Fe(AsO₄): A new iron(III) arsenate synthesized from thermal treatment of (NH₄)[Fe(AsO₄)F]

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The new orthorhombic Fe(AsO₄) phase has been synthesized by thermal treatment at 525 °C of a new (NH₄)[Fe(AsO₄)F] compound, with a [Fe(AsO₄)F]²⁻ skeleton showing channels where the ammonium cations are located. The crystal structure of Fe(AsO₄) has been solved from single-crystal data. The structure is formed by layers of edge-sharing dimeric octahedra, and interconnected by chains of alternating FeO₆ octahedra and AsO₄ tetrahedra.

The MIII(AsO₄) trivalent transition metal arsenates are scarce. To date only one ferric arsenate synthesized by the ceramic method, and estabilized in an oxoanion network is known.1–3 The crystal structure of this monoclinic phase was determined from high-resolution neutron powder diffraction data by Cheetham et al.2 More precise structural parameters were obtained from a single-crystal X-ray study by Reiff et al.3 The structure of this monoclinic Fe(AsO₄) compound consists of a three-dimensional network in which the iron(Ⅲ) cations are five-coordinated giving rise to pairs of FeO₅ trigonal bipyramid units with a common edge. This compound exhibits a strong antiferromagnetic behaviour with a Weiss-temperature of approximately −230 K. In this work we report on the synthesis and crystal structure of a new orthorhombic Fe(AsO₄) phase. As far as we are aware, Fe(AsO₄) represents the first example of iron(Ⅲ) arsenate obtained as single-crystals from thermal treatment at 525 °C of the (NH₄)[Fe(AsO₄)F] precursor,† by removing the (NH₄)⁺ counterion.

The crystal structure of the (NH₄)[Fe(AsO₄)F] precursor consists of a three-dimensional framework constructed from corner-sharing FeO₄F₂ octahedra and AsO₄ tetrahedra. The (NH₄)⁺ cations are located in the channels of the [Fe(AsO₄)F]⁻ open-framework, similarly to that found in the related (NH₄)[Fe(PO₄)F] compound.4 This structural feature favours the elimination of the cationic counterions as ammonium fluoride, giving rise to a new crystalline material with partial modifications of the structure of the ammonium precursor. The thermogravimetric analysis of (NH₄)[Fe(AsO₄)F] reveals a continuous weight loss of ca. 16.2% in the 180–500 °C temperature range. This loss can be attributed to the elimination of both the ammonium and fluoride ions of (NH₄)[Fe(AsO₄)F] (calc. 16.0%). The X-ray thermodiffractometry (Fig. 1) indicates that after losing both the ammonium and fluoride ions a new compound is obtained in the 450–630 °C range. This phase exhibits high crystallinity and corresponds to a novel Fe(AsO₄). It is worth mentioning that the unit-cell parameters of both the (NH₄)[Fe(AsO₄)F] precursor and the Fe(AsO₄) resulting compound are similar, which probably favours the attainment of single-crystals of Fe(AsO₄). The monoclinic Fe(AsO₄) phase† appears in the thermodiffractograms at temperatures higher than 630 °C.

Fig. 1 Thermodiffractograms of (NH₄)[Fe(AsO₄)F].

Fig. 2 View of the crystal structure of Fe(AsO₄) showing (a) the layers in the ab-plane and (b) the channels along the a-axis. The average Fe–As–O bond distances are 2.01(3) and 1.69(4) Å, respectively.
Taking into account the results obtained from the thermal analysis, the novel Fe(AsO₄) phase was obtained in the form of single-crystals by heating few single-crystals of (NH₄)Fe(AsO₄)F at 525 °C in air atmosphere, according to the chemical reaction:

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\text{(NH}_4\text{)}_2\text{[Fe(AsO}_4\text{)]F} (s) \rightarrow \text{Fe(AsO}_4\text{)} (s) + \text{NH}_4\text{F (g)}
\]

This synthetic procedure allowed us to obtain single-crystals of Fe(AsO₄), with high quality for the X-ray crystal resolution, without any further thermal treatment.†

Fe(AsO₄) crystallizes in the orthorhombic system.† The structure shows a three-dimensional skeleton constructed from sheets stacked along the [001] direction and interconnected by chains of alternating Fe(2)O₆ octahedra sharing vertex with the As(2)O₄ tetrahedra (Fig. 2a). The layers are formed by Fe(1)O₁₀ edge-sharing dimeric octahedra linked by common edges to the (1O₆)As-O₄ tetrahedra, which gives rise to tetrameric units connected to each other by common oxygen vertex (Fig. 2a). These sheets of Fe(AsO₄) result from the condensation and loss of the fluorine anions in the FeO₆F₂ octahedra which form the chains in the (NH₄)Fe(AsO₄)F precursor. Six-ring channels are observed along the c-axis of the three-dimensional network of Fe(AsO₄) (Fig. 2b). Similar structural packings of the FeO₆As₄ edge-sharing dimeric octahedra and XO₄ groups have been found in the crystalline forms of the Fe(AsO₄)K (X = V and Mo) phases.⁵

The magnetic study performed on the Fe(AsO₄) phase indicates the presence of strong antiferromagnetic interactions, with a Weiss constant of approximately −310 K and a magnetic moment at room temperature of 4.6 μₜ. The magnetic and spectroscopic properties of these phases will be published shortly.

