



# Dielectric properties and phase transitions of BiNbO<sub>4</sub> ceramic

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In the present work, HP-BiNbO<sub>4</sub> was found, by in situ X-ray diffraction, thermal expansion and differential thermal analysis, to transform to orthorhombic BiNbO<sub>4</sub> at around 680 °C along with an abrupt increase of volume, and to then transform to the triclinic BiNbO<sub>4</sub> at around 1000 °C with an endothermic phenomenon. The results indicate that the dielectric permittivity of HP-BiNbO<sub>4</sub> ceramic prepared via the high-temperature/high-pressure method was increased remarkably and this might work in other dielectric systems.

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BiNbO<sub>4</sub> has been widely studied over the world for more than half century due to its photocatalysis and dielectric properties since the phase equilibrium relation in the Bi<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> binary system was first reported by Roth and Waring [1–5]. In particular, since the excellent microwave dielectric properties and low sintering temperature (permittivity ~43, quality factor Qf ~10,000–20,000 GHz) of BiNbO<sub>4</sub> ceramic were reported by Kagata et al. [6], there have been a large number of works focusing on the modification and low-temperature co-firing of BiNbO<sub>4</sub> ceramic and film samples [7–9].

The low-temperature orthorhombic modification of BiNbO<sub>4</sub> ( $\alpha$  phase) and the phase transition to the high-temperature triclinic phase ( $\beta$  phase) above 1020 °C were first reported by Roth and Waring, who believed that the transformation could not be reversed

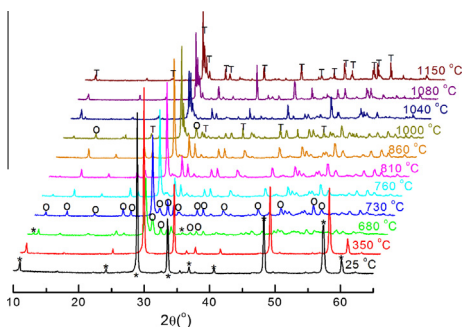
by cooling down to lower temperatures [5,10]. Single-crystal samples of  $\alpha$ -BiNbO<sub>4</sub> and  $\beta$ -BiNbO<sub>4</sub> were synthesized by Keve et al. [11] and Subramanian et al. [12] in 1993 and 1973, respectively, and detailed structure analysis was carried out. In our previous work [13], the phase transformation from  $\alpha$ -BiNbO<sub>4</sub> to  $\beta$ -BiNbO<sub>4</sub> in a ceramic sample was proved by X-ray diffraction (XRD) analysis and supported by differential thermal analysis, shrinkage and the dielectric spectrum. Recently, a third modification of BiNbO<sub>4</sub>, was called HP-BiNbO<sub>4</sub>, has been obtained by Xu et al. [14] using a high-pressure/high-temperature (HPHT) method. In the present work, the in situ X-ray diffraction, differential thermal analysis, thermal expansion and dielectric properties of the novel HP-BiNbO<sub>4</sub> ceramic are studied in detail.

BiNbO<sub>4</sub> was prepared via a solid-state reaction method. The calcination and temperature is 800 °C. After being remilled, the powders were pressed into cylinders (10 mm in diameter and 4–5 mm in height) in a steel die with the addition of 5 wt.% PVA binder under an

