

# Enhanced dielectric properties of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ thick films via cold isostatic pressing

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**Abstract** Dense  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films were prepared on  $\text{Ag}/\text{Al}_2\text{O}_3$  substrates using screen-printing technology at a lower temperature of 825 °C. A novel pretreatment of cold isostatic pressing was introduced to enhance the quality of thick films. After cold isostatic pressing prior to sintering, the microstructure of thick films was improved with a more compact morphology and better dielectric properties, and the permittivity and dielectric loss of thick films sintered at 900 °C were about 160 and 0.006. The obvious tunability of thick films was also observed, and the tunability value reached about 3 % for thick films sintered at 900 °C under 400 kV/cm. The enhanced properties and low-temperature sintering made this compound a potential candidate for Low Temperature Co-fired Ceramic (LTCC).

**Keywords**  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films · Dielectric properties · High milling technology · Cold isostatic pressing

## 1 Introduction

Cubic bismuth zinc niobate ( $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ ) pyrochlore ceramics exhibits high dielectric constant  $\sim 170$ , relatively low dielectric loss  $\sim 10^{-4}$ , compositionally adjustable temperature coefficients of capacitance (TCC), and the lower

firing temperature  $\sim 1000$  °C. These properties make this compound a potential candidate for integrated microwave resonators and decoupling capacitors [1–5]. To downsize the final device, the active material must be miniaturised and integrated into the substrate. Screen-printing technology has been shown to be a successful method for forming integrated films on a substrate, with the thickness ranging from a few micrometers to a few tens of micrometers.

In order to make this compound could be miniaturized and integrated into the substrate by using silver as internal electrode, lowering the processing temperature is of great interests. In previous work we obtained the dense  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  ceramics at 850 °C without any sintering aids by using high energy milling technology [6]. Compared to bulk ceramics, thick films show porous morphology caused by the strain shrinkage between films and bottom substrate. The films are likely to crack, and the dielectric properties degrade. Recently, the dielectric and sintering properties of  $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$  thick films was improved by using a novel pretreatment consisting of cold isostatic pressing of the green films before sintering [7].

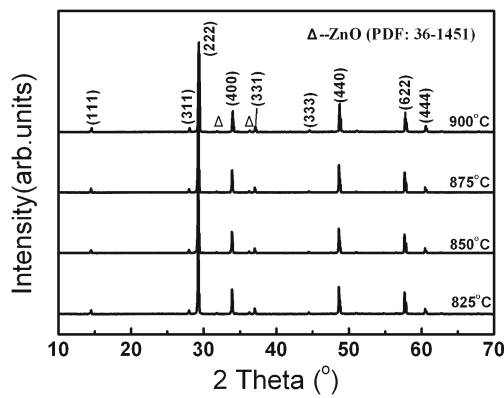
This work mainly aimed at fabricating low-temperature sintered  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films, while still achieving an acceptable microstructural properties and a good functional response. It was achieved by a novel pretreatment consisting of cold isostatic pressing of the green films. The ceramic powders were prepared by high energy milling technology. The sintering and dielectric properties of thick films also were investigated.

## 2 Experimental procedure

Proportionate amounts of reagent-grade starting materials of  $\text{Bi}_2\text{O}_3$  (>99 %, Shu-Du Powders Co. Ltd, Chengdu, China),  $\text{ZnO}$  (>99 %, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and  $\text{Nb}_2\text{O}_5$  (>99 %, Zhu-Zhou Harden Alloys

