

Nanopowder Preparation and Dielectric Properties of a $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ Binary System Prepared by the High-Energy Ball-Milling Method

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The high-energy ball-milling (HEM) method was used to synthesize the compositions of BiNbO_4 , $\text{Bi}_5\text{Nb}_3\text{O}_{15}$, and Bi_3NbO_7 in a $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ binary system. Reagent Bi_2O_3 and Nb_2O_5 were chosen as the starting materials. The X-ray diffraction patterns of the three compositions milled for different times were studied. Only the cubic Bi_3NbO_7 phase, Nb_2O_5 , and amorphous matters were observed in powders after being milled for 10 h. After heating at proper temperatures the amorphous matters disappeared and the proleptic phases of BiNbO_4 and $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ could be obtained. The Scherrer formula was used to calculate the crystal size and the results of nanopowders are between 10 and 20 nm. The scanning electron microscopy photos of Bi_3NbO_7 powders showed drastic aggregation, and the particle size was about 100 nm. The dielectric properties of ceramics sintered from the nanopowders prepared by HEM at 100–1 MHz and the microwave region were measured. Bi_3NbO_7 ceramics showed a good microwave permittivity ϵ_r of about 80 and a $Q \times f$ of about 300 at 5 GHz. The triclinic phase of BiNbO_4 ceramics reached its best properties with $\epsilon_r = 24$ and $Q \times f = 14000$ GHz at about 8 GHz.

I. Introduction

PHASES of the $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ binary system were first studied in detail by Roth and Waring.¹ Then, some researchers had carried out some work to modify and this system. The dielectric properties of some important compositions such as BiNbO_4 , $\text{Bi}_5\text{Nb}_3\text{O}_{15}$, and Bi_3NbO_7 , have also been studied.^{2–4} Since the microwave dielectric properties of BiNbO_4 ceramic were reported,⁵ some modifications in this composition by substitution or doping have been carried out.^{6–8} But the reaction between BiNbO_4 and the important electrode Ag limited its further application.^{9,10} Valant studied the microwave dielectric properties of Bi_3NbO_7 ceramics and found that they are suitable for LTCC modules and microwave application.⁴ Besides the modification of compositions, the novel and practical process methods also played an important role in the application.

In general, the conventional solid-state reaction method always needs relatively high temperatures and long times of reaction. In order to avoid these problems, mechanochemical activation synthesis of materials has become popular in recent years. High-energy ball-milling (HEM) was known as a very novel 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 pow-

ders,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). Hence, 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 a higher sinterability than those synthesized by a conventional solid-state reaction and most of the wet-chemical processes.¹⁴ Castro and Palem¹⁵ conducted some studies of the $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$, $\text{Bi}_2\text{O}_3\text{--Ta}_2\text{O}_5$, and $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5\text{--Ta}_2\text{O}_5$, systems using different starting compositions and mechanical activation devices (vibrating and planetary ball mills). They found that the amorphous precursors were easy to obtain first and Bi_3MO_7 ($M \sim \text{Nb, Ta}$) fluorites were obtained as the annealing temperature was further increased. In our previous work,¹⁶ the pure tetragonal phase of Bi_3NbO_7 ceramic was obtained by the HEM method. It has high stability and cannot be transformed to the cubic phase by heating at high temperatures.

In this work, the preparations of BiNbO_4 , $\text{Bi}_5\text{Nb}_3\text{O}_{15}$, and Bi_3NbO_7 powders by the HEM method using different milling times were described in detail. Ceramics were also obtained using a conventional solid-state reaction (CSR) method to make some comparisons. The phases and the microstructures of the powders were given. The dielectric properties of ceramics at 100–1 MHz and microwave region were measured and discussed.

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 compositions of BiNbO_4 , $\text{Bi}_5\text{Nb}_3\text{O}_{15}$, and Bi_3NbO_7 , respectively. A planetary mill (Nanjing Machine Factory, Nanjing, China) was used for mixing the starting oxides by setting the running speed at 150 rpm with the Zirconia balls (2 mm in diameter) as the milling media. The dried powders were calcined at 800°C for the CSR method. The HEM operation was carried out in a Fritsch Pulverisette P4™ vario-planetary HEM system (Fritsch, Germany) in air at room temperature for 10 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 various analyses described below. After being milled for 10 h, some of the powders were calcined at different temperatures for 2 h and other powders were uniaxially pressed into pellets and cylinders in a steel die with 5 wt% PVA binder for the dielectric behavior measurements.

