

Sintering and dielectric properties of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics via high-energy milling technology

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Abstract The dense $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics is synthesized by high-energy milling technology from the coarse $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore powders prepared by solid state route. The sintering and dielectric properties of the $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics are investigated, which show that the sintering temperature of the prepared ceramics could be effectively lowered to 800°C and the bulk density reach 6.889 g/cm³ approximately 97% of the theoretical density of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics. The excellent dielectric properties of the ceramics sintered at 850°C has been obtained with the relative permittivity of 160 and the dielectric loss of 10⁻⁴. This route would be a low-cost and mass production for lowering the sintering temperature of the $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics without sintering aids.

Keywords $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore · High-energy milling technology · Sintering behavior

1 Introduction

Cubic bismuth zinc niobate ($\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$) cubic pyrochlore ceramics exhibits high dielectric constant ~170, relatively low dielectric loss ~10⁻⁴, compositionally adjustable temperature

coefficients of capacitance (TCC), and the lower firing temperature ~1000°C. These properties make this compound a potential candidate for integrated microwave resonators and decoupling capacitors [1–6]. However, for RF applications of electronic equipments, further lowering the sintering temperature is still the topic of research due to being needed to co-fire with the cheaper electrodes with lower melting points, such as Ag, for multilayered device applications.

Several attempts have been made to lower the sintering temperature of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics. The addition of some sintering aids, such as V_2O_5 , CuO, and B_2O_3 [7, 8], are normally used to lower the sintering temperature, which could lower the sintering temperature but also increase the dielectric loss. Another attempt is related to wet chemical process, such as sol-gel, aqueous solution-gel method [9, 10], which could lower the sintering temperature by using very fine powders. These are possible to decrease the sintering temperature to ~800°C. However, it is relatively expensive and difficult to scale up for mass production. In order to avoid these disadvantages, mechanical high-energy milling technology is known as a perfect method to synthesize nanocrystalline oxides and improve the sinterability of the ceramics, which has been receiving increasing attention [11–13]. The researches by using this method mainly focus on synthesizing piezoelectric powders by the constituent oxides at room temperature. However, not much work about the effect of high-energy milling on coarse $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore powders prepared by solid state route especially for the effect on the sintering and related dielectric properties of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics are done.

The aim of this work is to determine the effect of high-energy milling on the sintering and dielectric properties of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics, pure $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore phase are obtained by solid state route and the nano-sized $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$

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cubic pyrochlore particles is produced by high-energy milling technology. The dielectric and sintering behaviors of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics are investigated in details.

2 Experimental

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd, Chengdu, China), ZnO (>99%, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co. Ltd, Zhuzhou, China) were prepared according to the compositions of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$. 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. For the solid state route, the dried powders were calcined at 880°C. The high-energy milling operation was carried out in a Fritsch Pulverisette P4™ vario-planetary high-energy milling system (Fritsch, Germany) in air at room temperature for 4 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. After being milled for 4 h, the dried powder of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ was pressed into cylindrical disks of 10 mm diameter and 2 mm thickness with 5 wt% PVA binder, by applying a pressure of 38.2 kN/cm². These green disks were sintered at 750, 800, 850, 900, 950 and 1000°C for 4 h, respectively. Electrodes were connected to both sides of the sintered disks using a silver paste and these samples were used to measure the dielectric properties. The relative permittivity, dielectric loss and its frequency dependence (100 Hz-1 MHz) at room temperature were measured using a high precision LCR meter (Agilent 4284A LCR meter). The electrical resistivity was measured by a HP 4339A high-resistance meter under a measuring voltage of 100 V. The temperature (from 50 to 600°C) dependence of the relative permittivity and dielectric loss were measured at different frequencies (1, 10, and 100 kHz) by placing the disks in an automatic measurement system consisting of a PC computer, an Agilent 4284A LCR meter and a temperature chamber.

