

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

Begoña Bazán,^b José L. Mesa,^{*a} José L. Pizarro,^b Andrés T. Aguayo,^c María I. Arriortua^b and Teófilo Rojo^{*a}

^a Departamento de Química Inorgánica, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain. E-mail: qiproapt@lg.ehu.es; Fax: 34-944648500; Tel: 34-946012458

^b Departamento de Mineralogía-Petrología, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain

^c Departamento de Ingeniería Química, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain

Received (in Cambridge, UK) 7th November 2002, Accepted 22nd January 2003

First published as an Advance Article on the web 6th February 2003

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]⁻ 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 M^{III}(AsO₄) trivalent transition metal arsenates are scarce. To date only one ferric arsenate synthesized by the ceramic method, and established 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 fluorine ions of (NH₄)[Fe(AsO₄)F] (calc. 16.0%). The X-ray thermodiffraction (Fig. 1) indicates that after losing both the ammonium and fluorine 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^{1–3} appears in the thermodiffractiongrams at temperatures higher than 630 °C.

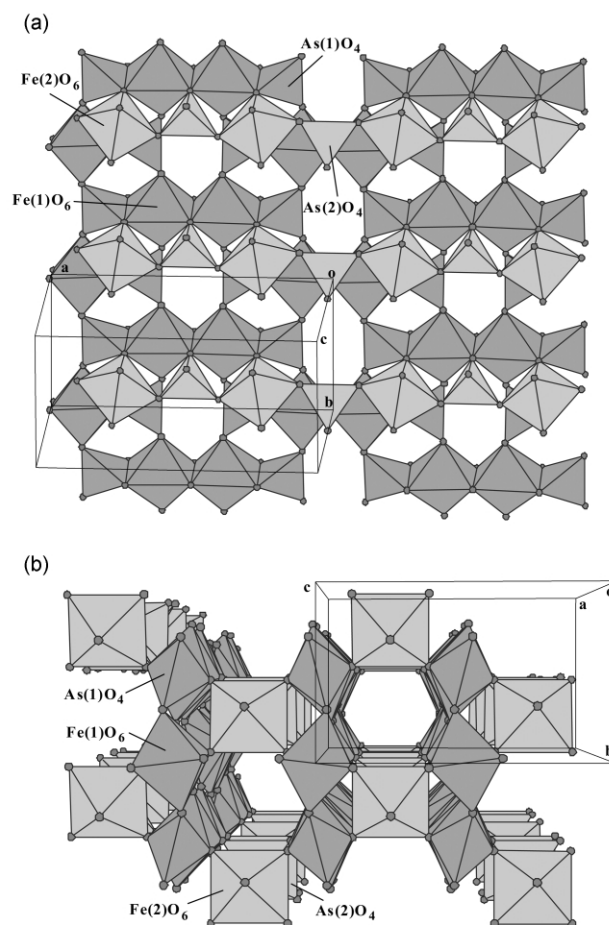


Fig. 2 View of the crystal structure of Fe(AsO₄) showing (a) the layers in the *ab*-plane and (b) the channels along the *a*-axis. The average Fe,As–O bond distances are 2.01(3) and 1.69(4) Å, respectively.

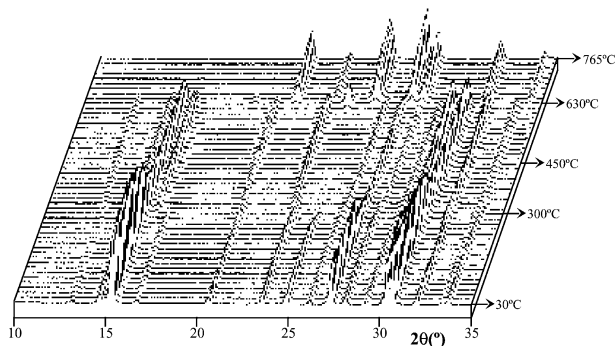
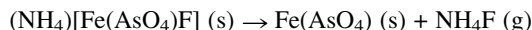


Fig. 1 Thermodiffractiongrams of (NH₄)[Fe(AsO₄)F].

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:



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)₂O₁₀ edge-sharing dimeric octahedra linked by common edges to the As(1)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 FeO₄F₂ octahedra which form the chains in the (NH₄)[Fe(AsO₄)F] precursor. Six-ring channels are observed along the *a*-axis of the three-dimensional network of Fe(AsO₄) (Fig. 2b). Similar structural packings of the Fe₂O₁₀ edge-sharing dimeric octahedra and XO₄ groups have been found in the crystalline forms of the Fe(XO₄) (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 μ_B. The magnetic and spectroscopic properties of these phases will be published shortly.

This work was financially supported by the Ministerio de Educación y Ciencia (BQU2001-0678) and Universidad del País Vasco/EHU (9/UPV00169.310-14199/2001, 9/UPV00130.310-13700/ 2001) which we gratefully acknowledge. B. Bazán thanks the University of Basque Country/Euskal Herriko Unibertsitatea for a doctoral fellowship.

