# Exploring the compression behavior of HP-$BiNbO_4$ under high pressure*

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In the present work, a third form, the so-called HP-$BiNbO_4$ synthesized at high pressure and high temperature is investigated with the *in-situ* angle-dispersive x-ray diffraction (ADXRD) measurements under high pressure. We explore the compression behavior and phase stability of HP-$BiNbO_4$. The structure of HP-$BiNbO_4$ is first determined. The x-ray diffraction data reveal that the structure HP-$BiNbO_4$ is stable under pressures up to 24.1 GPa. The ADXRD data yield a bulk modulus $K_o = 185(7)$ GPa with a pressure derivative $K_o' = 2.9(0.8)$. Furthermore, the data are compared with those of other $ABO_4$ compounds. The results show that the bulk modulus of HP-$BiNbO_4$ (about 185 GPa) is slightly higher than that of tetragonal $BiVO_4$ and significantly greater than those of the tungstates and molybdates.

**Keywords:** high pressure, $BiNbO_4$, x-ray diffraction, bulk modulus

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## 1. Introduction

Bismuth niobate fourfold oxide ($BiNbO_4$) belongs to the family of $ABO_4$ compounds. The structure of $ABO_4$ compound is versatile with *A* and *B* cations, and has been studied at high temperature and high pressure.[1]

In general, $BiNbO_4$ possess two polymorphs: a low-temperature orthorhombic ($\alpha$) phase[2–4] and a high-temperature triclinic ($\beta$) phase.[5–7] Recently, a new phase of $BiNbO_4$, called HP-$BiNbO_4$, has been obtained above 3 GPa and 800 °C. The phase transitions of $\alpha$-$BiNbO_4$ and $\beta$-$BiNbO_4$ were investigated at 0–5 GPa and 300–1800 °C.[8] It has been shown that the transition temperature decreases with increasing pressure and the phase transition is irreversible after cooling and decompressing. Furthermore, the *in-situ* x-ray diffraction, differential thermal analysis, thermal expansion and dielectric properties of the novel HP-$BiNbO_4$ ceramic were studied in detail by Zhou *et al.*[9] The results indicate that the energy density of HP-$BiNbO_4$ ceramic is four times higher than that of the $\alpha$-$BiNbO_4$ ceramic and the dielectric permittivity increases obviously.[9] However, to the best of our knowledge, the crystal structure of HP-$BiNbO_4$ has not been determined, and the behaviors of the novel HP- $BiNbO_4$ in a diamond anvil cell (DAC) have not yet been studied by using the angle-dispersive x-ray diffraction (ADXRD) measurements under high pressure with synchrotron radiation either. The differences in bulk modulus from those of other $ABO_4$ compounds remain to be studied.

In our work, we apply the *in-situ* synchrotron x-ray diffraction method to HP-$BiNbO_4$ under high pressures up to 24.1 GPa, and investigate the compression behavior and the phase stability. In addition, the equation of state (EOS) of HP-$BiNbO_4$ is determined. Here, we for the first time report on the new phase of HP-$BiNbO_4$ in DAC by using in-situ high pressure ADXRD with synchrotron radiation.

## 2. Experiment

The HP-$BiNbO_4$ was synthesized at 5 GPa and 1300 °C for 10 min through an HPHT method, using $\alpha$-$BiNbO_4$ powders as the raw material. $BiNbO_4$ ceramics were prepared by a solid-state reaction method from starting materials of $Bi_2O_3$ and $Nb_2O_5$ mixed in 1:1 stoichiometric ratio. The powders were compressed into cylinders, and then were sintered at 950 °C for 24 h to obtain the $\alpha$-$BiNbO_4$ ceramic. X-ray diffraction analysis (XRD; DX-2500, Dandong, China) using a Cu-Ka radiation source with $\lambda = 1.5404$ Å and scanning electron microscopy (SEM; JSM-6490, JEOL, Akishima, Japan) were performed on raw materials to detect the microstructures and compositions. The HP-$BiNbO_4$ powders with a small ruby chip were loaded into a diamond anvil cell (DAC) with a pair of 300 μm culets, and a stainless steel gasket was used with a sample hole of 100 μm diameter.[10–15] Methanol-ethanol (4:1) was used as a pressure-transmitting medium to minimize the uniaxial stress effect.[10] The pressures were determined by the ruby fluorescence shifts.[16]

