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13. ABSTRACT (*Maximum 200 words*)

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Two New Titanium Pyroarsenates: α-$TiAs_2O_7$ and β-$TiAs_2O_7$.

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ABSTRACT. — Two new titanium pyroarsenate phases, α-$TiAs_2O_7$ and β-$TiAs_2O_7$, have been prepared by high-temperature hydrothermal methods and characterized by single crystal X-ray diffraction techniques. Both structures are based on different three-dimensional networks of vertex-sharing TiO_6 octahedra and AsO_4 tetrahedra. The TiO_6 groups show little distortion from regular octahedral geometry and the arsenate anions are linked in pairs *via* As–O–As bonds to form pyroarsenate (As_2O_7) groups. α-$TiAs_2O_7$ is isostructural with a polymorph of SiP_2O_7; β-$TiAs_2O_7$ is a new structure.

Crystal data: α-$TiAs_2O_7$: monoclinic, space group $P2_1/n$ (No. 14), with a = 5.0992 (8) Å, b = 12.879 (3) Å, c = 8.219 (2) Å, α = 90 °, β = 91.313 (4) °, γ = 90 °, Z = 4, V = 539.62 Å^3, ρ_{calc} = 3.82 g/cm^3, 1712 observed reflections [$I > 3\sigma(I)$], R = 6.47% and R_w = 7.14%.

β-$TiAs_2O_7$: monoclinic, space group $C2/c$ (No. 15), with a = 6.8697 (7) Å, b = 7.9239 (6) Å, c = 9.4369 (8) Å, α = 90 °, β = 104.072 (4) °, γ = 90 °, Z = 4, V = 498.28 Å^3, ρ_{calc} = 4.13 g/cm^3, 880 observed reflections [$I > 3\sigma(I)$], R = 3.43%, R_w = 4.13%.

INTRODUCTION

Many titanium/phosphate-containing materials, including such technologically-important phases as KTP ($KTiOPO_4$), have been characterized to various extents. KTP and its many isomorphs are of interest for their exceptional non-linear optical properties [1]. Although $KTiOAsO_4$ [2], the As-containing analogue of KTP, has been prepared, much less is known about other materials in the titanium/arsenate phase space [3]. This paper reports the results of our exploratory synthesis by high-temperature/high-pressure hydrothermal methods and single crystal X-ray structural characterization of two titanium pyroarsenate phases, α-$TiAs_2O_7$ and β-$TiAs_2O_7$.

EXPERIMENTAL

Both of the title materials were prepared in the same hydrothermal reaction: 0.0809 g of TiO_2, 2.34 g of $As_2O_5{\cdot}nH_2O$ and 0.34 cm^3 of distilled water were sealed in a gold tube, dimensions $\frac{1}{4}'' \times 2\frac{1}{4}''$. This tube was placed in a LECO Tem-Pres high-pressure furnace, and thermally treated as follows: from room temperature, heat to 700 °C over a 1 hour period (estimated P_{max} = 60 000 psi); cool to 650 °C over 40 hours; cool to 350 °C over 36 hours; switch off and cool to ambient (overnight). The tube was broken open and the solid product recovered from the mother liquor (pH = 1) by suction filtration. A mass of transparent crystals, with sizes up to 2 mm, were recovered, including a few rods, many eqiaxial chunks, and other morphologies. The crystals from this reaction are stable in air for an indefinite period.

Suitable single crystals of α-$TiAs_2O_7$ and β-$TiAs_2O_7$ for structure determination were selected and mounted on thin glass fibers with cyanoacrylate glue. Intensity data were collected at room-temperature [25 (2) °C] for each phase using a Huber automated 4-circle diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) as outlined in Table I, by procedures fully described elsewhere [4]. After successful structure solution, the centrosymmetric space group $C2/c$ was assumed in all subsequent crystallographic analysis of β-$TiAs_2O_7$.

