrode were believed to have potential value in LTCC modules and microwave application.⁷ Valant and Suvorov⁸ studied the dielectric properties of $(1-x)\text{Bi}_2\text{O}_3-x\text{Nb}_2\text{O}_5$ ($0.10 < x < 0.29$) ceramics. The Bi_3NbO_7 ceramics were obtained at $x = 0.25$, where ϵ_r remained at 91, $Q \times f$ decreased from 700 to 300 GHz, and the temperature coefficients of resonant frequency τ_f decreased from +100 to -200 ppm/°C with the ST increasing from 870° to 940°C. An interesting phase transition was found wherein a pure cubic phase of Bi_3NbO_7 formed at 790° and 950°C, a pure tetragonal phase only formed at 850°C, and cubic and tetragonal phases coexisted at the ST range of 790°-850°C and 850°-950°C. And this transition was described as a homogeneous nucleation with a temperature-dependent induction time and growth kinetics.⁹ In the further study, different microwave dielectric properties for the two phases were found ($\epsilon_r \approx 100$, $Q \times f \approx 300$ GHz, and $\tau_f \approx -200$ ppm/°C for the cubic phase; $\epsilon_r \approx 90$, $Q \times f \approx 700$ GHz, and $\tau_f \approx +100$ ppm/°C for the tetragonal phase).¹⁰

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The reported Bi_3NbO_7 with low ST and good dielectric properties are promising in LTCC, but the large τ_f limited its further applications. Both modification of the composition and new preparation process are possible ways to solve the problem.

High-energy ball milling (HEM) was known as mechanical alloying and has been successfully used as a vehicle for the solid-state reaction. Recently, this mechanochemical ball milling has been used as a method to synthesize materials for various applications, such as nanocrystalline oxide powders,¹¹ solid-state solutions of ceramics,¹² and lead titanate powders,¹³ etc. The most valuable advantage of this technique is that the solid-state reaction is activated via mechanical energy instead of heating energy (high temperature). So this method skips the calcination step, which is necessary in the conventional solid-state method, and the initial reaction takes place at a temperature close to room temperature in a sealed container. Furthermore, the mechanically derived powders possess higher sinterability than those synthesized by a conventional solid-state reaction and most of those by wet-chemical processes.¹⁴

In this paper, the pure Bi_3NbO_7 ceramics were prepared by the HEM method and V_2O_5 was chosen as the additive in the conventional mixed oxides preparation. The sinterability, structure, and microwave dielectric properties of Bi_3NbO_7 ceramics were studied to improve its dielectric properties for LTCC applications.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Chengdu, China) and Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co. Ltd., Zhuzhou, China) were prepared according to the composition Bi_3NbO_7 . Powders were prepared by the conventional solid-state method calcined at 700°C for 4 h with 0.35 wt% V_2O_5 addition. A planetary mill (Nanjing Machine Factory, Nanjing, China) was used for mixing the starting oxides and pulverizing the calcined powders by setting the running speed at 150 rpm with the Zirconia balls (2 mm in diameter) as milling media. The HEM operation was carried out in a Fritsch Pulverisette P4™ vario-planetary HEM system (Fritsch, Idar-Oberstein, Germany) in air at room temperature for 8 h. A 225-mL tungsten carbide container and 50 tungsten carbide balls with a diameter of 10 mm were used as the milling medium. The milling speed of the main disk was set at 400 rpm and the speed of each pair was set at -800 rpm, which means that the rotation speed ratio (R ratio) was -2.0. The ball mass to powder mass ratio (M_B/M_P) was 15:1. The milling was stopped for 20 min for every 30 min of milling to cool down the system and was interrupted after each hour to decant samples for analysis. The tungsten contamination was detected with elemental analysis by alternating current arc atomic emission spectrum (AES; WPG-100 Grating Spectrograph, Rayleigh Analysis Instrument Company, Beijing, China).

Both kinds of powders were uniaxially pressed into pellets and cylinders in a steel dye with 5 wt% PVA binder. Then, the pellets and cylinders were sintered from 840° to 960°C for 2 h in air.