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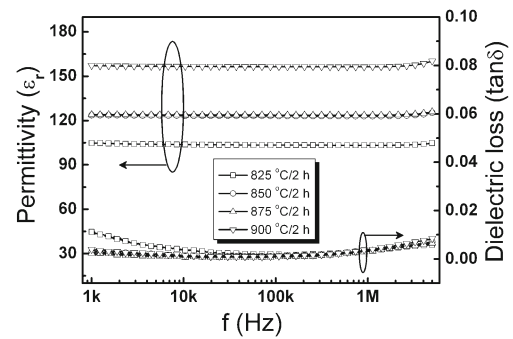
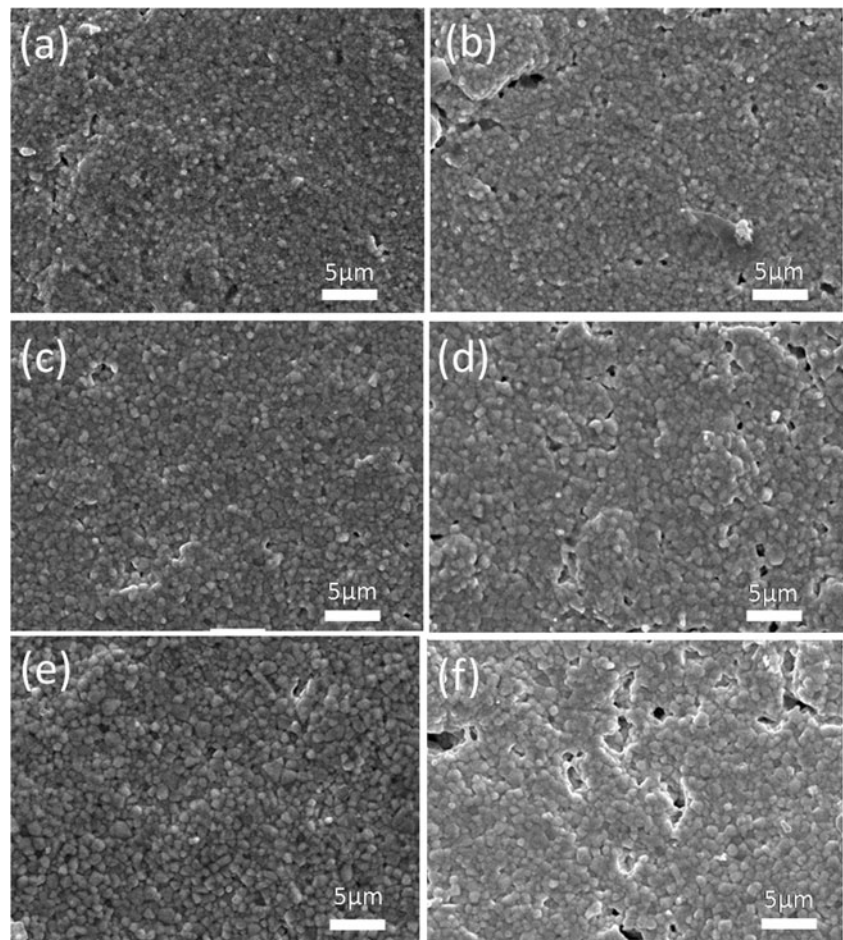
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**Fig. 1** XRD patterns of  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films sintered at different temperatures

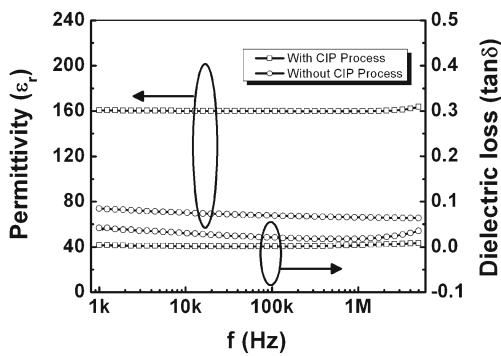
Co. Ltd, Zhuzhou, China) were prepared according to the compositions of  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ . A planetary mill (Nanjing Machine Factory, Nanjing, China) was used for mixing the starting oxides by setting the running speed at 150 rpm with the Zirconia balls (2 mm in diameter) as the milling media. The dried powders were calcined at 880 °C for the solid state route. The high energy mill operation was carried out in a Fritsch Pulverisette P4<sup>TM</sup> vario-planetary high energy

**Fig. 2** SEM photos of thick films with isostatic pressing process sintered at (a) 825, (c) 850, (e) 875 °C/2 h, and without isostatic pressing process sintered (b) 825, (d) 850, (f) 875 °C/2 h.



**Fig. 3** Frequency dependence of dielectric properties of thick films sintered at different temperatures

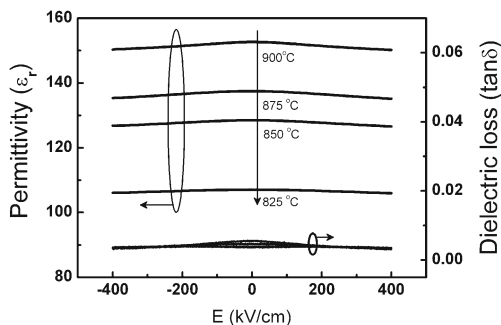
mill system (Fritsch, Germany) in air at room temperature for 4 h. A 225 mL tungsten carbide container and 50 tungsten carbide balls with a diameter of 10 mm were used as the milling medium. The milling speed of the main disk was set at 400 rpm and the speed of each pair was set at  $-800$  rpm, which 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 nanometer size powder was mixed



