Crystal Structure and Intercalation Properties of γ-$Zr(AsO_4)(H_2AsO_4) \times 2\ H_2O$

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The crystalline structure of γ-$Zr(AsO_4)(H_2AsO_4) \times 2\ H_2O$ (γ-ZrAs) has been refined by the Rietveld method. It has a monoclinic $P2_1$ layered structure built up from AsO_4 tetrahedra and ZrO_6 octahedra stacked along the 001 direction. The cell parameters are: a = 5.5752(6) Å, b = 6.8290(7) Å, c = 12.110(1) Å, and β = 103.03(1)°. The layered nature of γ-ZrAs is confirmed by the intercalation of n-alkylamines ($CH_3[CH_2]_nNH_2$; n = 0–5) as well as of cyclic amines (benzylamine, cyclohexylamine, piperidine, and pyridine). Among the linear amines, only with methyl-, ethyl-, and hexylamine is the maximum incorporation attained. With the cyclic amines, except in the case of pyridine, pure new phases are obtained, with the highest degree of intercalation being one mol of amine per mol of γ-ZrAs.

Introduction

Some insoluble acid salts of the general formula $M^{IV}(HXO_4)_2 \times n\ H_2O$ (M = Ti, Zr, Ce, Sn, Hf; X = P or As) have a layered structure, each layer consisting of a plane of tetravalent atoms sandwiched between tetrahedral phosphate or arsenate groups. Thus, these salts possess the typical characteristics of an intercalating agent and can be considered as hosts for the design and preparation of supramolecular solids with various functions.[1]

There are two major types of layered structures, usually denoted as α- and γ-layered forms.[1−4] The γ-compounds, presently formulated as $M(PO_4)(H_2PO_4) \times 2\ H_2O$, differ from the α-type in that half of the phosphate groups have all 4 oxygen atoms bonded to the metal atoms, while the other half are present as dihydrogen phosphate groups, bearing exchangeable protons.[4][5]

There is now an extensive body of literature dealing with the ion-exchange and intercalation chemistry of metal(IV) phosphates with α- and γ-type structures, the most studied compounds being α-$Zr(HPO_4)_2 \times H_2O$ (α-ZrP) and γ-$Zr(PO_4)(H_2PO_4) \times 2\ H_2O$ (γ-ZrP).[6−10] In contrast, the corresponding arsenates have been scarcely investigated. Only three layered α-type polyvalent metal arsenates are known: $Zr(HAsO_4)_2 \times H_2O$ (α-ZrAs), $Ti(HAsO_4)_2 \times H_2O$ (α-TiAs), and $Sn(HAsO_4)_2 \times H_2O$ (α-SnAs).

α-ZrAs was prepared by refluxing amorphous zirconium arsenate in arsenic acid[11][12] and the titration curves with hydroxides of alkali metal ions, Tl^+, Ba^{2+}, and $NH_4{}^+$ have been determined.[13] Although the windows connecting the cavities in α-ZrAs are about the same size as those in α-ZrP,[14] it seems that steric hindrance to the diffusion of large cations is less in α-ZrAs than in α-ZrP. Thus, the ion-exchange properties of the two compounds lead to differences in their abilities to function as sieves. α-TiAs has been scarcely studied to date; it is less stable than α-TiP and is strongly hydrolyzed, even in neutral media. Thus, ion-exchange experiments in aqueous solutions are restricted to acidic media, where only one proton is replaced by Li^+, Na^+, or K^+ ions.[15] α-SnAs has been prepared and the ion-exchange properties towards alkali metal ions have also been investigated.[16] This material is strongly hydrolyzed in alkaline media, hence it is a poor exchanger of limited utility, unless specific applications in acidic solution or in non-aqueous media are required.

To date, no γ-arsenates have been reported in the literature, although it is probable that the structure of $Ce(HAsO_4)_2 \times 2\ H_2O$ is of the γ-type.[17][18] Some properties of metal(IV) arsenates are compiled in Table 1.

