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ARTICLE TYPE

Synthesis of large MgAPO-11 single crystals in F^- free system

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Synthesis process of large magnesium substituted $AlPO_4$-11 single crystals （MgAPO-11）under hydrothermal condition has been reported. The crystal size and morphology sensitively depend on crystallization conditions and gel compositions. The addition of HF acid in the gel undermines rather than favours the growth of MgAPO-11 single crystals. Using the optimal gel composition with magnesium oxide as magnesium source, large MgAPO-11 single crystals with good quality have been synthesized in F- free system. The typical crystal dimension is 25 ×157×254μm^3, the synthesis temperature is 180°C, and the crystallization period is 60 hours.

1 Introduction

Since first reported in 1982, aluminophosphate($AlPO_4$-n) molecular sieves have attracted much attention due to their structural diversity and wide applications in catalysis, ion exchange, adsorption and separation. To date, many members in the family of aluminophosphates or their derivatives have been synthesized by changing the templates or crystallization conditions [1-10].

$AlPO_4$-11 (AEL) is one of the crystalline microporous aluminophosphates. The framework of the $AlPO_4$-11 crystal consists of alternating tetrahedral $(AlO_4)^-$ and $(PO_4)^+$, which form 1-D elliptical channel system. The diameters of the major and minor axes are 6.5 Å and 4.3 Å. In addition, a pure $AlPO_4$-11 crystal is optically transparent from ultraviolet to near-infrared with good insulation as well as excellent thermal stability. With these excellent physical properties and unique elliptical pore structures, $AlPO_4$-11 gives good performance as a template to control the alignment of neutral molecules and fabricate the smallest single-walled carbon nanotubes (SWNTs) with diameter of only 3 Å[11-13]. As the $AlPO_4$-11 framework is relatively inert chemically[14], the adsorption of the guest molecules (to the pore wall) is weak. As a result, the molecular wires formed inside the channels usually have a large density of atomic defects. The neutral framework of $AlPO_4$-11 also limits its applications in catalysis and ion exchange. One possibility to improve the quality of the framework is the isomorphous substitution of Al^{3+} by M^{2+}ions. When Al(III) is substituted by Mg(II) in the framework of $AlPO_4$-11 (MAPO-11), the negatively charged framework and Brønsted acid sites are generated. The adsorption potential of the channel walls is enhanced owing to the negative framework. It is interesting to note that the strong interaction between the pores and the guest speices can modulate the physical properties of guest speices. Moreover, the Brønsted acid sites can be used in catalytic cracking and isomerization of hydrocarbons.

Large MgAPO-11 crystals are essential for its wide applications in the structure analysis, the study of crystal growth mechanism, adsorption and diffusion of guest molecules, the determination of optical and electrical properties, and applications in advanced functional materials. Many works have dealt with the synthesis of MgAPO-11 crystals[15-18], but the size and quality or aspect ratio of the final crystals was not satisfying. HF acid was widely used as mineralizer in aluminophosphates synthesis systems to obtain large crystals[3, 7, 8, 18]. It is believed that the presence of F^- ion restrains the nucleation ratio and slows down the crystallization, and leads to the growth of larger crystals. However, the presence of F^- would affect the performance of the products when they are used as a template to fabricate SWNTs. In our previous work, we reported that the F^- ion would reduce the quality and filling density of the SWNTs inside the channels of $AlPO_4$-5 crystals[19]. Also, HF is highly toxic and caustic. Avoiding the use of HF acid would be advantageous for aluminophosphates synthesis on an industrial scale.

In this paper, large MgAPO-11 crystals (25× 157 ×254 μm^3) with proper aspect ratio have been synthesized successfully without F^- ions. To our best knowledge, they are the largest MgAPO-11 single crystals reported so far. The influence of parameters such as crystallization duration and temperature, molar ratio of MgO/Al_2O_3, amount of the organic template dipropylamine (DPA) and HF as well as different magnesium sources upon the properties of the products have been evaluated.

