



## Ionothermal synthesis of gallophosphate molecular sieves in 1-alkyl-3-methyl imidazolium bromide ionic liquids

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### ABSTRACT

Gallopophosphate ( $\text{GaPO}_4$ ) molecular sieves were ionothermally prepared in 1-alkyl-3-methyl imidazolium bromide ionic liquids (ILs) with alkyl chain length varying from 2 to 6 carbons for the first time. Three kinds of  $\text{GaPO}_4$  materials such as  $\text{GaPO}_4$ -a, cloverite (denoted as CLO below) and  $\text{GaPO}_4$ -LTA were obtained, and their structures and morphologies were characterized by powder and single crystal XRD, SEM and multi-nuclear NMR. In the case of 1-ethyl-3-methyl imidazolium bromide ionic liquid, large single crystals of  $\text{GaPO}_4$ -LTA with well-defined octahedral morphology was obtained in both sealed (ca. 400  $\mu\text{m}$  in size) and open vessels (ca. 300  $\mu\text{m}$  in size). Ionothermal synthesis is an effective method for the preparation of large single crystal of molecular sieves. With the alkyl chain length of the ionic liquids increasing from 2 carbons to 6 carbons, the size of  $\text{GaPO}_4$ -LTA decreased sharply. The organic template cations in the as-synthesized  $\text{GaPO}_4$ -LTA crystals may have two different kinds of conformational structures. Fluorine plays a role of co-template along with organic cations of ILs in the synthesis of  $\text{GaPO}_4$ -LTA and CLO, while only  $\text{GaPO}_4$ -a was obtained in the absence of fluorine. The reaction temperature can also affect the structure of the final structure. In the reaction medium of 1-ethyl-3-methyl imidazolium bromide IL,  $\text{GaPO}_4$ -LTA was obtained at 180 °C, while CLO was obtained at 150 °C.

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### 1. Introduction

Microporous crystalline molecular sieves are widely applied in the fields of catalysis, gas adsorption and ion-exchangers etc., [1,2]. Conventionally, they are prepared under hydrothermal or solvothermal conditions in the presence of organic amines or quaternary ammonium ions [1–4]. Based on the elemental composition, molecular sieves can be divided into three main groups, silicates (zeolites etc.), phosphates ( $\text{AlPO}_4$  etc.), and the others (all-carbon molecular sieves, pillared clays etc.) [4]. Once  $\text{AlPO}_4$ -*n* series molecular sieves were reported by Flanigen and co-workers in 1982 [5], many other phosphates molecular sieves with new compositions or with new structure topologies have been reported, and some of them were prepared by partly or completely replacing aluminium with other metals [6].  $\text{GaPO}_4$  is one important family of phosphate molecular sieves by substituting aluminium with gallium. Gallium exhibits crystal chemistry features similar to aluminium with a flexible coordination ranging from four to five or six [6]. It results in the

formation of complicated structures, which drastically differ from the aluminosilicate structures. In combination of fluorine route [7], using fluorine anions instead of hydroxide anions as the mineralizing agents for crystallization, more attention has been paid on the study of the amine–fluorine–gallium–phosphate system and a large number of new network topologies have been reported [8,9]. Several research groups have done predominant works on the synthesis of  $\text{GaPO}_4$  porous materials, including Kessler and co-workers in Mulhouse [9], Xu's group in Jilin University [10–12], and Ferey's group in Versailles [13,14], etc. Two unusual samples of  $\text{GaPO}_4$  molecular sieves are twenty-ring ( $13.2 \times 6.0 \text{ \AA}$  in size) CLO [15–17] and eight-ring ( $4.1 \times 4.1 \text{ \AA}$  in size)  $\text{GaPO}_4$ -LTA [18,19], which is isostructural with the aluminosilicate zeolite-A. CLO was first reported by Estermann et al. using quinuoline as template under hydrothermal conditions [15], while  $\text{GaPO}_4$ -LTA was synthesized with di-*n*-propylamine (DPA) as template [18]. Both CLO and  $\text{GaPO}_4$ -LTA build from double four rings (D4R) hosting a fluorine anion in their center. The Ga atoms are penta-coordinated in a distorted trigonal bipyramidal environment, and the P atoms remain tetrahedrally coordinated [15,19]. To the best of our knowledge,  $\text{GaPO}_4$ -LTA has been so far prepared only through the fluorine route.

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As the only precedent, Parnham et al. have recently reported the preparation of GaPO<sub>4</sub>-LTA in the absence of fluorine in the medium of deep-eutectic solvents [20].