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The high-pressure ADXRD experiments were performed at 4W2 beamline, Beijing Synchrotron Radiation Facility (BSRF, China) with a wavelength of 0.6199 Å. The monochromatic x-ray beam was focused into a spot with a size of approximately 38 μm × 16 μm. The diffraction patterns at various pressures were recorded with a Mar345 imaging plate detector. High-purity $CeO_2$ powder was used to calibrate the geometrical parameters of the detector. The collected two-dimensional (2D) diffraction patterns were integrated into one-dimensional (1D) profiles with software FIT2D.[15,17] The GASA program was applied to the Rietveld refinements of sample x-ray diffraction data.[18]

## 3. Results and discussion

X-ray diffraction patterns of the $\alpha$-$BiNbO_4$ samples prepared via a solid-state reaction method and the HP-$BiNbO_4$ samples synthesized through an HPHT method are shown in Figs. 1(a) and 1(b). The results of the synthesized $\alpha$-$BiNbO_4$ and HP-$BiNbO_4$ are demonstrated to be consistent with previous results.[8] The insets in Figs. 1(a) and 1(b) show the scanning electron microscopy (SEM) images of $\alpha$-$BiNbO_4$ and HP-$BiNbO_4$, respectively, and reveal their different microstructures.

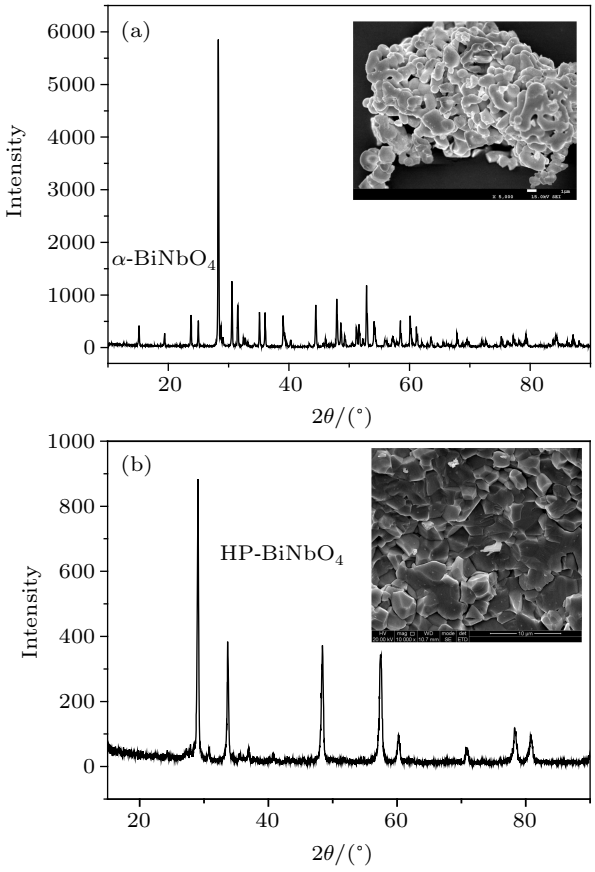



**Fig. 1.** X-ray diffraction patterns of $BiNbO_4$. (a) x-ray diffraction patterns of the $\alpha$-$BiNbO_4$ prepared via a solid-state reaction. (b) x-ray diffraction patterns of the HP-$BiNbO_4$ sintered at 5 GPa and 1100 °C. Insets show the SEM micrographs of (a) $\alpha$-$BiNbO_4$ and (b) HP-$BiNbO_4$.