Notes and references

† *Synthesis*: (NH₄)[Fe(AsO₄)F] was synthesized from a mixture in 30 mL of water of FeCl₃·6H₂O (0.408 mmol), As₂O₅·3H₂O (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 (fill 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)[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.⁶ Crystals of (NH₄)[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)[Fe(AsO₄)F], size 0.3 × 0.2 × 0.1 mm, *M*_r = 231.81, orthorhombic, space group *Pna*2₁ (no. 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}, *ρ*_{calcd} = 3.222

g cm^{−3}, *ρ*_{obs} = 3.27(2) g cm^{−3}, *F*(000) = 888. 5301 reflections were measured in the 3.07° ≤ *θ* ≤ 29.96° range, being 2750 independent reflections (*R*_{int} = 0.0170) and 2539 observed applying the criterion *I* > 2σ(*I*). Fe(AsO₄), size 0.25 × 0.2 × 0.1 mm, *M*_r = 194.77, orthorhombic, space group *Imam* (no. 74), *a* = 13.468(2), *b* = 6.525(1), *c* = 10.768(2) Å, *V* = 946.3(3) Å³, *Z* = 12, *μ* = 15.014 mm^{−1}, *ρ*_{calcd} = 4.101 g cm^{−3}, *ρ*_{obs} = 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 (*R*_{int} = 0.0424) and 432 observed with *I* > 2σ(*I*). The structures were solved by direct methods (SHELXS 97)⁷ and refined by the full-matrix least-squares procedure based on *F*², using the SHELXL 97 computer program⁸ belonging to the WINGX software package.⁹ The scattering factors were taken from ref. 10. All non-hydrogen atoms were assigned anisotropic thermal parameters. The unit-cell parameters of (NH₄)[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 *Pna*2₁ (*abc*) or the centric *Pnna* (*−acb*) space group. When the refinement is performed in the acentric space group the ammonium cations are placed in two different crystallographic positions (*R*1 = 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 (*R*1 = 0.053). Therefore, taking into account that the space group utilised to describe the KTiO(PO₄)-type structures^{4,11} is the acentric *Pna*2₁ we have considered the solution in this space group, with final *R* factors *R*1 = 0.030 (all data) [*wR*₂ = 0.065]. For the Fe(AsO₄) phase values of *R*1 = 0.022 (all data) [*wR*₂ = 0.041] were obtained. Maximum and minimum peaks in final difference synthesis were 0.687, −0.879 eÅ^{−3} and 0.383, −0.849 eÅ^{−3} for the (NH₄)[Fe(AsO₄)F] and Fe(AsO₄) phases, respectively. The goodness of fit on *F*² was 1.113 and 1.002 in every compound. A simulation based on the (NH₄)[Fe(AsO₄)F] and Fe(AsO₄) single-crystal structures was in excellent agreement with the X-ray powder data, indicating the presence of pure phases with high crystallinity. CCDC 197540 and 197541. See <http://www.rsc.org/suppdata/cc/b2/b210998k/> for crystallographic data in CIF or other electronic format.

- 1 E. C. Shafer, M. W. Shafer and R. Roy, *Z. Kristallogr.*, 1956, **108**, 263–275.
- 2 A. K. Cheetham, R. B. J. Jakeman, W. I. F. David, M. M. Eddy, M. W. Johnson and C. C. Torardi, *Nature*, 1986, **320**, 46–48.
- 3 W. M. Reiff, M. J. Kwiecien, R. J. B. Jakeman, A. K. Cheetham and C. C. Torardi, *J. Solid State Chem.*, 1993, **107**, 401–412.
- 4 Th. Loiseau, Y. Calage, P. Lacorre and G. Ferey, *J. Solid State Chem.*, 1994, **111**, 390–396.
- 5 (a) B. Robertson and E. Kostiner, *J. Solid State Chem.*, 1972, **4**, 29–37; (b) Y. Oka, T. Yao, N. Yamamoto, Y. Ueda, S. Kawasaki and M. Azuma and M. Takano, *J. Solid State Chem.*, 1996, **123**, 54–59; (c) A. W. Sleight, B. L. Chamberland and J. F. Weiher, *Inorg. Chem.*, 1968, **7**, 1093–1098.
- 6 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 1997.
- 7 G. M. Sheldrick, SHELXS 97: *Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1997.
- 8 G. M. Sheldrick, SHELXL 97: *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
- 9 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
- 10 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, UK, 1974, vol. IV, p. 99.
- 11 (a) I. Tordjman, R. Masse and J. C. Guitel, *Z. Kristallogr.*, 1974, **139**, 103–115; (b) T. Loiseau, C. Pautet, N. Simon, V. Munch, F. Taulle and G. Ferey, *Chem. Mater.*, 2000, **12**, 1393–1399.