ILs are special molten salts entirely containing inorganic anions and organic cations, such as quaternary ammonium, quaternary phosphine and other bulk organic cations [21–23]. They have low melting point (usually less than 100 °C), relatively low viscosity, high electric and thermal stability, and, importantly, have negligible vapor pressure, and are good solvents for a wide range of organic and inorganic materials [21–23]. These characteristics enable ILs to be widely used as a “green” solvent, functional solvent, or catalyst in organic synthesis, inorganic preparation, electrochemistry, as well as other areas [21–23]. The most used ILs are imidazolium-based ILs [24]. Imidazolium-based cations are quaternary ammoniums in nature, and 1-methylimidazole has served as template in the hydrothermal synthesis of AlPO<sub>4</sub> molecular sieves [8,25]. In 2004, Morris et al. reported a new synthesis methodology of molecular sieves, named as ionothermal synthesis [26], in which ILs or eutectic mixtures [27] were used as both synthesis media and template. This new synthesis method is currently receiving a growing amount of interest within the zeolite community due to its interesting features and potential advantages [20,26,28–35]. For example, it can be performed at high temperature while keeping the pressure at ambient level [26]. The crystallization time of molecular sieves could be markedly reduced to tens of minutes by combining microwave heating with ionothermal synthesis [32]. Cai et al. prepared a highly oriented SAPO<sub>4</sub>-11 film by using microwave-assisted ionothermal synthesis [35]. Furthermore, ionothermal synthesis allows one to address the questions that are difficult to study in conventional synthesis methods. We have studied the effects of the addition of amines and water into the ionothermal synthesis mixture [33,36]. Therefore, to explore more fully the potential of this new ionothermal synthesis method is still of great interest.

To date, much of the work on ionothermal synthesis of molecular sieves has been concentrated predominately on the preparation of AlPO<sub>4</sub> or metal–AlPO<sub>4</sub> family materials [20,26,28–35], with the exception of only one study, in which GaPO<sub>4</sub>-LTA was prepared [20]. However, the reaction medium of this GaPO<sub>4</sub> material was deep-eutectic solvent [20]. In this work, we report the synthesis of GaPO<sub>4</sub> molecular sieves in 1-alkyl-3-methyl imidazolium bromide ILs with alkyl chain length varying from 2 to 6 carbons. Three kinds of GaPO<sub>4</sub> materials were obtained, GaPO<sub>4</sub>-a [37], CLO, and GaPO<sub>4</sub>-LTA. Particularly, large single crystals of GaPO<sub>4</sub>-LTA with size of ca. 400 μm were obtained.

## 2. Experimental section

### 2.1. Synthesis of ILs

ILs used in the present study, including 1-ethyl-3-methyl imidazolium bromide ([C<sub>2</sub>mim]Br), 1-propyl-3-methyl imidazolium bromide ([C<sub>3</sub>mim]Br), 1-butyl-3-methyl imidazolium bromide ([C<sub>4</sub>mim]Br), 1-pentyl-3-methyl imidazolium bromide ([C<sub>5</sub>mim]Br), 1-hexyl-3-methyl imidazolium bromide ([C<sub>6</sub>mim]Br), were prepared according to the procedure reported in Ref. [38].

### 2.2. Synthesis of GaPO<sub>4</sub> samples

The gallium source (gallium oxyhydroxide, denoted as GaOOH) was prepared from the reaction of gallium metal with H<sub>2</sub>O at 200 °C for 72 h. Phosphoric acid solution (H<sub>3</sub>PO<sub>4</sub>, 85 wt% in H<sub>2</sub>O) and hydrofluoric acid solution (HF, 40 wt% in H<sub>2</sub>O) were used as purchased.

In a typical synthesis, a plastic beaker was charged consecutively with IL (15.0 g), H<sub>3</sub>PO<sub>4</sub> and GaOOH. HF was added if re-

**Table 1**

Details of the synthesis and conditions for the preparation of GaPO<sub>4</sub> materials using various imidazolium-based ILs.

| Sample               | ILs                    | Ga:P:F:IL: H <sub>2</sub> O<br>(molar ratio) | Temperature<br>(°C) | Time<br>(d) |
|----------------------|------------------------|--|---------------------|-------------|
| GaPO <sub>4</sub> -a | [C <sub>2</sub> mim]Br | 1:3:0:20:3                                   | 150                 | 2           |
| CLO                  | [C <sub>2</sub> mim]Br | 1:3:1:20:4.5                                 | 150                 | 12          |
| LTA-C <sub>2</sub>   | [C <sub>2</sub> mim]Br | 1:3:1:20:4.5                                 | 180                 | 8           |
| LTA-C <sub>3</sub>   | [C <sub>3</sub> mim]Br | 1:2:1:20:3.5                                 | 180                 | 2           |
| LTA-C <sub>4</sub>   | [C <sub>4</sub> mim]Br | 1:2:1:40:3.5                                 | 180                 | 2           |
| LTA-C <sub>5</sub>   | [C <sub>5</sub> mim]Br | 1:2:1:40:3.5                                 | 150                 | 2           |
| LTA-C <sub>6</sub>   | [C <sub>6</sub> mim]Br | 1:2:1:40:3.5                                 | 150                 | 2           |

quired. After stirred homogeneously at 70 °C in an oil bath, the reaction mixture was then transferred to a Teflon-lined stainless-steel autoclave (volume 30 mL) for crystallization at the required temperature for certain time. After cooling to room temperature, the obtained solid product was filtered, washed thoroughly with distilled water and ethanol, and dried at 100 °C overnight. Details of the initial reaction mixture compositions, the synthesis conditions and the structure of the final products are given in Table 1. LTA-C<sub>n</sub> was used to label GaPO<sub>4</sub>-LTA products obtained in [C<sub>n</sub>mim]Br (*n* = 2–6) ILs with different alkyl chain length.