The crystalline structures of samples were investigated using X-ray diffraction with Cu K α radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). The surface morphology and microstructures of the sintered samples were determined by scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). A high-resolution transmission electron micro-

scope (TEM) was also applied to check the $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore powders prepared using high-energy milling (TEM-4000EX, JEOL). The apparent densities of sintered ceramics were measured by Archimedes method.

3 Results and discussion

The XRD patterns of the $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics sintered at the temperatures ranging from 750 to 1000°C for 4 h is shown in Fig. 1. In XRD analysis, all peaks of the samples could be indexed as the pure cubic pyrochlore (PDF 54-971) besides a weak peak at about 22° which is identified as a superlattice reflection from the ordered $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore lattices and can be indexed as (211). The relative intensity of this peak gradually increases with the sintering temperature increasing, which indicates that the structure ordering of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore is enhanced. This phenomenon has been observed in La_2O_3 modified Bi_2O_3 - ZnO - Nb_2O_5 system [14]. The intensities of peaks of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore phase increase with sintering temperature increasing, and reach the maximum values at 950°C. This suggests that the sample sintered at 950°C has larger crystalline particles than the samples sintered at lower sintering temperature. When the sintering temperature is above 1000°C, the relative intensities begin to decrease, which relates to a significant change in the microstructure of ceramics. It is supported by the SEM observation (Fig. 2).

Figure 2 shows the SEM images of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics sintered at different temperatures. It can be seen that $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics sintered at 800°C for 4 h exhibits a porous microstructure with small grains. However, a dense microstructure develops and the grain size increases to about 1–2 μm as the sintering temperature increasing to 850°C. Above 900°C, abnormal grain growth is observed, and some of the larger grains reach

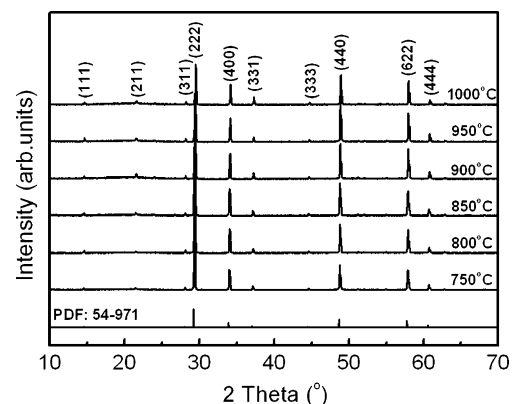
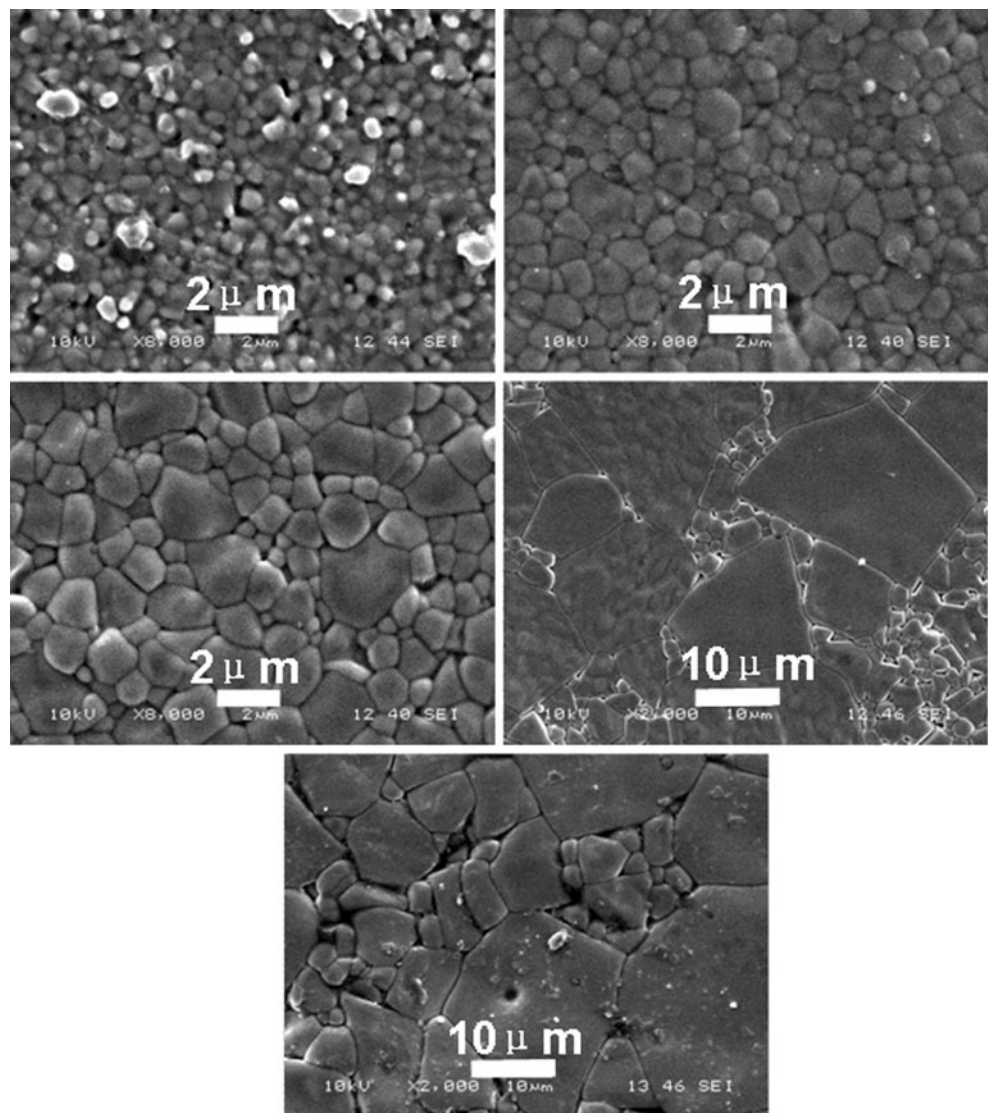


