

# Ionothermal synthesis of $\beta$ - $\text{NH}_4\text{AlF}_4$ and the determination by single crystal X-ray diffraction of its room temperature and low temperature phases

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## Abstract

$\beta$ - $\text{NH}_4\text{AlF}_4$  has been synthesised ionothermally using 1-ethyl-3-methylimidazolium hexafluorophosphate as solvent and template provider.  $\beta$ - $\text{NH}_4\text{AlF}_4$  crystals were produced which were suitable for single crystal X-ray diffraction analysis. A phase transition occurs between room temperature (298 K) and low temperature (93 K) data collections. At 298 K the space group =  $I4/mcm$  (no. 140),  $a = 11.642(5)$ ,  $c = 12.661(5)$  Å,  $Z = 2$  ( $10\text{NH}_4\text{AlF}_4$ ),  $wR(F^2) = 0.1278$ ,  $R(F) = 0.0453$ . At 93 K the space group =  $P4_2/nm$  (no. 138),  $a = 11.616(3)$ ,  $c = 12.677(3)$  Å,  $Z = 2$  ( $10\text{NH}_4\text{AlF}_4$ ),  $wR(F^2) = 0.1387$ ,  $R(F) = 0.0443$ . The single crystal X-ray diffraction study of  $\beta$ - $\text{NH}_4\text{AlF}_4$  shows the presence of two different polymorphs at low and room temperature, indicative of a phase transition. The  $[\text{AlF}_4/2\text{F}_2]^-$  layers are undisturbed except for a small tilting of the  $\text{AlF}_6$  octahedra in the  $c$ -axis direction.

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## 1. Introduction

Ionothermal synthesis is the use of an ionic liquid [1] or eutectic mixture [2] as the reaction solvent and, in many cases, structure directing agent (SDA) in the synthesis of microporous materials [3–10]. To date most studies have concentrated on the ionic liquid 1-ethyl-3-methylimidazolium bromide. However an ionic liquid is made of two components which can be varied, the organic or inorganic anion and usually a large organic cation. By varying the anion and cation, the properties of any ionic liquid, including viscosity, solvating ability, catalytic activity and melting point, can be altered dramatically [11,12]. This means that the solvents can be designed with a particular end use in mind, or to possess a particular set of properties. Hence the term “designer solvents” is often used when describing ionic liquids [13].

Here we report the first investigation of the use of an ionic liquid with a hexafluorophosphate ( $\text{PF}_6^-$ ) counter

anion in the ionothermal synthesis of a material. Ionic liquids based on the anion  $\text{PF}_6^-$  come under the class of hydrophobic ionic liquids [14]. This is in contrast to the ionic liquids based on the anion  $\text{Br}^-$ , commonly used in ionothermal synthesis, which are highly hygroscopic. This makes the ionic liquids based on the anion  $\text{PF}_6^-$  easier to handle than those based on the  $\text{Br}^-$  anion.

In a system where an ionic liquid acts as both solvent and template the negatively charged atoms at the surface of a growing framework will always be interacting primarily with the templating cation rather than with a mixture of template and solvent. It must be noted however that even after a moderate drying process these hydrophobic ionic liquids still often contain as much as 500 ppm water [15].

The downside to the advantages of ease of handling of hydrophobic ionic liquids is that the relatively non-polar nature of the solvents results in poor solubilisation of inorganic cations and anions. This makes them far from ideal as solvents for inorganic materials synthesis. One method of improving the solubility of inorganic species is the use of mineralisers. Mineralisers, such as fluoride or hydroxide ions, added to the reaction mixtures in the

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correct quantities are often vital for crystallisation of the desired molecular sieve products. Fluoride in particular has recently been an extremely useful mineraliser for aluminophosphates (AlPOs) [16] and silicate [17,18] synthesis. In addition to helping solubilise the starting materials under the reaction conditions there is evidence that fluoride itself can play a structure directing role [19–22] and is intimately involved in SDA ordering in certain materials [23,24]. In ionothermal synthesis the addition of fluoride also seems to be important in determining the phase selectivity of the reaction [1].

