Dielectric properties and phase transitions of BiNbO$_4$ ceramic

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In the present work, HP-BiNbO$_4$ was found, by in situ X-ray diffraction, thermal expansion and differential thermal analysis, to transform to orthorhombic BiNbO$_4$ at around 680 $^\circ$C along with an abrupt increase of volume, and to then transform to the triclinic BiNbO$_4$ at around 1000 $^\circ$C with an endothermic phenomenon. The results indicate that the dielectric permittivity of HP-BiNbO$_4$ 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$_4$ 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$_2$O$_3$–Nb$_2$O$_5$ binary system was first reported by Roth and Waring [1–5]. In particular, since the excellent microwave dielectric properties and low sintering temperature (permittivity $\sim$43, quality factor $Q_f \sim$10,000–20,000 GHz) of BiNbO$_4$ 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$_4$ ceramic and film samples [7–9].

The low-temperature orthorhombic modification of BiNbO$_4$ ($\alpha$ phase) and the phase transition to the high-temperature triclinic phase ($\beta$ phase) above 1020 $^\circ$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$_4$ and $\beta$-BiNbO$_4$ 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$_4$ to $\beta$-BiNbO$_4$ 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$_4$, was called HP-BiNbO$_4$, 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$_4$ ceramic are studied in detail.

BiNbO$_4$ was prepared via a solid-state reaction method. The calcination and temperature is 800 $^\circ$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...
uniaxial pressure of 100 MPa. The samples were sintered at 990 °C for 2 h to obtain the α-BiNbO₄ ceramic. The HP-BiNbO₄ was prepared through an HPHT method, using α-BiNbO₄ 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-BiNbO₄ ceramic, the α-BiNbO₄ 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 Kα 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⁻¹. 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 α-BiNbO₄ and HP-BiNbO₄ ceramics, as seen from Figure S1 in the Supplementary Information. The in situ XRD patterns of HP-BiNbO₄ 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-BiNbO₄, the diffraction peaks of α-BiNbO₄ could also be observed, and this indicates that the sample had partially transformed to α phase at this temperature. When the temperature was further increased to 730 °C, only the peaks of α-BiNbO₄ were revealed, indicating that the phase transformation from HP to α phase was complete when the temperature increased to 1000 °C. peaks of β BiNbO₄ were observed, which means that the α-BiNbO₄ had started to transform to β BiNbO₄ at this temperature. As seen from the XRD patterns at 1040 °C, there are no peaks of α-BiNbO₄ observed, so the phase transformation from α to β was complete at this temperature.

The thermal expansion and DTA curves of HP-BiNbO₄ ceramic are presented in Figure 2. It can be seen that the length of the HP-BiNbO₄ ceramic increased linearly with temperature below 680 °C, and the thermal expansion coefficient is calculated to be around 10 ppm °C⁻¹. 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 α phase and indicates that the α-BiNbO₄ has a larger cell volume than the HP-BiNbO₄. As seen from the thermal expansion curve in the cooling course, the thermal expansion coefficient of α-BiNbO₄ is also around 10 ppm °C⁻¹, which is similar to that of the HP-BiNbO₄. The temperature difference as a function of the temperature of the HP-BiNbO₄ ceramic is presented.

Figure 1. The in situ XRD patterns of the HP-BiNbO₄ sample (25–1150 °C). *, HP phase; o, α phase; T, β phase.

Figure 2. The thermal expansion (a) and DTA curves (b) of the HP-BiNbO₄ ceramic.
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-BiNbO₄ ceramic transformed to α-BiNbO₄ at around 726 °C in an exothermic reaction and then transformed to β-BiNbO₄ 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 α-BiNbO₄ and HP-BiNbO₄ 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-BiNbO₄ ceramic decreased slightly from 237 to 220, which is nevertheless almost five times larger than that of α-BiNbO₄ ($\varepsilon_r = 48–45$). In the frequency range 100 Hz–10 kHz, the dielectric loss of the α-BiNbO₄ ceramic ($\tan \delta = 0.05–0.01$) is larger than that ($\tan \delta = 0.02–0.01$) of the HP-BiNbO₄ ceramic. The large dielectric loss of both the α-BiNbO₄ and HP-BiNbO₄ ceramics might be due to the electric conduction at low frequency. The electrical resistivities of the α-BiNbO₄ and HP-BiNbO₄ ceramics are $4 \times 10^{13}$ and $2 \times 10^{12}$ $\Omega \cdot \text{cm}$, 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-BiNbO₄ 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-BiNbO₄ to α-BiNbO₄ 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-BiNbO₄, there is no abnormality observed for the α-BiNbO₄ sample, which indicates that there is no phase transition in the temperature range 25–750 °C for α-BiNbO₄. It should be noted that, when the frequency was increased to above 100 kHz, the dielectric permittivity of HP-BiNbO₄ 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 α-BiNbO₄ ceramic ($\sim 0.2%$). All the results above indicate that the HP-BiNbO₄ ceramic possesses a large dielectric permittivity ($\sim 240$) and a low dielectric loss ($\sim 0.01$) comparable with α-BiNbO₄ at a frequency above 10 kHz. More
importantly, when the frequency is above 100 kHz, the
dielectric permittivity of HP-BiNbO₄ remains stable in
the wide temperature range from 25 to 650 °C.

The polarization field (P–E) loops of the α-BiNbO₄
and HP-BiNbO₄ 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
~0.4 mm, and they were electrically broken down at
~85 kV cm⁻¹. The energy density is defined as
follows:

\[
\text{energy density} = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2
\]

The energy density of α-BiNbO₄ is only 0.02 J cm⁻³
at 83 kV cm⁻¹ due to the low breakdown strength at
room temperature. With enhanced dielectric permittiv-
ity, the energy density of HP-BiNbO₄ is about
0.08 J cm⁻³ at 81 kV cm⁻¹, which is four times higher
than that of α-BiNbO₄. With an increase in temperature
to 100 °C, the dielectric permittivity and the dielectric
loss of HP-BiNbO₄ 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 BiNbO₄ 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-BiNbO₄ transformed to
the α-BiNbO₄ phase along with an exothermic phenom-
enum. The dielectric permittivity of HP-BiNbO₄ was
found to be 237–220, which is almost five times larger
than that of α-BiNbO₄ (εᵣ = 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-BiNbO₄ ceramic is four times higher than
that of the α-BiNbO₄ ceramic. All the results indicate
that the HP-BiNbO₄ 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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