



Crystal Structure Refinements of the Lead(II) Oxoarsenates(V) Pb₂As₂O₇, Pb(H₂AsO₄)₂, Pb₅(AsO₄)₃OH and NaPb₄(AsO₄)₃ from Single-Crystal X-ray Data

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Copyright: © 2021 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Division of Structural Chemistry, Institute for Chemical Technologies and Analytics, TU Wien, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria; Matthias.Weil@tuwien.ac.at † Dedicated to the late Ekkehard Tillmanns. He will be remembered as a human and scientific role model.

Abstract: Single-crystals of lead(II) oxoarsenates(V) were grown from the melt (Pb₂As₂O₇), from solution (Pb(H₂AsO₄)₂ and Pb₅(AsO₄)₃OH), and under hydrothermal conditions (NaPb₄(AsO₄)₃). Crystal structure refinements from single-crystal X-ray diffraction data revealed isotypism for both Pb₂As₂O₇ and Pb(H₂AsO₄)₂ with the corresponding barium and phosphate phases. A quantitative comparison of the crystal structures showed a high similarity for the isotypic $M_2X_2O_7$ structures (M = Pb, Ba; X = As, P), whereas for the $M(H_2XO_4)_2$ structures only the pair Pb(H₂AsO₄)₂ and Pb(H₂PO₄)₂ is similar, but not Ba(H₂AsO₄)₂. Pb₅(AsO₄)₃OH adopts the apatite structure type in space group $P6_3/m$, with the hydroxyl group disordered around Wyckoff position 2 *b* (0, 0, 0) in the channels of the structure. NaPb₄(AsO₄)₃ represents a lacunar apatite with two of the three metal positions occupationally disordered by Pb and Na. In contrast to a previous X-ray powder study of NaPb₄(AsO₄)₃ that reported an apatite-type structure in space group $P6_3/m$, the current single-crystal data clearly revealed a symmetry reduction to space group $P\overline{3}$. Hence, NaPb₄(AsO₄)₃ is the first lacunar apatite that comprises only tetrahedral anions and adopts the belovite structure type.

Keywords: lead; oxoarsenates; solid state synthesis; hydrothermal synthesis; crystal chemistry; apatite structure type; belovite structure type; crystal structure comparison

1. Introduction

To date, in the system Pb/As/O/(H), two approved and crystallographically fully characterized mineral phases are known to exist, *viz*. paulmooreite, $Pb^{II}_2As^V{}_2O_5$, and schultenite, $Pb^{II}HAs^VO_4$. Paulmooreite represents a lead(II) oxoarsenate(III) with a pyroarsenite anion, $As_2O_5^{4-}$ [1], whereas schultenite is a lead(II) oxoarsenate(V) with a hydrogenarsenate anion, $HAsO_4^{2-}$ [2]. Other synthetic phases for which their crystal structures have been determined include lead(II) arsenite, $Pb^{II}As^{III}{}_2O_4$ [3], the lead(II) oxoarsenates(V) $Pb^{II}_3(As^VO_4)_2$ [4], $Pb_8^{II}O_5(As^VO_4)_2$ [5], and $Pb^{II}As^{II}_2O_6$ [6], as well as the lead(IV) oxoarsenate(V) $Pb^{IV}(HAs^VO_4)_2(H_2O)$ [7]. Although other synthetic lead(II) oxoarsenates(V) have been reported to exist and compiled in one of the older handbooks on lead and its compounds [8], structural details of these phases still are missing. Since these compounds might also be present in nature as yet-unidentified mineral phases, detailed structure analyses were desirable.

In this article, single-crystal growth procedures and crystal structure refinements of $Pb^{II}_2As^V_2O_7$, $Pb^{II}(H_2As^VO_4)_2$, $Pb^{II}_5(As^VO_4)_3OH$, and $NaPb^{II}_4(As^VO_4)_3$ are reported and the results comparatively discussed with related phases, expanding our knowledge about the crystal chemistry of lead(II) oxoarsenates(V).

2. Materials and Methods

2.1. Syntheses and Single-Crystal Growth Procedures

All used chemicals were of pro analysis quality.

Pb₂**As**₂**O**₇. Single-crystals of lead(II) diarsenate(V) were obtained from the melt, starting with polycrystalline PbHAsO₄. The latter was prepared by slow addition of aqueous solutions of Na₂HAsO₄ (1.9 g in 50 mL water) to Pb(NO₃)₂ (3.3 g in 50 mL water) in a molar ratio of 1:1. The precipitated PbHAsO₄ was filtered off, washed with water and ethanol, and dried overnight. X-ray powder diffraction revealed a single-phase material. An amount of 0.5 g of PbHAsO₄ was then placed in a platinum crucible covered with a lid. The crucible was heated within 24 h to 850 °C and then cooled within 99 h to room temperature. Crystals of Pb₂As₂O₇ were present as a minor constituent in the recrystallized melt with Pb₃(AsO₄)₂ as the main constituent because Pb₂As₂O₇ melts incongruently [9]. Polycrystalline single-phase Pb₂As₂O₇ was prepared by heating PbHAsO₄ at 600 °C for one day.

Pb(H_2AsO_4)₂. A concentrated Pb(NO_3)₂ solution (10 g in 50 mL water) was refluxed for one day with 8 mL concentrated arsenic acid (80%_{wt}). After cooling to room temperature, plate-like crystals could be isolated next to recrystallized Pb(NO_3)₂ crystals. The latter were easily distinguishable from the bis(dihydrogen)arsenate due to their cubic symmetry.

