Synthesis and characterization of the layered titanium arsenate $Ti_2O_3(H_2AsO_4)_2{\cdot}2H_2O$

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A new metastable layered titanium arsenate, isostructural with $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$, has been synthesized by acid treatment of the framework compound $NH_4TiOAsO_4$ at ambient temperature. Based on elemental analysis, IR spectroscopy, X-ray diffraction and thermogravimetry the formula $Ti_2O_3(H_2AsO_4)_2{\cdot}2H_2O$ was assigned to the novel compound. The layered nature of the compound was confirmed from amine intercalation and the ion exchange behavior towards alkali and alkaline earth metals.

Among the various inorganic materials of current interest, layered polyvalent metal (Ti, Zr, Sn) phosphates and phosphonates occupy a pivotal position. Owing to such properties as thermal, radiation and chemical stability, resistance to oxidation and developed porosity, these materials have received much attention in recent years, and are regarded as promising catalysts and ionic conductors, selective ion exchangers, materials for non-linear optics, radioactive waste hosts and convenient matrices for functionalization, *etc.*[1–6] Traditional methods of their preparation include the reactions between reagents in solution at elevated temperature (reflux technique) or at hydrothermal conditions. At the present time two main types of crystalline layered polyvalent metal phosphates are known, the α and γ phases.[7,8] Both of them contain two phosphorus atoms per metal atom. The difference between them is that the α phase has only one type of functional group, HPO_4, and its formula can be represented as $M(HPO_4)_2{\cdot}H_2O$ (M = Ti, Zr, Sn),[1,7] whereas in the corresponding γ phase half of the phosphorus atoms exist in the form of H_2PO_4 and the remainder in the form of PO_4 groups and hence the formula is $M(H_2PO_4)(PO_4){\cdot}2H_2O$ (M = Ti, Zr).[9,10] A search for novel compounds with valuable properties carried out actively in the last few years resulted in the discovery of several novel metastable phases of layered polyvalent metal phosphates. Among them are a layered zirconium-rich phosphate of formula $Zr_2O_3(HPO_4){\cdot}nH_2O$[11,12] and two layered titanium phosphates with a molar ratio P : Ti = 1 : 1: $TiO(OH)(H_2PO_4){\cdot}2H_2O$[13] and $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$.[14] It was found that the latter compound, having a characteristic first reflection in the XRD powder pattern at *ca.* 10.0 Å, could be formed as an intermediate product of α-TiP preparation [the formula $Ti(OH)_2(HPO_4){\cdot}H_2O$ was assigned to this compound previously[15]] and, possibly, as a product of $KTiOPO_4$ treatment with concentrated HNO_3.[16] $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ was synthesized as a single phase by the reaction of layered sodium titanates ($Na_2Ti_3O_7$ or $Na_4Ti_9O_{20}$) with 1–2 M phosphoric acid solution at 120–150 °C.[14]

In this paper, we present the results of the synthesis and preliminary characterization of a novel metastable phase of a layered titanium arsenate (TiAs) which is isostructural with $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$.

Experimental

Reagents

All reagents were of analytical grade (Aldrich).

Synthesis of the layered titanium arsenate

For the preparation of the layered titanium arsenate the framework ammonium titanyl arsenate ($NH_4TiOAsO_4$) was used as the initial compound. Ammonium titanyl arsenate was synthesized hydrothermally according to the following procedure. Titanium isopropoxide (3.0 ml) was thoroughly mixed with 13 ml of an aqueous solution containing 2.8 g of $As_2O_5{\cdot}3H_2O$ and 2.4 g of urea. The reaction mixture was transferred into a 30 ml Teflon lined stainless steel autoclave, sealed and treated at 190 °C for 10 days without stirring. The resultant solid (ammonium titanyl arsenate) was recovered by filtration, washed thoroughly with demineralized water and dried in air at 60 °C. In order to prepare the layered titanium arsenate, $NH_4TiOAsO_4$ was treated with an excess of 12 M HNO_3 solution at ambient temperature for 14 days. The resultant white fine dispersed powder of TiAs was filtered off, washed and dried in air at ambient temperature.