2 Experimental

2.1. Synthesis

The syntheses of MgAPO-11 crystals were carried out in aqueous media under hydrothermal conditions and autogenous pressure. Aluminum trisopropoxide(98 wt.% Aldrich), magnesium sulfate and orthophosphoric acid (85 wt.%, Aldrich) were used as sources of aluminum , magnesium and phosphorus , respectively . Dipropylamine (DPA, 99% Aldrich) was adopted as structure

directing agent. The composite of Al_2O_3:1.04P_2O_5: 0.2MgO:172DPA: 500H_2O was used as initial gel. The typical synthesis procedure was as follows: (1) the aluminum tri-isopropoxide and magnesium sulfate were dissolved in distilled water and stirred vigorously for 2 hrs to form a white gel (A), meanwhile orthophosphate, DPA and distilled water reacted under stirring to yield a clear solution (B). (2) Solution B was dropwise added into solution A under vigorous stirring for another 3 hrs .The prepared gel solution was sealed in a Teflon-lined stainless autoclave and heated to 150 – 210°C under autogenous pressure for 10 – 80 hrs. After crystallization, the final products were filtered and washed with distilled water, then dried at 80°C for 2 hrs.

2.2. Characterization

The powder XRD patterns of the as-synthesized MgAPO-11 crystals were recorded on a D8 ADVANCE diffractometer at 40 kV and 40 mA. The X-ray source was Cu target. The scanning angle ranged from 5 to 40 degree and the scanning speed was 6 degree/min. The crystal size and morphology were examined by scanning electron microscopy (JEOL Co, Model: JSM-6490LA).

3 Results and discussion

3.1 Effect of the crystallization duration

The influence of crystallization duration on the quality and size of MgAPO-11 crystals was investigated. The crystallization temperature was set at 190°C. The crystallization duration varies from 10 to 80 hrs. Fig. 1 shows the SEM images of the productions synthesized under different crystallization duration. When the crystallization duration is 10 h, small MgAPO-11 phase with irregular morphology appears, accompanied by some intergrowth phase (Fig. 1(a)). As the duration of crystallization increases, the quality and yield of the crystals are obviously improved. When the crystallization duration reaches 60 h, the crystal size reaches the maximum with the aspect ratio of 1.2 (Fig. 1(c)). However, the size of the crystals becomes smaller at prolonged the crystallization duration to 80 h (Fig. 1(d)). Thus, the optimal crystallization duration for the growth of large MgAPO-11 single crystals is set as 60 hrs.

It is interesting to note that the size of the intergrowth phase also increases with the extension of crystallization duration (Fig.1). During the single crystal growth period, nucleation occurs in the solution only when the supersaturation degree reaches a certain point. According to this point, a higher supersaturation degree leads to more nuclei. In the earliest stages of the reaction, nucleations of MgAPO-11 crystals occur in the gel. With the increase of crystallization duration, the number of nuclei increases. Under the effect of organic template, the second nucleation that has an AEL structure will occur on the surface of first nucleation, leading to secondary growth. This procedure is repeated, resulting in the formation of intergrowth morphology with rough surface.

Fig. 2 shows the XRD patterns of the productions synthesized under different crystallization duration. As can be seen that the powder XRD pattern corresponds well with the standard one for AEL crystals[20], which indicates the productions are of AEL structure. The intensity of signals increases significantly with an increase in the crystallization duration from 10 to 60 h. However, with further prolonging the crystallization duration to 80 h, the intensity of signals decreases. Thus, the optimal crystallization duration is around 60 h. These results are in accordance with SEM images (Fig. 1)

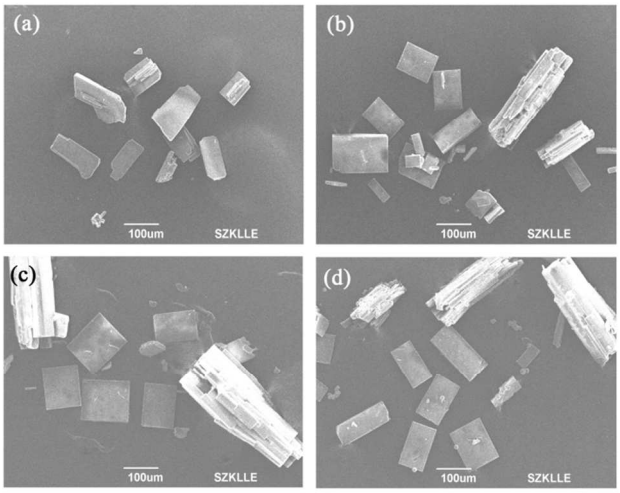

Fig.1 SEM images of the crystals synthesized under different crystallization duration: (a) 10 h (b) 40 h (c) 60 h and (d) 80 h.