The powder samples were investigated using X-ray diffractometry with $\text{CuK}\alpha$ radiation (Rigaku D/MAX-2400 X-ray

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diffraction, Tokyo, Japan). To calculate the crystal size of the samples, the Scherrer formula was used:

$$D_{hkl} = \frac{K \times \lambda}{(\text{FWHM} - \text{FW}) \times \cos \theta} \quad (1)$$

where K is the shape factor, often valued between 0.89 and 0.94, λ is the wavelength of incidence, FWHM is the calculated width of half-height, FW is the broadening from the equipment (valued at 0.2 here), and θ is the Bragg angle. To investigate the morphology of the samples, the powder samples were observed by scanning electron microscopy (SEM) (JEOL JSM-6460, Tokyo, Japan).

Dielectric behaviors between 100–1 MHz were measured by an LCR analyzer (4284, Agilent, Santa Clara, CA). Microwave dielectric properties were measured by the TE₀₁₈ shielded cavity method with a network analyzer (8720ES, Agilent, Santa Clara, CA).

III. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of BiNbO₄ samples milled for different times by the HEM method, calcined, and sintered at different temperatures. After being milled for half an hour, the XRD patterns show mixed phases of the original materials. Then, the main phase of cubic-Bi₃NbO₇ was

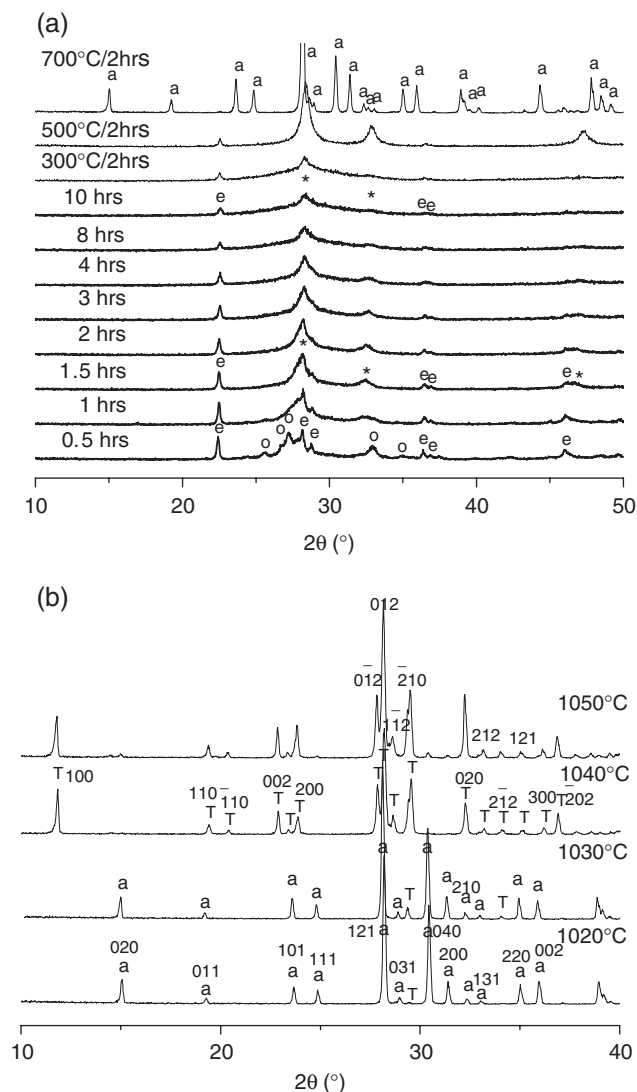


Fig. 1. X-ray diffraction patterns of BiNbO₄ powder samples (a) and sintered pellet samples (b) prepared by the high-energy ball milling method.

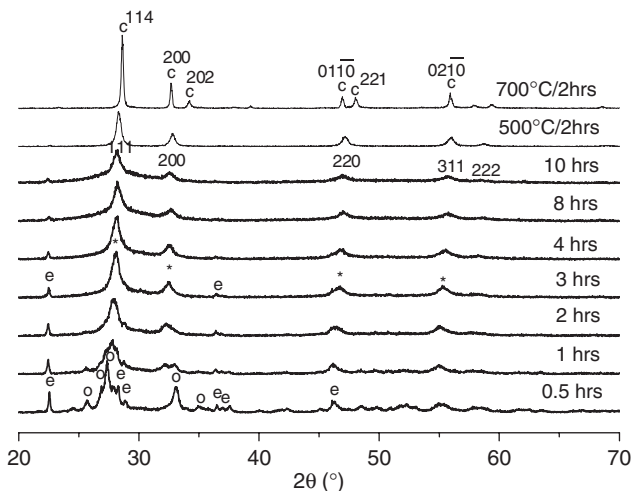


Fig. 2. X-ray diffraction patterns of Bi₅Nb₃O₁₅ samples prepared by the high-energy ball milling method.

