

Cite this: *CrystEngComm*, 2012, 14, 7907–7914

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PAPER

pH-driven hydrothermal synthesis and formation mechanism of all BiPO₄ polymorphs†

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Received 9th March 2012, Accepted 17th August 2012

DOI: 10.1039/c2ce25337b

Understanding of formation mechanism of inorganic solids by solution chemistry is always disturbed by the interference effect of the impurities from starting materials. Herein, we exploited a new two-step route to the selective synthesis of BiPO₄ of different polymorphs with an aim to eliminate the impurity interference effect. The first step is the room-temperature solution synthesis of a hexagonal phase (HP), and the second step involves sufficient washing of HP and a subsequent hydrothermal treatment of HP under given conditions. The formation mechanism of BiPO₄ nanocrystals of different polymorphs was studied by monitoring the reaction parameters like pH, reaction temperature, time, and impurity ions as well as by sample characterizations using X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. It is found that the pH of the solution is the determinant parameter for the selective synthesis of BiPO₄ polymorphs. Namely, at 240 °C and under strong acidic conditions (pH < 1), HP underwent a phase transformation to a low-temperature monoclinic phase (LTMP), while under neutral or weakly acidic conditions (3 < pH < 7), HP transferred to a high-temperature monoclinic phase (HTMP). Further increasing the solution pH value up to 14 led to the formation of P-doped Bi₂O₃, a phase which is never accessible by conventional solution chemistry but firing in air at $T > 750$ °C. Based on these observations, two kinds of phase transition mechanisms were discussed.

1. Introduction

Understanding of the formation mechanism of inorganic solids is very important, since the majority of inorganic solid materials have unique properties and therefore can be used for a wide variety of applications. Consequently, many solution chemistry routes have been developed to synthesize inorganic solid materials.^{1–3} To understand the relevant formation or growth processes involved in solution chemistry, several mechanisms, like Ostwald ripening (OR) and oriented attachment (OA) have been put forward.^{4–7} Indeed, these mechanisms have played certain key roles in interpreting morphological control occurring in solution. Nevertheless, for all these solution chemistry routes, soluble metal salts usually have to be used as the starting materials. As a result, some unwanted impurity species from starting materials would be introduced into the reaction systems, which will bring some unknown interference effects and thus disturb the formation process, making it very difficult to control

the phase structures for desired properties. For instance, when using hydrothermal synthesis, raw material TiCl₄ will give rise to rutile-type TiO₂, while raw material TiOSO₄ will yield anatase or brookite-type TiO₂.^{8,9} Therefore, it is necessary to develop a synthetic approach to inorganic solids that can eliminate the unwanted ions from the starting materials.

We feel that a two-step crystallization method may have the great potential to eliminate the impurity interference effect. This proposition is based on the following dual considerations: (i) a crystalline precursor is first formed in solution at room temperature, then it could be relatively easier to wash off the unwanted species mainly adsorbed on surfaces of the crystalline precursors, and (ii) the subsequent transformation of crystalline precursor to other phase structures under hydrothermal treatments would have a definite formation process with less impact from the impurity ions. The key to this two-step crystallization method lies in the choice of target materials.

We choose bismuth phosphate (BiPO₄) as a target material because BiPO₄ is a typical compound known to crystallize in three phases: hexagonal phase (HP), low-temperature monoclinic phase (LTMP), and high-temperature monoclinic phase (HTMP).¹⁰ Up to now, preparations of BiPO₄ crystals are mainly based on one-pot solution chemistry. For example, HP nanorods were prepared *via* a sonochemical method in a surfactant/ligand-free system.¹¹ Qian *et al.*¹² reported the synthesis of HP nano-cocoons and LTMP nanorods by

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† Electronic supplementary information (ESI) available: SEM image of the HP precursor prepared at room temperature. XRD patterns of the samples prepared by one-pot hydrothermal approach. XRD patterns of the LTMP and HTMP hydrothermal treatment under given condition. See DOI: 10.1039/c2ce25337b

solvothermal method. Depending on the solvent used,¹³ HP or LTMP was also prepared at room temperature. Even so, the formation mechanism for these phase structures deserves to be made clear, since many examples of one-pot solution chemistry popularly ignored the impact of unwanted impurity species from starting materials.

Herein, we report a two-step crystallization method to the selective synthesis of BiPO₄ nanocrystals. The effects of pH, reaction temperature, time, and impurity ions on the phase stability and transition reaction were systematically studied and relevant transformation mechanism were discussed. This approach is reproducible and could be extended to the synthesis of other inorganic solids for tailored polymorphs.

2. Experimental section

2.1 Two-step sample preparation

Room-temperature synthesis. HP precursor was prepared by a simple co-precipitation method at room temperature without adding any surfactant. In a typical synthesis, 10 mmol Bi(NO₃)₃·5H₂O was added to 100 mL deionized water to form a white precipitate, into which 100 mL of 0.1 M NH₄H₂PO₄ aqueous solution was slowly dropped under vigorously stirring. Then the mixed solution was further stirred for 2 h at room temperature. The resultant white precipitate was filtered, washed with distilled water, and HP precursor was obtained.