Starting positions for the heavy atoms (Ti and As) were obtained by direct-methods using the program SHELXS-86 [5] in each case, and the oxygen

TABLE I: Crystallographic Parameters

	α-$TiAs_2O_7$	β-$TiAs_2O_7$
emp. formula	As_2TiO_7	As_2TiO_7
mol wt.	309.74	309.74
habit	colorless shard	colorless lump
crystal size (mm)	0.6 × 0.1 × 0.05	0.4 × 0.4 × 0.3
crystal system	monoclinic	monoclinic
a (Å)	5.092 (8)	6.8697 (7)
b (Å)	12.879 (3)	7.9239 (6)
c (Å)	8.219 (2)	9.4369 (8)
β (°)	91.313 (4)	104.072 (4)
V (Å^3)	539.62	498.28
Z	4	4
systematic absences	$h0l$, $h+l$; $0k0$, k	hkl, $h+k$; $h0l$, h,l; $0k0$, k
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
T (°C)	25 (2)	25 (2)
λ(Mo Kα) (Å)	0.71073	0.71073
ρ_{calc} (g/cm^3)	3.81	4.13
μ (cm^{-1})	137.0	148.3
absorption correction	DIFABS [17]	ψ-scans
extinction parameter	110 (9)	124 (6)
hkl-limits	±7,+19,+12	±10,+11,+14
total data	2233	2011
observed data§	1712	880
parameters	92	49
$R(F_o)^a$ (%)	6.47	3.43
$R_w(F_o)^b$ (%)	7.14	4.13

§ $I > 3\sigma(I)$

$R^a = \Sigma\,||F_o| - |F_c||/|F_o|$, $R_w{}^b = [\,\Sigma\, w(\,|F_o| - |F_c|\,)^2/\Sigma w|F_o{}^2|\,]^{1/2}$

atoms were located from Fourier difference maps following refinement of the heavy-atom positions (refinement software: CRYSTALS [6]). No particular problems were encountered during the refinements, and tables of anisotropic thermal factors and observed and calculated structure factors are available from the authors.

RESULTS

A. *α-Titanium Pyroarsenate, α-$TiAs_2O_7$*

Final atomic positional and thermal parameters for α titanium pyroarsenate, α-$TiAs_2O_7$, are listed in Table II, with selected bond distance/angle data in Table III. This new phase (Figure 1) consists of a three-dimensional network of octahedral TiO_6 groups and pairs of tetrahedral AsO_4 groups, linked together *via* Ti–O–As and As–O–As bonds, the latter linkage leading to pyroarsenate (As_2O_7) units.

TABLE II: Atomic Positional Parameters for α-$TiAs_2O_7$

Atom	*x*	*y*	*z*	U_{eq}*
Ti(1)	−0.2963 (2)	0.34590 (7)	0.3467 (1)	0.0100
As(1)	0.2044 (1)	0.18862 (4)	0.44008 (6)	0.0096
As(2)	−0.1869 (1)	0.48443 (4)	0.69056 (6)	0.0095
O(1)	0.0029 (8)	0.2569 (3)	0.3210 (5)	0.0134
O(2)	−0.4105 (8)	0.3206 (3)	0.1273 (5)	0.0131
O(3)	−0.1612 (9)	0.3835 (3)	0.5648 (5)	0.0151
O(4)	−0.6049 (8)	0.4271 (3)	0.3811 (5)	0.0139
O(5)	−0.4834 (8)	0.2246 (3)	0.4276 (5)	0.0155
O(6)	−0.1047 (9)	0.4654 (3)	0.2580 (5)	0.0159
O(7)	0.1840 (8)	0.0612 (3)	0.3694 (5)	0.0141

*$U_{eq}(\text{Å}^2) = (U_1 U_2 U_3)^{1/3}$

α-$TiAs_2O_7$ contains 10 species in the asymmetric unit—1 Ti atom, 2 As atoms and 7 O atoms. The titanium atom bonds to 6 of the 7 oxygen atoms, all of which bridge to an adjacent As-atom center. Each As atom makes 3 As–O–Ti links and its remaining vertex [O(7)] is the bridging oxygen atom of