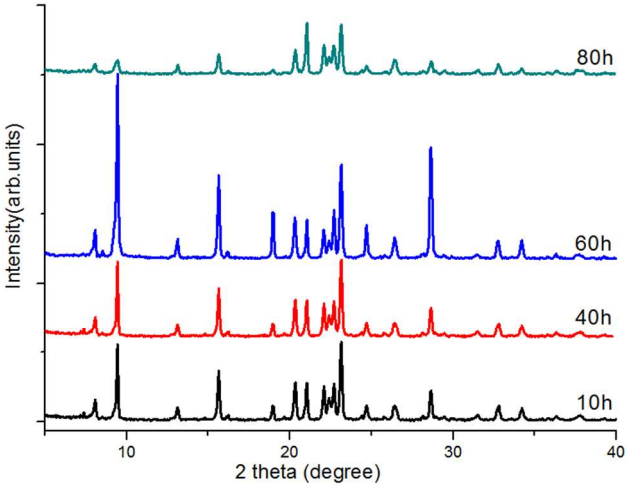

Fig. 2 XRD patterns of crystals synthesized under different crystallization duration.

3.2. Effect of the crystallization temperature

To find out the optimal temperature for the preparation of MgAPO-11 crystals, the crystallization duration is fixed at 60 h and the crystallization temperature ranges from 150 to 210°C. The SEM micrographs of the as-synthesized samples at different crystallization temperature are shown in Fig. 3. When the crystallization temperature is 150°C, the reaction mixture remains slurry and no crystallization appears. As the temperature reaches 160°C，irregularly-shaped crystals with slight intergrowth are observed (Fig. 3(a)). By elevating growth temperature up to 170°C, well-shaped single crystals appear. Large single crystals with a typical dimension of 25 × 115 × 173 μm^3 are obtained when the temperature reaches 180°C (Fig.3(c)). At the same time, the intergrowth phases are very serious. When the temperature is

further increased, the crystal size decreases (Fig.3 (d)), accompanied by deterioration of the crystal quality, owing to the occurrence of some granules on the crystal surface. These results indicate that a slightly lower crystallization temperature favours the formation of larger MgAPO-11 crystals. It is interesting to note that the change of intergrowth phase is not obvious when the crystallization temperature increases from 170°C to 180°C. As the temperature rises to 200°C, the length of the symbiotic crystal becomes shorter (Fig.3 (d)). It is probably because higher temperature can restrain the intergrowth crystal growth along the c-direction.

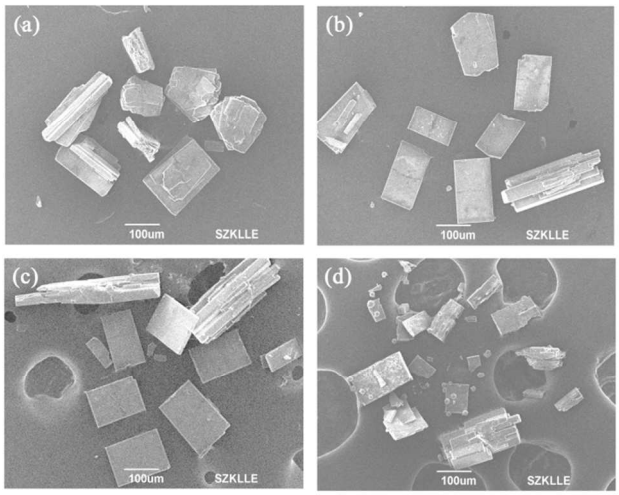

Fig.3 SEM images of the crystals synthesized under different crystallization temperature: (a) 160°C (b) 170°C (c) 180°C and (d) 200°C.

3.3. Gel composition

In order to study the effect of gel composition on the synthesis of MgAPO-11 crystals, we have conducted a series of experiments with the crystallization temperature and duration are set as 180°C and 60 h. Three batches of crystals were synthesized to investigate the influence of ratio MgO/Al_2O_3, DPA and HF content, respectively. Every batch has at least eight samples with different gel compositions, and they were synthesized under the same conditions synchronously.