Hydrothermal treatment. Selective synthesis of BiPO₄ polymorphs was carried out by hydrothermal treatment of the HP precursor under the given conditions. In a typical treatment process, about 0.2 g of the as-synthesized HP precursor was put into a Teflon cup containing 75 mL of deionized water to form a suspension. The pH of the suspension in the cup was adjusted to an array of target values (*i.e.*, 0–14) with either HNO₃ or NaOH. After stirring for 15 min, the Teflon cup with the suspension were sealed and put into a 100 mL Teflon-lined stainless steel autoclave, which was put into an electric oven and held at 160, 200, or 240 °C for the required time then cooled to room temperature naturally. The pH of the reacted suspension was determined again. The obtained powders were separated from the suspension by centrifugation, washed with distilled water, and dried for the determination of phase content and particle size.

For comparison purposes, the popular one-pot hydrothermal synthesis was also conducted: 10 mmol Bi(NO₃)₃·5H₂O was added to 100 mL deionized water to form a white precipitate, into which 100 mL of 0.1 M NH₄H₂PO₄ aqueous solution was slowly dropped under vigorously stirring and the mixed solution was adjusted by dropping HNO₃ or NaOH solutions to wanted pH values and then transferred into a 100 mL Teflon-lined stainless steel autoclave for hydrothermal treatment.

2.2 Sample characterization

All samples were characterized by X-ray diffraction (XRD) on a Rigaku 2000 apparatus with Cu-K α irradiation. Scanning electron microscope (SEM) images were used to determine particle size and morphology of BiPO₄ polymorphs. Infrared spectrum of the sample was performed on a Perkin-Elmer IR

spectrometer using a KBr pellet technique. The mass ratio of the sample to KBr is set at 4%. The solubility measurements were conducted as follows: in order to form saturated solution at given conditions, approximately 100 mg portions of BiPO₄ samples were suspended in 50 mL of given pH value solutions, which were adjusted by controlling the additive amount of HNO₃ or NaOH. Then, the suspension was incubated for two weeks. In order to increase the separating efficiency of solid from solution, at the end of the equilibration periods, suspensions were centrifuged at 12 000 rpm for 30 min. Finally, the supernatant was analyzed for Bi with inductively coupled plasma mass spectroscopy (ICP-MS).

3. Results

3.1 Room temperature synthesis of crystalline precursor HP

Synthesis of BiPO₄ nanocrystals usually requires hydrothermal or solvothermal condition. In the present work, the HP precursor was prepared by a co-precipitation method at room temperature. Fig. 1 shows the XRD patterns for the precursor. All diffraction peaks are sharp, which indicates high crystallinity. All diffraction peaks can be indexed to a hexagonal phase (space group: *P*3₁21, JCPDS card no. 45-1370), while no other peaks can be detected. Therefore, the precursor HP is present in a pure phase. HP is composed of an open framework structure due to the symmetrical arrangement of chains of alternating PO₄ tetrahedra and BiO₈ polyhedra with lattice water molecules that are located in the channels parallel to the *c*-axis, as illustrated in the insert of Fig. 1. The infrared spectrum of the precursor was measured to investigate chemical species absorbed on the sample surfaces. As indicated in Fig. S1,[†] there are no other absorption peaks except for the peaks corresponding to the surface absorbed water and eigenvibrations of precursor HP, which indicates that the unreacted ions from the starting materials were effectively washed off. This provides favorable conditions for the phase formation in the following hydrothermal treatment.

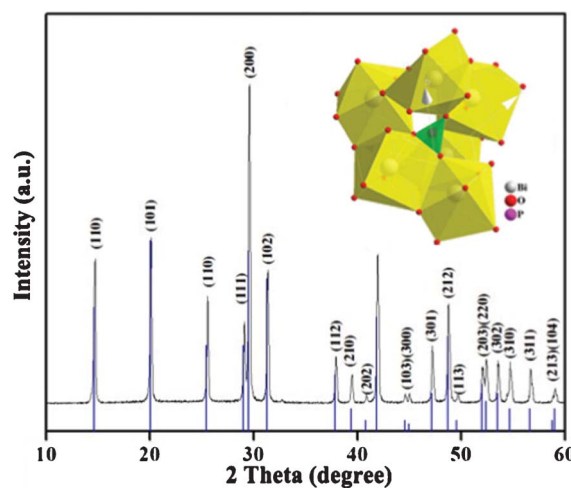


Fig. 1 XRD pattern of the HP precursor prepared at room temperature. Inset shows the corresponding lattice structure. PO₄ tetrahedra are shown in green and BiO₈ polyhedra in yellow.