After the surface was polished, the crystalline structures of the samples were investigated using X-ray diffractometry with $\text{CuK}\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). To investigate the morphology of the samples, the surface of the sintered specimens was observed by an SEM (JEOL JSM-6460, Tokyo, Japan). A laser-scattering Particle Size Analyzer (Brookhaven BI-90, Holtsville, NY) was used for particle size measurement.

Dielectric behaviors at microwave frequency were measured by the $\text{TE}_{0,18}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA). The temperature coefficients of resonant frequency τ_f were measured with the 8720ES network analyzer and a DELTA 9023 temperature chamber (Delta Design, Poway, CA) using the $\text{TE}_{0,18}$ shielded cavity method. The τ_f was calculated by the following formula:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \quad (1)$$

where f_T, f_0 are the $\text{TE}_{0,18}$ resonant frequencies at 85° and 25°C , respectively.

III. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of Bi_3NbO_7 ceramics sintered at different temperatures by both methods. The cubic phase was found to form in both samples sintered at 700°C for 4 h either by the conventional method with sharp peaks or by HEM with broader peaks, which might be caused by the stress generated by HEM as well as smaller particles (particle size analysis results showed that the HEM method produced particles about 100 nm in average while the conventional method yielded particles about 800 nm in average). For samples prepared by the conventional mixed oxides method with V_2O_5 addition, the tetragonal phase formed at $840^\circ\text{--}960^\circ\text{C}$. The XRD patterns for sample sintered at 900°C showed a trace of an unknown phase (like $\text{Bi}_5\text{Nb}_3\text{O}_7$) and this is similar to Valant and Suvorov's results.⁸ This phenomenon needs to be studied further and the occurrence of the unknown phase was only related to the ST. In Valant and Suvorov's work,⁸ a cubic-tetragonal-cubic phase transition occurred. However, the cubic phase was not observed in the densified ceramics in this work. This implies that the addition of V_2O_5 effectively restrained the occurrence of the cubic phase, and a pure tetragonal phase could be obtained. For samples prepared by the HEM method, only the cubic phase was obtained in the samples sintered between 870° and 960°C and the peak became sharper with increasing ST. The tungsten contamination was

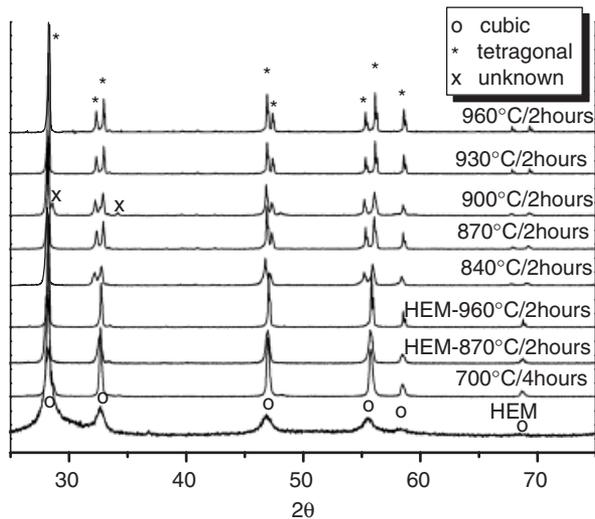


Fig. 1. X-ray diffraction patterns of Bi_3NbO_7 ceramics sintered at different temperatures by both methods.