### 2.3. Characterization

All the solid products were characterized by powder X-ray diffraction (PXRD) analyses on a PANalytical X'Pert PRO diffractometer fitted with Cu Kα radiation ( $\lambda = 1.5406 \text{ \AA}$ ) operating at 40 mA and 40 kV. The products were also characterized by scanning electron microscopy (SEM) on a Hitachi S4800 field-emission scanning electron microscope. Single crystal X-ray diffraction was performed on a Bruker Smart APEX II X-diffractometer equipped with graphite monochromated Mo-Kα radiation ( $\lambda = 0.71073 \text{ \AA}$ ). <sup>31</sup>P MAS NMR, <sup>71</sup>Ga MAS NMR and <sup>13</sup>C CP/MAS NMR measurements were performed on a Varian Infinityplus-400 spectrometer. Solution <sup>13</sup>C NMR spectra were recorded at 80 °C on Bruker DRX-400 spectrometer. <sup>71</sup>Ga MAS NMR spectra were acquired at 121.90 MHz with samples spun in a 2.5 mm rotor at 25 kHz. The spectra were accumulated with 36,000 scans and a 2 s pulse delay. <sup>31</sup>P MAS NMR spectra with <sup>1</sup>H decoupling were recorded at 161.8 MHz with a spinning rate of 10 kHz. The spectra were accumulated with 200 scans and a 4 s pulse delay. <sup>1</sup>H→<sup>13</sup>C CP/MAS NMR spectra were recorded at 100.5 MHz with a spinning rate of 4 kHz. The spectra were accumulated with 2100 scans, a 2 s pulse delay and contact time of 4 s.

## 3. Results and discussion

Table 1 gives the details of the initial gels, crystallization conditions and the structure of the products. It is apparent that a small quantity of water is added with H<sub>3</sub>PO<sub>4</sub> and HF solution, and this water has an important effect on the crystallization as reported elsewhere [36]. In each kind of ILs used in the present work, GaPO<sub>4</sub>-a [37], an open structure containing 8-ring channels, was exclusively produced in the absence of HF. However, on addition of HF, CLO or GaPO<sub>4</sub>-LTA was produced depending on both the structure of the IL used and the reaction temperature employed. In the case of [C<sub>2</sub>mim]Br, CLO was obtained at 150 °C, while GaPO<sub>4</sub>-LTA was produced at 180 °C. Increasing the alkyl chain length of ILs to 3–6 carbons resulted only in GaPO<sub>4</sub>-LTA without reference to reaction temperature. Attributing to negligible vapor pressure of ILs [21–23], GaPO<sub>4</sub>-a, GaPO<sub>4</sub>-LTA and CLO can also be prepared in open vessel, representing the safe and simple characters of this new synthetic method. In addition to its mineralizing effect, F<sup>-</sup> played a co-template role along with the organic cations

of ILs as well as in conventional synthesis of CLO and GaPO<sub>4</sub>-LTA [15,18]. Additionally, the amount of HF was also found to affect the synthesis process to a large extent.

### 3.1. Synthesis of CLO

As given in Table 1, CLO was produced in [C<sub>2</sub>mim]Br in the presence of fluorine, while GaPO<sub>4</sub>-a was obtained in the absence of fluorine. PXRD patterns of as-synthesized CLO, along with that of GaPO<sub>4</sub>-a, is shown in Fig. 1. SEM images of GaPO<sub>4</sub>-a and CLO are shown in Fig. 2. GaPO<sub>4</sub>-a crystal comprises hexagonal prism fairly regular in shape and approximately 120 μm in length. The crystals of CLO are poorly cubic with a size ranging from 5 to 20 μm.

The <sup>13</sup>C CP/MAS NMR spectra (Fig. 3) of CLO and GaPO<sub>4</sub>-a prepared in [C<sub>2</sub>mim]Br confirm that [C<sub>2</sub>mim]<sup>+</sup> cations located in the final products and keep intact [38]. In literatures, many organic amines, including quinuclidine, methylquinuclidium iodide, 3-azabicyclo(3,2,2)nonane, piperidine and hexamethyleneimine, have been used as template for the preparation of CLO [8]. Considering the similarities between those molecules, it is not difficult to understand that [C<sub>2</sub>mim]<sup>+</sup> can work as template in this study. Based on systematic studies of CLO with quinuclidine as template, Ozin et al. speculated the location of quinuclidine molecules in the framework of CLO, and they concluded that 8 quinuclidine molecules cooperated to direct the formation of one CLO supercage, and 4 quinuclidine molecules directed the formation of one 20-member ring [39]. In this work, CLO was produced only in [C<sub>2</sub>mim]Br IL, while increasing the alkyl chain length of 1-alkyl-3-methyl imi-

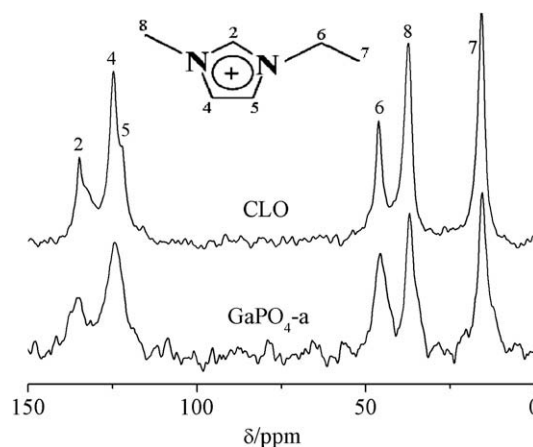


Fig. 3. <sup>13</sup>C CP/MAS NMR spectra of CLO and GaPO<sub>4</sub>-a prepared in [C<sub>2</sub>mim]Br.

dazolium bromide ILs to 3–6 carbons resulted in only GaPO<sub>4</sub>-LTA. Therefore, we can deduce that 1-alkyl-3-methyl imidazolium bromide ILs with alkyl chain length longer than 2 carbons are only proper for the formation of LTA cages in structures of GaPO<sub>4</sub>-LTA, but are probably too large to direct the formation of CLO cages/RPA cages/20-member ring in CLO structures. The structure character of template molecules seems vital for the synthesis of CLO.

