

The study of the structure stability of hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ under high pressure

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In this work, the structure stability of hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ has been investigated by high-pressure synchrotron X-ray diffraction measurements. The results show that the structure is stable within the pressure up to 18.3 GPa. The diffraction data are refined and the lattice constants a and c are determined, which is compressed by 6.3(7)% and 3.5(0)% within the experimental pressure, respectively. By fitting the pressure dependence of V/V_0 (unit cell volume divided by that at ambient pressure) with the second-order Birch equation of state, the bulk modulus B_0 is given to be about 87.1(0) GPa.

Keywords: BiPO_4 ; high-pressure synchrotron; structure stability.

1. Introduction

Inorganic phosphates have been studied comprehensively due to their multifunctional applications. For example, zirconium phosphate $\text{Zr}_2\text{O}(\text{PO})_4$ and $\text{NaZr}_2(\text{PO}_4)_3$ are used to clean the high-level nuclear wastes.^{1,2} BiPO_4 are studied as catalyst,³ humidity sensor,^{4,5} microwave dielectric⁶ and host for luminescent

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ions.⁷ BiPO_4 exhibits three different phases, i.e., hexagonal phase, high-temperature metastable monoclinic phase (HTMP) and low-temperature monoclinic phase (LTMP). Using simple co-precipitation method hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ can be synthesized. After the dehydration at high temperature, BiPO_4 transforms into HTMP with the space group of $P21/m$. The LTMP (space group: $P21/n$) and HTMP can be inversely transformed by heating or hand-grinding.⁸ More interesting, it is easy to synthesize LTMP and HTMP BiPO_4 by controlling pH values in the solution.⁹ Recently, the phase transition of BiPO_4 was studied by high-pressure synchrotron X-ray diffraction.¹⁰ When HTMP is used as the starting material, it starts to transform into LTMP at approximately 0.8 GPa. For the starting material of hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$, it transforms to LTMP within 0.2 GPa. LTMP is stable up to 31 GPa. It is reported that $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ is a metastable phase, in which H_2O molecules play a crucial role in the retention of this phase.¹⁰ Under high temperature, $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ loses H_2O molecules. However, it is questionable that whether the role of high pressure is identical to that of high temperature because H_2O molecules in the $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ may be retained and thereby the structure of $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ should be more stable under high pressure.

Here, we study the hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ stability under high pressure. The results show that the hexagonal phase is stable up to 18.3 GPa, which contradicts with Ref. 10. The most possible reason for this is from the different grain size of raw hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$, which leads to the presence of distinct kinetic barrier hindering the occurrence of the phase transition.

2. Experimental

The sample was prepared through a co-precipitation method. In a typical experiment, 2 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 5 mL ethylene glycol and 2 mmol $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in 100 mL of deionized water. A white precipitation was formed. After stirring at room temperature for 12 h, the suspension was collected and washed by deionized water. The $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ sample was obtained after drying at 60°C for 4 h.

The high-pressure synchrotron X-ray diffraction measurements were carried out at the Beijing Synchrotron Radiation Facility at room-temperature with a wavelength 0.6199 Å. The high pressure was generated by using a symmetric type diamond-anvil cell (DAC) with 300 μm culets. The sample was loaded into the high pressure chamber with a T301 stainless steel gasket. The pressure was measured by using the ruby fluorescence technique. The crystal structures were refined using GSAS package.¹¹

3. Results and Discussion

Figure 1(a) shows the high-pressure synchrotron X-ray diffraction patterns of hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ and Fig. 1(b) is the typical refinement result at 3.7(0) GPa. The sharp diffraction peaks indicate a high quality of our sample. All peaks can