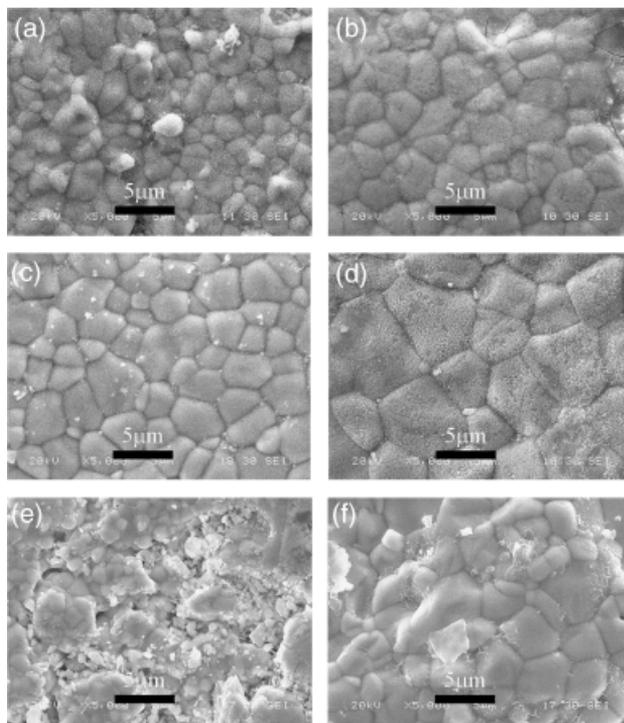


Fig. 2. SEM micrographs for $\text{Bi}_3\text{NbO}_7\text{-V}_2\text{O}_5$ ceramics sintered at (a) 840°C , (b) 870°C , (c) 900°C , and (d) 930°C , and for high-energy ball milling samples sintered at (e) 870°C and (f) 900°C .

found to be incorporated into the samples during the HEM method and its amount reached 0.15 wt% by the AES analysis. Besides the high-energy mechanical activation, the tungsten contamination might be a reason for the high stability of the cubic phase in the samples by HEM.

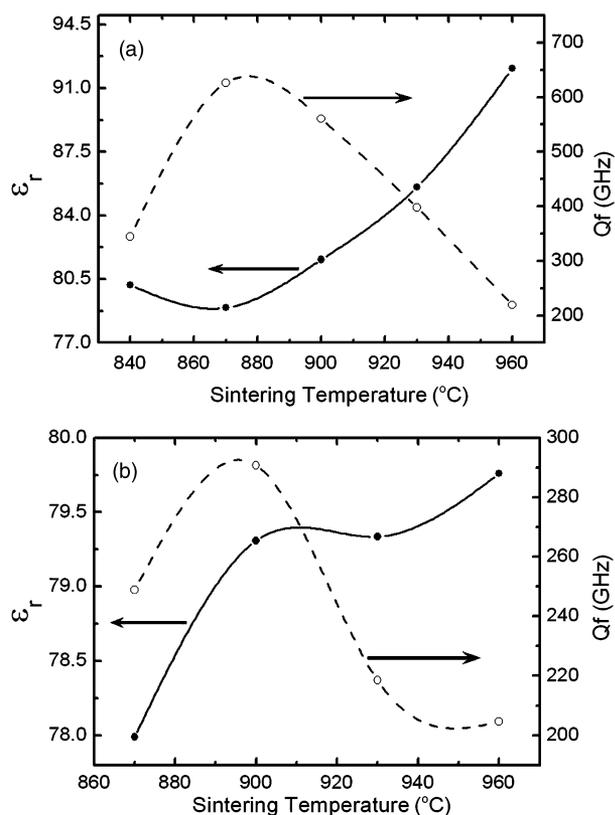


Fig. 3. Dielectric properties as a function of sintering temperature for Bi_3NbO_7 ceramics with V_2O_5 addition (a) and for that prepared by high-energy ball milling (b).

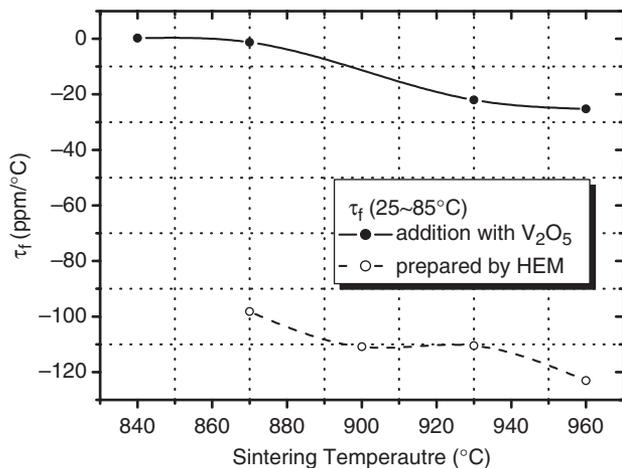


Fig. 4. τ_f as a function of sintering temperature of Bi_3NbO_7 ceramics.