In this study,  $\beta$ - $\text{NH}_4\text{AlF}_4$  crystals, large enough for single-crystal X-ray diffraction, were produced by ionothermal synthesis. In this case fluoride, rather than acting only as a mineraliser, has formed a major component of the material itself.  $\beta$ - $\text{NH}_4\text{AlF}_4$  is the unique intermediate of  $\kappa$ - $\text{AlF}_3$ , i.e., on heating  $\beta$ - $\text{NH}_4\text{AlF}_4$  to 450 °C the  $\text{AlF}_4$  layers join together to form the three-dimensional (3D)  $\kappa$ - $\text{AlF}_3$  structure with the loss of  $\text{NH}_4\text{F}$  [25]. The different  $\text{AlF}_3$  polymorphs are of industrial importance as catalysts in the manufacturing of fluorochemicals, in particularly CFCs and the new CFC alternatives [26].  $\beta$ - $\text{NH}_4\text{AlF}_4$  undergoes a phase transition between 298 and 93 K. Whilst the room temperature (298 K) phase has been previously solved by powder X-ray diffraction [25] this is the first report of the low temperature phase.

## 2. Experimental

### 2.1. Synthesis

*1-ethyl-3-methylimidazolium bromide* (EMIBr), m.p. = 81–83 °C [27]. Under inert atmosphere conditions, degassed ethylbromide (86.04 g, 0.790 mol, Avocado) was added to the redistilled *N*-methyl imidazole (49.86 g, 0.607 mol, Aldrich), with constant stirring. This was refluxed at 40 °C for 3 h then allowed to cool to room temperature. Ethyl acetate was added and the product crashed out of solution. This was filtered, washed with ethyl acetate and dried under vacuum at 25 °C for 10 h to give 1-ethyl-3-methylimidazolium bromide as a white solid. The product was stored under an inert atmosphere. Yield 94%.  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta$  1.41 (t, 3H,  $J = 7.3$  Hz), 3.81 (s, 3H), 4.15 (q, 2H,  $J = 7.3$  Hz), 7.38 (d, 2H,  $J = 21.0$  Hz), 8.66 (s, 1H). NMR comparable with literature values [28].

*1-ethyl-3-methylimidazolium phosphorus hexafluoride* (EMIPF<sub>6</sub>), m.p. = 59–62 °C [15]. EMIBr (58 g, 0.304 mol) was placed in a plastic container and dissolved in about 250 mL distilled water. HPF<sub>6</sub> (86 g, 0.354 mol, 60 wt% in H<sub>2</sub>O, Aldrich) was added drop wise and a white precipitate formed. The liquid phase was decanted and a further 250 mL distilled water added and the mixture stirred vigorously. This step was repeated until the liquid phase measured about pH = 7. The EMIPF<sub>6</sub> was dried at 40 °C on a vacuum line for 7 h and stored under Argon. Yield 48%.

$\beta$ - $\text{NH}_4\text{AlF}_4$ : a Teflon-lined autoclave (volume 23 mL) was charged with EMIPF<sub>6</sub> (1.62 g), Al[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (0.100 g, Aldrich) and H<sub>3</sub>PO<sub>4</sub> (0.174 g, 85 wt% in H<sub>2</sub>O, Aldrich). This gives a ratio of Al[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub>:EMIPF<sub>6</sub>:H<sub>2</sub>O (from the aqueous H<sub>3</sub>PO<sub>4</sub>) as 1.0:3.1:13:2.9. The stainless steel autoclave was then heated in an oven to 190 °C for 96 h. The colourless crystals were suspended in water, sonicated then filtered under suction and washed with water and acetone.

### 2.2. Characterisation

Single crystal X-ray diffraction data for  $\beta$ - $\text{NH}_4\text{AlF}_4$  were collected using a Rigaku rotating anode single-crystal X-ray diffractometer at the University of St. Andrews. Initially the two full structure determinations were carried out on different crystals at different temperatures 93 and 298 K. A subsequent variable temperature study on the same crystal showed that the phase change is reversible. The structures were solved using standard direct methods and refined using least-squares minimisation techniques against  $F^2$ . The hydrogen atoms were located using difference Fourier maps and the N–H bond distances fixed at 0.98 Å using the DFIX restraint in the refinement programme SHELXL-97 [29]. Full details of the data collection and refinement can be found in the accompanying CIF files in the supplementary information.