Rietveld refinement is employed to solve the crystal structure of the HP-$BiNbO_4$ phase. Cubic structure ($A_2B_2O_7$) is chosen as a starting model,[19] since this compound has a formula unit potentially similar to that of $BiNbO_4$. Figure 2 displays the powder x-ray diffraction data of the synthesized HP-$BiNbO_4$ and the results of Rietveld refinements, with $Sm_2Sn_2O_7$ and $Dy_3NbO_7$ used as starting model, by using the program GASA,[18] the agreement factors are $R_P = 1\%$, $W_{RP} = 1.6\%$, $R(F^2) = 5.4\%$, and $CHI^2 = 6.745$; $R_P = 1.5\%$, $W_{RP} = 2.5\%$, $R(F^2) = 6.1\%$, and $CHI^2 = 15.64$, respectively. However, the $Dy_3NbO_7$ structure cannot explain the two peaks at 14–16 angles. The cubic $Sm_2Sn_2O_7$ structure fitting is better for HP-$BiNbO_4$ structure than for $Dy_3NbO_7$ structure. The crystal HP-$BiNbO_4$ is found to have a cubic microstructure.

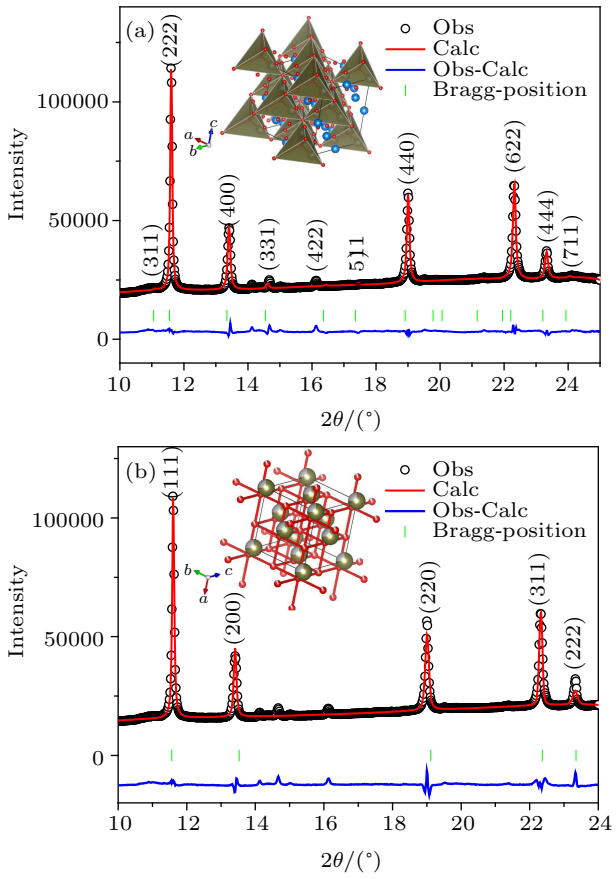



**Fig. 2.** (color online) The x-ray diffraction and Rietveld refinement patterns of HP-$BiNbO_4$ about 1 GPa. (a) The HP-$BiNbO_4$ sample based on $Sm_2Sn_2O_7$. (b) The HP-$BiNbO_4$ sample based on $Dy_3NbO_7$. Empty circle: observed curve; red line: calculated curve; green short vertical lines: all possible Bragg positions; bottom line: difference curve.

In a previous paper,[8] to study the stability of HP-$BiNbO_4$, the samples were annealed at different temperatures under atmospheric pressure. It has been found that HP-$BiNbO_4$ remains stable up to 500 °C. At above 600 °C, the HP-$BiNbO_4$ is converted into $\alpha$-$BiNbO_4$ and transformed into $\beta$-$BiNbO_4$ when the annealed temperature is increased to 1150 °C. However, there has been not enough research