The stability of CLO is a serious question for its further application. Several works have concentrated on this issue [17,39]. In this

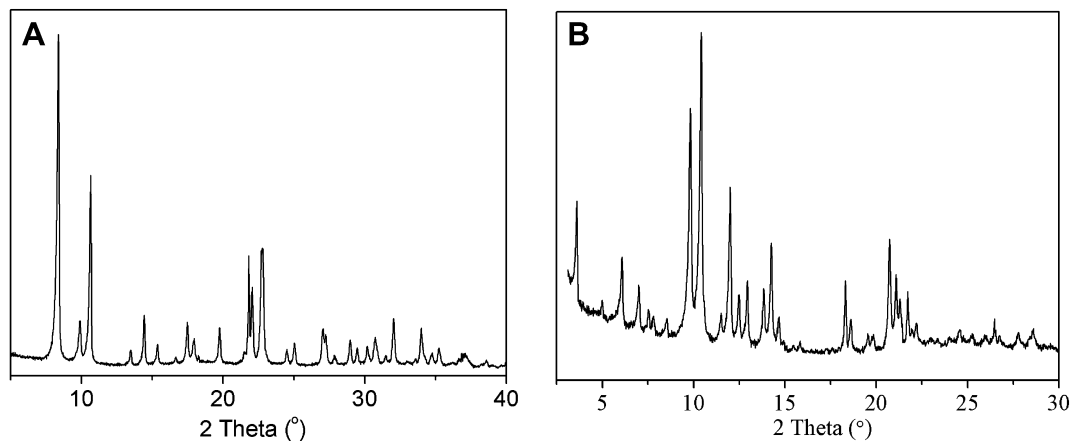


Fig. 1. PXRD patterns of GaPO<sub>4</sub>-a and CLO prepared in [C<sub>2</sub>mim]Br.

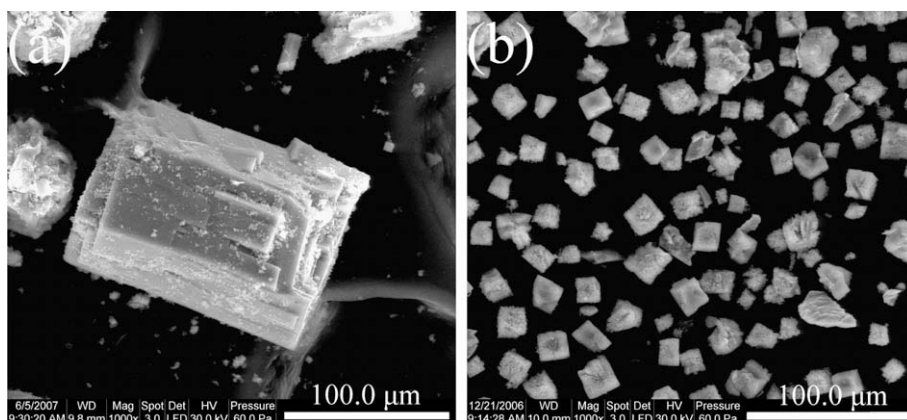


Fig. 2. SEM images of (a) GaPO<sub>4</sub>-a prepared in [C<sub>2</sub>mim]Br and (b) CLO.

work, no distinct enhancement of the thermal stability was observed in this sample prepared ionothermally. Further effective methods should be explored to improve its stability.

### 3.2. Synthesis of large single crystal of GaPO<sub>4</sub>-LTA

In order to study the effect of the reaction temperature, the crystallization temperature was increased to 180 °C, and GaPO<sub>4</sub>-LTA was formed (sample LTA-C<sub>2</sub> in Table 1). The XRD patterns and SEM images of as-synthesized LTA-C<sub>2</sub> are shown in Figs. 4 and 5, respectively. LTA-C<sub>2</sub> is unique crystal with octahedral morphology. The size of the crystals prepared in sealed vessel ranges from 200 to 400 μm, while the crystals obtained in open vessel varies from 100 to 300 μm. Single crystal of GaPO<sub>4</sub>-LTA has been reported using hydrothermal [18] and solvothermal synthesis methods [40]. However, all of them were performed in sealed vessels. Ionothermal synthesis provides a safe, simple and effective method for the preparation of large single crystal of molecular sieves.

Along with fluorine route, the extraordinary low surface tension of ILs [21–23] and the elimination of the competition between template-framework and solvent-framework interaction in ionothermal synthesis [27] all favor to the nucleation at low supersaturation level. Attributing to the unique characters of ILs, such as high viscosity, high density and the ionization environment etc. [21–23], the convection currents of ionothermal synthesis systems are much lower than those of hydrothermal and solvothermal syn-

thesis systems. Therefore, in the ionothermal synthesis, both secondary nucleation and crystallization by sedimentation are effectively suppressed in a manner analogous to that in solvothermal synthesis [4,41,42]. Accordingly, crystal growth is the dominant reaction, favoring the form of large crystals.