Elemental analysis was carried out using a Carlo Erba 1106 CHN Elemental Analyser. A Jeol JSM-5600 scanning electron microscope (SEM) integrated with an energy dispersive X-rays (EDX) system for analytical elemental analysis was used to confirm the presence of fluorine in the  $\beta$ - $\text{NH}_4\text{AlF}_4$ .

## 3. Results

At room temperature  $\beta$ - $\text{NH}_4\text{AlF}_4$  is the same material as that previously synthesised and reported by Herron et al. [25] This material was characterised by powder diffraction at room temperature and reported with a space group of  $I4/mcm$ . Ionothermal syntheses of this product produced large single crystals (cubic 0.15 mm) suitable for data collection on the Rigaku rotating anode single-crystal X-ray diffractometer at the University of St. Andrews. The data were initially collected at 93 K. This resulted in data that indicated a space group of  $P4_2/nm$ . A further data set was collected at room temperature (298 K) and this gave a space group of  $I4/mcm$ . The crystal data and refinement details for the structure determinations are given in Table 1. The final atomic coordinates for the high and low temperature phases are given in Tables 2 and 3, respectively.

The space group identification for the two data sets was confirmed by checking the systematic absences in the reflections and these showed unambiguously the I centering for the room temperature phase ( $h+k+l = 2n+1$  absent). The structural changes between the low and room

Table 1  
Crystal and refinement data for the 298 and 93 K structure determinations of NH<sub>4</sub>AlF<sub>4</sub>

Identification code	$\beta$ -NH <sub>4</sub> AlF <sub>4</sub> temp. = 298(2) K	$\beta$ -NH <sub>4</sub> AlF <sub>4</sub> temp. = 93(2) K
Empirical formula	10NH <sub>4</sub> AlF <sub>4</sub>	10NH <sub>4</sub> AlF <sub>4</sub>
Formula weight	1210.22	1210.22
Wavelength	0.7107 Å	0.7107 Å
Crystal system, space group	Tetragonal, <i>I4/mcm</i>	Tetragonal, <i>P4<sub>2</sub>/ncm</i>
Unit cell dimensions	$a = 11.642(5)$ Å, $\alpha = 90.000^\circ$ $b = 11.642$ Å, $\beta = 90.000^\circ$ $c = 12.661(5)$ Å, $\gamma = 90.000^\circ$	$a = 11.616(3)$ Å, $\alpha = 90.000^\circ$ $b = 11.616$ Å, $\beta = 90.000^\circ$ $c = 12.677(3)$ Å, $\gamma = 90.000^\circ$
Volume	1716.0(12) Å <sup>3</sup>	1710.5(7) Å <sup>3</sup>
Z, Calculated density	2, 2.342 Mg/m <sup>3</sup>	2, 2.350 Mg/m <sup>3</sup>
Absorption coefficient	0.533 mm <sup>-1</sup>	0.534 mm <sup>-1</sup>
<i>F</i> (000)	1200	1200
Crystal size	0.1 × 0.08 × 0.08 mm	0.15 × 0.15 × 0.15 mm
Theta range for data collection	2.47–25.30°	2.48–25.28°
Limiting indices	$-10 \leq h \leq 14$ $-13 \leq k \leq 14$ $-14 \leq l \leq 14$	$-13 \leq h \leq 13$ $-10 \leq k \leq 13$ $-14 \leq l \leq 14$
Reflections collected/unique	5008/437 [ <i>R</i> (int) = 0.0203]	9085/827 [ <i>R</i> (int) = 0.0233]
Completeness to $\theta = 25.30$	97.50%	98.20%
Data/restraints/parameters	437/4/61	827/7/104
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.146	1.134
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0451, w <i>R</i> <sub>2</sub> = 0.1276	<i>R</i> <sub>1</sub> = 0.0438, w <i>R</i> <sub>2</sub> = 0.1380
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0453, w <i>R</i> <sub>2</sub> = 0.1278	<i>R</i> <sub>1</sub> = 0.0443, w <i>R</i> <sub>2</sub> = 0.1387
Largest diff. peak and hole	1.820 and $-0.356$ e Å <sup>-3</sup>	1.648 and $-0.387$ e Å <sup>-3</sup>