3.2 Hydrothermal treatment of HP to give different polymorphs

pH effect. Here, we employed nitric acid or sodium hydroxide to adjust the pH values of the reaction solutions. The amount of HP precursor in each feedstock was fixed at 0.2 g. Reaction conditions were fixed at 240 °C for 24 h. Fig. 2 shows the XRD patterns of the samples obtained after hydrothermal treatments at different pH values. It can be seen that in a strong acidic medium (pH = 0), pure phase LTMP was obtained. When the pH value increased to 1, a mixture of LTMP and HTMP was formed. As the pH values further increased to 3 and 7, pure HTMP was generated. This result is strikingly different from those recently reported using an one-pot hydrothermal method.^{11,14} For the latter cases, varying pH between 0.5 and 5 with chlorine acid has led to LTMP contaminated by BiOCl.¹¹ The preparation of pure-phase HTMP has to proceed in the presence of a high concentration of H₃PO₄.¹⁴

Continuously increasing the pH value to 10, a mixture of LTMP and HTMP occurred again. Further increasing solution pH to 13 led to the disappearance of LTMP or HTMP and the formation of a yellowish unknown phase. Once in a strong alkaline solution of pH = 14, the HP precursor completely transformed to a yellowish P-doped bismuth oxide, Bi₁₂P_{0.86}O_{20.14} (PDF#44-0189). This seems to be the first example of the low-temperature synthesis of such compounds, since the previous preparation usually needed a high temperature of 750 °C.¹⁵ These results indicate that the pH value of the solution plays a vital role in the two-step synthesis of BiPO₄ polymorphs.

The morphologies of these phase structures obtained in various pH solutions were examined by SEM images. As shown in Fig. 3, the sample had a rod-like shape (Fig. 3a, b) under acidic conditions. Under neutral conditions, the sample was composed of irregular polyhedron particles (Fig. 3c). As shown in Fig. 3d, the morphology of the sample changed from polyhedron to sheet-like aggregations as the pH value increased

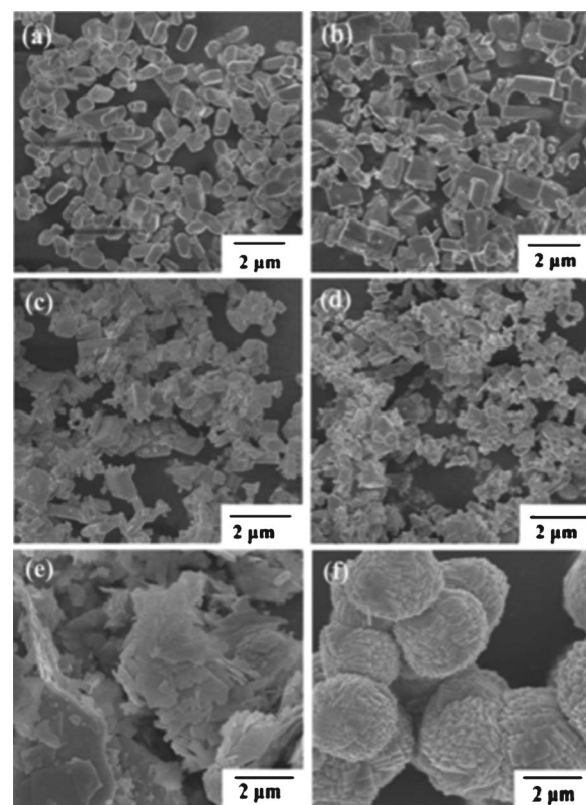


Fig. 3 SEM images of the samples obtained after hydrothermal treatment of the HP precursor at given pH solutions: (a) pH = 0; (b) pH = 3; (c) pH = 7; (d) pH = 10; (e) pH = 13; (f) pH = 14.

from 10 to 13. Uniform microspheres with a rough surface were observed in the samples, as shown in Fig. 3f, when the pH value further increased to 14.

Temperature effect. Fig. 4 shows the XRD patterns of the samples synthesized at different reaction temperatures with a fixed reaction time of 12 h. At 160 °C, it is seen that part of the HP precursor converted into a mixture of LTMP and HTMP in acidic solution. As to the transformation in neutral solution, only a bit of HP transformed into LTMP. HP remained after hydrothermally treated in basic solution (pH = 13). With the increase of reaction temperature to 200 °C, phase transformation obviously accelerated. As can be seen, HP completely converted into LTMP in acidic solution (pH = 0). In the pH case of 7, the main product was HTMP with a scrap of LTMP and HP. It is interesting to note that HP completely converted into a yellowish P-doped bismuth oxide Bi₁₂P_{0.86}O_{20.14} (PDF#44-0189) in strong basic solution (pH = 14). According to these results, we concluded that phase transformation accelerated with the increase of temperature.

The effect of reaction temperature on the morphology was illustrated in Fig. 5. At 160 °C, the particle size and morphology of the samples was almost the same in different pH solutions. The samples were mainly composed of rice-like particles about 300 nm in size, which is similar with that of the HP precursor (Fig. S2†), which also indicates that the phase transformation was slow at this reaction temperature. For the case of 200 °C, however, the particle size and morphology apparently altered.

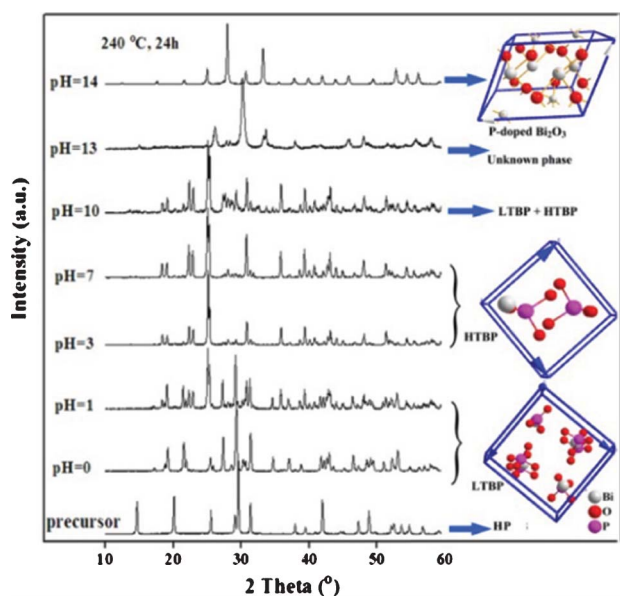


Fig. 2 XRD patterns for the samples obtained after hydrothermal treatments of HP precursor at 240 °C for 24 h at given pH values.