To determine the structure, LTA-C<sub>2</sub> was further characterized by single crystal XRD. The results determines a Fm-3c cubic unit cell with  $a = 24.058(2) \text{ \AA}$ ,  $\alpha = 90.00^\circ$  (CIF file in supplementary data). The PXRD of LTA-C<sub>2</sub> conforms to the simulated XRD pattern from single crystal XRD data very well (Fig. 4), indicating the bulk product is a pure phase of GaPO<sub>4</sub>-LTA. Like SIZ-6 [28], the [C<sub>2</sub>mim]<sup>+</sup> cations in the framework are severely disordered, and we are unable to model all the electron density in the framework satisfactorily. However, the results of check CIF/PLATON program served by IUCr on web [43] indicate that the total number of electrons near one 8-ring is approximately 56.2, which is comparable to the 60 electrons required by one [C<sub>2</sub>mim]<sup>+</sup> cation. Therefore, the negative charge of the structure is compensated by [C<sub>2</sub>mim]<sup>+</sup> cations, and the unit cell chemical composition is proposed as [Ga<sub>96</sub>P<sub>96</sub>O<sub>384</sub>] · 24[C<sub>2</sub>mim]F · 44.16 H<sub>2</sub>O.

In the <sup>13</sup>C CP/MAS NMR spectrum of LTA-C<sub>2</sub> (Fig. 6), despite all the distinct resonances of [C<sub>2</sub>mim]<sup>+</sup> cations are observed in the expected regions [38], two more peaks are observed at 49.8 and 57.8 ppm. To ascertain what species those two peaks belong to, we study the solution <sup>13</sup>C NMR spectra of reaction supernatant fluid after crystallization and HCl solution of dissolved LTA-C<sub>2</sub> (Fig. 7). However, the spectra are just analogous to that of [C<sub>2</sub>mim]Br [38], indicating that there is no new species formed.

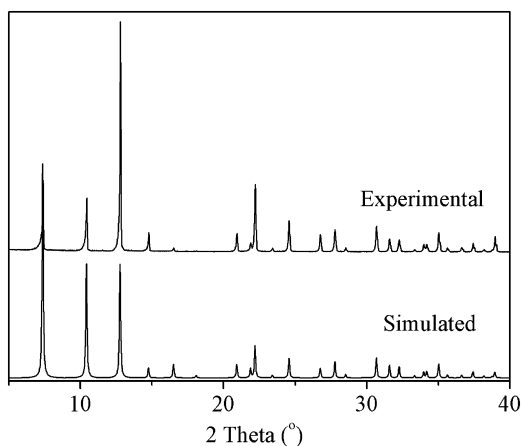


Fig. 4. XRD patterns of LTA-C<sub>2</sub>.

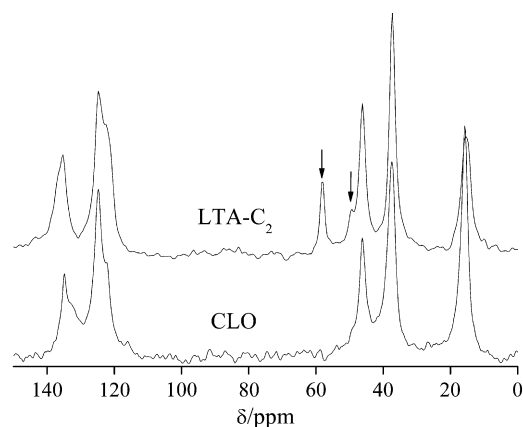


Fig. 6. <sup>13</sup>C CP/MAS NMR spectra of CLO and LTA-C<sub>2</sub>.

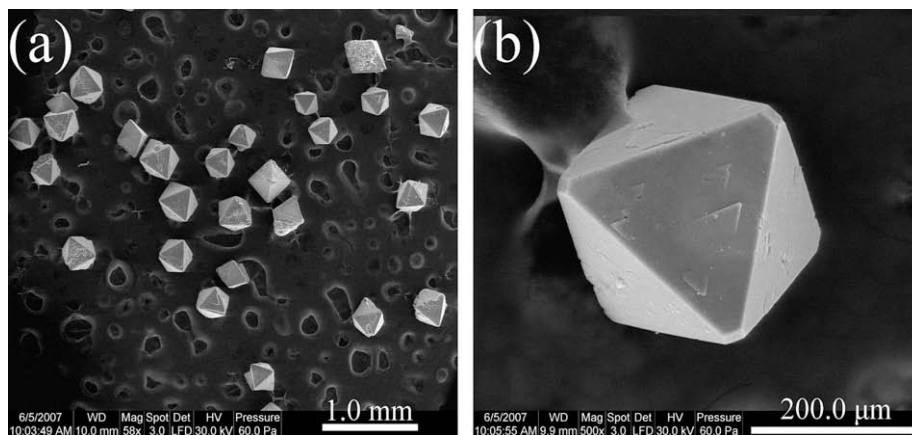


Fig. 5. SEM images of (a) LTA-C<sub>2</sub> in sealed and (b) open vessel.