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uniaxial pressure of 100 MPa. The samples were sintered at 990 °C for 2 h to obtain the  $\alpha$ -BiNbO<sub>4</sub> ceramic. The HP-BiNbO<sub>4</sub> was prepared through an HPHT method, using  $\alpha$ -BiNbO<sub>4</sub> powders as the raw material. In our work, HPHT experiments were carried out with a DS6X8MN cubic press, in which the pressure and temperature were calibrated. To obtain the HP-BiNbO<sub>4</sub> ceramic, the  $\alpha$ -BiNbO<sub>4</sub> powders were first compressed under a pressure of about 5 GPa, then sintered at 1200 °C for 10 min. The samples were subsequently cooled naturally to room temperature by turning off the electric power, then decompressed to ambient pressure as described in our previous work [14]. High-temperature XRD was performed in the temperature range from room temperature to 1150 °C using a XRD with Cu K<sub>α</sub> radiation (X'Pert PRO, PANalytical, Holland). Prior to examination, sintered pellets were crushed to a powder in a mortar and pestle. The diffraction pattern was obtained between 10 and 65° (2θ) at a step size of 0.02°. The thermal expansion parameters were measured using a dilatometer (DIL402C, NETZSCH, Germany). Differential thermal analysis (DTA) was carried out using a thermoanalyzer system (Netzsch STA-449C, Netzsch, Selb, Germany) with heating rate of 10 °C min<sup>-1</sup>. The sintered samples were machined into pellet samples with a thickness of 0.4 mm and a diameter of ~8 mm. Gold was then sputtered onto both sides of the pellet samples as electrodes with a diameter of 6 mm for the electric measurements. The room-temperature electrical resistivity was measured using an HP4339A-HP16339A instrument. The room-temperature dielectric constant and dielectric loss were measured using an HP 4294 instrument (Hewlett-Packard, Palo Alto, CA) in the frequency range 100 Hz–10 MHz. The temperature dependence of the dielectric permittivity and the loss were determined at the frequencies of 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz, using an LCR meter (4980, Agilent) with a home-made high-temperature system. The high-field polarization–electric field loops were recorded with a modified Sawyer–Tower circuit. All samples were subjected to two successive triangle waves, with a frequency of 10 Hz.

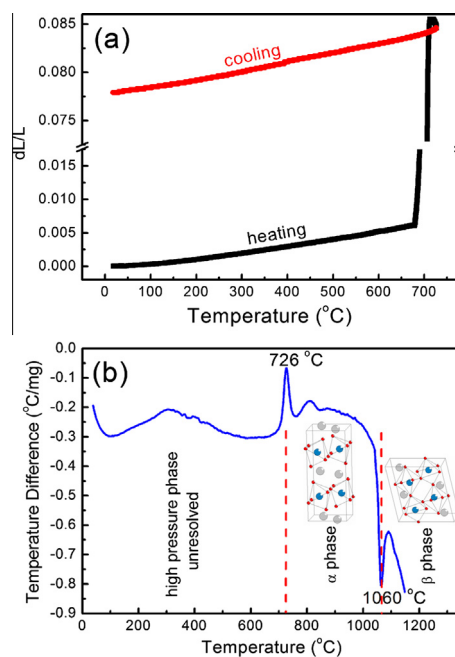
A homogeneous microstructure with virtually no pores could be observed for both  $\alpha$ -BiNbO<sub>4</sub> and HP-BiNbO<sub>4</sub> ceramics, as seen from Figure S1 in the



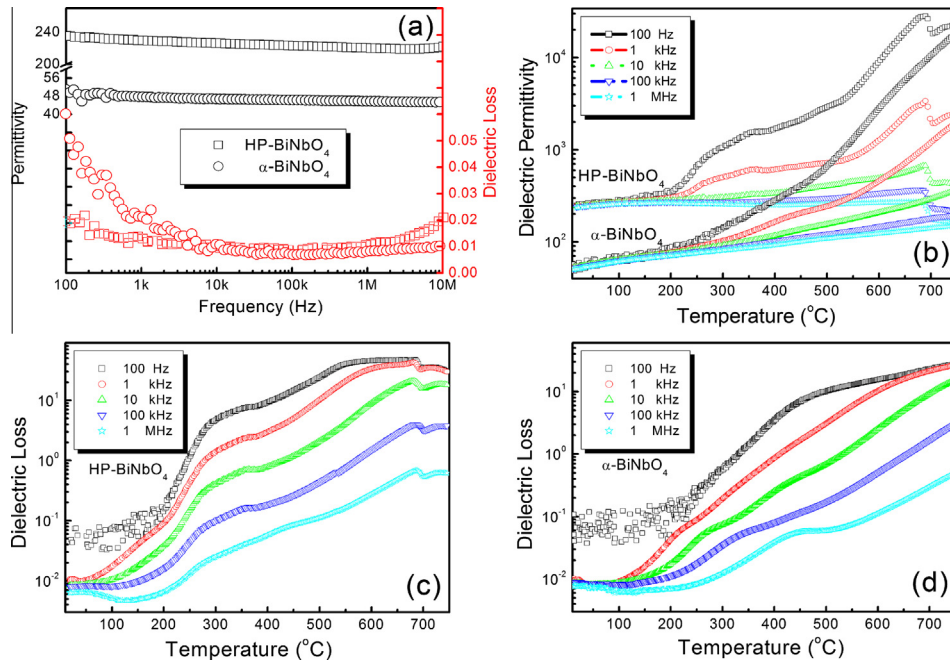
**Figure 1.** The in situ XRD patterns of the HP-BiNbO<sub>4</sub> sample (25–1150 °C). \*, HP phase; o,  $\alpha$  phase; T,  $\beta$  phase.