formed while remnant Nb₂O₅ also existed after being milled for about 2 h. These two main phases remain in the powders despite being milled for 10 h. As the milling time increased, the peaks were broadened slightly and became weaker and weaker because of the formation of the amorphous matters. After being calcined at 300° and 500°C for 2 h, the amorphous matters formed nanocrystals and the crystal particles grew larger and larger. The XRD peaks became sharp again. After being calcined at 700°C for 2 h, the cubic Bi₃NbO₇ and the remnant Nb₂O₅ reacted and the pure phase of α-BiNbO₄ was observed as shown in Fig. 1(a). Figure 1(b) shows the XRD patterns of pellet samples sintered at different temperatures for 2 h. When the sintering temperature reached 1020°C, a triclinic phase of BiNbO₄ appeared. As the sintering temperature increased, more and more orthorhombic phase transformed into a triclinic phase. For the sample sintered at 1040°C/2 h, only the pure triclinic phase could be observed. Similar corresponding results were reported by Keve and Skapski.¹⁷ Ceramics prepared by both the methods showed similar XRD results.

Figure 2 shows the XRD patterns of Bi₅Nb₃O₁₅ samples milled for different times and calcined at different temperatures by the HEM method. Similar to the results of the BiNbO₄ samples, the main phases of cubic-Bi₃NbO₇ and Nb₂O₅ were revealed after being milled for about 2 or 3 h. These two phases exist in powders after being milled for 10 h. After being calcined at 500°C for 2 h, peaks of the cubic-Bi₃NbO₇ phase became sharp and nearly no trace of Nb₂O₅ phase was revealed. Compared with the results of the BiNbO₄ samples mentioned above, Nb₂O₅ might be the main source of amorphous matters. After the powders were calcined at 700°C for 2 h, a pure orthorhombic Bi₅Nb₃O₁₅ phase was formed and the peaks matched well with the results reported by Takenaka *et al.*³ Table I shows the crystal size of Bi₅Nb₃O₁₅ powders calculated from the Scherrer formula using different crystal directions. The crystal sizes changed

Table I. Crystal Size (nm) of Bi₅Nb₃O₁₅ Samples Calculated from the Scherrer Formula

Milling time (h)	Crystal direction			
	111	200	220	311
3	14.6	19.2	10.7	11.8
4	14.2	16.1	10.5	16.3
8	13.3	17.7	13.3	10.4
10	14.0	20	11.3	15
Calcined at 500°C/2 h	38.4	43.4	40.5	47.5

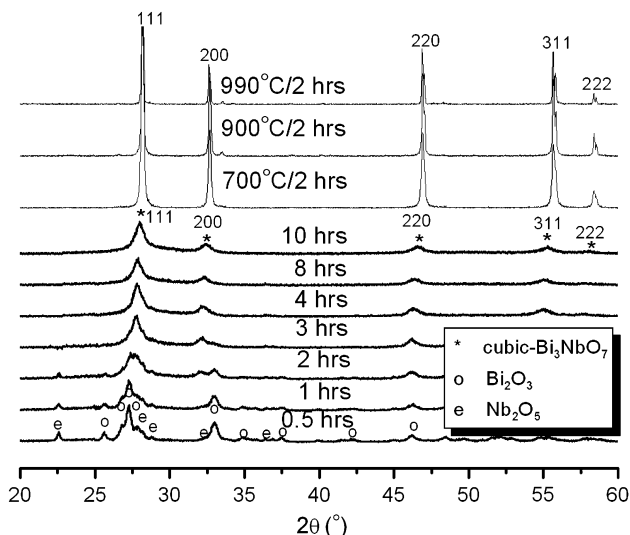


Fig. 3. X-ray diffraction patterns of Bi_3NbO_7 samples prepared by the high-energy ball milling method.

between 10 and 20 nm for various powder samples. There were many factors that influenced the calculated sizes drastically. The choice of angles' range of the calculated peaks and the different broadening to different peaks from the equipment dominate the main errors. There is no clear rule for the crystal sizes calculated by the same peak with increasing milling time. The results calculated from different crystal directions differ from each other but the errors were acceptable. The crystal size reached about 40 nm for powders calcined at 500°C for 2 h. The heat treatment accelerates the growth of the crystal particles and that of crystallization amorphous matters.