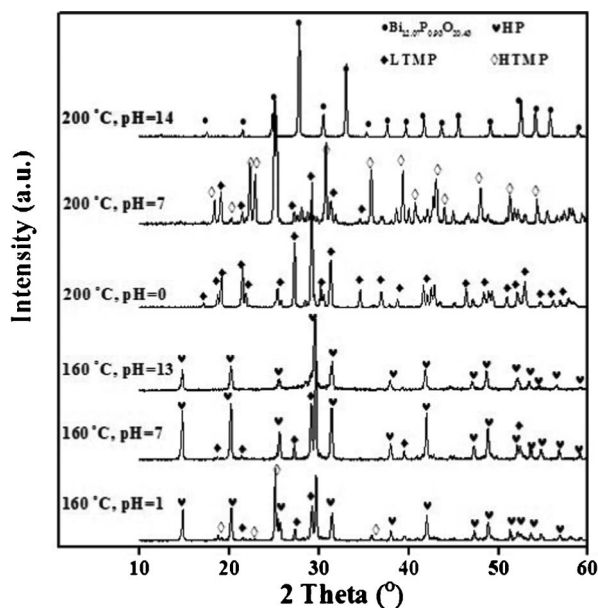


Fig. 4 XRD patterns for the samples obtained after hydrothermal treatments of HP precursor for 12 h under given condition.

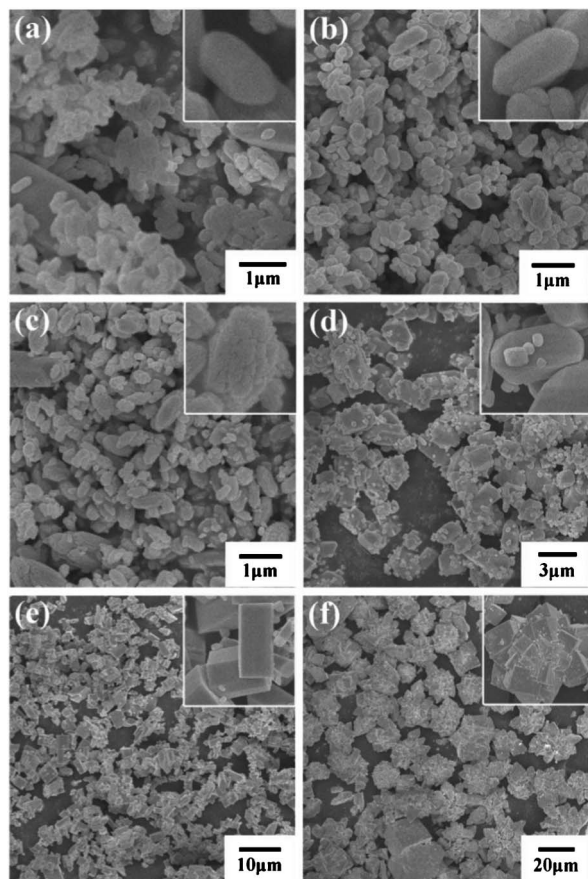


Fig. 5 SEM images of the samples obtained after hydrothermal treatments of HP precursor at given conditions: 160 °C (a) pH = 1, (b) pH = 7, (c) pH = 13 and 200 °C (d) pH = 0, (e) pH = 7, (f) pH = 14.

For pH = 0, polyhedron particles with different sizes from 200 nm to 1 μm were observed; for pH = 7, the sample was mainly composed of rod-like particles of about 2 μm in size; for pH = 14, polyhedron aggregates of about 10 μm were observed. Apparently, with the increase of pH value, the particle size of the samples increases. In combination with the morphology of the samples prepared at 240 °C (Fig. 3), it is noted that higher reaction temperature is favorable for the morphology uniformity of particles, which may be ascribed to the increased crystallized rate at a higher temperature.¹⁶

Time effect. Another influencing factor for the phase transformation is reaction time. In order to study the effect of reaction time on the phase transformation from HP to LTMP and HTMP, we executed time-variable experiments at given temperature and pH value solutions. Fig. 6 shows the phase evolution process in the strong acidic solution (pH = 0). It can be seen that a fraction of HP transformed into LTMP after being hydrothermally treated at 240 °C for 1 h. As reaction time prolonged to 2 h, the HP precursor completely transformed into LTMP, and further transformation was not observed even for periods of up to 16 h, which means that LTMP was the most stable phase in a strong acidic environment even under hydrothermal conditions. In addition, Fig. 7 shows the phase evolution process in the solution with pH = 3. Compared to phase transition in strong acidic solution, it is found that phase transition became tardy. As can be seen, the HP precursor remained after hydrothermal treatment for 1 h. Moreover, it should be noted that after hydrothermal treatment for 2 h, the HP precursor completely disappeared and a mixture of LTMP and HTMP was observed. Further increasing the hydrothermal