Fig. 1 X-ray diffraction patterns of the $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics sintered at 750, 800, 850, 900, 950, and 1000°C for 4 h, respectively

Fig. 2 SEM photos of the samples sintered at (a) 800, (b) 850, (c) 900, (d) 950, and (e) 1000°C for 4 h, respectively



3 and 15 μm for the samples sintered at 900 and 950°C, which is different with the ceramics synthesized by solid state route. When the sintering temperature is above 1000°C, more pores near the grain boundary are observed, which is due to the evaporation of the compound.

It is interesting that the dense samples are obtained at 850°C. In stress the effect of high-energy milling, the TEM photos of the high-energy milled powders and the coarse powders is provided. As shown in Fig. 3, the particle size of the coarse powders is about 1–2 μm (Fig. 3(a)). However,

Fig. 3 TEM photos of the powder (a) prepared using high-energy milling and (b) calcined coarse powders

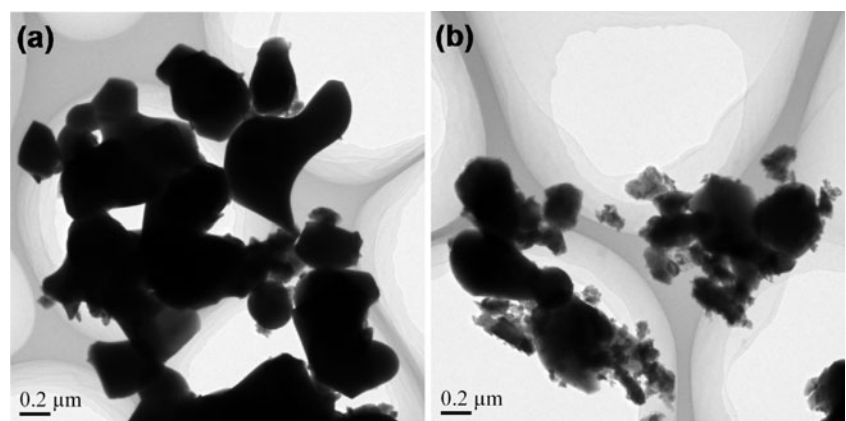
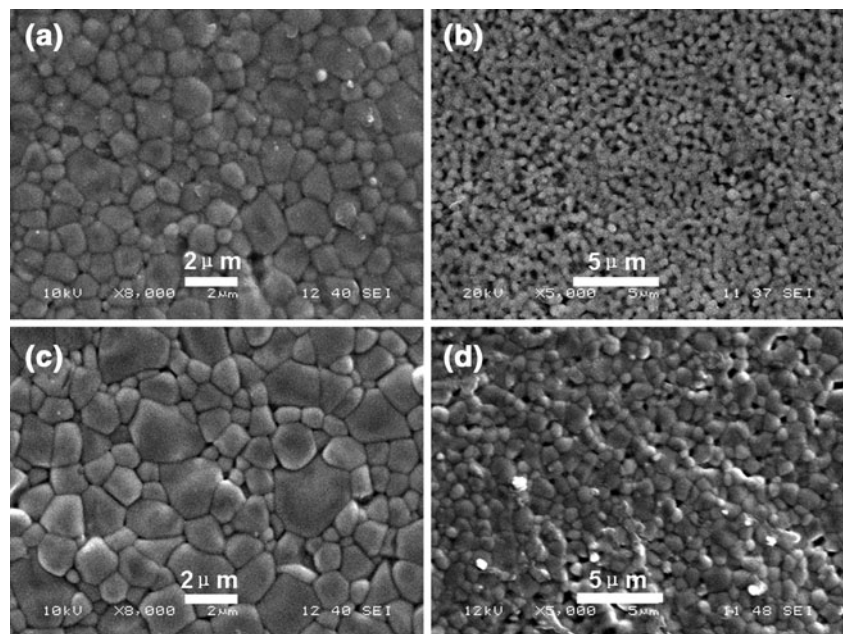


Fig. 4 SEM photos of the samples prepared by high-energy milling sintered at: (a) 850, (c) 900°C for 4 h, and prepared by solid state route sintered at: (b) 850, (d) 900°C for 4 h



more fine powders are observed in the samples prepared by high-energy milling technology (Fig. 3(b)). It concludes that high-energy milling technology could efficiently reduce the particle size of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore powders prepared by solid state route, and thus lower the sintering temperatures of the $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ ceramics.

In order to further determine the improvement of sintering properties of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore based on high-energy milling, the SEM photos of the samples prepared using high-energy milling (Fig. 4(a) and (c)) and prepared using solid state route (Fig. 4(b) and (d)) are given as shown in Fig. 4. It is clear that the densification of the samples is improved significantly in the presence of high-energy milling process. Due to the fine powder could lower the sintering temperature. However,

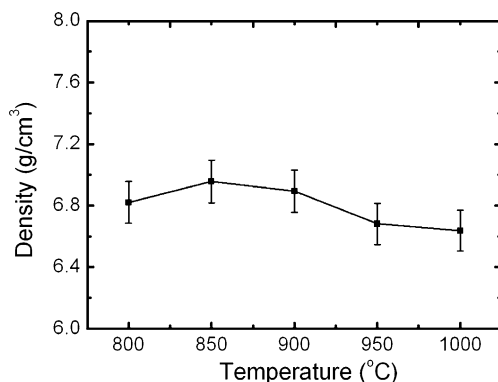


Fig. 5 Bulk density of the ceramics sintered at 800, 850, 900, 950, and 1000°C for 4 h, respectively

obvious microstructure changing is observed for the samples prepared by solid state route above 900°C.