Table 1. Some properties of metal(IV) arsenates

	d [Å][a]	Free area [Å][b]	IEC [meq/g][c]	Ref.
α-$Zr(HAsO_4)_2 \times H_2O$	7.78	24.68	5.14	[14]
α-$Ti(HAsO_4)_2 \times H_2O$	7.77	22.20	5.78	[15]
α-$Sn(HAsO_4)_2 \times H_2O$	7.87	22.60	4.80	[16]

[a] Interlayer spacing. − [b] Area associated with each OH group on the plane. − [c] Ion-exchange capacity.

In a previous paper[19] we reported the hydrothermal synthesis of γ-ZrAs via its half-exchanged ammonium phase, and some preliminary data towards its characterization. In this paper, we describe the refinement of the crystal structure of γ-ZrAs by the Rietveld procedure. Furthermore, the layered nature of the compound is confirmed by the intercalation of n-alkylamines ($CH_3[CH_2]_nNH_2$; n = 0−5) and

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cyclic amines (benzylamine, cyclohexylamine, piperidine, and pyridine).

Results and Discussion

The γ-$Zr(AsO_4)(H_2AsO_4) \times 2\ H_2O$ formula for the synthesized compound was determined by means of the analytical procedures indicated in the Experimental Section.

A summary of the crystallographic data is given in Table 2, and final positional parameters are listed in Table 3. The final Rietveld refinement plot is shown in Figure 1.

Table 2. Crystallographic data for $Zr(AsO_4)(H_2AsO_4) \times 2\ H_2O$

Empirical formula	$ZrAs_2O_{10}H_6$
Molecular mass	407.1
Crystal system	monoclinic
$\rho_{calcd.}$ [g cm^{-3}]	3.01
Z	2
space group	$P2_1$
No. of contributing reflections	620 (K_α doublets)
No. of distance constraints	31
As−O distance constraint [Å]	1.67(1)
Zr−O distance constraint [Å]	2.07(1)
O···O distance constraint for PO_4 [Å]	2.72(1)
O···O distance constraint for ZrO_6 (*cis*) [Å]	2.93(1)
No. of parameters	54
R_{wp}	0.21
R_F	0.068
χ^2	37.3

$$R_{wp} = \left\{\frac{\sum_i w_i(y_{i,obs}-y_{i,calc})^2}{\sum_i w_i(y_{i,obs})^2}\right\}^{1/2},\ R_F = \frac{\sum_K |(I_{K',obs'})^{1/2}-(I_{K,calc})^{1/2}|}{\sum_K (I_{K',obs'})^{1/2}},$$

$$\chi^2 = \sum_i \frac{w_i(y_{i,obs}-y_{i,calc})^2}{(N_{obs}-N_{var})}$$

where N_{obs}, N_{var} = number of observations and variables.

Table 3. Atomic positional parameters for $Zr(AsO_4)(H_2AsO_4) \times 2\ H_2O$

Atom	x	y	z
Zr	0.816(1)	0.25	0.1384(3)
As1	0.220(1)	0.2429(9)	0.9381(4)
As2	0.405(1)	0.1393(9)	0.3181(4)
O1	0.027(2)	0.275(2)	0.0211(7)
O2	0.168(2)	0.0457(9)	0.8657(8)
O3	0.181(5)	0.445(1)	0.856(1)
O4	0.506(1)	0.244(1)	0.009(1)
O5	0.110(1)	0.181(2)	0.2634(6)
O6	0.588(1)	0.259(1)	0.2508(9)
O7	0.458(2)	0.8964(9)	0.312(1)
O8	0.472(2)	0.207(2)	0.4549(6)
OW1	0.036(2)	0.377(2)	0.6768(8)
OW2	0.01(1)	0.541(3)	0.479(2)

Compared with the unit cell of γ-ZrP, that of γ-ZrAs is extended in the *a* and *b* directions and compressed in the *c* direction. Accordingly, γ-ZrAs has a larger cell volume but a smaller interlayer distance (11.80 Å) than γ-ZrP (12.27 Å).