**Supplementary Information.** The in situ XRD patterns of HP-BiNbO<sub>4</sub> sample (25–1150 °C) are shown in Figure 1. Only the peaks of the HP phase were observed at room temperature. However, the resolution of this novel structure requires further work. When the temperature was increased to 680 °C, besides the peaks of HP-BiNbO<sub>4</sub>, the diffraction peaks of  $\alpha$ -BiNbO<sub>4</sub> could also be observed, and this indicates that the sample had partially transformed to  $\alpha$  phase at this temperature. When the temperature was further increased to 730 °C, only the peaks of  $\alpha$ -BiNbO<sub>4</sub> were revealed, indicating that the phase transformation from HP to  $\alpha$  phase was complete. When the temperature was increased to 1000 °C, peaks of  $\beta$  BiNbO<sub>4</sub> were observed, which meaning that the  $\alpha$ -BiNbO<sub>4</sub> had started to transform to  $\beta$  BiNbO<sub>4</sub> at this temperature. As seen from the XRD patterns at 1040 °C, there are no peaks of  $\alpha$ -BiNbO<sub>4</sub> observed, so the phase transformation from  $\alpha$  to  $\beta$  was complete at this temperature.

The thermal expansion and DTA curves of HP-BiNbO<sub>4</sub> ceramic are presented in Figure 2. It can be seen that the length of the HP-BiNbO<sub>4</sub> ceramic increased linearly with temperature below 680 °C, and the thermal expansion coefficient is calculated to be around 10 ppm °C<sup>-1</sup>. When the temperature was increased to around 680 °C, the length increased sharply to about 1.085 times larger than normal. This was caused by the phase transition from the HP phase to the orthorhombic  $\alpha$  phase and indicates that the  $\alpha$ -BiNbO<sub>4</sub> has a larger cell volume than the HP-BiNbO<sub>4</sub>. As seen from the thermal expansion curve in the cooling course, the thermal expansion coefficient of  $\alpha$ -BiNbO<sub>4</sub> is also around 10 ppm °C<sup>-1</sup>, which is similar to that of the HP-BiNbO<sub>4</sub>. The temperature difference as a function of the temperature of the HP-BiNbO<sub>4</sub> ceramic is presented



**Figure 2.** The thermal expansion (a) and DTA curves (b) of the HP-BiNbO<sub>4</sub> ceramic.

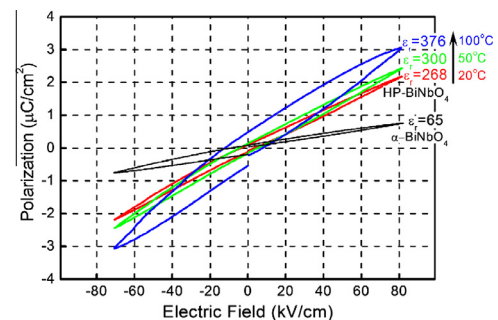


**Figure 3.** Dielectric properties of  $\alpha$ -BiNbO<sub>4</sub> and HP-BiNbO<sub>4</sub> as a function of frequency (100 Hz–10 MHz) (a), dielectric permittivity (b) and dielectric loss (c, d) as a function of temperature (25–750 °C).

in Figure 2(b). It can be observed that there is an exothermic and an endothermic peak in DTA curves, at about 726 and 1060 °C, respectively. This indicates that the HP-BiNbO<sub>4</sub> ceramic transformed to  $\alpha$ -BiNbO<sub>4</sub> at around 726 °C in an exothermic reaction and then transformed to  $\beta$ -BiNbO<sub>4</sub> at about 1060 °C in an endothermic reaction. The latter phenomenon corresponds well with our previous results [13], and all the results supported the XRD analysis above.