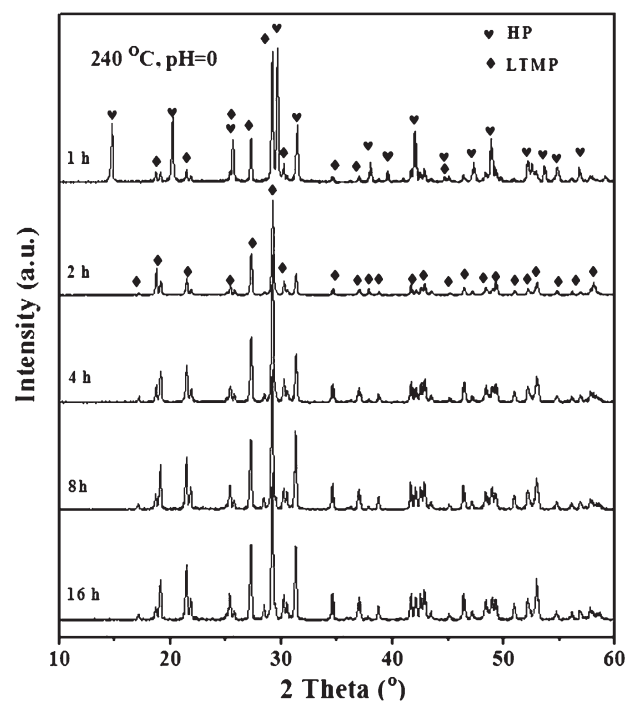


Fig. 6 XRD patterns of the samples obtained after hydrothermal treatment of HP precursor at 240 °C in pH = 0 solution for different times.

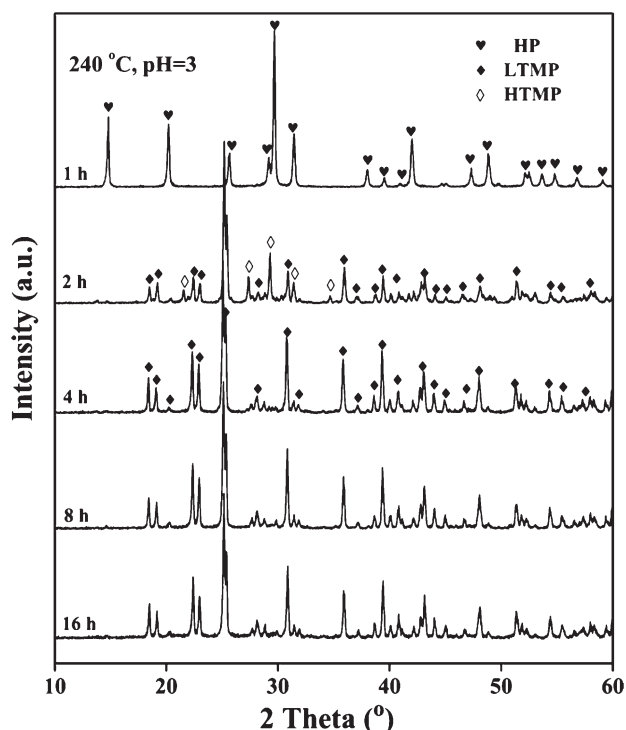


Fig. 7 XRD patterns of the samples after hydrothermal treatment of HP precursor at 240 °C in pH = 3 solution for different times.

time up to 4 h, LTMP disappeared and pure HTMP was obtained. These results indicated that under this condition, HP transformed into LTMP and HTMP simultaneously at the beginning. The newly generated LTMP was unstable and inclined to transform to HTMP quickly. The obtained HTMP still remained even after hydrothermal treatment for 96 h.

Fig. 8 shows the morphology evolution in the phase transition process. In strong acidic solution (pH = 0), morphology change at different reaction stages corresponding to a reaction time of 1, 2 and 4 h are shown in Fig. 8(a)–(c). It is seen that after hydrothermal treatment for 1 h, the sample exhibits a rice-like morphology with an average size of 200 nm (Fig. 8a) which is similar to that of the HP precursor, although partial LTMP had already appeared as indicated by XRD results shown in Fig. 6. When the time prolongs to over 2 h, an LTMP sample with cubic shape was obtained (Fig. 8b and c). Distinguishingly, the morphology change was more obvious for the phase transition in the solution with pH = 3, as illustrated in Fig. 8(d)–(f). When the reaction time is 1 h, the sample shows irregular aggregates which are composed of small particles of about 100–200 nm in size. When the reaction prolongs from 2 to 4 h, these small particles tend to disappear and larger particles gradually occur.