The powder pattern of γ-ZrAs reveals a certain degree of structural disorder. This is manifested by the appearance of two principal zones of extra-Bragg scattering, around 2θ = 18° and 29°. A similar effect is observed in the pattern of γ-TiP[20]. In the case of γ-TiP these zones appear as broad humps, whereas for γ-ZrAs sharper, better defined peaks are seen. These observations clearly indicate that both samples have a characteristic partially disordered structure.

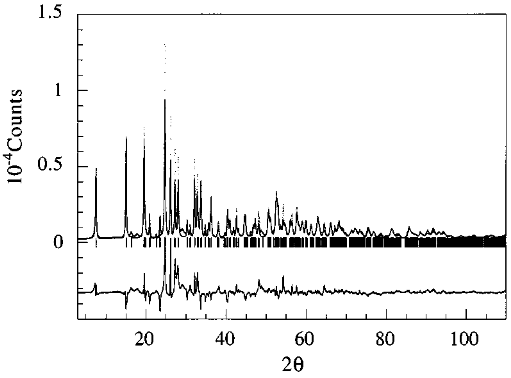

Figure 1. Rietveld refinement pattern of γ-ZrAs; points correspond to observed data; the solid line represents the calculated profile; tick marks show the positions of allowed reflections; a difference curve, on the same scale, is plotted at the bottom of the pattern

Although the Rietveld refinement is not completely satisfactory due to the aforementioned disorder, it can clearly be stated that γ-ZrAs has a mean crystal structure akin to other known γ-phases, namely a monoclinic $P2_1$ layered structure built up from AsO_4 tetrahedra and ZrO_6 octahedra stacked along the [001] direction. A polyhedral plot of the structure is shown in Figure 2. Six-sided cavities are present between the layers. The water molecules reside inside the cavities, where they are held by hydrogen bonds.

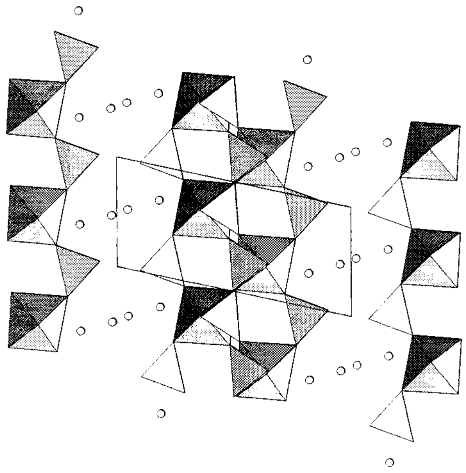

Figure 2. Polyhedral plot of the crystal structure viewed down the *b* axis; the *c* axis is vertical and the *a* axis is horizontal

Intercalation reactions of γ-ZrAs with amines were carried out in order to confirm the layered nature of the structure. The amines were chosen so as to represent the following classes: (a) primary linear amines (*n*-alkylamines), (b) primary cyclic amines (cyclohexylamine), (c) secondary cyclic amines (piperidine), (d) primary aromatic amines (benzylamine), and (e) heterocyclic amines (pyridine).

X-ray patterns of the intercalates showed the formation of new phases with basal spacings larger than in the case of γ-ZrAs (Table 4) and the total disappearance of the reflection at 11.80 Å, which is characteristic of the initial compound, except in the case of pyridine where this reflection persisted with a noticeable intensity. The intercalates maintain the lamellar structure, but a decrease in the order of the crystalline structure is observed.