Analytical procedures

A Seifert–Scintag PAD-V diffractometer with Cu-Kα radiation was utilized. Thermogravimetry was performed with a DuPont Instruments TA 4000 unit (under nitrogen at a heating rate of 10 °C min^{-1}). The arsenic and titanium contents in the solids were determined by using a microprobe analysis with a Link detector Pentatet (EXL-100) operating at 20 kV. IR spectra were obtained on a Perkin-Elmer 1720-X FT spectrophotometer by the KBr pellet technique. Micrographs were recorded with a JEOL JSM-6100 electron microscope operating at 20 kV.

Amine intercalation

n-Alkylamine intercalation compounds were obtained by exposure of the titanium arsenate in an atmosphere saturated with amine vapor during 10–30 days at room temperature.

Ion exchange studies

Uptake of alkali and alkaline earth metal cations by the TiAs was studied using 0.05 N MCl_n–$M(OH)_n$ (M = Li, Na, K, Cs, Ca, Sr, Ba; $n = 1,2$) solutions with $V/m = 200/1$ (ml g^{-1}), at room temperature. The affinity of this exchanger towards some heavy metal cations was studied in 1×10^{-3} M MCl_n solutions ($M = Cr^{3+}$, Cd^{2+}, Hg^{2+}, Pb^{2+}, $Cu^{2+}$and Co^{2+}, $n = 2,3$) at $V/m = 200/1$ (ml g^{-1}). In all cases the contact time was 5 days under continuous shaking. The pH of the solutions after equilibration with the exchanger was measured using a Corning 340 pH meter. Initial and final concentrations of alkali and alkaline earth ions in solutions were measured using a Varian SpectrAA-250 atomic absorption spectrometer.

The affinity of the exchanger for alkali, alkaline earth and some transition metal elements was expressed through the distribution coefficient (K_d, ml g^{-1}) values, according to the formula $K_d = (C_o - C_i/C_i)V/m$, where C_o, C_i are the ion concentrations in the initial solution and in the solution after equilibration with adsorbent, respectively; V/m is the volume to mass ratio.

Results and Discussion

The X-ray powder diffraction pattern of the novel layered titanium arsenate is shown in Fig. 1(*a*). TiAs has the first most intense reflection at 10.2 Å, which is close to that found previously for the layered titanium phosphate $Ti_2O_3(H_2PO_4)_2 \cdot 2H_2O$ (9.9 Å). Under the given experimental conditions the acid transformation of $NH_4TiOAsO_4$ results in the formation of a moderately crystalline compound, whose X-ray pattern is not sufficiently developed to allow solution of its crystal structure by the powder diffraction method. The SEM photographs of the precursor ammonium titanyl arsenate and layered TiAs at 2000× and 15 000× magnification, respectively, are presented in Fig. 2(*a*), (*b*). It is seen that their morphology differs considerably. $NH_4TiOAsO_4$ consists of small polygonal plates with the size from 1 to > 10 μm, whereas TiAs consists of agglomerations (average size of 3–5 μm) of extremely thin flakes fused together.

According to the elemental analysis TiAs contains 21.08% Ti and 33.50% As, which indicates that the molar ratio As : Ti in the solid is close to 1 : 1.

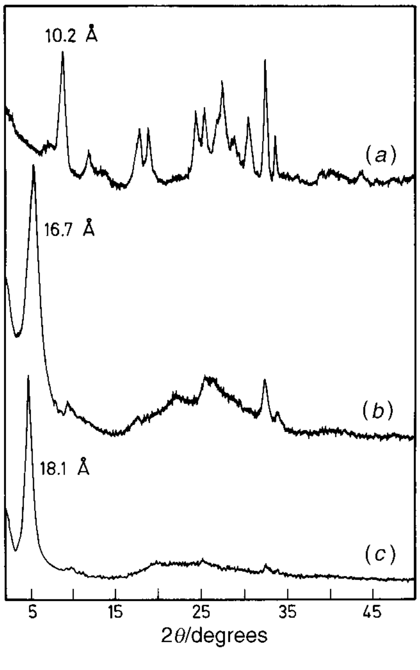

Fig. 1 The XRD powder patterns of $Ti_2O_3(H_2AsO_4)_2 \cdot 2H_2O$ (*a*) and its *n*-propylamine (*b*) and *n*-butylamine (*c*) intercalates