The dielectric permittivity and dielectric loss of  $\alpha$ -BiNbO<sub>4</sub> and HP-BiNbO<sub>4</sub> as a function of frequency (100 Hz–10 MHz) and temperature (25–750 °C) are shown in Figure 3. As can be seen in Figure 3(a), as the frequency increased from 100 Hz to 10 MHz, the dielectric permittivity of the HP-BiNbO<sub>4</sub> ceramic decreased slightly from 237 to 220, which is nevertheless almost five times larger than that of  $\alpha$ -BiNbO<sub>4</sub> ( $\epsilon_r = 48$ –45). In the frequency range 100 Hz–10 kHz, the dielectric loss of the  $\alpha$ -BiNbO<sub>4</sub> ceramic ( $\tan\delta = 0.05$ –0.01) is larger than that ( $\tan\delta = 0.02$ –0.01) of the HP-BiNbO<sub>4</sub> ceramic. The large dielectric loss of both the  $\alpha$ -BiNbO<sub>4</sub> and HP-BiNbO<sub>4</sub> ceramics might be due to the electric conduction at low frequency. The electrical resistivities of the  $\alpha$ -BiNbO<sub>4</sub> and HP-BiNbO<sub>4</sub> ceramics are  $4 \times 10^{13}$  and  $2 \times 10^{13} \Omega\cdot\text{cm}$ , respectively. In the high-frequency range (10 kHz–10 MHz), the dielectric loss became quite stable with frequency, maintaining a value of  $\sim 0.01$ . As seen in Figure 3(b)–(d), both the dielectric permittivity and the dielectric loss increased rapidly with temperature when the temperature was above 200 °C. For the HP-BiNbO<sub>4</sub> ceramic, there is an abrupt decrease in dielectric permittivity at  $\sim 690$  °C, and this phenomenon can be observed at all of the frequencies (100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz), which corresponding with the phase

transition from HP-BiNbO<sub>4</sub> to  $\alpha$ -BiNbO<sub>4</sub> phase. Meanwhile, a similar fluctuation could also be observed in the curves of dielectric loss vs. temperature at the same temperature point. Compared with the results of HP-BiNbO<sub>4</sub>, there is no abnormality observed for the  $\alpha$ -BiNbO<sub>4</sub> sample, which indicates that there is no phase transition in the temperature range 25–750 °C for  $\alpha$ -BiNbO<sub>4</sub>. It should be noted that, when the frequency was increased to above 100 kHz, the dielectric permittivity of HP-BiNbO<sub>4</sub> ceramic became quite stable with the temperature below the phase transition point, as seen in Figure 3(b), and the largest derivation of dielectric permittivity between 50 and 650 °C is  $\sim 0.02\%$  (at 1 MHz), which is much lower than that of the  $\alpha$ -BiNbO<sub>4</sub> ceramic ( $\sim 0.2\%$ ). All the results above indicate that the HP-BiNbO<sub>4</sub> ceramic possesses a large dielectric permittivity ( $\sim 240$ ) and a low dielectric loss ( $\sim 0.01$ ) comparable with  $\alpha$ -BiNbO<sub>4</sub> at a frequency above 10 kHz. More



**Figure 4.** The P–E loops of  $\alpha$ -BiNbO<sub>4</sub> and HP-BiNbO<sub>4</sub> ceramic samples.

importantly, when the frequency is above 100 kHz, the dielectric permittivity of HP-BiNbO<sub>4</sub> remains stable in the wide temperature range from 25 to 650 °C.