Figure 3 shows the X-ray patterns of some of the intercalates. It can be seen that in the case of *n*-alkylamines, the interlayer distances increase linearly with increasing number of carbon atoms in the alkyl chain (Figure 4). The resulting straight-line plot fits the equation $d_{002} = 10.0 + 2.48\ n_c$, with the slope corresponding to 2.48 Å per carbon atom. Since the increment in the alkyl chain length in a *trans-trans* conformation is generally estimated to be 1.27 Å per each additional carbon atom, the observed slope indicates, in agreement with the compositional data, that the *n*-alkylamines are arranged between the layers as a bimolecular film. The average angle α of inclination of the molecules with respect to the sheet amounts to $\sin^{-1}(2.48/2.54) = 77.5°$. Similar behaviour has been observed for α-MP compounds (M = Zr, Ti, Hf).[21]

Tentative formulae for the intercalates were determined from elemental analysis and TG data, assuming that in all cases the final product of thermal transformations is ZrO_2 and that the change in weight is only due to amine and water losses and to γ-ZrAs decomposition with As_2O_5 release. Carbon and nitrogen contents, the total weight losses at 800°C, and the tentative formulae of the intercalates are compiled in Table 4. Analysis of these data shows that among the *n*-alkylamines, maximum uptake was only attained with methyl-, ethyl-, and hexylamine, whereas the others were only incorporated to an extent of ca. 4/3 mol of amine per mol of γ-ZrAs.

In the case of cyclic amines, the uptake does not reach the saturation level of the compound, only 1 (piperidine) and 0.3 (pyridine) mol of amine per mol of γ-ZrAs being incorporated. It was not possible to assign formulae in the case of cyclohexylamine or benzylamine since the C and N analysis values, the total weight loss at 800°C, and the apparent solidification of the amine, seemed to suggest that some amine polymerization had occurred.

Some typical TG curves for γ-ZrAs amine intercalates are reproduced in Figure 5. As can be seen, thermal decomposition on going from room temperature to 800°C occurs in several steps. Below 150°C, loss of water of crystallization takes place, and then between 150 and 450°C amine elimination occurs. At temperatures in excess of 500°C, ZrAs decomposition with As_2O_5 release and elimination of water due to condensation of the hydrogen arsenate groups take place. The As_2O_5 release takes place at lower temperatures than in the case of unintercalated γ-ZrAs,[19] probably due

Table 4. D-spacings, microanalytical data (C, N), experimental weight loss at 800°C, and tentative formulae of the intercalates

Amine	*d* [Å]	% C	% N	% weight loss	Formula
Methylamine	12.4	5.29	6.24	72.62	$Zr(AsO_4)(H_2AsO_4) \times 2\ CH_5N \times H_2O$
Ethylamine	14.7	10.08	4.55	74.25	$Zr(AsO_4)(H_2AsO_4) \times 2\ C_2H_7N \times H_2O$
n-Propylamine	18.0	10.41	4.09	72.50	$Zr(AsO_4)(H_2AsO_4) \times 1.3\ C_3H_9N$
n-Butylamine	20.1	13.35	3.92	73.52	$Zr(AsO_4)(H_2AsO_4) \times 1.3\ C_4H_{11}N$
n-Pentylamine	22.2	16.08	3.79	74.55	$Zr(AsO_4)(H_2AsO_4) \times 1.3\ C_5H_{13}N$
n-Hexylamine	24.9	23.68	4.57	79.79	$Zr(AsO_4)(H_2AsO_4) \times 2\ C_6H_{15}N \times 2\ H_2O$
Benzylamine	23.5	67.15	11.19	95.42	–
Cyclohexylamine	21.0	58.21	11.32	93.68	–
Piperidine	18.4	12.19	2.83	74.96	$Zr(AsO_4)(H_2AsO_4) \times C_5H_{11}N \times 2\ H_2O$
Pyridine	12.3	4.58	1.06	68.81	$Zr(AsO_4)(H_2AsO_4) \times 0.3\ C_5H_5N$