of compression behavior of HP-$BiNbO_4$. The *in-situ* high-pressure angle-dispersive x-ray diffraction data are shown in Fig. 3(a) for both compression and decompression procedures. The highest pressure applied is 24.1 GPa. Five major diffraction peaks of HP-$BiNbO_4$ are observed, the other peaks are relatively weak. All the diffraction peaks shift toward larger diffraction angles with pressure increasing, and there no new peaks appear. The pressure dependence of d-spacing of different planes is shown in Fig. 3(b). Under compression, we do not find any evidence of pressure-induced phase transition nor chemical decomposition, indicating that the cubic structure remains stable at pressures up to 24.1 GPa. In addition, as the pressure increases to 24.1 GPa, peak broadening increases. This fact can be attributed to the stress during the experiment. X-ray diffraction data of the decompression sample further prove the result.

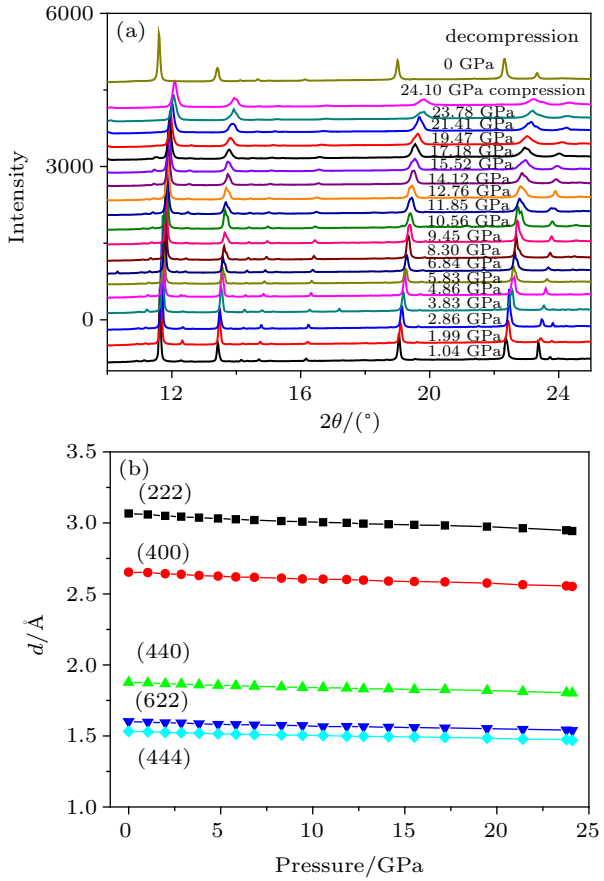



**Fig. 3.** (color online) (a) X-ray diffraction patterns of HP-$BiNbO_4$ under various pressures, (b) pressure dependence of $d$-spacing of the mainly five planes.

As starting parameters, the refined cell parameters ($a = b = c = 10.6754$ Å) with space group $Fd$-$3m$ (No. 227) are used. The pressure dependence of the unit-cell parameters of HP-$BiNbO_4$ is plotted in Fig. 4. The present pressure–volume data are fitted to a third-order Birch–Murnaghan equation,[20,21]

$$P = 1.5K_0\left[\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}}\right] \times \left\{1 - 0.75\left(4 - K_0'\right)\left[\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right]\right\}, \quad (1)$$

where $K_o$ and $V_o$ are the bulk modulus and unit-cell volume in ambient condition, respectively, and $K_o'$ is the pressure derivative of $K_o$. The equation of cubic HP-$BiNbO_4$ is determined: $K_o = 185(7)$ GPa, $K_o' = 2.9(0.8)$. For comparison, the results obtained in earlier studies of $BiNbO_4$ and other $ABO_4$ compounds are collected in Table 1. We can see that the bulk moduli differ widely among these $ABO_4$ compounds. The bulk modulus of HP-$BiNbO_4$ (about 185 GPa) is slightly larger than that of tetragonal $BiVO_4$ and significantly greater than those of the tungstates and molybdates. Hazen *et al.*[1] and Mariathasan *et al.*[22] reported that $ABO_4$ compound has bulk modulus that is primarily a function of 8-coordinated site valence, and higher valence, the less compressibility.[22] Therefore, the compressibility values of divalent cation polyhedrons in these tungstates and molybdates are both greater than that of the $Bi^{3+}$ polyhedron, leading to the difference. For the same $A$–O bonds, such as HP-$BiNbO_4$ and tetragonal $BiVO_4$, the difference in bulk modulus is attributed to the structure. The HP-$BiNbO_4$ is a dense high pressure phase compared with the tetragonal $BiVO_4$. Calculated values of $\alpha$-$BiNbO_4$ and