Table 2  
Atomic coordinates (× 10<sup>4</sup>) for NH<sub>4</sub>AlF<sub>4</sub> at 298 K

	<i>x</i>	<i>y</i>	<i>z</i>
Al(1)	743(1)	2077(1)	0
Al(2)	0	5000	0
F(1)	764(2)	2072(2)	1382(2)
F(2)	2163(2)	2837(2)	0
F(3)	1415(2)	679(2)	0
F(4)	0	5000	1389(3)
F(5)	-13(2)	3451(2)	0
N(1)	0	0	2500
N(2)	1601(2)	6601(2)	1992(3)
H(1A)	0(200)	680(40)	2960(50)
H(2A)	1120(40)	7120(40)	2420(50)
H(2B)	1021(12)	6021(12)	1810(60)
H(2C)	1940(50)	6940(50)	1360(40)

Tetragonal unit cell *I4/mcm* (no. 140),  $a = 11.642(5)$ ,  $c = 12.661(5)$  Å.

temperature phases appear to be similar to that reported by Bulou et al. [30] for the  $\alpha$ -NH<sub>4</sub>AlF<sub>4</sub> structure with a tetragonal unit cell of  $a = 5.0875(1)$ ,  $c = 12.7313(3)$  Å. The  $\alpha$ -NH<sub>4</sub>AlF<sub>4</sub> structure is made of layers of corner-linked AlF<sub>6</sub> octahedra connected to form four-rings. This is in contrast to the  $\beta$ -NH<sub>4</sub>AlF<sub>4</sub> layered structure where the corner-linked AlF<sub>6</sub> octahedra connect to form three-, four-, and five-rings (Fig. 1). The layers in the  $\beta$ -NH<sub>4</sub>AlF<sub>4</sub> structure are stacked with adjacent layers having the five and three-membered rings overlaid on one another. Between the layers are the ammonium cations. In the  $\alpha$ -NH<sub>4</sub>AlF<sub>4</sub> structure, at room temperature, the NH<sub>4</sub><sup>+</sup> are statistically distributed over two different orientations and the space group is *I4/mcm*. In the low temperature phase,

Table 3  
Atomic coordinates (× 10<sup>4</sup>) for NH<sub>4</sub>AlF<sub>4</sub> at 93 K

	<i>x</i>	<i>y</i>	<i>z</i>
Al(1)	7500	7500	2534(1)
Al(2)	10425(1)	6755(1)	2472(1)
F(1)	7500	7500	3931(2)
F(2)	7500	7500	1145(2)
F(3)	9656(1)	5344(1)	2273(2)
F(4)	10439(1)	6525(2)	3827(1)
F(5)	11829(1)	6090(1)	2353(1)
F(6)	9049(1)	7512(1)	2545(1)
F(7)	10423(1)	6940(1)	1086(1)
N(1)	9075(2)	5925(2)	-436(2)
N(2)	5886(2)	5886(2)	541(2)
N(3)	12500	7500	0
H(1A)	9660(20)	6340(30)	-20(30)
H(1B)	9400(40)	5600(40)	-1080(30)
H(1C)	8495(7)	6505(7)	-620(40)
H(2A)	5150(20)	6110(50)	860(40)
H(2B)	6461(8)	6461(8)	740(40)
H(2C)	5910(50)	5910(50)	-232(3)
H(3A)	11,850(20)	7450(30)	490(20)

*P4<sub>2</sub>/ncm* (no. 138),  $a = 11.616(3)$ ,  $c = 12.677(3)$  Å.

there is ordering of the NH<sub>4</sub><sup>+</sup> and the space group is *P4<sub>2</sub>/mbc*.