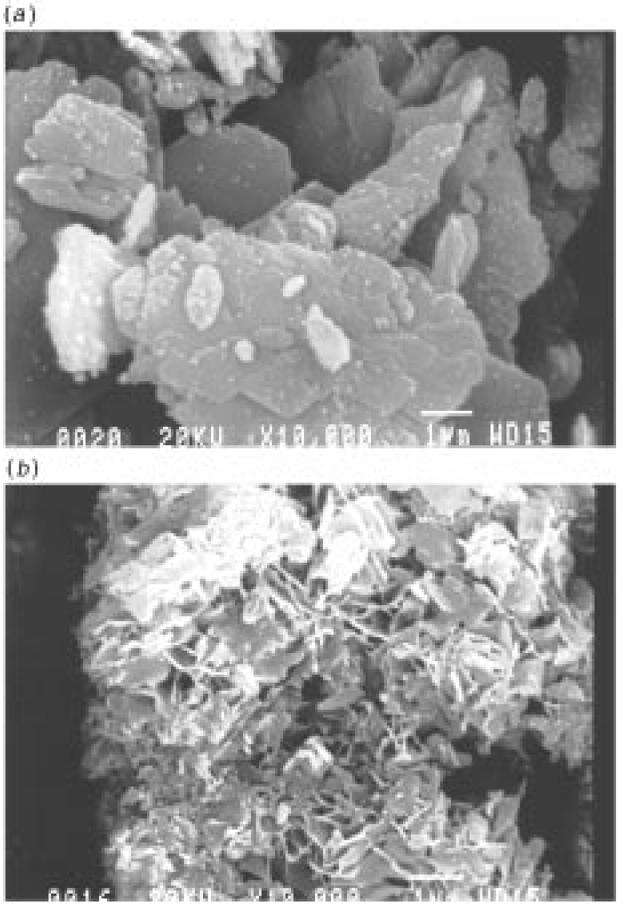

Fig. 2 SEM images: (*a*) NH_4TiAsO_4 (2000× magnification); (*b*) $Ti_2O_3(H_2AsO_4)_2 \cdot 2H_2O$ (15 000× magnification)