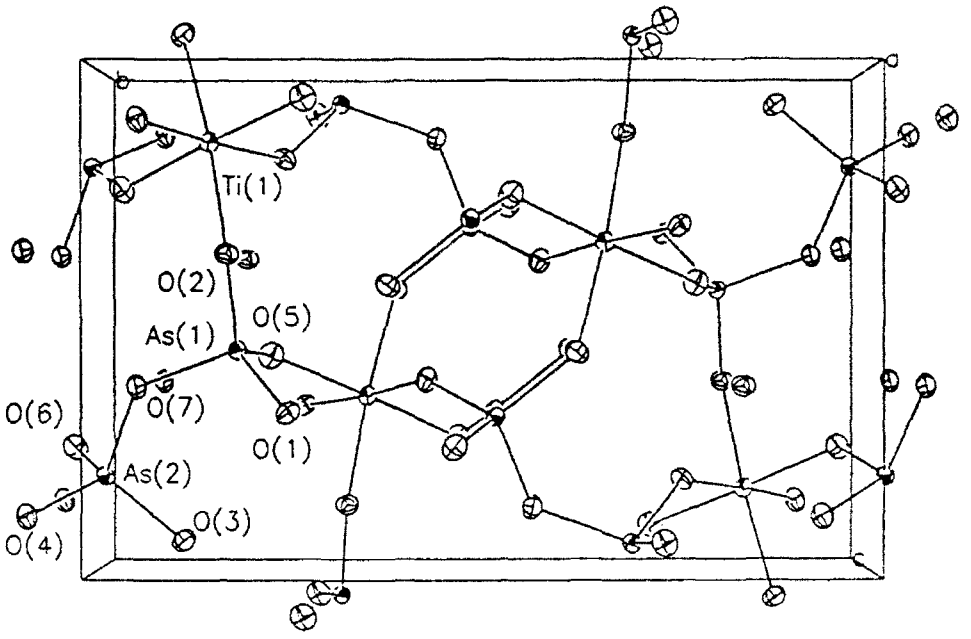

Figure 1: ORTEP [15] view of the crystal structure of α-$TiAs_2O_7$, viewed down [100]. Thermal ellipsoids are drawn at the 50% level.

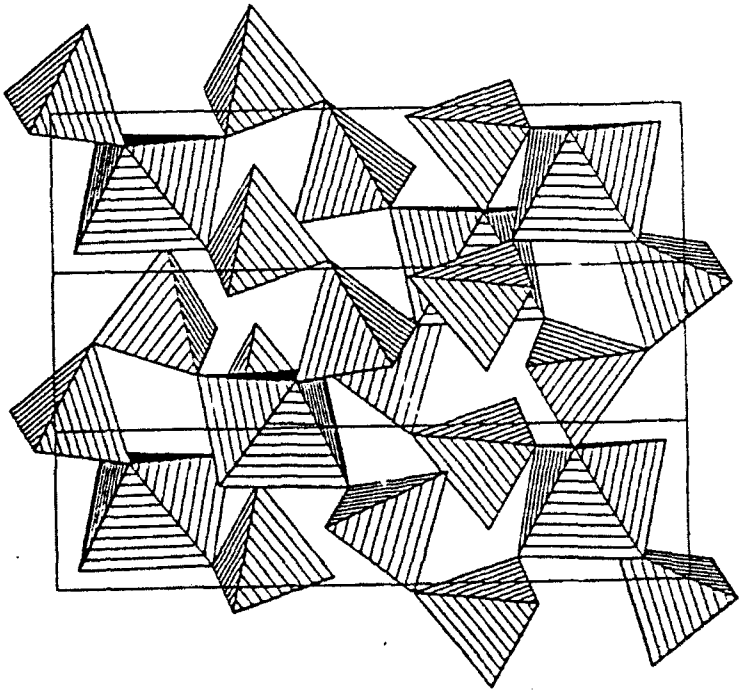

Figure 2: Polyhedral plot (STRUPLO: [16]) of the crystal structure of α-$TiAs_2O_7$, viewed down [201].

the pyroarsenate group. The Ti–O distances are typical [d_{av} = 1.942(2) Å] and there is no distinct, short, "titanyl" Ti=O bond [d(Ti–O) < 1.75 Å], as is found for octahedral Ti^{4+} in $KTiOAsO_4$ [2] and similar phases. The six As–O bonds which link to titanium atoms are also characteristic [d_{av} = 1.662(2) Å], and the average Ti–O–As bond angle is 138.3(1)°. The As–O bonds in the pyroarsenate linkage are somewhat lengthened [d_{av} = 1.735(3) Å] compared to the As–O bonds in the As–O–Ti links, akin to the extended P–O bonds in the P–O–P bridge in pyrophosphate species [7].