Fig. 2 shows the slight framework distortion which occurs during the phase transition from room temperature to low temperature. The Al1 octahedra tilt slightly, and the hanging Al–F bonds are no longer parallel to the *c*-axis. This is in contrast to the room temperature structure where both the Al1–F and Al2–F are parallel to the *c*-axis.

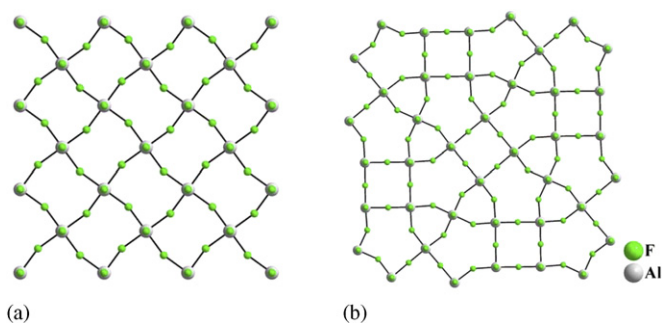


Fig. 1. Ball and stick diagram of a layer along the *c*-axis for room temperature: (a)  $\alpha$ - $\text{NH}_4\text{AlF}_4$  and (b)  $\beta$ - $\text{NH}_4\text{AlF}_4$

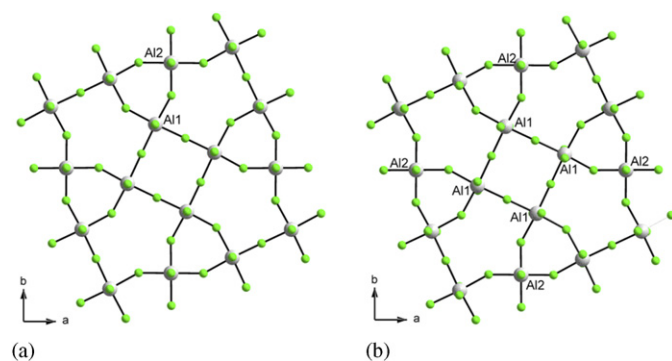


Fig. 2. Ball and stick diagram of  $\beta$ - $\text{NH}_4\text{AlF}_4$  showing the slight framework distortion (a) room temperature to (b) low temperature.

It is however the orientation of the hydrogen atoms around the nitrogens which characterises the different structures of the low temperature and room temperature phases. At low temperature the asymmetric unit contains three independent nitrogen sites (N1, N2, and N3) but at room temperature the asymmetric unit only contains two independent nitrogen sites (N4 and N5). Fig. 3 shows the arrangement of the nitrogens between the  $\text{AlF}_4$  layers. At low temperature N1, N2 and N3 are surrounded by ordered hydrogens, i.e. ordered  $\text{NH}_4^+$  groups. The data is of high enough quality for the individual hydrogen atoms to be located from the difference Fourier maps. Each site is crystallographically independent of the others due to the orientation of the hydrogens. At room temperature N4 is surrounded by ordered hydrogen atoms but for the N5 atom there are two equally probable, but different orientations for the  $\text{NH}_4^+$  tetrahedra. It is this orientation of the hydrogens around the nitrogens which breaks the symmetry of the room temperature space group. Again this is similar to the phase change seen for  $\alpha$ - $\text{NH}_4\text{AlF}_4$  [30].

To confirm the presence of fluorine in the  $\beta$ - $\text{NH}_4\text{AlF}_4$  structure, the crystals were analysed using EDX, giving an Al:F atomic ratio of 1:3.7. CHN was carried out to confirm the presence of ammonium. The values were as follows: C = 0.08, H = 2.95, N = 10.85% which are not too dissimilar to the calculated values of C = 0.00, H = 3.33, N = 11.57%.