Figure 6 shows the dielectric properties of the $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics sintered at 800–1000°C for 4 h. At 800°C, it is obviously that the relative permittivity and dielectric loss of the ceramics decrease with the frequency increasing. This phenomenon, as discussed by Wang et. al [9], can be attributed to the localized electric charge carriers contribution related to the formation of pores and defects along the grains boundaries in the ceramics sintered at lower sintering temperature. The relative permittivity of the sample sintered at 850°C reaches the maximum value of 160 at 1 MHz, and the dielectric loss keeps at 10^{-4} level, which is comparable to that of the samples sintered at 1020°C prepared by solid state route. Furthermore, the relative permittivity and dielectric loss of the ceramics sintered above 850°C keep stable with frequencies increasing. It can be attributed to the dense microstructure with homogenous grains (1–2 μm). As shown in Fig. 5, the bulk density of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics reaches the peak value of about 160 at 850°C. Then the bulk densities of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics drop gradually with the sintering temperature rising further. The relative permittivity keeps

Table 1 The electrical resistivity of the $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics sintered at different temperature

Sintering temperature	800°C	850°C	900°C	950°C	1000°C
ρ ($\Omega\cdot\text{cm}$)	1.629×10^{13}	2.941×10^{12}	2.659×10^{13}	1.063×10^{14}	7.938×10^{14}

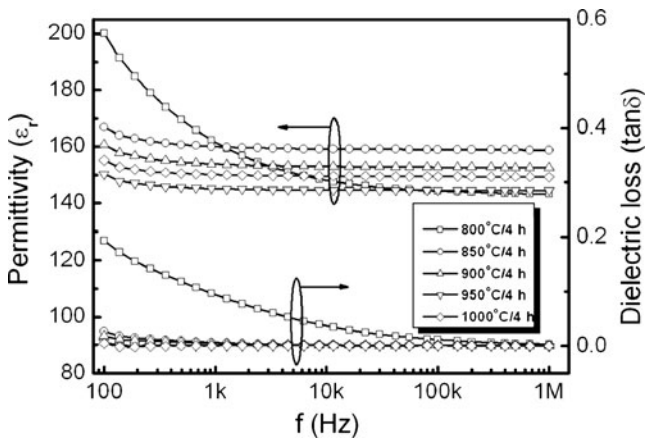


Fig. 6 Dielectric properties of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics sintered at 800, 850, 900, 950, and 1000°C for 4 h, respectively

the same trend and slightly decreases with sintering temperature rising, whereas the dielectric loss keeps at 10^{-4} level. According to our previous work [10], in polycrystalline ceramic materials, the grain and grain boundary structure has a great influence on the dielectric properties of the ceramics. The more homogenous grains are, the better dielectric properties of ceramics are. Thus the

ceramics sintered above 900°C with inhomogeneous grains show a lower permittivity than the ceramics sintered at 850°C with the homogenous grains. The electrical resistivity of the ceramics is listed in Table 1, it can be seen that the electrical resistivity of the ceramics increases from 10^{12} to 10^{14} $\Omega\cdot\text{cm}$ as sintering temperature rising from 800 to 1000°C Fig. 6.

Figure 7 shows the dependence of dielectric properties on temperature for the samples sintered at 800–950°C for 4 h. All samples show the same trend, whose relative permittivity initially gradually decreases with temperature rising, then increases sharply with temperature above 350°C. The dielectric loss almost keeps the same with the temperature rising initially, whereas significantly increases in the higher temperature range, especially for those measured under lower frequencies. Such variations are strongly dependent on the frequencies. Dielectric loss at high frequencies is much lower than those occurring at low frequencies (1 and 10 kHz). This is typically associated with dielectric loss by conduction [9]. As the temperature increasing, electrical conductivity increases owing to the increase in thermally activated drift mobility of electric charge carriers according to the hopping conduction mechanism. Therefore, the increase in dielectric polarization causes a remarkable increase in permittivity and dielectric loss as the temperature increasing.