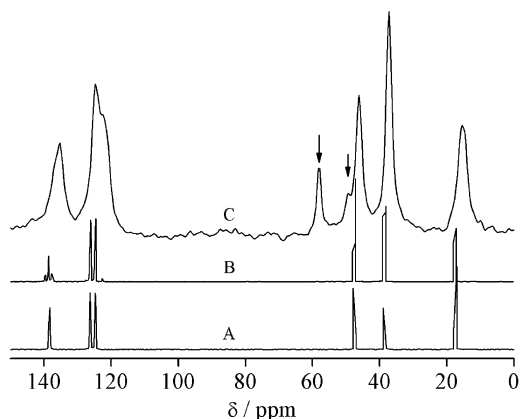


Fig. 7. Solution  $^{13}\text{C}$  NMR spectra of (A) reaction supernatant fluid after crystallization and (B) HCl solution of dissolved LTA-C<sub>2</sub>, along with (C)  $^{13}\text{C}$  CP/MAS NMR of LTA-C<sub>2</sub>.

So those two peaks should ascribe to crystallographically inequivalent  $[\text{C}_2\text{mim}]^+$  cations. The analogous cases are also observed in other fluorogallophosphate materials, such as Mu-15 [44]. Nevertheless, a clear assignment of the different signals to the different carbon atoms is not straightforward. Indeed, two types of organic molecule in crystallography are present in the fluorogallophosphate and strong interactions may exist between the  $[\text{C}_2\text{mim}]^+$  cations and the inorganic framework. Morris et al. have reported that the presence of fluorine ion in the framework of zeolite IFR led to dramatic change of the symmetry and ordering of the organic template [45]. Fluorine may cause the disorder of  $[\text{C}_2\text{mim}]^+$  cations in LTA-C<sub>2</sub> in the same manner.

The  $^{31}\text{P}$  and  $^{71}\text{Ga}$  MAS NMR spectra of LTA-C<sub>2</sub> are reported in Fig. 8. Two distinct peaks are observed in  $^{31}\text{P}$  MAS NMR spectrum of LTA-C<sub>2</sub> at  $-5.0$  and  $-12.6$  ppm, respectively. And the peak area ratio is ca. 1:3. According to the LTA structure, in which only one crystallographic site for P is present, only one NMR peak should be observed for phosphorus. Patarin et al. have studied  $\text{GaPO}_4\text{-LTA}$  with DPA as template by  $^{31}\text{P}$  MAS NMR technique [19]. Two peaks with area ratio of 1:3 were also observed in the same regions. They attributed the peak at low field to the phosphorus atoms, which were influenced by the strong hydrogen bond between the N atom of DPA and one O atom in 8-member ring. And only one quarter phosphorus atoms were affected by N atom of DPA. In the imidazolium ring of  $[\text{C}_2\text{mim}]^+$  cations, only the C atom between the two N atoms is substantially positive, while the other two C atoms and the formally positive N atoms carry sig-

nificant negative charge [46]. Therefore, only the C atom between two N atoms in  $[\text{C}_2\text{mim}]^+$  cation can form hydrogen bond with O atom of the 8-member ring, and these interactions should account for the emergence of the peak at low field in the  $^{31}\text{P}$  MAS NMR spectra of LTA-C<sub>2</sub>. Accordingly, these interactions lead to the appearance of two more peaks in the  $^{13}\text{C}$  CP/MAS NMR spectra of LTA-C<sub>2</sub> as shown in Fig. 6. The occurrence of two more peaks can be ascribed to two different kinds of conformational structures that  $[\text{C}_2\text{mim}]^+$  cations may take.

$^{71}\text{Ga}$  MAS NMR spectrum of LTA-C<sub>2</sub> is also given in Fig. 8. It is poorly resolved, presumably due to a quadrupolar effect. The broad peak at  $-33.7$  ppm is attributed to penta-coordinated gallium atoms [18,19], which is in good agreement with the structure determination of single crystal XRD date. The peak at  $55.3$  ppm is attributed to the extra-framework Ga species, unreacted  $\text{GaOOH}$ .

### 3.3. Effect of alkyl chain length of 1-alkyl-3-methyl imidazolium bromide ILS on the synthesis of $\text{GaPO}_4$ materials

To study the effect of the structure of ILS on the synthesis, 1-alkyl-3-methyl imidazolium bromide ILS with alkyl chain length of 3–6 carbons were also employed as reaction media. When no HF was added, only  $\text{GaPO}_4\text{-a}$  was obtained in these ILS. Once HF was added,  $\text{GaPO}_4\text{-LTA}$  was produced. The PXRD patterns of LTA-C<sub>n</sub> ( $n = 3\text{--}6$ ) are given in Fig. 9. It was noteworthy that no CLO was obtained even changing the reaction temperature. Furthermore, with the alkyl chain length of the ILS increasing from 3 to 6 carbons, dense phase became dominant in the final products, and the resultant products became very sensitive to the reaction temperature.

Fig. 10 shows the SEM images of LTA-C<sub>3</sub>, LTA-C<sub>4</sub>, LTA-C<sub>5</sub> and LTA-C<sub>6</sub>. Taking the results of Fig. 5 into account, it can be seen that, with the alkyl chain length of ILS increasing from 2 to 6 carbons, the sizes of  $\text{GaPO}_4\text{-LTA}$  crystals decrease sharply, meanwhile the morphologies of  $\text{GaPO}_4\text{-LTA}$  vary from octahedron (LTA-C<sub>2</sub>, LTA-C<sub>3</sub> and LTA-C<sub>4</sub>) to truncated octahedron (LTA-C<sub>5</sub>), and ultimately to cube (LTA-C<sub>6</sub>).