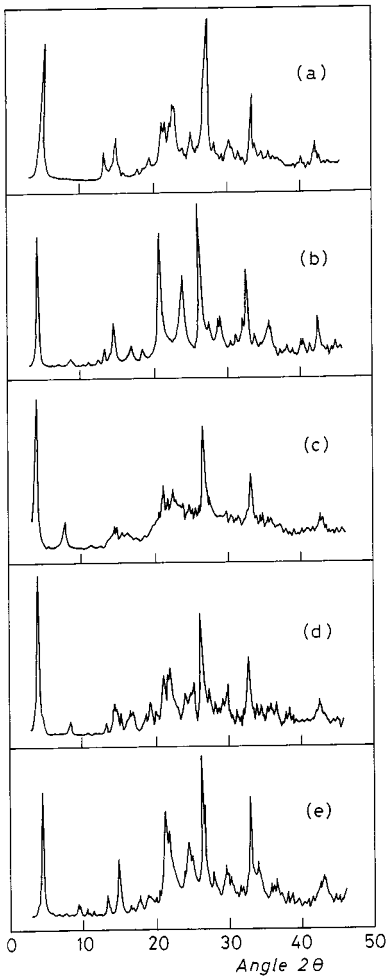

Figure 3. X-ray patterns of selected intercalates: (a) *n*-propylamine, (b) *n*-butylamine, (c) *n*-hexylamine, (d) cyclohexylamine, and (e) piperidine

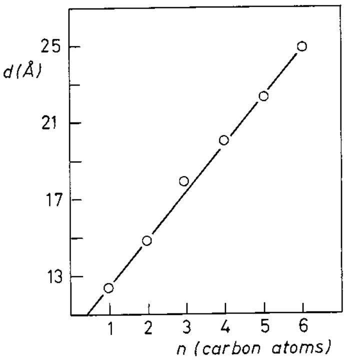

Figure 4. Interlayer distances in *n*-alkylamine intercalate compounds of γ-ZrAs as a function of the number of carbon atoms in the alkyl chain

to the loss of stability of the crystalline structure as a consequence of the presence of the amine in the interlayer space. From Figure 5, it is apparent that propylamine and butylamine intercalates do not contain water of crystallization, in contrast to the phases containing hexylamine and piperidine. For cyclohexylamine (total weight loss 93.68%) two well-differentiated losses can be observed, the first between 75 and 150 °C (80.77%) corresponding to about 15.8 mol of amine per mol of γ-ZrAs, and the second at temperatures above 450 °C (12.91%) corresponding to the release of As_2O_5 from γ-ZrAs and to the elimination of water upon condensation of the hydrogen arsenate groups.

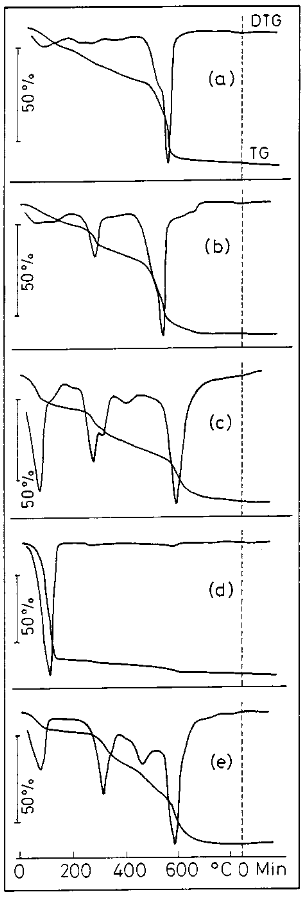

Figure 5. TG curves for selected γ-ZrAs intercalates: (a) *n*-propylamine, (b) *n*-butylamine, (c) *n*-hexylamine, (d) cyclohexylamine, and (e) piperidine

Conclusion

The crystal structure of γ-zirconium arsenate has been refined from X-ray powder diffraction data by the Rietveld method. It has a monoclinic $P2_1$ layered structure built up from AsO_4 tetrahedra and ZrO_6 octahedra stacked along the [001] direction. The final agreement factors are: $R_{wp} = 0.21$ and $R_F = 0.068$. The average As−O bond length is 1.66(1) Å.

It can be concluded that γ-ZrAs reacts readily with *n*-alkylamines, giving rise to new phases with expanded interlayer distances, which confirms its layered nature. In the case of cyclic amines, the intercalation becomes more difficult and cyclohexylamine and benzylamine form as yet uncharacterized, probably polymeric solids, the nature and composition of which will be the subject of future investigations.