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Notes and references

† Synthesis: (NH₄)₂[Fe(AsO₄)F] was synthesized from a mixture in 30 mL of water of FeCl₃·6H₂O (0.408 mmol), As₂O₃·2H₂O (1.500 mmol), HF (13.928 mmol) and ammonium hydroxide to increase the pH up to 4. The reagents were stirred and sealed in a PTFE-lined stainless steel pressure vessels (till factor 75%). After that the mixture was heated at 170 °C for 5 days, followed by slow cooling to room temperature. Well formed light-green single-crystals with (NH₄)₂[Fe(AsO₄)F] composition appeared. Calcd: N, 6.0; As, 32.3; Fe, 24.1; F, 8.2. Found: N, 5.9; As, 32.0; Fe 23.9; F, 7.7. The pH at the end of the reaction did not show any appreciable change. The IR spectrum does not show bands above 3500 cm⁻¹, in accordance with the absence of (OH)⁺ groups in the crystal structure. Crystals of (NH₄)₂[Fe(AsO₄)F] slowly heated under air at 525 °C for 24 h in a tubular furnace transform into single-crystals of the Fe(AsO₄) phase (yield ca. 85%). The morphology of the single-crystals used in the experiment was maintained before and after the thermal transformation. Chemical analysis of Fe(AsO₄) indicates the absence of the (NH₄)⁺ and F⁻ ions.

† Crystal data: (NH₄)₂[Fe(AsO₄)F], size 0.3 × 0.2 × 0.1 mm, Mᵦ = 231.81, orthorhombic, space group Pna₂₁ (n. 33), a = 13.270(2), b = 6.629(1), c = 10.866(1) Å, V = 955.8(2) Å³, Z = 8, μ = 9.971 mm⁻¹, ρₐbd = 3.222 g cm⁻³, ρcalc = 3.27(2) g cm⁻³, F(000) = 888. 580 reflections were measured in the 3.07° ≤ θ ≤ 29.96° range, being 2750 independent reflections (Rint = 0.0170) and 2539 observed applying the criterion I > 2σ(I). Fe(AsO₄), size 0.25 × 0.2 × 0.1 mm, Mᵦ = 194.77, orthorhombic, space group Immm (n. 74), a = 13.468(2), b = 6.525(1), c = 10.786(2) Å, V = 194.6(3) Å³, Z = 12, μ = 15.014 mm⁻¹, ρcalc = 4.101 g cm⁻³, ρcalc = 2.79(5) g cm⁻³, F(000) = 1092. The reduction of the experimental density of Fe(AsO₄) up to approximately 2/3 of that obtained from the X-ray measurements is in accordance with a textural porosity for this phase. The value of the BET surface area is 1.57(2) m² g⁻¹. 3756 reflections measured in the 4.74° ≤ θ ≤ 25.87° range gave 484 independent reflections (Rint = 0.0424) and 432 observed with I > 2σ(I). The structures were solved by direct methods (SHELXS 97) and refined by the full-matrix least-squares procedure based on F² using the SHELXL 97 computer program belonging to the WINGX software package. The scattering factors were taken from ref. 10. All non-hydrogen atoms were assigned anisotropic thermal parameters. The unit-cell parameters of (NH₄)₂[Fe(AsO₄)F] are close to those found for the KTiO(PO₄)-type materials. 4,11 The crystal structure can be solved in either the acentric Pna₂₁ (ab) or the centric Pna₂₁ (−ab) space group. When the refinement is performed in the acentric space group the ammonium cations are placed in two different crystallographic positions (R₁ = 0.030). However, if the centric space group is used the ammonium cations must be considered as disordered with occupancy factors of 50%, maintaining the pseudoinversion centre of the [Fe(AsO₄)F]⁻ inorganic skeleton (R₁ = 0.055). Therefore, taking into account that the space group utilised to describe the KTiOPO₄-type structures5,11 is the acentric Pna₂₁ we have considered the solution in this space group, with final R factors R₁ = 0.030 (all data) [wR₂ = 0.065]. For the Fe(AsO₄)F phase values of R₁ = 0.022 (all data) [wR₂ = 0.041] were obtained. Maximum and minimum peaks in final difference synthesis were 0.687, −0.879 e Å⁻³ and 0.383, −0.849 e Å⁻³ for the (NH₄)₂[Fe(AsO₄)F] and Fe(AsO₄)F₃ phases, respectively. The goodness of fit on F² was 1.113 and 1.002 in every compound. A simulation based on the (NH₄)₂[Fe(AsO₄)F] and Fe(AsO₄)F₃ single-crystal structures was in excellent agreement with the X-ray powder data, indicating the presence of pure phases with high crystallinity, CCDC 197340 and 197541. See http://www.rcsb.org/pdb/submitdata/ cht/bi20998k/ for crystallographic data in CIF or other electronic format.