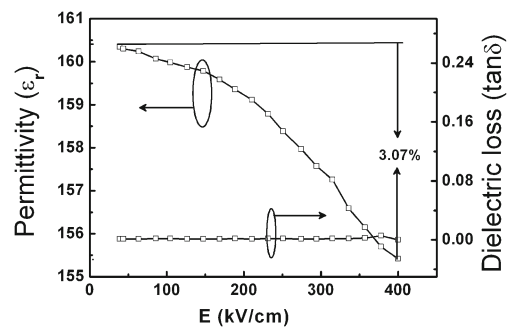
**Fig. 4** Frequency dependence of dielectric properties of thick films with and without cold isostatic pressing process sintered at 900 °C/2 h

with organic vehicle (the weight ratio of ceramic powder: organic vehicle=66.7: 33.3 wt%) by stirring for about 1 h to form paste for screen-printing technology. The Ag /Al<sub>2</sub>O<sub>3</sub> substrate was prepared by printing Ag paste on the Al<sub>2</sub>O<sub>3</sub> substrate and fired at 900 °C for 10 min. The Bi<sub>1.5</sub>ZnNb<sub>1.5</sub>O<sub>7</sub> paste was printed on the fired Ag /Al<sub>2</sub>O<sub>3</sub> substrate, the screen-printing process was repeated until desired thickness was reached. Each layer of the films was preheated at 100 °C for 10 min subsequently. In order to improve the microstructure of thick films, a high isotatic pressure of 140 MPa was applied on the green films for 1 min before sintering. The resultant films were then sintered from 825 to 900 °C for 2 h in furnace. In order to determine the effect of cold isostatic pressing process on dielectric properties of Bi<sub>1.5</sub>ZnNb<sub>1.5</sub>O<sub>7</sub> thick films, the samples without cold isostatic pressing process was sintered at 900 °C for 2 h.

The phases of the printed thick films were identified by X-ray diffraction with CuK $\alpha$  radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). A scanning electron microscope (JSM-6460, JEOL, Tokyo, Japan), was used for the overall microstructural analysis. For the frequency measurements of the Bi<sub>1.5</sub>ZnNb<sub>1.5</sub>O<sub>7</sub> thick films, top electrodes with dimensions of 3.14 mm<sup>2</sup> were deposited by gold sputtering. The relative permittivity and dielectric losses were measured with a high



**Fig. 5** Bias dependence of dielectric properties of thick films sintered at different temperatures



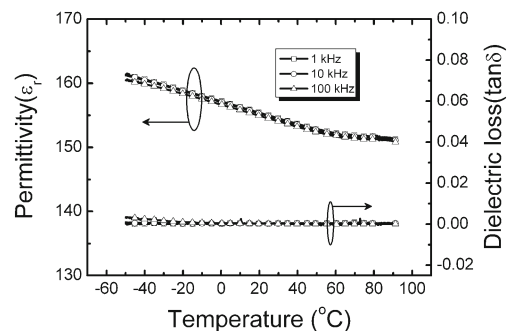
**Fig. 6** Bias dependence of permittivity and loss of thick films sintered at 900 °C/2 h under high voltage

precision LCR meter (Agilent 4294A LCR meter). It was also used to measure the tunability under the DC bias of 40 V at 1 MHz. The temperature dependence of the relative permittivity and dielectric losses was measure from -50 to 85 °C by 4284A (Agilent 4284A, Palo Alto, CA, USA). The tunability under high voltage was measured up to the maximum DC bias of 300 V at 10 kHz by TH 2816 LCR (TH 2816 LCR, Changzhou, China).

### 3 Results and discussion

Figure 1 shows XRD patterns of the Bi<sub>1.5</sub>ZnNb<sub>1.5</sub>O<sub>7</sub> thick films sintered from 825 to 900 °C for 2 h. In XRD analysis, the patterns are all indexed as the pure cubic pyrchlore phase (PDF 54–971) besides a small amount of ZnO. Levin et al. [8] systematically studied this phenomenon. They found the structure of Bi<sub>1.5</sub>ZnNb<sub>1.5</sub>O<sub>7</sub> is composed of unusual cubic pyrochlore single phase consisting Bi<sub>1.5</sub>Zn<sub>0.92</sub>Nb<sub>1.5</sub>O<sub>6.92</sub> and small amounts of ZnO, and the ZnO is always distributed at the boundary of the Bi<sub>1.5</sub>Zn<sub>0.92</sub>Nb<sub>1.5</sub>O<sub>6.92</sub> structure.

In our previous work, the sintering temperature of Bi<sub>1.5</sub>ZnNb<sub>1.5</sub>O<sub>7</sub> ceramics could successfully lower to 850 °C by using high energy milling technology. However, the densification mechanism of thick films is different from the ceramics, the ceramics could shrink freely to get a dense



**Fig. 7** Temperature dependence of dielectric properties of thick films sintered at 900 °C for 2 h from -50 to 85 °C

microstructure, the tight contact between films and bottom electrode of substrate would limited the shrinkage of the films. As shown in Fig. 2 (b), (d) and (f), the thick films sintered at 825 °C without cold isostatic pressing show porous microstructure, and the pores would join each other to form the larger size pores with the sintering temperatures increasing. Cold isostatic pressing is an efficient method to improve the microstructure of the thick films. As shown in Fig. 2 (a), (c) and (e), a dense thick films sintered at 825 °C with fine grains of about 500 nm is obtained (Fig. 2 (a)). As the sintering temperatures increasing from 850 (Fig. 2 (c)) to 875 °C (Fig. 2 (e)), the microstructures of the thick films is improved accompanied with the grain growth increasing from 0.5 to 1.5  $\mu\text{m}$ .