Experimental Section

Synthesis: Crystalline γ-ZrAs, $Zr(AsO_4)(H_2AsO_4) \times 2\ H_2O$, was prepared by treatment of the half-exchanged ammonium phase γ-$Zr(AsO_4)[(NH_4)HAsO_4]$ with an excess of 2 M HCl, washed with deionized water, and dried in air. The half-exchanged ammonium phase was synthesized by adding a solution of $As_2O_5 \times 3\ H_2O$ and urea in an approximate mass ratio of 4:1 to zirconium propoxide (70% solution in *n*-propanol). The mixture was hydrothermally treated at 180 °C for 6 d without stirring.[19] The solid obtained was characterized by X-ray diffraction, IR spectroscopy, and chemical and thermal analysis.

Structure Refinement: A sample of $Zr(AsO_4)(H_2AsO_4) \times 2\ H_2O$ (γ-ZrAs) was finely ground using an agate mortar and side-loaded onto a flat sample holder in order to minimize any preferred orientation effects. Step-scanned X-ray powder data were collected by means of a Philips PW 1050 computer-controlled automated diffractometer operating at 40 kV and 30 mA with a copper target and graphite-monochromated radiation. Data were collected in the range $3° < 2\theta < 110°$ with increments of 0.02° and a count time of 10 s per step. 22 low-angle unambiguously characterized reflections were extracted from the data and indexed by trial-and-error methods implemented in the program TREOR[22] with a monoclinic cell, giving figures of merit of $M_{20} = 28$[23] and $F_{20} = 42(0.00837, 57)$.[24] Crystal data of γ-ZrAs are compared with those of γ-$M(PO_4)(H_2PO_4) \times 2\ H_2O$ (M = Ti, Zr, Hf) in Table 5.

Table 5. Crystal data for γ-phases

	γ-ZrAs	γ-HfP[25]	γ-ZrP[26]	γ-TiP[20]
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a [Å]	5.5752(6)	5.3499(3)	5.3825(2)	5.186(1)
b [Å]	6.8290(7)	6.5949(4)	6.6337(1)	6.3505(8)
c [Å]	12.110(1)	12.3939(8)	12.4102(4)	11.865(3)
β [°]	103.03(1)	98.594(5)	98.687(2)	102.52(3)
V [Å^3]	449.21	432.37	438.03	381.47

In view of the similarities in the crystal data, the structural parameters of γ-ZrP[26] were used as the initial values for the Rietveld refinement using the program FULLPROF.[27] A pseudo-Voigt profile function was selected. After initial refinement of the scale, background, profile, and cell parameters, the atomic positions were refined using soft constraints for the AsO_4 tetrahedra and ZrO_6 octahedra. Additional distance constraints were needed for water molecules. All atoms were refined isotropically with a common temperature factor, $B = 1.23(8)$. No corrections were made for anomalous dispersion or absorption. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Fachinformationszentrum Karlsruhe (FIZ), D-76344 Eggenstein-Leopoldshafen, Germany, as supplementary publication No. FIZ-408717.

Intercalation Procedure: γ-ZrAs was equilibrated over a period of 7 d with the pure *n*-alkylamines or cyclic amines at 25°C according to the batch method. The solid was present in the solution in an approximate ratio of 1 g per 100 mL. The solids were subsequently separated by centrifugation, dried at 50°C for 24 h, and characterized by X-ray diffraction and thermal and chemical analysis.

Analytical Procedures: Zr and As contents of the solid samples were determined by elemental analysis using a SpectraSpec DCP-AEC spectrometer, following the dissolution of weighed amounts in HF. X-ray powder diffraction patterns were recorded with a Philips PW 1729/1720 computer-controlled diffractometer using Cu-K_α radiation ($\lambda = 1.542$ Å). Microanalytical data (C, N) were obtained with a Perkin-Elmer model 2400 elemental analyzer. The TG curves were obtained under nitrogen with a Mettler TA 4000 (TG 50) thermoanalyzer, employing a heating rate of 10°C min^{-1}.

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