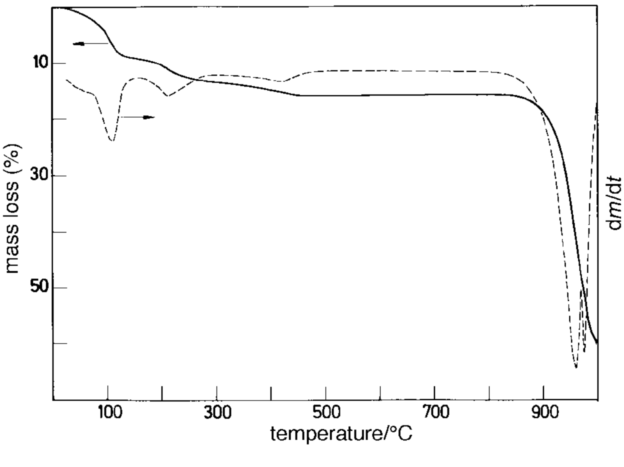

Fig. 3 TG (—) and DTG (– – –) curves for $Ti_2O_3(H_2AsO_4)_2 \cdot 2H_2O$

The TG curve for the TiAs is presented in Fig. 3. The mass loss up to 800 °C is 15.83% and the product isolated at this temperature was identified as $Ti_2O(AsO_4)_2$ ($M = 389.8$). Thus, the formula mass initially was 463.1. On the assumption that this increase in mass is totally due to water, the original solid contained 4.07 mol of H_2O. The mass loss in the temperature range 20–800 °C occurs in three steps. In the first stage, which takes place in the temperature range 50–120 °C, a mass loss of 8.10% was found, which we assign to 2.08 molecules of released interlayer crystal water. The mass losses in the second ($T = 120$–275 °C) and the third ($T = 275$–445 °C) stages, 5.07 and 2.66 mass%, respectively, are attributed to the release of 1.99 moles of structurally bound water due to the condensation processes of the functional groups of the titanium arsenate. In the last stage ($T > 800$ °C) $Ti_2As_2O_9$ undergoes further decomposition with the release of As_2O_5. Based on X-ray diffraction data, elemental analysis, thermogravimetry and IR spectroscopy the formula, $Ti_2O_3(H_2AsO_4)_2 \cdot 2H_2O$, is proposed for the titanium arsenate. This suggests that the novel titanium arsenate is isostructural to the dititaniumtrioxobis(dihydrogenphosphate) dihydrate $Ti_2O_3(H_2PO_4)_2 \cdot 2H_2O$, reported earlier.[14]

The novel titanium arsenate was further characterized by IR spectroscopy, TG and by studying its intercalation and ion exchange properties. As seen from Fig. 4(*a*) the IR spectrum of the TiAs has several intense, medium and weak bands at 3425vs, 1629m, 1123w, 1052w, 991w, 899m, 791vs, 695m, 500m and 427m cm^{-1}. The positions and intensities of bands observed are characteristic for the spectra of the polyvalent metal arsenates.[17] The adsorption bands at 1123, 1052, 991,

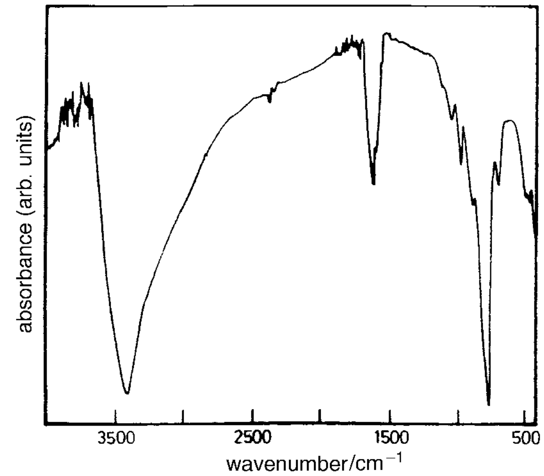

Fig. 4 IR spectrum of $Ti_2O_3(H_2AsO_4)_2{\cdot}2H_2O$

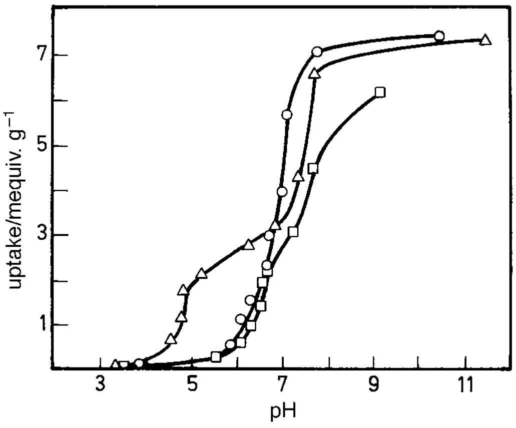

Fig. 6 Uptake of Ca^{2+} (○), Sr^{2+} (□) and Ba^{2+} (△) ions by $Ti_2O_3(H_2AsO_4)_2{\cdot}2H_2O$ as a function of pH

899, 791 and 695 cm^{-1} could be assigned to symmetric and antisymmetric stretching modes of As—O bonds in the H_2AsO_4 or $HAsO_4$ group. The two bands at 500 and 427 cm^{-1} are assigned to the vibration of Ti—O bonds of the TiAs matrix. A strong intense band at 3425 cm^{-1} and a medium intensity band at 1629 cm^{-1} arise from the presence of the free As—OH groups and/or physically bound water.