The pretreatment of isostatic pressing is important for the improvement of the dielectric properties of the thick films, because the pores with low relative permittivity are progressively eliminated. The dependence of dielectric properties on frequencies for the samples sintered at the temperatures ranging from 825 to 900 °C for 2 h is showed in Fig. 3. It is obvious that the permittivity increase from 100 to 160 with the sintering temperatures increasing from 825 to 900 °C. No obvious dependence of relative permittivity and dielectric loss on frequencies is observed except for the thick films sintered at 825 °C. The relative permittivity of the thick films sintered at 900 °C is about 160 and keeps very constant with increasing frequencies from 100 Hz to 1 MHz, which is comparable to the reported values for bulk samples [11]. The dielectric properties of thick films with and without cold isostatic pressing process sintered at 900 °C are shown in Fig. 4, it is obvious the dielectric properties of thick films have been enhanced via cold isostatic pressing process, and the relative permittivity of the thick films without isostatic pressing process is about 70.

It is interesting that obvious tunability of the  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films is observed, which is always found in thin films under higher DC bias voltage. Figure 5 shows the tunability value of  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films sintered at different temperatures. As shown in Fig. 5, the relative permittivity and dielectric loss of  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films as a function of applied DC bias in a frequency of 1 MHz. It is obvious the tunability value strongly depend on the relative permittivity of the thick films at zero DC bias measured at 1 MHz, and the tunability value increase from 0.8 % to 1.03 %, with the sintering temperatures increasing from 825 to 900 °C. As the DC bias voltage increasing to 400 kV/cm, the tunability value increases to about 3.1 % (Fig. 6). According to reference [9], the tunability value of the thin films is 55 % under a bias field of 2.4 MV/cm. Therefore, higher tunability value of thick films could be expected to be obtained by

improving the quality of thick films and further increasing the bias voltage.

The dependence of dielectric properties on temperature is investigated. The result is shown in Fig. 7. The relative permittivity decrease gradually from 160 to 151 and the dielectric loss keep  $10^{-4}$  as the temperature increasing from  $-50$  to 85 °C. This phenomenon is due to the dielectric relaxation of thick films. In reference [10],  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  shows obvious dielectric relaxation and the films stresses can significantly the dielectric properties of films, which always wide the relaxation peaks [11].

## 4 Conclusions

The dielectric and sintering properties of  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films on  $\text{Ag}/\text{Al}_2\text{O}_3$  via high energy milling technology were investigated. The isostatic pressing process was introduced to improve the densification of the thick films. The dense thick films with fine grain were obtained as low as 825 °C, the permittivity and dielectric loss are about 160 and 0.006 for the thick films sintered at 900 °C. The tunability of  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films was also observed. It is concluded that high energy milling technology consisting with isostatic pressing is a useful method to lower the sintering temperature of  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  thick films.

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## References

1. R.G. Li, S.W. Jiang, L.B. Gao, L.Y. Wang, Y.R. Li, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **58**(6), 1140–1144 (2011)
2. J. Singh, S.B. Krupanidhi, Appl. Surf. Sci. **257**(6), 2214–2217 (2011)
3. K. Sudheendran, K.C. James Raju, J. Mater. Sci: Mater. Electron. **22**(6), 626–630 (2011)
4. A. Mergen, H. Zorlu, M. Ozdemir, Ceram. Int. **37**(1), 37–42 (2011)
5. D. Grebennikov, O. Ovchar, A. Belous, P. Mascher, J. Appl. Phys. **108**(11), 114109 (2010)
6. W.H. Liu, H. Wang, J. Electroceram. **27**, 209–214 (2011)
7. M.H. Zhang, H. Wang, H.B. Yang, W.H. Liu, H.F. Zhou, X. Yao, J. Electroceram. **26**, 99–104 (2011)
8. L. Levin, T.G. Amos, J.C. Nino, T.A. Vanderah, C.A. Randall, J. Solid State Chem. **168**, 69–75 (2002)
9. F. Xiang, H. Wang, M.H. Zhang, X. Sun, X. Yao, Ceram. Int. **34**, 925–928 (2008)
10. S. Kamba, V. Porokhonskyy, A. Pashkin, V. Bovtun, J. Petzelt, Phys. Rev. B **66**, 054106 (2002)
11. A. Bartaszyte, O. Chaix-Pluchery, J. Kreisel, C. Jimenez, F. Weiss, J. Appl. Phys. **103**, 014103 (2008)