The SEM micrographs of the samples sintered at different temperatures by both methods are shown in Fig. 2. For $Bi_3NbO_7-V_2O_5$ ceramics, the grain size is between 1 and 3 μm sintered at 840°C and the grain growth is not homogeneous as shown in Figs. 2(a). With increasing ST, homogeneous fine microstructures with almost no pores were revealed in the samples sintered at 870°C and 900°C as shown in Fig. 2(b) and (c). When ST increased to 930°C, the secondary grain growth was observed with a grain size larger than 5 μm , which would deteriorate the microwave properties. For samples prepared by HEM, the porous microstructures were observed for the sample sintered at 870°C and a well-densified ceramic was obtained sintered at 900°C as shown in Figs. 2(e) and (f).

The microwave dielectric properties of $Bi_3NbO_7-V_2O_5$ ceramics were shown in Fig. 3(a). With an increase in ST from 840° to 870°C, the $Q \times f$ values increased from about 350 GHz to about 640 GHz. Then, the $Q \times f$ values decreased with increasing ST further because of the secondary growth of grains. The ϵ_r reached minimum of 79 at 870°C and then increased to 92 when the ST increased to 960°C. In Valant and Suvorov's study,⁸ pure Bi_3NbO_7 ceramics could be obtained at 790°–950°C after being calcined twice at different temperatures. Its ϵ_r changed between 90 and 100 while $Q \times f$ were between 300 and 700 GHz. So it is obvious that the addition of V_2O_5 decreases the ϵ_r of Bi_3NbO_7 ceramics slightly but has little effect on the $Q \times f$ values. Fig. 3(b) shows the dielectric properties of samples prepared by the HEM method. The permittivity changes between 78 and 80 while $Q \times f$ was between 200 and 290 GHz. The best properties have been obtained in the samples sintered at 900°C and this corresponds well with the microstructures. The cubic phase seems to have a larger dielectric loss in the microwave region than that of the tetragonal phase of Bi_3NbO_7 ceramics, while their permittivities are similar.

The τ_f of $Bi_3NbO_7-V_2O_5$ ceramics decreased from +0.2 to -1.2 ppm/°C, and -21.9 ppm/°C with an increase in ST from 840° to 870° and 930°C as shown in Fig. 4. In Valant and Suvorov's work,⁸ the τ_f values of pure Bi_3NbO_7 ceramics changed between +100 and -200 ppm/°C. This implies that

the addition of V_2O_5 effectively improves the properties of τ_f values and thus the Bi_3NbO_7 ceramics with V_2O_5 addition is more close to practical applications. Moreover, the τ_f values are not very sensitive to the ST. The τ_f of samples prepared by HEM is shown in Fig. 4. It decreased from -98 to -125 ppm/°C as the ST increased from 870° to 960°C. This implies that the cubic phase of Bi_3NbO_7 prepared by HEM may not suitable for application due to its very large τ_f value.

IV. Conclusion

Pure tetragonal phase Bi_3NbO_7 were obtained at an ST range of 840°–960°C by the conventional mixed oxides method with V_2O_5 addition. The best properties of the samples with $\epsilon_r = 79$, $Q = 198$, and $Q \times f = 640$ GHz, $\tau_f = -1.2$ ppm/°C have been obtained at ST 870°C. For the samples prepared by HEM, a pure cubic phase was obtained between 870° and 960°C, and the best properties of the ceramics with $\epsilon_r = 79.3$, $Q \times f = 290$ GHz, $\tau_f = -110$ ppm/°C were obtained at ST 900°C. This work provides simple and dependable methods to prepare a pure phase of Bi_3NbO_7 ceramics and also makes it promising for LTCC applications.

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