Figure 3 shows the XRD patterns of Bi_3NbO_7 samples milled for different times by the HEM method and calcined at different temperatures. After being milled for about 2 or 3 h, a pure cubic- Bi_3NbO_7 phase was formed. The peaks became slightly weak and broadened as the milling time increased. This indicates that the powders of the pure cubic- Bi_3NbO_7 phase with no Nb_2O_5 were influenced weakly by the milling time, and the amount of amorphous matter was also less than that of powders with remnant Nb_2O_5 . The mixed phases of cubic and tetragonal Bi_3NbO_7 were observed in ceramics sintered at 900°C prepared by the traditional mixed-oxide method by Valant and Suvorov.⁴ But in this work, after calcination at 700° , 900° , and 990°C for 2 h, only the pure cubic- Bi_3NbO_7 phase was observed in the XRD patterns. This phenomenon may be caused by the activation of mechanochemistry or the contamination introduced by the HEM method as discussed in our previous work.¹⁶ The crystal sizes of Bi_3NbO_7 samples calculated from the Scherrer formula are shown in Table II. The crystal sizes change between 13 and 23 nm for various powder samples.

Figures 4(a) and (b) shows the SEM photos of BiNbO_4 and Bi_3NbO_7 compositions after being milled for 10 h. It is obvious that the aggregation of the nanocrystals is prevalent in the powders. It is difficult to distinguish between the nanocrystals and amorphous matters. The ideal model is that the nanocrystals

Table II. Crystal Size (nm) of Bi_3NbO_7 Samples Calculated from the Scherrer Formula

Milling time (h)	Crystal direction			
	111	200	220	311
3	13.7	20.9	22.2	13.3
4	14.7	16.8	15.8	15.6
8	15.3	18.4	14.1	13.5
10	15.2	15.5	15.1	15.6

scatter in the amorphous matters. The size of the aggregated particle is larger than 100 nm, which includes hundreds of nanocrystals and amorphous matters as shown in Figs. 4(a) and (b). The defects and stress introduced by the high energy from mechanochemistry caused high surface activation of the nanocrystals and it also accelerated the formation of large and firm particles. There are no simple and efficient methods to smash the large aggregated particles; thus, the respective studies of the nanocrystal and amorphous matters were slightly difficult. SEM photos of the natural surface and the fracture surface of ceramics sintered at 990°C for 2 h prepared by HEM and CSR methods are shown in Figs. 4(c)–(f). The grain size of ceramics prepared by the two methods was between 1 and 3 μm . The natural surface looked more densified than the fracture surface. From microstructure of fracture surface, ceramics prepared by HEM seemed to have little pores compared with that of ceramics prepared by CSR. From Fig. 4(g) (SEM photo with small magnifying multiples of ceramics sintered at $990^\circ\text{C}/2$ h prepared by HEM), several of microcracks on the sample's surface could be observed. This phenomenon should be attributed to the characteristic of initial nanopowder powders prepared by HEM. These microcracks led to the smaller densities of the ceramics prepared by HEM than that of the ceramics prepared by CSR.