The polarization field (P–E) loops of the  $\alpha$ -BiNbO<sub>4</sub> and HP-BiNbO<sub>4</sub> ceramic samples measured at 10 Hz are shown in Figure 4. All the P–E loops are almost linear. The thicknesses of the ceramic samples are  $\sim$ 0.4 mm, and they were electrically broken down at  $\sim$ 85 kV cm<sup>-1</sup>. The energy density is defined as follows: energy density =

$$\frac{1}{2} \epsilon_0 \epsilon_r E^2 \quad (1)$$

The energy density of  $\alpha$ -BiNbO<sub>4</sub> is only 0.02 J cm<sup>-3</sup> at 83 kV cm<sup>-1</sup> due to the low breakdown strength at room temperature. With enhanced dielectric permittivity, the energy density of HP-BiNbO<sub>4</sub> is about 0.08 J cm<sup>-3</sup> at 81 kV cm<sup>-1</sup>, which is four times higher than that of  $\alpha$ -BiNbO<sub>4</sub>. With an increase in temperature to 100 °C, the dielectric permittivity and the dielectric loss of HP-BiNbO<sub>4</sub> ceramic both increased, resulting in a lossy loop and temperature-stable energy density. However, the weak breakdown strength of the ceramic sample caused the low energy density.

The phase transitions in BiNbO<sub>4</sub> ceramic from the HP to the orthorhombic structure at around 680 °C, then to the triclinic structure at around 1000 °C, were directly observed by the in situ XRD method. An abrupt volume expansion could be observed from the thermal expansion curve when the HP-BiNbO<sub>4</sub> transformed to the  $\alpha$ -BiNbO<sub>4</sub> phase along with an exothermic phenomenon. The dielectric permittivity of HP-BiNbO<sub>4</sub> was found to be 237–220, which is almost five times larger than that of  $\alpha$ -BiNbO<sub>4</sub> ( $\epsilon_r = 48$ –45), in the frequency range 100 Hz to 10 MHz, while the dielectric loss remains below 0.02. Meanwhile, the energy density of the HP-BiNbO<sub>4</sub> ceramic is four times higher than that of the  $\alpha$ -BiNbO<sub>4</sub> ceramic. All the results indicate that the HP-BiNbO<sub>4</sub> ceramic prepared via the HPHT method possesses a smaller cell volume and this results in a remarkable increase in the dielectric permittivity, and also introduces a new way of designing novel dielectrics.

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Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.scriptamat.2014.02.022>.

- [1] Z. Zou, J. Ye, K. Sayama, H. Arakawa, *Chem. Phys. Lett.* 343 (2001) 303.
- [2] B.C. Wang, J. Nisar, B. Pathak, T.W. Kang, R. Ahuja, *Appl. Phys. Lett.* 100 (2012) 182102.
- [3] S. Kamba, H. Wang, M. Berta, F. Kadlec, J. Petzelt, D. Zhou, X. Yao, *J. Eur. Ceram. Soc.* 26 (2006) 2861.
- [4] S. Chattopadhyay, P. Ayyub, R. Pinto, M.S. Multani, *J. Mater. Res.* 13 (1998) 1113.
- [5] R.S. Roth, J.L. Waring, *J. Res. Nat. Bur. Stand.* 66A (1962) 451.
- [6] H. Kagata, T. Inoue, J. Kato, I. Kameyama, *Jpn. J. Appl. Phys.* 31 (1992) 3152.
- [7] E.S. Kim, W. Choi, *J. Eur. Ceram. Soc.* 26 (2006) 1761.
- [8] N. Wang, M.Y. Zhao, Z.W. Yin, *Mater. Sci. Eng., B* 99 (2003) 238.
- [9] D. Zhou, L.X. Pang, X. Yao, H. Wang, *Mater. Chem. Phys.* 115 (2009) 126.
- [10] R.S. Roth, J.L. Waring, *Am. Mineral.* 48 (1963) 1348.
- [11] M.A. Subramanian, J.C. Calabrese, *Mater. Res. Bull.* 28 (1993) 523.
- [12] E.T. Keve, A.C. Skapski, *J. Solid State Chem.* 8 (1973) 159.
- [13] D. Zhou, H. Wang, X. Yao, X.Y. Wei, F. Xiang, L.X. Pang, *Appl. Phys. Lett.* 90 (2007) 172910.
- [14] Ch. Xu, D.W. He, Ch.M. Liu, H.K. Wang, L.L. Zhang, P. Wang, Sh. Yin, *Solid State Commun.* 156 (2013) 21.