Molecular simulation study of 1-alkyl-3-methyl imidazolium family ILS predicts the presence of polar domains that are formed by the head groups of the cations and anions and of nonpolar domains that are formed by the alkyl groups [46]. With the alkyl chain length of 1-alkyl-3-methyl imidazolium bromide ILS increasing from 2 to 6 carbons, the nonpolar domain becomes larger and more connected, while the polar domain becomes more and more permeated by nonpolar regions [47]. Accordingly, as the alkyl chain length increases, the supersaturation level in the polar domain becomes higher, and leads to the decrease of crystal sizes of  $\text{GaPO}_4\text{-LTA}$ . Meanwhile, the changes in gel rheology and

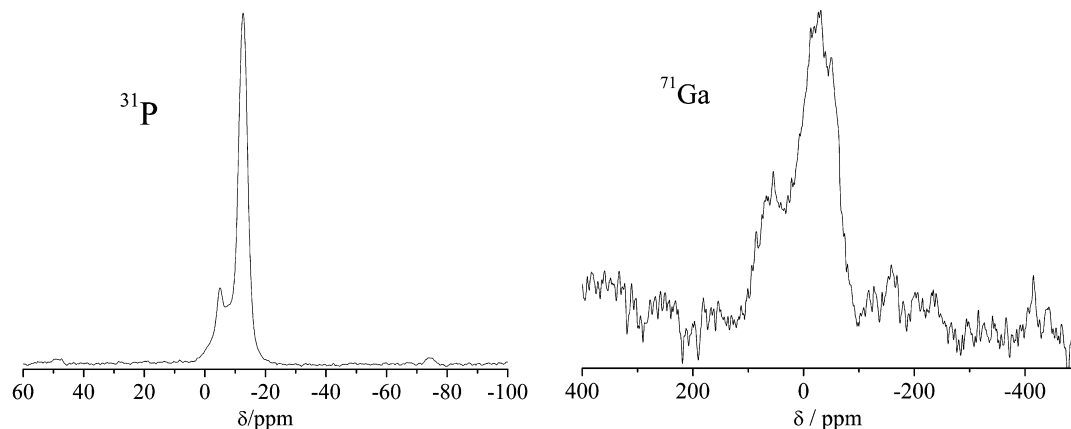
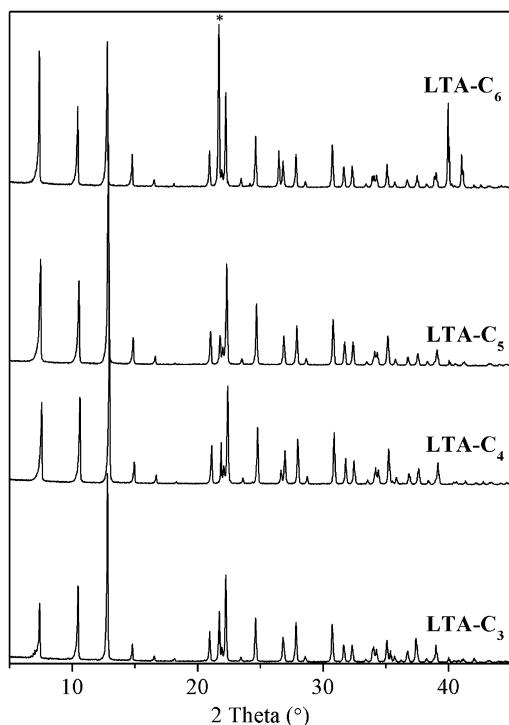


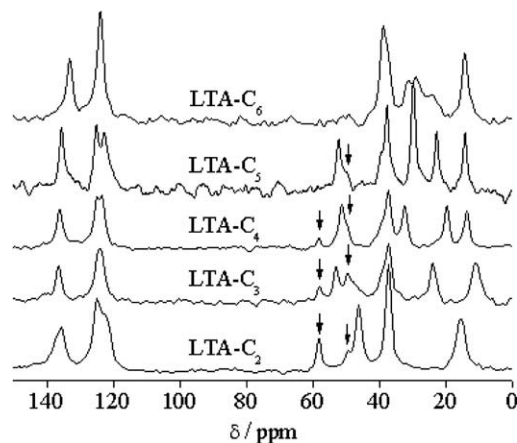
Fig. 8.  $^{31}\text{P}$  and  $^{71}\text{Ga}$  MAS NMR spectra of LTA-C<sub>2</sub>.



**Fig. 9.** PXRD patterns of LTA-C<sub>3</sub>, LTA-C<sub>4</sub>, LTA-C<sub>5</sub> and LTA-C<sub>6</sub>. The peak labeled by asterisk belongs to dense phase.