TABLE III: Bond Distances (Å) and Angles (°) for α-$TiAs_2O_7$

Ti(1)–O(1)	1.924(4)	Ti(1)–O(2)	1.910(4)
Ti(1)–O(3)	1.966(4)	Ti(1)–O(4)	1.916(4)
Ti(1)–O(5)	1.955(4)	Ti(1)–O(6)	1.971(4)
As(1)–O(1)	1.655(4)	As(1)–O(2)	1.663(4)
As(1)–O(5)	1.663(4)	As(1)–O(7)	1.743(4)
As(2)–O(3)	1.668(4)	As(2)–O(4)	1.656(4)
As(2)–O(6)	1.667(4)	As(2)–O(7)	1.727(4)
O(2)–Ti(1)–O(1)	91.1(2)	O(3)–Ti(1)–O(1)	89.1(2)
O(3)–Ti(1)–O(2)	174.6(2)	O(4)–Ti(1)–O(1)	176.0(2)
O(4)–Ti(1)–O(2)	89.9(2)	O(4)–Ti(1)–O(3)	90.2(2)
O(5)–Ti(1)–O(1)	87.4(2)	O(5)–Ti(1)–O(2)	92.5(2)
O(5)–Ti(1)–O(3)	92.9(2)	O(5)–Ti(1)–O(4)	88.7(2)
O(6)–Ti(1)–O(1)	91.4(2)	O(6)–Ti(1)–O(2)	85.8(2)
O(6)–Ti(1)–O(3)	88.8(2)	O(6)–Ti(1)–O(4)	92.5(2)
O(6)–Ti(1)–O(5)	177.9(2)	O(2)–As(1)–O(1)	111.0(2)
O(5)–As(1)–O(1)	113.5(2)	O(5)–As(1)–O(2)	115.8(2)
O(7)–As(1)–O(1)	105.8(2)	O(7)–As(1)–O(2)	102.8(2)
O(7)–As(1)–O(5)	106.9(2)	O(4)–As(2)–O(3)	112.0(2)
O(6)–As(2)–O(3)	112.2(2)	O(6)–As(2)–O(4)	112.6(2)
O(7)–As(2)–O(3)	107.4(2)	O(7)–As(2)–O(4)	106.4(2)
O(7)–As(2)–O(6)	105.7(2)	As(1)–O(1)–Ti(1)	137.3(2)
As(1)–O(2)–Ti(1)	141.2(3)	As(2)–O(3)–Ti(1)	136.5(2)
As(2)–O(4)–Ti(1)	147.7(3)	As(1)–O(5)–Ti(1)	135.9(2)
As(2)–O(6)–Ti(1)	131.0(2)	As(2)–O(7)–As(1)	125.6(2)

This Ti/As/O connectivity leads to the polyhedral networks illustrated in

Figure 2: interleaved layers of vertex-sharing TiO_6 and As_2O_7 groups are roughly aligned in the ac-plane. The smallest identifiable atomic-connectivity "loops" include –Ti–As–Ti–As– "4-rings" and –Ti–As–As–Ti–As– "5-rings" (linking O-atoms omitted). α-$TiAs_2O_7$ has an interesting structural analogue in one of the polymorphs of SiP_2O_7 [8], which is one of the few crystal structures containing octahedrally-coordinated silicon atoms.

A. *β-Titanium Pyroarsenate, β-$TiAs_2O_7$*

Final atomic positional and thermal parameters with e.s.d.'s for β titanium pyroarsenate, β-$TiAs_2O_7$, are listed in Table IV, with selected geometrical data in Table V. This structure (Figure 3) is also built up from TiO_6 and As_2O_7 units, but the connectivity is different from that found in α-$TiAs_2O_7$.

TABLE IV: Atomic Positional Parameters for β-$TiAs_2O_7$

Atom	x	y	z	U_{eq}*
Ti(1)	0	0	0	0.0125
As(1)	0.30569 (7)	0.13280 (6)	−0.19848 (5)	0.0119
O(1)	1/2	0.0277 (6)	−1/4	0.0152
O(2)	0.2412 (5)	0.0075 (5)	−0.0763 (4)	0.0157
O(3)	0.1294 (5)	−0.1614 (5)	0.1472 (4)	0.0152
O(4)	0.1064 (6)	0.1811 (5)	0.1300 (4)	0.0178

*U_{eq}(Å^2) = $(U_1 U_2 U_3)^{1/3}$

There are six asymmetric atoms (one octahedral Ti, one tetrahedral As, three Ti–O–As bridging-O, one As–O–As bridging-O), which all show their characteristic bonding geometries: d_{av}(Ti–O) = 1.938 (2) Å, d_{av}(As–O_{Ti}) = 1.664 (3) Å, d(As–O_{As}) = 1.740 (3) Å, θ_{av}(Ti–O–As) = 141.8 (2)°. The Ti atom is located at an inversion center, and is in a very regular coordination environment; the pyroarsenate-group bridging oxygen atom, O(1), is located on a two-fold axis, and the other atoms occupy general crystallographic positions. Compared to α-$TiAs_2O_7$, the most significant geometrical change is the expanded Ti(1)–O(4)–As(1) bond angle: the As–O–As angle is virtually unchanged in the two structures.