3.3.1. Effect of the molar ratio MgO/Al_2O_3

In Ref. 7, L. Fu et al found that the molar ratio SiO_2/Al_2O_3 influences the average size and morphology of SAPO-11 crystals, as well as product purity. In our experiment, the molar ratio MgO/Al_2O_3 affects only the size and quality of MgAPO-11 crystals. The gel composition of Al_2O_3:1.04P_2O_5:xMgO: 1.72DPA:500H_2O was selected to investigate the effect of molar ratio MgO/Al_2O_3 on the synthesis of MgAPO-11 crystals, x varies from 0.1 to 0.4. As shown in Fig. 4, the crystal size and morphology sensitively depend on the MgO/Al_2O_3 molar ratio. When x = 0.1, irregular-shaped AEL phase are observed (Fig. 4(a)). With the molar ratio x increasing to 0.2, the crystal integrity increases and the crystal size is up to 23 × 85 × 132 μm^3(Fig. 4(b)) . When x = 0.28 was adopted in the starting gel, the crystals are of regular shape and have a good morphology, indicating high crystalline quality. Also the crystal size reaches the maximum (Fig. 4(c)). The size of final products decreases noticeably with further increasing the molar ratio of MgO/Al_2O_3, accompanied by a deterioration of the crystal surface. The optimal MgO/Al_2O_3 molar ratio for the synthesis of large MgAPO-11 single crystals is 0.28.

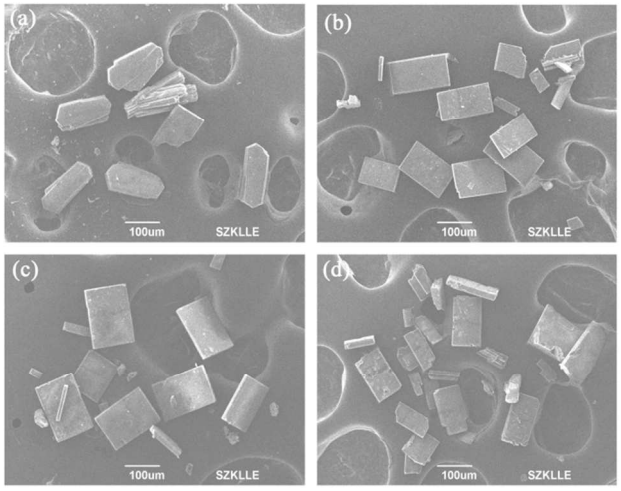

Fig. 4 SEM images of the crystals synthesized from the gel composition of Al_2O_3: 1.04P_2O_5:xMgO:1.72DPA::500H_2O: (a) x = 0.1 (b) x = 0.2 (c) x = 0.28 and (d) x = 0.4.

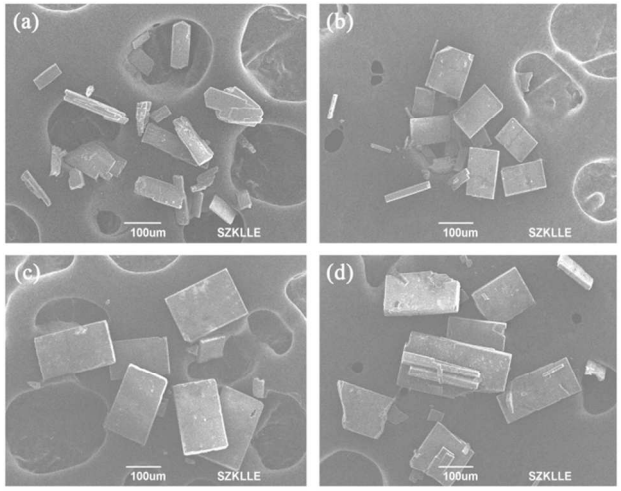

Fig. 5 SEM images of the crystals synthesized from the gel composition of Al_2O_3:1.04P_2O_5:0.28MgO: yDPA:500H_2O:(a) y = 1.1 (b) y = 1.57 (c) y = 1.9 and (d) y = 2.35.