Figure 5 shows the dielectric properties of three kinds of ceramics sintered at their densified temperatures as a function of frequency (100–1 MHz). The permittivity of BiNbO_4 and $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ ceramics decreased from 42 to 28 and from 152 to 143, respectively, as the frequency increased from 100 Hz to 1 MHz while Bi_3NbO_7 's permittivity remained about 86. Dielectric losses at 1 MHz were about 0.001, 0.0011, and 0.015, respectively, for BiNbO_4 , Bi_3NbO_7 , and $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ ceramics. Figure 6 shows the microwave dielectric properties of Bi_3NbO_7 and BiNbO_4 ceramics, prepared by HEM and CSR, as a function of sintering temperatures. (Dielectric loss of $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ ceramics is too large in the microwave region to be measured by the TE_{018} -shielded cavity method.) The permittivity of Bi_3NbO_7 ceramics changed from 74 to 84 as the sintering temperature increased from 870° to 930°C , while the $Q \times f$ values decreased from 300 to 200 GHz (the resonant frequency is about 5 GHz), and this result is similar to our previous work¹⁸ and the comparison of the properties of ceramics prepared by HEM and CSR methods also discussed there. For BiNbO_4 ceramics prepared by HEM, permittivity firstly increased from 19.3 to 29.8 as the sintering temperature increased from 960° to 1020°C and then decreased to 24.9 when the sintering temperature was 1050°C . The permittivity is slightly smaller than that of ceramics prepared by the CSR method but the change trend is similar as shown in Fig. 6. The $Q \times f$ values firstly remained about 10 000 GHz below 1030°C and then sharply increased to about 14 000 GHz (the resonant frequency is about 8 GHz). This change might be attributed to the phase transition of $\alpha\text{-BiNbO}_4$ to $\beta\text{-BiNbO}_4$. It was reported that both the permittivity and $Q \times f$ values of $\beta\text{-BiNbO}_4$ are slightly smaller than that of $\alpha\text{-BiNbO}_4$,¹⁸ but the $Q \times f$ values of $\beta\text{-BiNbO}_4$ ceramic seemed to be slightly larger than that of $\alpha\text{-BiNbO}_4$ in this work, and the average $Q \times f$ values of BiNbO_4 ceramic prepared by HEM are slightly larger than that of ceramics prepared by CSR. As is well known, a pure BiNbO_4 ceramic was hard to be densified without low-melting oxide addition or substitution.⁵ Pores would decrease the microwave permittivity and increase the dielectric loss of BiNbO_4 ceramics prepared by CSR drastically. In general, HEM could replace the calcinations of the conventional solid reaction method without drastic deterioration of the dielectric properties. But the sintering course of nanopowders prepared by HEM must be improved to obtain more densified ceramics.

IV. Conclusions

The nanocrystals with a size between 10 and 20 nm and amorphous matters could be obtained using a HEM method for the