Figure 4 indicates the TiO_6/As_2O_7 polyhedral connectivity. Once again, interlinked sheets of Ti- and As-centered polyhedra may be identified, this

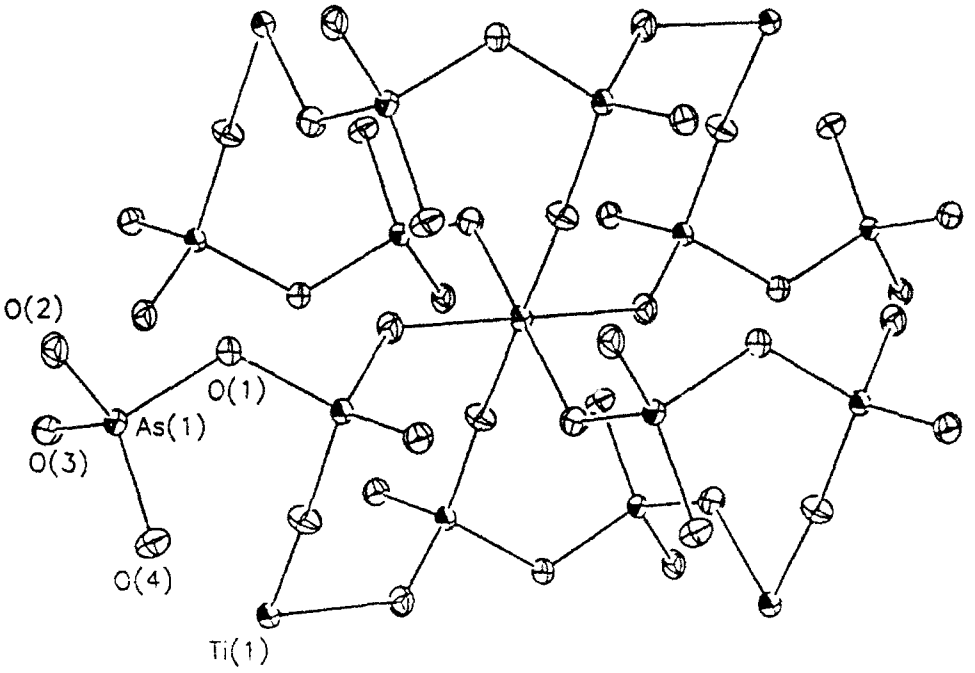

Figure 3: ORTEP view of an *ab*-slice of the crystal structure of β-$TiAs_2O_7$, viewed down the c-direction. Thermal ellipsoids are drawn at the 50% level.

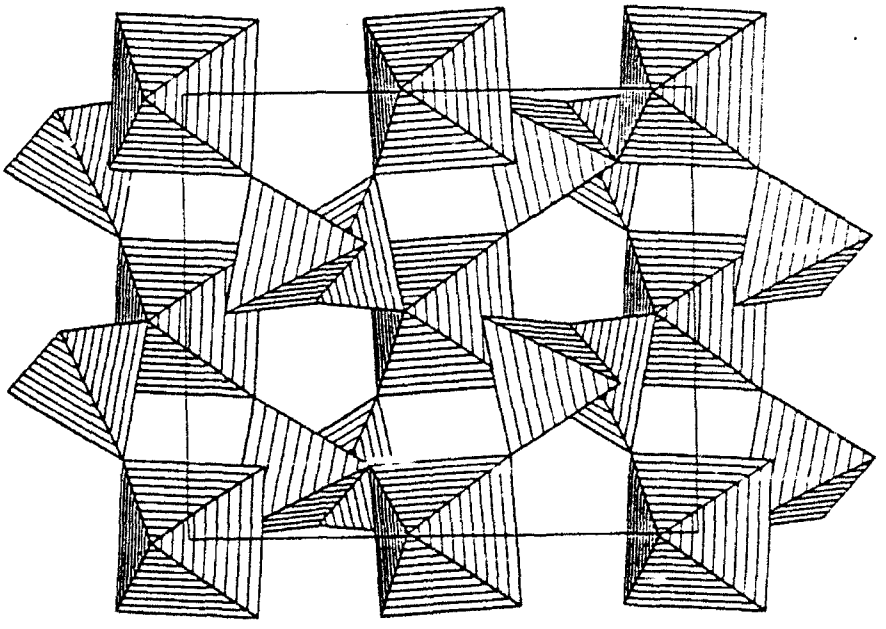

Figure 4: Polyhedral plot (STRUPLO) of the crystal structure of β-$TiAs_2O_7$, viewed down [100].

time in the *ab*-plane. Similar 4- and 5-rings make up the Ti/As/O linkages.