3.3.2. Effect of the DPA content

To determine the optimal molar ratio of DPA for the preparation of large MgAPO-11 single crystals, we adopted the following initial gel composition: Al_2O_3:1.04P_2O_5:0.28MgO:yDPA:500H_2O, where y varies from 1.1 to 2.35. The as-synthesized MgAPO-11 crystals are shown in Fig. 5. It can be seen that only a few small-sized crystals with complete shape appear when the molar ratio of DPA in the reaction mixture composition is 1.1. As y increases to 1.57, large crystals with perfect morphology are prepared (Fig. 5(b)). A gel with y = 1.9 provides crystals with a size of 26×130×182 μm^3 (Fig. 5(c)). However, the quality of the crystals decreases when y reaches 2.35, demonstrated by rough surface and slight intergrowth. At a high molar ratio of DPA, not all DPA can be dissolved in the solution, and the undissolved DPA molecules can

be mixed into the MAPO-11 crystal phase, leading to the crystals having a rough morphology. A similar phenomenon has been reported in Ref. 7. Therefore, it can be considered that 1.9 is the optimal molar ratio of DPA for the formation of large MgAPO-11 single crystals.

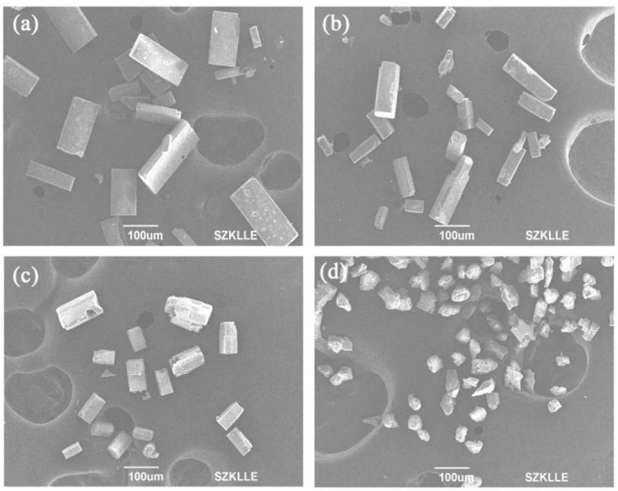

Fig. 6 SEM images of the crystals synthesized from the gel composition of Al_2O_3:1.04 P_2O_5:0.28MgO: 1.9DPA: 500H_2O: z HF: (a) z = 0.4 (b) z = 1.04 (c) z = 1.6 and (d) z = 2.08.

3.3.3. Effect of the HF acid content

In many hydrothermal systems, HF was used to reduce the supersaturation degree of the solution and supply nutrients for the growth of large aluminophosphate single crystals[3, 7, 8, 18]. In order to study the effect of HF content on the size and quality of MgAPO-11 single crystals, HF was introduced to our experiment system , and the gel composition was Al_2O_3:1.04 P_2O_5:0.28MgO: 1.9DPA: 500H_2O: z HF , where z varies from 0.4 to 2.08. The experimental procedure is the same as that mentioned in the synthesis part, except that HF was added to solution B. Fig. 6 shows the SEM images of the resulting samples. It can be seen that the HF content strongly affects the average size and morphology of MgAPO-11 crystals. In comparison with Fig.5 (c) (z = 0), the size of product samples decreases evidently while the aspect ratio increases a lot when a gel composition with z = 0.4 was employed (Fig. 6(a)). Further increasing the HF content, the size of as-prepared crystals becomes smaller and the thickness becomes larger (Fig. 6(b) and (c)). As shown in Fig. 6(d), the final products are small particles with irregular shape when z increases to 2.08. To verify whether the HF causes structural change of the crystals, the XRD patterns of products with z=1.6 and 2.08 were measured. The powder XRD patterns are similar and look identical with the standard one for $AlPO_4$-11[20] (Fig. 7).It is interesting to note that the intensity of sample with z=2.08 is stronger than that of sample with z=1.6. Maybe a slightly higher conten of HF in the reaction gel can lead to higher crystallinity of the products. Obviously, the existence of HF in the reaction solution has a notable effect on the size and morphology of MgAPO-11 crystals. Higher content of HF in the reaction solution leads to smaller size and worse morphology of the resulting products. But the structure of crystals is unaffected. In the certain range, the crystallinity of the products increases with the increase of concentration of HF in the reaction solution. Based on the above discussion, optimal parameters for the synthesis of large size MgAPO-11 single crystals can be summarized as follows: the gel composition is Al_2O_3:1.04 P_2O_5:0.28MgO:1.9DPA:500H_2O, crystallization temperature is 180°C, crystallization duration is 60 h.