**Table 1.** List of the values of bulk modulus ($K_o$), pressure derivative ($K_o'$) of $BiNbO_4$, compared with previous results. Bulk moduli of some $ABO_4$ compounds are listed for comparison.

| Compounds | $K_o$/GPa | $K_o'$ | Techniques | Reference |
|---|---|---|---|---|
| HP-$BiNbO_4$ | 185 | 2.9 | experiment | This work |
| $\alpha$−$BiNbO_4$ | 201 | 4.52 | calculation | [23] |
| $\beta$−$BiNbO_4$ | 206 | 4.55 | calculation | [23] |
| $CaWO_4$ | 68 | 4 | experiment | [1] |
| $CaMoO_4$ | 81.5 | 4 | experiment | [1] |
| $PbWO_4$ | 64 | 4 | experiment | [1] |
| $PbMoO_4$ | 64 | 4 | experiment | [1] |
| $CdMoO_4$ | 104 | 4 | experiment | [1] |
| $BiVO_4$ | 150 | 4 | experiment | [22] |

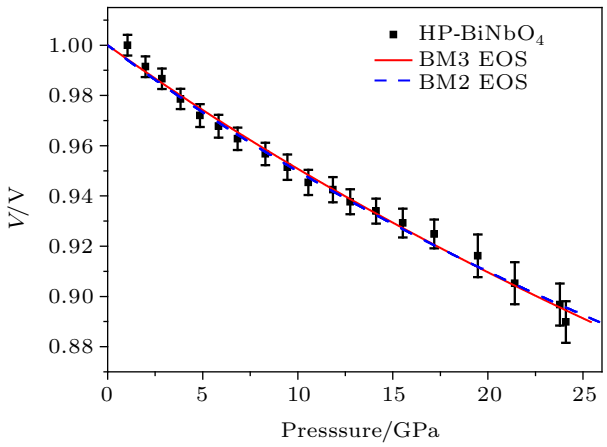



**Fig. 4.** (color online) Normalized unit cell volumes of HP-$BiNbO_4$ as a function of pressure. The red solid line represents experimental fitting of third-order Birch–Murnaghan equation. The blue dashed line denotes the best fitting of second-order Birch–Murnaghan equation.

$\beta$-$BiNbO_4$ are slightly higher than that of HP-$BiNbO_4$, for which the main reason, we think, is that there exist some discrepancies between the experimental result and theoretical calculation due to the fact that the parameters used in theoretical calculation are obtained from the crystal in ambient conditions.

## 4. Conclusions

In this paper, the structure of HP-$BiNbO_4$ is revealed to be a cubic structure by XRD refinements, with cubic $Sm_2Sn_2O_7$ and $Dy_3NbO_7$ used as starting model. The compressibility and phase stability of HP-$BiNbO_4$ are investigated at high pressure under quasi-hydrostatic conditions by using synchrotron x-ray diffraction. The HP-$BiNbO_4$ is found to have a stable cubic structure at pressures up to 24.1 GPa. The derived bulk modulus is 185 GPa, which is about 10% lower than the reported theoretical calculation values for $\alpha$-$BiNbO_4$ and $\beta$-$BiNbO_4$ (201 GPa), but it is significantly greater than those of the $BiVO_4$ (150 GPa), tungstates and molybdates (60 to 105 GPa). The results indicate that the HP-$BiNbO_4$ ceramic is synthesized via the HPHT method, and the bulk modulus of HP-$BiNbO_4$ ceramic is improved obviously.

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