Impurity effect. Impurity ions in solution can affect not only structures and sizes but also morphologies of the final product by changing the ionic strength of the solution. As we know, it is necessary to introduce some ions in the one-pot hydrothermal method. For example, to synthesize BiPO_4 nanoparticles, the introduction of NH_4^+ cation is required if $\text{NH}_4\text{H}_2\text{PO}_4$ was chosen as the raw material. In order to investigate the influence of NH_4^+ cation, we carried out a one-step hydrothermal method at the same reaction temperature, time and pH value, using $\text{NH}_4\text{H}_2\text{PO}_4$ and

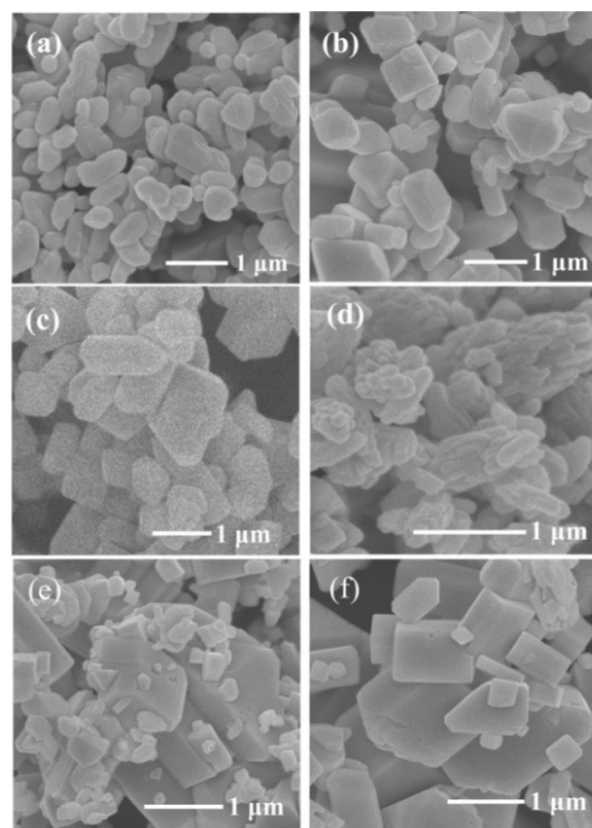


Fig. 8 SEM images of the samples after hydrothermal treatment of HP precursor for different time in corresponding solutions. (a) 1 h, (b) 2 h, and (c) 4 h in the solution with pH = 0; (d) 1 h, (e) 2 h, and (f) 4 h in the solution with pH = 3.

$\text{Bi}(\text{NO}_3)_3$ as the raw materials. The NH_4^+ effect on the final product is summarized in Table 1 (XRD patterns of the samples prepared in different pH solutions are given in Fig. S3†). In the experimental pH range, only LTMP was prepared under the one-pot hydrothermal conditions. Evidently, polymorph selective synthesis was not realized by the one-pot hydrothermal method, which indicates that the presence of NH_4^+ cation in the present system has a great influence on phase formation and crystal growth of BiPO_4 . It is noted that the effect of NH_4^+ cation on the phase transition of BiPO_4 has not been reported in previous literature, possibly because of the complex interference effect of the impurities from starting materials in one-pot solution chemistry.

4. Discussion

4.1 pH role

Although the three phases of BiPO_4 have the same chemical compositions and similar atomic coordination environments,

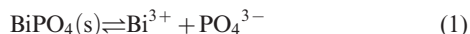
Table 1 Comparison between two-step and one-pot hydrothermal methods at 240 °C for 24 h^a

pH	0	1	3	7	10	14
Two-step method	L	L+H	H	H	L+H	$\text{Bi}_{12}\text{P}_{0.86}\text{O}_{20.14}$
One-pot hydrothermal	L	L	L	L	L	$\text{Bi}_{12}\text{P}_{0.86}\text{O}_{20.14}$

^a L denotes LTMP, H denotes HTMP.

they exhibit different physiochemical properties, such as photocatalytic and dielectric properties.^{17,18} It is well documented that solubility is dependent on the polymorphic state, since different polymorphs have different energies and thus different solubilities.^{19,20} According to conventional precipitation transformation theory, if there are two or more homogeneous polycrystallines in the solution system, a soluble phase always tends to transform into an insoluble phase. Therefore, the examination of the solubility distinction among these polymorphs in different pH value solutions may give some inspiration to help to understand the crystallization mechanism in solution. The solubility parameters for the HP, LTMP and HTMP polymorphs in different solutions are determined by ICP-MS, shown in Table 2.

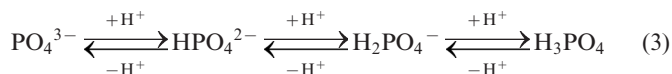
As illustrated in Table 2, the solubility of BiPO₄ polymorphs is dependent on the pH value of the solution. In strong acidic medium (pH = 0), all polymorphs showed their largest solubilities with 464.58, 334.60, and 357.48 mg L⁻¹ for HP, LTMP, and HTMP, respectively. With increasing pH values from 0 to 7, the solubility for all polymorphs decreased greatly. While further increasing pH value to 10, the solubility increased. In acid solution, LTMP is the most insoluble phase with the smallest solubility, while in neutral and basic solution, HTMP is the most insoluble phase. The effect of pH on the solubility can be interpreted from the precipitation–dissolution equilibrium point. Let us consider a saturated solution of bismuth phosphate in equilibrium with some crystals of bismuth phosphate. The equilibrium can be expressed by:



Applying the law of chemical equilibrium to this system, at fixed temperature and pressure, we obtain the following expression:

$$K_{\text{sp}} = [\text{Bi}^{3+}][\text{PO}_4^{3-}] \quad (2)$$

Namely, in the saturated solution of bismuth phosphate, the product of Bi³⁺ and PO₄³⁻ concentration is constant at fixed temperature and pressure. In the acidic solution, such as pH = 0, a new chemical equilibrium between H⁺ and PO₄³⁻ ions was established, which is expressed as follows:

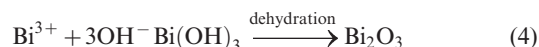


In strong acidic solution, PO₄³⁻ ion reacted with H⁺ to form several other species, such as HPO₄²⁻, and H₂PO₄⁻, and the number of PO₄³⁻ decreased. To keep K_{sp} constant, the reaction will shift the equilibrium to the right side, which would dissolve more Bi³⁺ and PO₄³⁻ ions, and thus more BiPO₄ crystal dissolved in acidic solution, as supported by the solubility

Table 2 The solubility of BiPO₄ polymorphs in different pH value solutions at ambient temperature and pressure (units: mg L⁻¹)

pH	0	1	7	10
HP	464.58	51.19	0.15	51.46
LTMP	334.60	1.14	0.15	3.80
HTMP	357.48	1.64	0.013	3.25

results displayed in Table 2. On the other hand, in basic solution, the following chemical equilibrium results in the formation of Bi(OH)₃ due to the strong complex ability between Bi³⁺ and OH⁻:

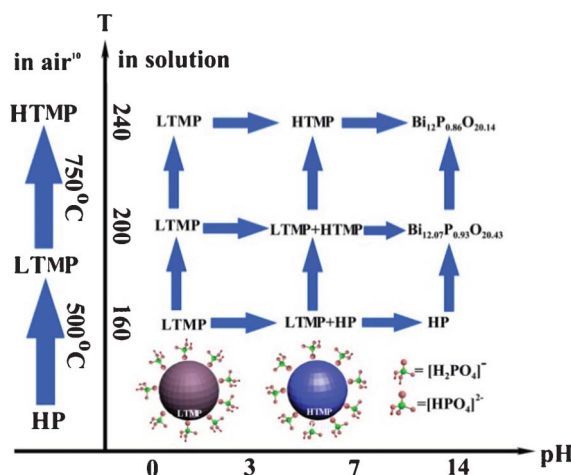


Under hydrothermal condition, Bi(OH)₃ tended to become Bi₂O₃ and therefore more BiPO₄ crystals should be dissolved in order to keep the K_{sp} constant. In similar way, comparison with that in pure water, the solubility of BiPO₄ was also increased, as indicated in the case of pH = 10.

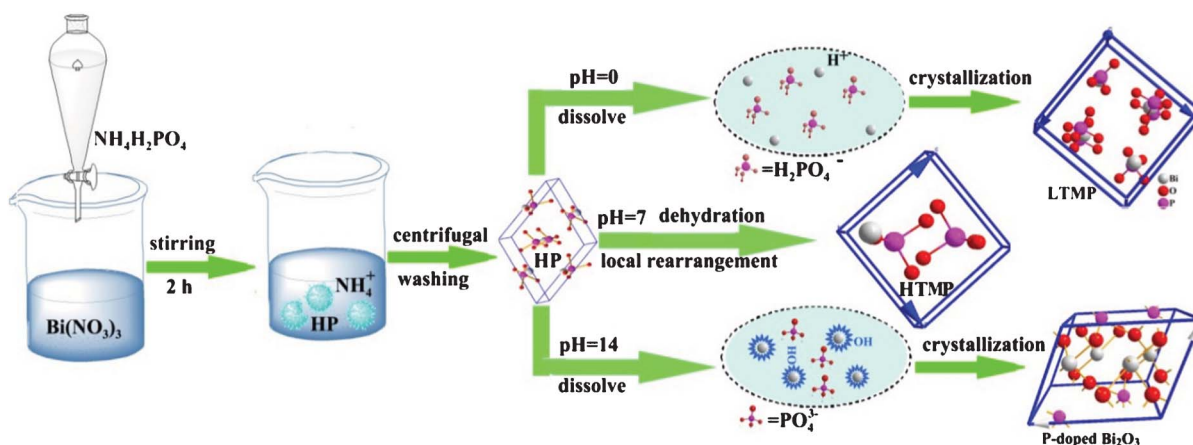
4.2 Understanding on the phase stability and feasible transformation mechanism

Although HP, LTMP, and HTMP are all constructed by PO₄ and BiO₈ units, their densities are different from each other, which are 5.77, 6.82, and 6.22 g cm⁻³, respectively.¹⁷ HP is the metastable phase of BiPO₄, typically associated with its high free energy. HP undergoes a transformation into LTMP upon thermal treatment, typically at 400–500 °C in the solid state, while LTMP would transform into HTMP when it is heated above 750 °C.¹⁰ It is well known that phase stability and transformation in aqueous solution is distinct from that in the solid state. Based on the experimental results, effects of temperature and pH on BiPO₄ polymorphs can be summarized in Scheme 1. It is apparent that polymorphic stability was strongly dependent on both the temperature and pH of the solution. As shown in Fig. 3, only part of the HP precursor transformed into LTMP at 160 °C in the solution of pH = 7, while HP completely converted into LTMP in acidic solution at the same temperature. Moreover, when it comes to the transformation at 160 °C in basic solution, HP remained unchanged and neither LTMP nor HTMP was detected in the XRD patterns. This means that polymorphic stability was strongly dependent on the pH of the solution.