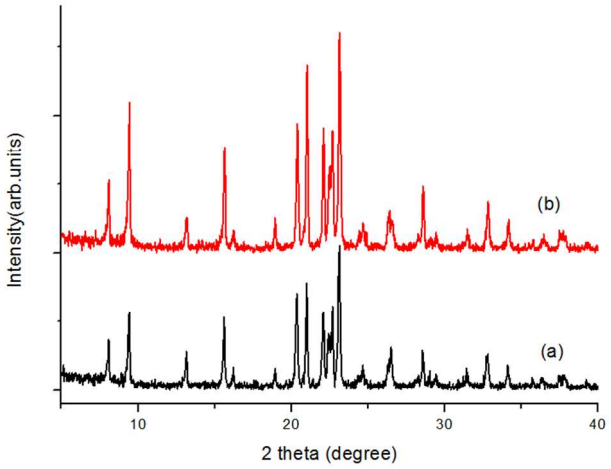

Fig.7 XRD patterns of the crystals synthesized using the gel composition of Al_2O_3:1.04 P_2O_5:0.28MgO: 1.9DPA: 500H_2O: z HF: (a) z = 1.6 and (b) z = 2.08.

3.4. Effect of different magnesium sources

In order to investigate the influence of different magnesium source on the size and morphology of MgAPO-11 crystals, we conducted some experiments with different magnesium sources. The synthesis condition and gel composition is the same with the optimal conditions mentioned above, with the exception of replacing magnesium sulfate with magnesium oxide or magnesium acetate. It is found that the effect of magnesium source on the crystal size is obvious. Fig. 8 shows the SEM images of MgAPO-11 single crystals synthesized using different magnesium sources. In comparison with magnesium sulfate and magnesium acetate, the crystals grown from a gel containing magnesium oxide are largest in size (25× 157×254 μm^3) with perfect morphology (Fig. 8 (b)). The resulting products with magnesium acetate as magnesium source are a little smaller (Fig. 3 (c)), but larger than those grown with magnesium sulfate (Fig.8 (a)). The size difference between the crystals synthesized using different magnesium sources may originate from the solubility difference between magnesium sulfate, magnesium oxide and magnesium acetate. The solubility difference affects the reaction kinetics, and then influences the crystal size.

4 Conclusions

By optimizing the crystallization duration and temperature as well as the gel composition including the molar ratio of MgO/Al_2O_3 and DPA content, large crystalline MgAPO-11 single crystals with high quality have been synthesized in F- free system. The size and quality of MgAPO-11 single crystals sensitively depend on the synthesis condition and gel compositions. The crystal size is also affected by different magnesium sources used during the synthesis process. HF is

found to disfavour the growth of large MgAPO-11 single crystals. The as-synthesized crystals were characterized by SEM and powder-X ray diffraction. Powder-X ray diffraction measurement shows that the resulting crystals are of pure AEL structure. The largest well-shaped crystal we prepared is 25× 157×254 μm^3.

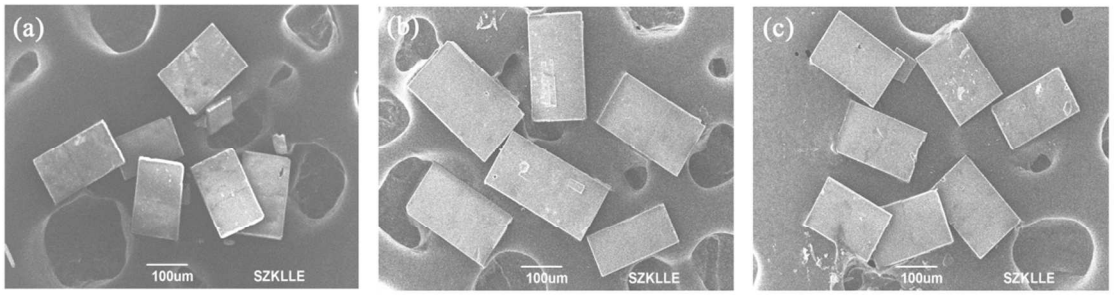

Fig.8 SEM images of the crystals synthesized using different magnesium sources: (a) magnesium sulfate (b) magnesium oxide (c) magnesium acetate.

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Graphical Abstract

Large-sized MgAPO-11 single crystals (25 ×157×254μm^3) have been successfully synthesized by hydrothermal method in F- free system.