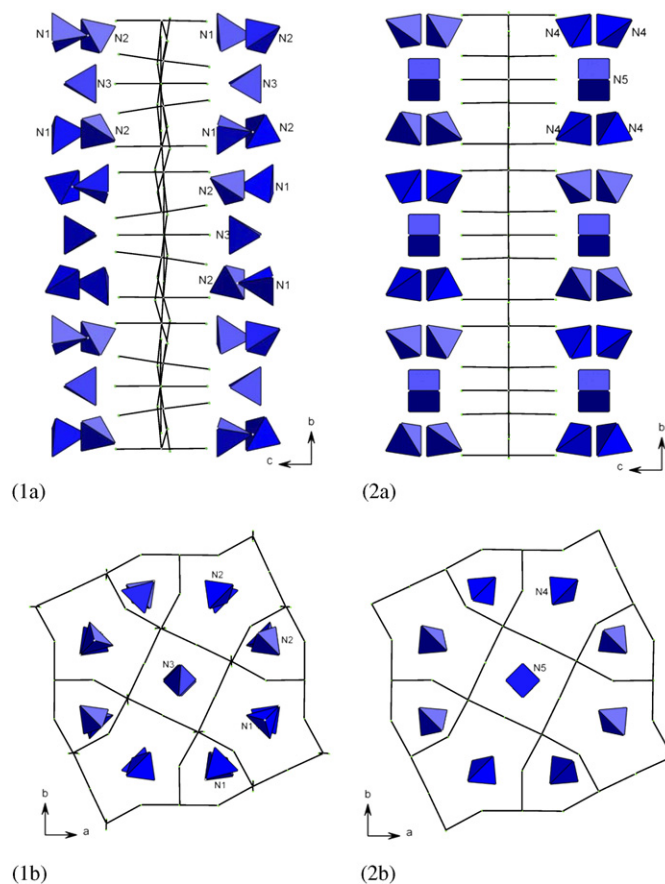


Fig. 3. Diagram to show the orientation of the crystallographically different  $\text{NH}_4$  shown as polyhedra, in Fig. 1a and b the low temperature data and in Fig. 2a and b the room temperature data.

#### 4. Discussion and conclusion

The single crystal X-ray diffraction study of  $\beta$ - $\text{NH}_4\text{AlF}_4$  at low (93 K) and room temperature (298 K) unambiguously shows the presence of two different polymorphs, indicative of a phase transition. Variable temperature studies on the same single crystal indicate that the phase change is reversible and that the crystals can be cycled several times without loss of structural integrity. The  $[\text{AlF}_4/2\text{F}_2]^-$  layers are undisturbed except for a small tilting of the  $\text{AlF}_6$  octahedra in the *c*-axis direction at low temperature. The two phases occur due to the orientation of the hydrogens around the nitrogens which breaks the symmetry of the room temperature space group. This phase change is similar to that observed by neutron powder profile refinement for  $\alpha$ - $\text{NH}_4\text{AlF}_4$  [30].

With regard to the synthesis, if no phosphoric acid was added to the reaction mixture, no product was formed. With the addition of phosphoric acid it was hoped that an AIPO framework would form, however the  $\beta$ - $\text{NH}_4\text{AlF}_4$  structure resulted. This raises many questions about the reaction conditions required to produce AIPOs and other materials using ionic liquids as the solvent and template. Perhaps the EMIPF<sub>6</sub> ionic liquid solubilised the



phosphorus source so efficiently that no AlPO structure can form.

Another issue with using an ionic liquid with the  $\text{PF}_6^-$  anion is the formation of HF. Ionic liquids containing the  $\text{PF}_6^-$  anion are sparingly water soluble. In the presence of water,  $\text{PF}_6^-$  undergoes hydrolysis to produce HF and  $\text{PO}_4^{3-}$  [15]. It would appear from the necessity to add phosphoric acid to this reaction that the water present in the phosphoric acid is in fact necessary for the formation of HF. The exact quantity of water present in the reaction is difficult to control, making reproducibility tricky. The quantity of water will affect the amount of HF present in the reaction, hence the pH. It is likely that large amounts of HF may lead to the break up of the imidazolium cation, hence the template in this structure is ammonium.

This research is in the early stages and there are many more anions to be tested in the ionothermal synthesis of materials. When changing the anion many different reaction conditions are altered. However we can conclude from the work presented in this paper that the anion does affect the reaction synthesis hence the final product produced.

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### Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at: [doi:10.1016/j.jssc.2006.09.024](https://doi.org/10.1016/j.jssc.2006.09.024).

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