It has been reported that Bi³⁺ and PO₄³⁻ ions exist in various phases, depending on solution pH.²² As mentioned above, Bi³⁺



Scheme 1 The effects of temperature and pH on the polymorphic stability of BiPO₄.



Scheme 2 Possible pathway for the phase formation under hydrothermal condition.

and H_2PO_4^- were the main ionic species in strong acidic solution. In the pH range of 7 to 10, Bi^{3+} and PO_4^{3-} ions mostly exist in the form of $\text{Bi}(\text{OH})_2^-$ and HPO_4^{2-} , respectively. Considering that lattice water coordinated to the Bi atoms can stabilize the HP structure and suppress the phase transition to LTMP,¹⁰ we proposed that the surface ionic layer adsorbed on BiPO_4 nanocrystals, which is directly coordinated to the Bi and P atoms, may account for polymorph selectivity in different pH solution under hydrothermal treatment. In basic solution, such as pH = 13, $\text{Bi}(\text{OH})_2^-$ and HPO_4^{2-} adsorbed on BiPO_4 surface may stabilize HP in a way similar to the lattice water. In very acidic solution (pH = 0), the excess H_2PO_4^- and Bi^{3+} might suppress the conversion from LTMP to HTMP by the adsorption on the surface of LTMP crystals. The effect of surface adsorbed species on the phase transformation has been reported in previous work.^{21,23,24} For example, monoclinic and tetragonal BiVO_4 crystals were selectively synthesized by changing the ratio of vanadium to bismuth in the starting materials.^{23,24} In neutral solution, the metastable HTMP was stabilized under the hydrothermal condition. A possible pathway for the phase formation under different hydrothermal conditions is summarized in Scheme 2.

To further study the mechanism of the phase transition, LTMP and HTMP were also used as precursors to check the phase transition behavior with other hydrothermal parameters remaining unchanged. It is interesting to find that phase transition was also dependent on the precursor. For instance, when using HTMP as precursor, it does not convert into LTMP in strong acidic solution. Similarly, at 240 °C, even up to 7 days, LTMP also remains unchanged in pH = 3–7 solution (XRD patterns of the samples after hydrothermal treatment are given in Fig. S4†). This phenomenon may help to clarify the pathway by which the phase transition took place under hydrothermal condition for BiPO_4 . Transformations between solid phases in contact with a solvent can proceed by the mechanism that crystals of the stable phase grow at the expense of the crystals of metastable phase. In acidic solution, the transformation from HP to LTMP should take place *via* a dissolution–crystallization process in view of the fact that the solubility for the HP precursor under hydrothermal should be larger than 464.58 mg L⁻¹. A similar mechanism was also reported by Finnegan in the case of anatase to rutile TiO_2 phase transition.^{25,26} On the other hand, with the pH value increased to 7, solubility of the precursor is so small that the dissolution–

crystallization process is limited. As we know, the structure of HP was stabilized by structural water coordinated directly to the bismuth atom. Therefore, phase transition *via* dehydration *in situ* and local rearrangement should be much easier than that *via* the dissolution–crystallization process. This kind of phase transition mechanism was not alone. Another case of phase transition in solution by this mechanism was reported in iron oxide.^{27,28} The dehydration *in situ* and local rearrangement can give a rational explanation of the phenomenon that transition between LTMP and HTMP was not observed in our experimental conditions for there was no lattice water in their crystals. Further increasing the solution pH value up to 14 led to the formation of $\text{Bi}_{12}\text{P}_{0.86}\text{O}_{20.14}$. Phase transition from HP to $\text{Bi}_{12}\text{P}_{0.86}\text{O}_{20.14}$ should also take place by a dissolution–crystallization process.

5. Conclusions

The main results reported in this work are summarized as follows:

- (1) LTMP and HTMP polymorphs were selectively prepared *via* phase transition reaction under hydrothermal conditions.
- (2) The pH of the reaction medium is the determinant factor for polymorphic control of BiPO_4 . Pure LTMP was formed in strong acidic condition (pH = 0 or 1) while metastable HTMP with pure phase was obtained in neutral or weakly acidic condition (pH = 3 or 7). In strong basic solution with pH value up to 14, P-doped Bi_2O_3 , a phase which is never accessible by conventional solution chemistry but firing in air at $T > 750$ °C, was obtained.
- (3) Based on the phase transformation behavior of BiPO_4 polymorphs, two different kinds of phase transformation mechanisms under hydrothermal condition were proposed.

Different from other solution chemistry, we eliminated the interference effect of impurity ions and synthesized BiPO_4 with controlled phase structures by two-step crystallization method. The method reported here may be used to prepare other metastable structures.

Acknowledgements

We acknowledge the support by NSFC (No. 21025104, 51072198, 50972143, 91022018) and the National Basic Research Program of China (2011CBA00501).

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