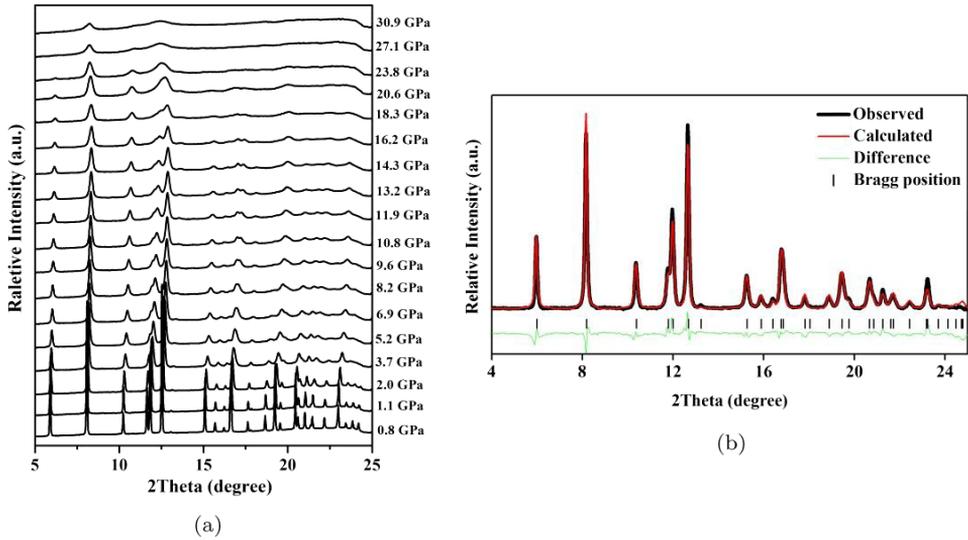


Fig. 1. (Color online) (a) High-pressure synchrotron X-ray diffraction patterns of hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$. (b) The typical refinement results of X-ray diffraction at 3.7 GPa. The refinement converges to $R_{wp} = 3.83\%$ and $R_p = 2.61\%$, respectively.

be indexed according to a hexagonal phase (space group: $P3121$, JCPDS, card no. 45-1370), indicating a pure phase. When pressure increases within 18.3 GPa, all the peaks shift to high angle direction and no new peak appears, which demonstrates that pressure compresses the crystal lattice and the hexagonal phase is stable within that pressure. When pressure increases more than 18.3 GPa, the peaks are significantly broaden, suggesting the amorphization under high pressure. After decompression, the hexagonal phase is recovered. The stability of hexagonal phase under 18.3 GPa obviously contradicts the results reported in Ref. 10, which may derive from the difference of starting material, such as the grain size. The kinetic barriers between different polymorphs always hinder the occurrence of the phase transition.

Figure 2(a) shows the lattice parameters of a and c as a function of pressure. As indicated, the axis of a and c are compressed with the increase of pressure. However, they exhibit anisotropic compressions. The axis of a decreases by 6.3(7)% almost linearly within 18.3 GPa, while c shrinks about 3.0(0)% at 13.2 GPa and then presents great compression resistance. Figure 2(b) presents the plot of unit cell volume ratio (V/V_0 , V_0 is the unit volume at ambient pressure and V corresponds to that of high pressure) versus pressure (P). The Birch–Murnaghan equation is used to deduce the bulk modulus B_0 . The solid lines are the fitted results using the second-order Birch equation of state. It is clear that the unit cell volume shrinks monotonously and no abrupt jump of V/V_0 is observed as the pressure increasing. These observations indicates that hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ is not sensitive to the pressure, which is not consistent with the role of high temperature. It may

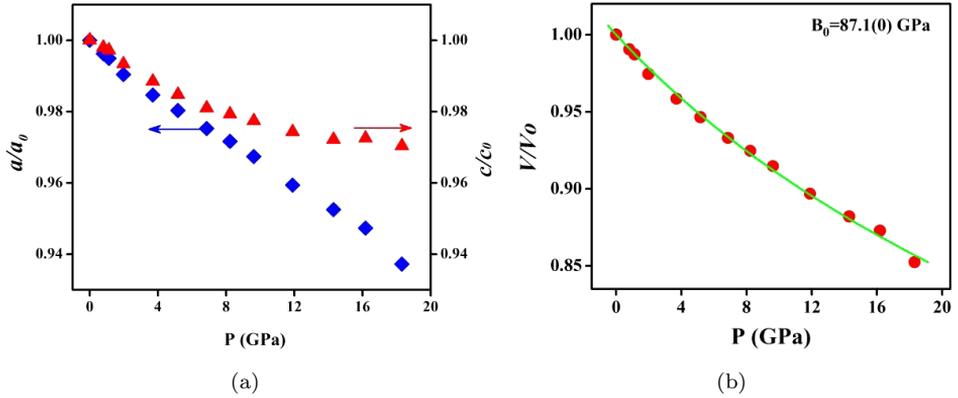


Fig. 2. (Color online) (a) Pressure dependence of changes of lattice parameters (a and c); (b) pressure dependent of unit cell volume of $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$. The solid line are fitting results according to the Brich–Murnaghan equation.

related to the effect of pressure to the structure of $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$. Because H_2O molecules in $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ are restrained and thereby stabilizes the crystal structure.

$$P(\text{GPa}) = \frac{3}{2}B_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \times \left\{ 1 - \left(3 - \frac{3}{4}B'_0 \right) \times \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}.$$

With B'_0 fixed at 4, the bulk modulus $B_0 = 87.1(0)$ GPa is obtained.

4. Conclusion

In this work, the structure stability of hexagonal $\text{Bi}(\text{PO}_4)(\text{H}_2\text{O})_{0.67}$ under high pressure has been studied. The hexagonal structure is stable within our experimental pressure of 18.3 GPa, in which the lattice constants a and c are compressed by 6.3% and 3.5%, respectively. The bulk modulus B_0 is about 87.1(0) GPa.

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