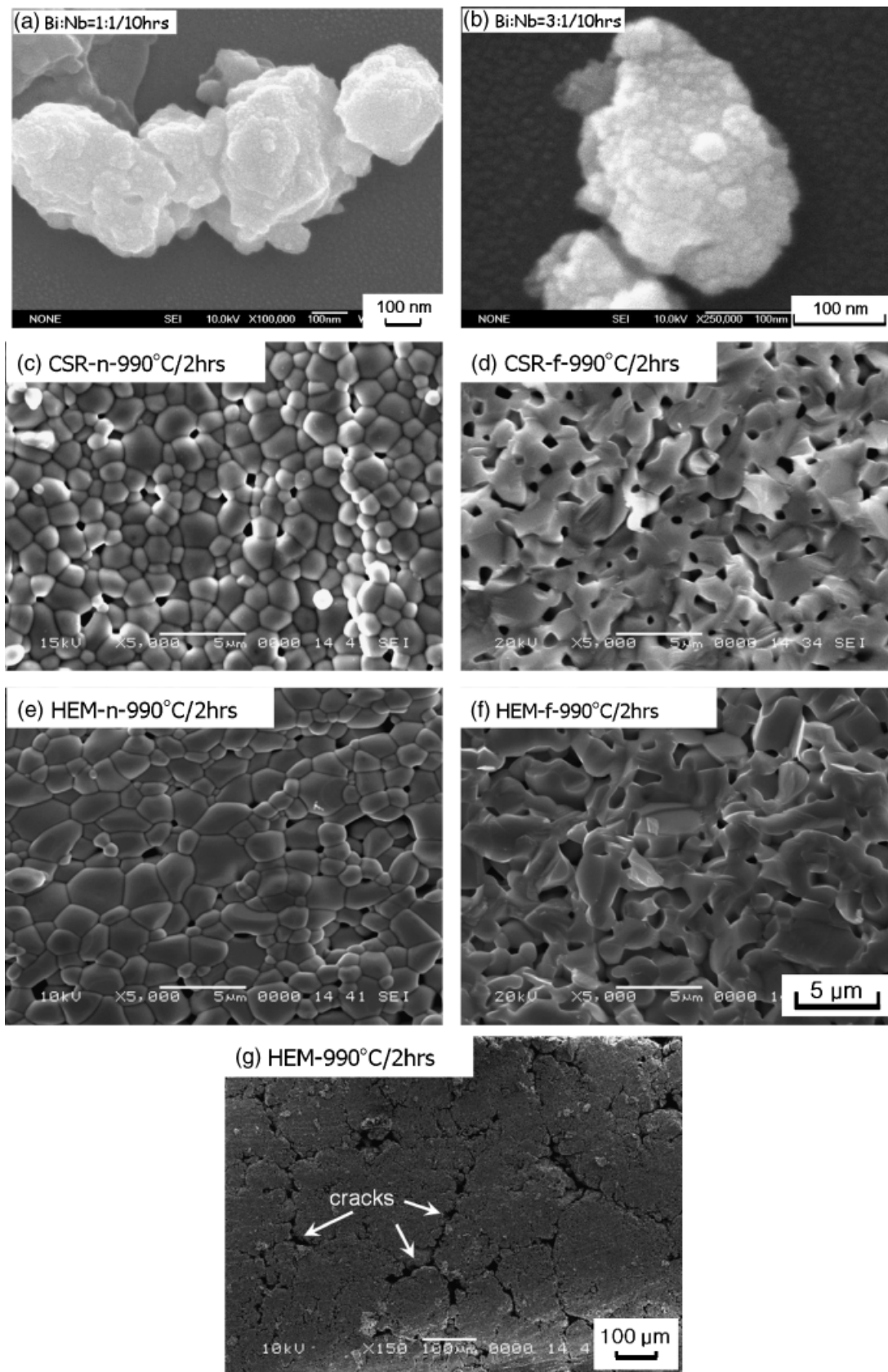


Fig. 4. Scanning electron microscopy photos of powders after being milled for 10 h for BiNbO_4 (a) and Bi_3NbO_7 (b) compositions, photos of natural sintered surface (c) and fracture surface (d) for a ceramic sintered at $990^\circ\text{C}/2\text{ h}$ prepared by conventional solid-state reaction, photos of natural-sintered surface (e), (g), and fracture surface (f) for ceramic sintered at $990^\circ\text{C}/2\text{ h}$ prepared by high-energy ball milling.

$\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ binary system. The cubic phase of Bi_3NbO_7 was easier to be formed, and the redundant Nb_2O_5 did not react with the Bi_3NbO_7 phase during the course of milling. After heating at proper temperatures, the amorphous matters disap-

peared and the proleptic phases of BiNbO_4 and $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ could be obtained. The aggregation phenomenon was considerable in the powders prepared by HEM because of the defects and stress. The cubic Bi_3NbO_7 phase formed was very

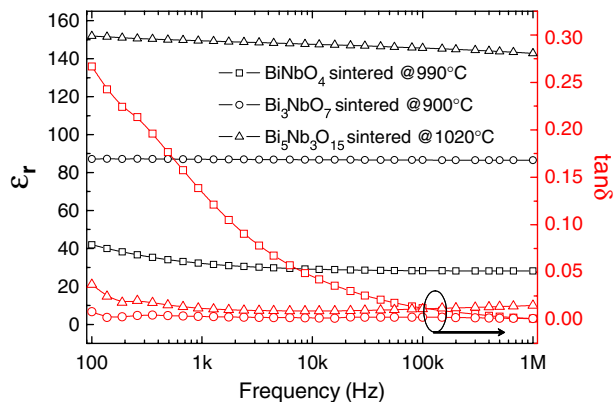


Fig. 5. Dielectric properties of ceramics as a function of frequency (100–1 MHz).

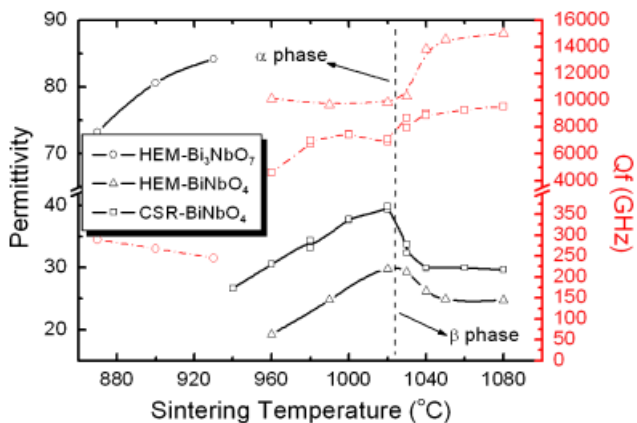


Fig. 6. Microwave permittivity (line) and dielectric loss (dash-dot) of ceramics prepared by high-energy ball milling (HEM) and conventional solid-state reaction (CSR) methods as a function of sintering temperature.

stable and it is hard to be transformed into a tetragonal phase, which could be obtained by the traditional mixed-oxide method. The microwave dielectric properties of BiNbO_4 were not poor, and the HEM method could replace the calcinations in a conventional solid reaction method.

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