TABLE V: Bond Distances (Å) and Angles (°) for β-$TiAs_2O_7$

Ti(1)–O(2)	1.962(3) × 2	Ti(1)–O(3)	1.938(4) × 2
Ti(1)–O(4)	1.914(4) × 2	As(1)–O(1)	1.740(3)
As(1)–O(2)	1.662(4)	As(1)–O(3)	1.668(4)
As(1)–O(4)	1.663(4)		
O(2)–Ti(1)–O(2)′	180‖	O(3)–Ti(1)–O(2)	90.1(1)
O(3)–Ti(1)–O(2)	89.9(1)	O(3)–Ti(1)–O(3)′	180‖
O(4)–Ti(1)–O(2)	89.3(2)	O(4)–Ti(1)–O(2)	90.7(2)
O(4)–Ti(1)–O(3)	89.9(2)	O(4)–Ti(1)–O(3)	90.1(2)
O(4)–Ti(1)–O(4)′	180‖	O(2)–As(1)–O(1)	105.1(2)
O(3)–As(1)–O(1)	105.3(1)	O(3)–As(1)–O(2)	115.3(2)
O(4)–As(1)–O(1)	107.6(2)	O(4)–As(1)–O(2)	113.1(2)
O(4)–As(1)–O(3)	109.7(2)	As(1)–O(1)–As(1)′	122.8(3)
As(1)–O(2)–Ti(1)	131.6(2)	As(1)–O(3)–Ti(1)	130.2(2)
As(1)–O(4)–Ti(1)	163.7(3)		

‖by symmetry

DISCUSSION

Two new titanium pyroarsenates, α-$TiAs_2O_7$ and β-$TiAs_2O_7$, have been prepared and structurally characterized. Their octahedral/tetrahedral networks may be rationalized in terms of the typical crystallochemical behavior of their component species. The unit-cell volumes and densities of these two phases differ by about 8% (β-$TiAs_2O_7$ more dense than α-$TiAs_2O_7$), suggesting that β-$TiAs_2O_7$ might be the stable form of titanium pyroarsenate at higher pressures. Of course, many materials, including zirconium pyrophosphate, ZrP_2O_7 [9], and silicon pyrophosphate, SiP_2O_7 [10], show such polymorphism, but the co-synthesis of the two Ti/As/O polymorphs in one reaction is a typical feature of the non-equilibrium conditions often present in hydrothermal reactions.

Neither material reported here is isomorphous with any titanium pyrophosphate phases, or other $M^{IV}As_2O_7$ types. The $M^{IV}P_2O_7$ family has been quite

extensively studied [7,11] and a number of related phases reported: M = Hf, Ge, Np, Zr, Sn, Si, U, Th, Ti, Re, Si, Pb, Ce. These are probably all based on a large (a = ~22–23 Å) cubic cell [12], whereas earlier work indicated a a/3 subcell, which would require the presence of linear P–O–P bridging links in the pyrophosphate group. The few characterized $M^{IV}As_2O_7$-type phases (M = Zr, Th, Np) are apparently isomorphs of the cubic $M^{IV}P_2O_7$ phase [11].

Both materials reported here are notable for the regularity of the TiO_6 octahedral grouping. The distortion of the TiO_6 group in KTP has recently been discussed in terms of a molecular-orbital model, in which O–Ti–O bond distortion is viewed in terms of orbital mixing as the TiO_6 geometry changes [13]. The resulting TiO_6 configuration reflects the competition between the stabilization gained by the distortion *versus* the destabilizing effect on other occupied molecular orbitals. In both α-$TiAs_2O_7$ and β-$TiAs_2O_7$, all six Ti–O vertices connect to an As center, thus, it appears that any additional stability which the TiO_6 octahedron might attain on distortion is offset by the destabilizing effect on the As_2O_7 group, and the TiO_6 moiety is essentially regular. We have also noticed that in materials containing dimeric Ti_2O_{11} and trimeric Ti_3O_{16} groupings [14], the Ti–O distortion is greatly reduced compared to that found in KTP-type materials.

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