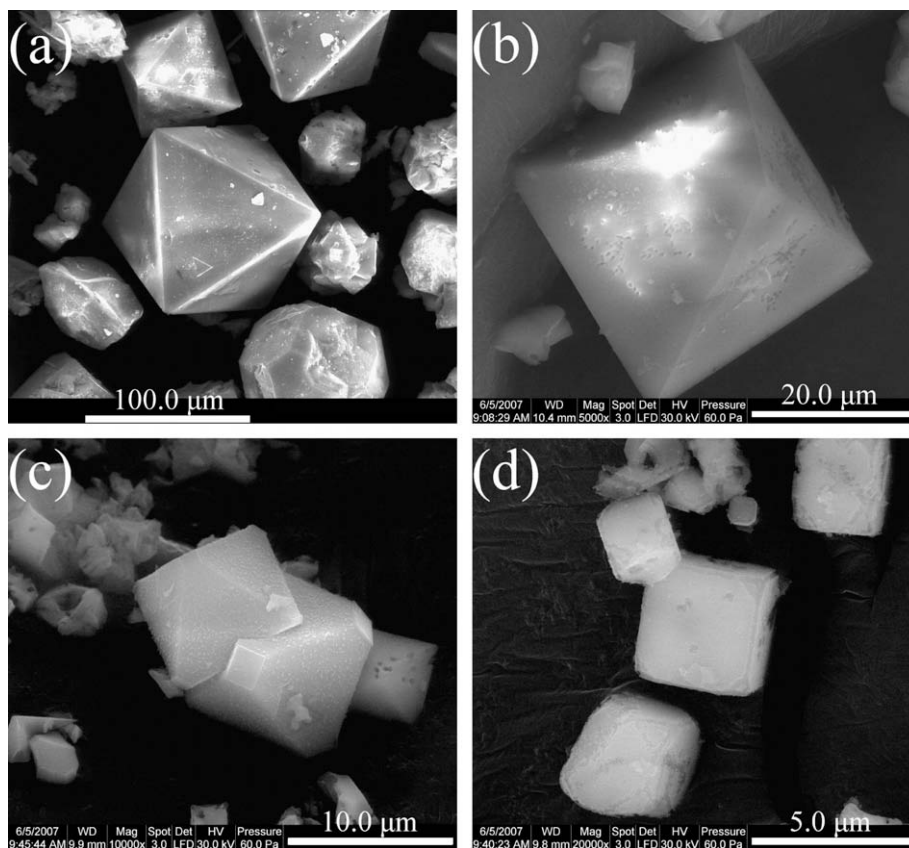
crystal kinetics lead to the varying of the morphologies of GaPO<sub>4</sub>-LTA.

GaPO<sub>4</sub>-LTA samples prepared in [C<sub>n</sub>mim]Br (*n* = 3–6) ILs are also characterized by <sup>13</sup>C CP/MAS NMR (Fig. 11). Besides the peaks of



**Fig. 11.** <sup>13</sup>C CP/MAS NMR spectra of LTA-C<sub>n</sub> (*n* = 2–6).

the IL used, two more distinct peaks at 49.8 and 57.8 ppm are also observed as in LTA-C<sub>2</sub>, and the intensities of those two peaks decrease with increasing the alkyl chain length from 2 to 5 carbons, and disappear for LTA-C<sub>6</sub>. Therefore, taking the results of <sup>31</sup>P and <sup>71</sup>Ga MAS NMR spectra of LTA-C<sub>2</sub> (Fig. 8) into account, we can deduce that, with the increasing of alkyl chain length of ILs from 2 to 6 carbons, the stereo-hindrance effect becomes severer, and the trend of the organic templates to take the second conformational structure corresponding to peaks at 49.8 and 57.8 ppm becomes more difficult. Morris et al. have studied the <sup>13</sup>C CP/MAS NMR spectra of AlPO<sub>4</sub> molecular sieves ionothermally synthesized in imidazolium-based ILs [30]. They found that the addition of HF led to the formation of dimethyl imidazolium cations, which served as the template of the final AlPO<sub>4</sub> molecular sieves. The



**Fig. 10.** SEM images of (a) LTA-C<sub>3</sub>, (b) LTA-C<sub>4</sub>, (c) LTA-C<sub>5</sub> and (d) LTA-C<sub>6</sub>.

NMR peaks of dimethyl imidazolium cation could be overlapped by those of the IL initially added. Therefore, the formation of a small amount of dimethyl imidazolium cations cannot be eliminated absolutely in this work.

#### 4. Conclusions

For the first time, GaPO<sub>4</sub> molecular sieves were ionothermally prepared in 1-alkyl-3-methyl imidazolium bromide ILs. Three kinds of GaPO<sub>4</sub> materials were obtained, GaPO<sub>4</sub>-a, CLO and GaPO<sub>4</sub>-LTA. The alkyl chain length of [C<sub>n</sub>mim]Br (*n* = 2–6) ILs, reaction conditions and fluorine can affect the structure, morphology, and size of the final products. In the case of [C<sub>2</sub>mim]Br, large single crystal of GaPO<sub>4</sub>-LTA with well-defined octahedral morphology was obtained in both sealed and open vessel. This suggests that ionothermal synthesis is an effective, simple, and safe method for the preparation of large single crystal of molecular sieves. With the alkyl chain length of [C<sub>n</sub>mim]Br ILs increasing from 2 to 6 carbons, size of the as-synthesized GaPO<sub>4</sub>-LTA decreased sharply, meanwhile the morphology varied from octahedron (LTA-C<sub>2</sub>, LTA-C<sub>3</sub> and LTA-C<sub>4</sub>) to truncated octahedron (LTA-C<sub>5</sub>), and ultimately to cube (LTA-C<sub>6</sub>). The template cations in the as-synthesized GaPO<sub>4</sub>-LTA crystals may have two different kinds of conformational structures. HF plays a role of co-template along with the organic cations of IL.

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