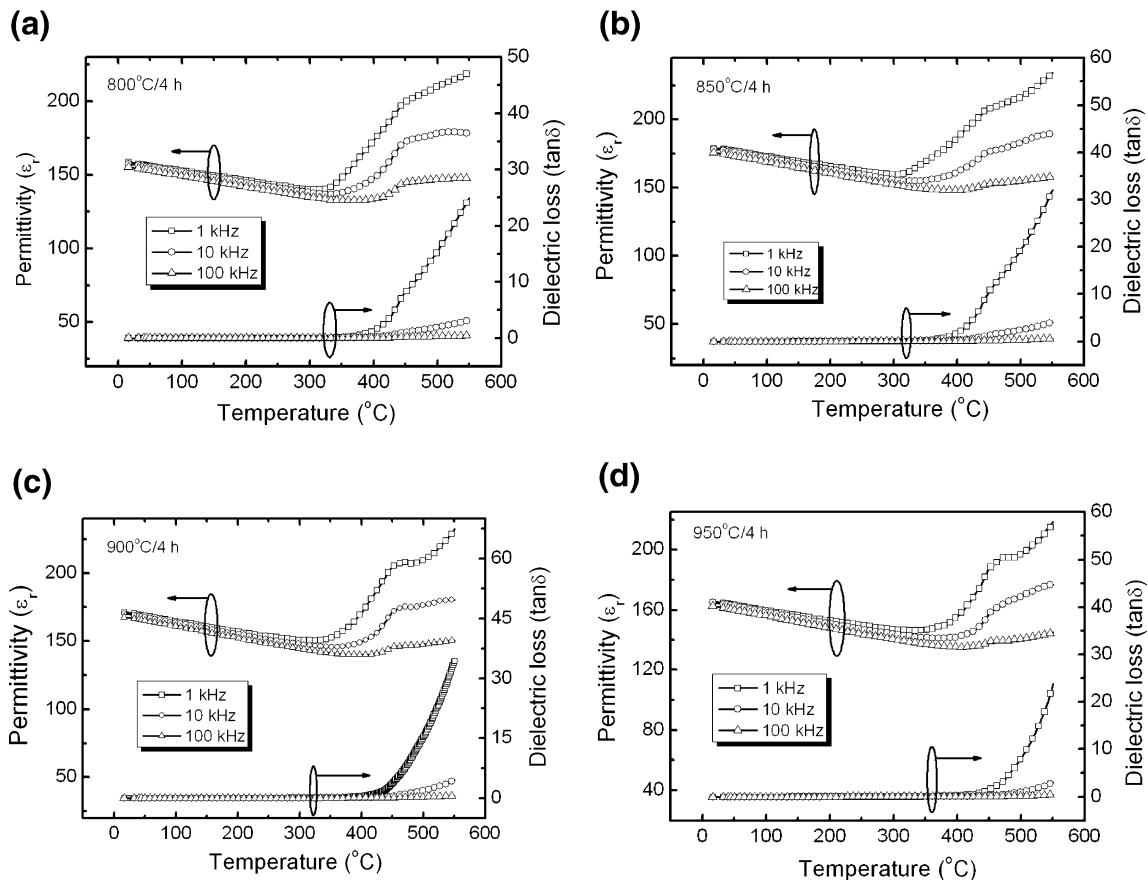


Fig. 7 Dependence of dielectric properties on temperature for the samples sintered at (a) 800, (b) 850, (c) 900, and (d) 950°C for 4 h, respectively

4 Conclusion and discussion

$\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics is synthesized by high-energy milling technology. In TEM analysis, which show that high-energy milling technology could effectively reduce the grain size of the powder derived from the calcined coarse powders, which attributes to effectively lowered its sintering temperature to 800°C. The relative permittivity and dielectric loss of the sample sintered at 850°C are about 160 and 10^{-4} at 1 MHz respectively, which is comparable to that of the sample sintered at 1020°C prepared by solid state route. The electrical resistivity value increases from about 10^{12} to 10^{14} $\Omega\cdot\text{m}$ with sintering temperature rising. The abnormal grains growth is observed in the samples sintered above 900°C, while the large grain sizes of the samples sintered at 900 and 950°C are 3 and 15 μm . It concludes that high-energy milling technology is a superior method to lower the sintering temperature of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ cubic pyrochlore ceramics without aids addition.

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