It was found that $Ti_2O_3(H_2AsO_4)_2{\cdot}2H_2O$ reacts readily with *n*-alkylamine vapours giving the corresponding amine intercalates with interlayer distances larger than that of the initial material [Fig. 1(*b*), (*c*)]. This expansion of the *d*-spacing indicates that the compound has a layered structure. It is notable that the interlayer distances of TiAs amine intercalates are considerably smaller than those found for dititaniumtrioxobis(dihydrogenphosphate) amine intercalates.[14] For example, the data on *d*-spacings of propylamine and butylamine intercalates in titanium arsenate (16.7 and 18.1 Å, respectively) are comparable with those found for the corresponding $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ amine intercalates (18.8 and 20.8 Å). At the same time these values are very close to those found for α-TiP amine intercalates.[18]

The presence in the structure of the TiAs of dihydrogenarsenate functional groups and its layered nature indicate that this material should behave as a cation exchanger with a theoretical ion exchange capacity (IEC) of 8.66 mequiv. g^{-1}, assuming that all the protons are exchangeable. The experimental curves which show the dependence of alkali metal ions uptake by TiAs from 0.05 M MCl–MOH (M = Li,Na,K,Cs) solutions are presented in Fig. 5. Analysis of these data shows that the layered titanium arsenate behaves as a weak acid cation exchanger. It starts the uptake of alkali metals at a pH close to 3.0–3.5 (<0.3 mequiv. g^{-1}) and its ion exchange capacity increases with increase of pH till 7.5–9.0 and then drops gradually in alkaline media. In acid solution titanium arsenate exhibits the following selectivity series to alkali metal cations: $K^+ > Na^+ \geqslant Li^+ > Cs^+$. In the pH range 6.8–7.8 a change of selectivity takes place: $K^+ > Na^+ > Cs^+ > Li^+$. The maximum value of alkali metal ions uptake found at pH = 7.5–9.0 is 2.2–2.5 mequiv. g^{-1} which is only 25–29% of the theoretical IEC. This could be related to two factors: steric hindrance for exchange of both protons on cations in H_2AsO_4 groups and, primarily a low hydrolytic stability of the exchanger in neutral and, especially, in alkaline media as was observed for the titanium phosphate analogue previously.[14] $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ starts to release phosphorus in the solution in the pH range 7–8, depending on the cation type (hydrolytic stability decreases in the series Cs > K > Na > Li) and loses practically all of it at pH = 9.0–9.5, when H_2PO_4 groups become completely dissociated. TiAs should hydrolyze even more readily.

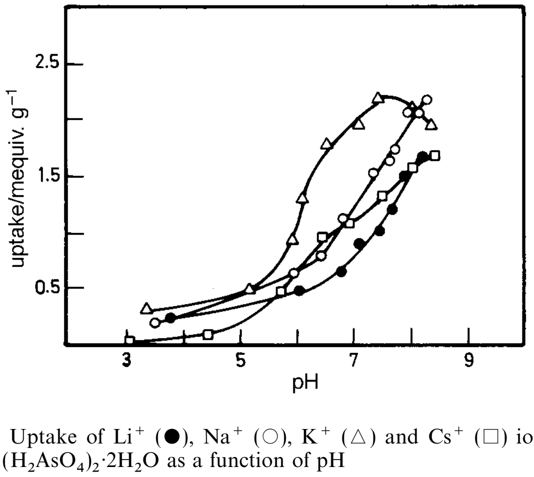

Fig. 5 Uptake of Li^+ (●), Na^+ (○), K^+ (△) and Cs^+ (□) ions by $Ti_2O_3(H_2AsO_4)_2{\cdot}2H_2O$ as a function of pH

Exchange of alkaline earth metal ions by TiAs was studied from 0.025 M MCl_2–$M(OH)_2$ solutions. As seen in Fig. 6, titanium arsenate does not exchange alkaline earth metal cations in acid solutions (pH < 3.5) and exhibits a low affinity towards calcium and strontium ions in the pH range 3.5–6.0 (IEC < 1 mequiv. g^{-1}). Exchange of these cations occurs in one step: a drastic increase in Ca^{2+} and Sr^{2+} ions uptake takes place in the pH range 6.5–8.5, reaching a maximum value of *ca.* 7.3 mequiv. g^{-1} (for Sr^{2+}) at pH higher than 8. Exchange of barium ion starts at lower pH (3.5–4.0) and occurs in two steps. In the first step (pH 4–7) *ca.* 3.0–3.5 mequiv. g^{-1} is taken up, whereas in the second step (pH 7–8) *ca.* 3.5 mequiv. g^{-1} more of barium is exchanged. The barium uptake totals to 7.2 mequiv. g^{-1} at pH 11. The IEC values of alkaline earth metal uptake by TiAs are close to but less than the theoretical ion exchange capacity (IEC 8.66 mequiv. g^{-1}). However this does not exclude the possibility of adsorption owing to the formation of insoluble alkaline earth metal arsenates in the pores of exchanger as was found in case of $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$.[14]

Conclusions

By treatment of the framework ammonium titanyl arsenate with a 12 M aqueous solution of HNO_3 a new metastable phase of a layered titanium arsenate has been prepared. Elemental data, thermogravimetry, IR spectroscopy and X-ray diffraction suggest that the synthesized material has formula $Ti_2O_3(H_2AsO_4)_2{\cdot}2H_2O$ and that it is isostructural with the dititaniumtrioxobis(dihydrogenphosphate) dihydrate. The novel phase readily reacts with *n*-alkylamine vapors, giving the corresponding amine intercalates.

The ion exchange properties of the layered titanium arsenate were also studied. It behaves as a weak acid cation exchanger towards alkali metals. It does not exchange alkaline earth cations in acid solutions ($pH < 3.5$) and exhibits a low affinity for them, with the exception of barium, in the pH range 3.5–6.0.

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References

1 *Inorganic Ion Exchange Materials*, ed. A. Clearfield, CRC Press, Boca Raton, FL, 1982.
2 A. Clearfield, in *Design of New Materials*, ed. D. L. Cocke and A. Clearfield, Plenum Press, New York, 1987.
3 G. Alberti, in *Recent Developments in Ion Exchange*, ed. P. A. Williams and M. J. Hudson, Elsevier, London, 1987.
4 G. Alberti and U. Costantino, in *Inclusion Compounds. Inorganic and Physical Aspects of Inclusion*, ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, Oxford, 1991, vol. 5.
5 G. D. Stucky, M. L. F. Phillips and T. E. Gier, *Chem. Mater.*, 1989, **1**, 489.
6 A. Clearfield, *Prog. Inorg. Chem.*, in press.
7 A. Clearfield and G. D. Smith, *Inorg. Chem.*, 1969, **8**, 431; J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311.
8 A. Clearfield, R. H. Blessing and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2249.
9 A. N. Christensen, E. K. Andersen, I. G. Andersen, G. Alberti, M. Nielsen and M. S. Lehmann, *Acta Chem. Scand.*, 1990, **44**, 865.
10 M. Salvado, S. Garcia-Granda and J. Rodriguez, *Mater. Sci. Forum*, 1994, **166**, 619.
11 A. I. Bortun, L. N. Bortun and A. Clearfield, *Solv. Extr. Ion Exchange*, 1997, **15**, 305.
12 A. Clearfield, A. Bortun, L. Bortun and J. R. Garcia, *Chem. Commun.*, submitted.
13 Y. J. Li and M. S. Whittingham, *Solid State Ionics*, 1993, **63–65**, 391.
14 A. I. Bortun, L. N. Bortun, A. Clearfield, M. A. Villa-García, J. R. García and J. Rodríguez, *J. Mater. Res.*, 1996, **11**, 2490.
15 A. Bortun, E. Jaimez, R. Llavona, J. R. García and J. Rodríguez, *Mater. Res. Bull.*, 1995, **30**, 413.
16 R. H. Jarman, *Solid State Ionics*, 1989, **32/33**, 45.
17 N. G. Chernorukov, I. A. Korshunov and M. I. Zhuk, *Russ. J. Inorg. Chem.*, 1982, **27**, 1728.
18 J. R. García, R. Llavona, M. Suárez and J. Rodríguez, *Trends Inorg. Chem.*, 1993, **3**, 209.

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