Pb₅(AsO₄)₃OH. Hydrothermal treatment of PbHAsO₄ in 20%_{wt} ammonia solution at 210 °C for five days (300 mg loading, Teflon container with 6 mL capacity, filling degree ca. 2/3) resulted in single-phase material of synthetic hydroxymimetite, Pb₅(AsO₄)₃OH, but with crystals too small for standard laboratory single-crystal X-ray diffraction. Larger single-crystals were grown by following a slight modification of the procedure reported by McDonnell and Smith [10]. PbHAsO₄ (see above) was added to 20 mL of a warm KOH (10%wt) solution until saturation. The solution was separated from the remaining material by filtration. The clear filtrate was then poured into 150 mL of cold water, resulting in a colorless flocculent precipitate. After standing and sedimentation for about 30 min, the solid was filtered off, and the filtrate was allowed to slowly evaporate at room temperature. After about five days, the solution became cloudy and after three additional days, an off-white solid started to crystallize. Rod-shaped single-crystals of Pb₅(AsO₄)₃OH were manually isolated from this material under a polarizing microscope. Phase analysis of the bulk using the program HIGHSCORE [11] revealed $Pb_5(AsO_4)_3OH$ as the main phase $(80\%_{wt})$, and KPb₂(CO₃)₂(OH) [12] and Pb₃(CO₃)₂(OH)₂ (hydrocerrusite) [13] as minor side products (10%_{wt} each).

NaPb(AsO₄)₃. The sodium lead arsenate phase was obtained as a minor by-product during single-crystal growth studies of Pb₅(AsO₄)₃OH under hydrothermal conditions. For that purpose, 0.3 g PbHAsO₄ were suspended in 6 mL water to which 1 g NaOH were added. The mixture was placed in a Teflon container (filling degree 70%) that was heated under autogenous pressure in a steel autoclave at 210 °C for five days. Crystals of NaPb(AsO₄)₃ appeared as block-like crystals next to yet-unidentified polycrystalline material.

Pb₄**As**₂**O**₉. Attempts to prepare Pb₄As₂O₉ were made by heating a mixture of PbO (0.795 g) and As₂O₅ (0.205 g) in the molar ratio 4:1 and a mixture of PbO (0.398 g) and PbHAsO₄ (0.618 g) in the molar ratio 1:1, respectively. For both batches, the educts were thoroughly milled and heated in a platinum crucible for three days at 750 °C for the first and at 680 °C for the second batch, followed by intermediate grindings after each day. Phase analysis of the products by PXRD revealed Pb₃(AsO₄)₂ and Pb₈(AsO₄)₂O₅ as the only reaction products in both cases, with an approximate ratio of 2:1 (program HIGHSCORE [11]).

2.2. Single-Crystal X-ray Diffraction and Structure Analysis

Single-crystals were optically preselected under a polarizing microscope, embedded in perfluorinated polyether for protection from air and humidity, and mounted on MiTeGen MicroLoopsTM. The X-ray diffraction studies were conducted at room temperature on a Bruker APEX-II CCD diffractometer (Bruker-AXS, Madison, WI, USA) using MoK α radiation. Data collection was handled and optimized with APEX-2 [14], data reduction was performed with Saint [14] and absorption effects were corrected with the semi-empirical

multi-scan procedure of SADABS [15]. Experimental details of the data collections and refinements are collated in Table 1.

Table 1. Details of single-crystal X-ray data collections and structure refinements.

Compound	$Pb_2(As_2O_7)$	Pb(H ₂ AsO ₄) ₂	Pb ₅ (AsO ₄) ₃ OH	NaPb ₄ (AsO ₄) ₃	
Temperature/°C		- 23(1)—		
Diffractometer	— Bruker-AXS APEX-II CCD detector —				
Radiation; $\lambda/\text{\AA}$	— Мо К <i>а</i> ; 0.71073 —				
Space group (# no.)	P1 (# 2)	P1 (# 2)	P6 ₃ /m (# 176)	P3 (# 147)	
Formula units Z	4	2	2	2	
Formula weight	676.22	489.06	1469.72	1268.51	
Crystal dimensions/mm	0.10 imes 0.03 imes 0.03	$0.10\times 0.06\times 0.01$	$0.10\times0.01\times0.01$	0.04 imes 0.04 imes 0.02	
Crystal description	light-yellow fragment	colorless plate	light-yellow needle	colorless block	
a/Å	7.13790(10)	7.9497(10)	10.1266(3)	10.0230(14)	
b/Å	7.14000(10)	8.6137(10)	10.1266(3)	10.0230(14)	
c/Å	13.0681(3)	5.9984(8)	7.5010(2)	7.3117(15)	
$\alpha/^{\circ}$	83.3602(11)	108.888(5)	90	90	
β/°	86.6710(10)	96.128(5)	90	90	
$\gamma/^{\circ}$	89.9469(10)	108.449(6)	120	120	
$V/Å^3$	660.42(2)	358.51(8)	666.16(4)	636.1(2)	
μ/mm^{-1}	60.851	32.693	70.429	60.606	
X-ray density/g·cm ⁻³	6.801	4.531	7.327	6.623	
Range $\theta_{\min} - \theta_{\max}$	1.57 - 40.18	2.69-36.73	2.32-30.00	2.35-30.28	
Range h	$-$ 12 \rightarrow 12	$-13 \rightarrow 13$	$-14 \rightarrow 14$	-14 ightarrow 14	
k k	$-$ 12 \rightarrow 12	-14 ightarrow 14	-14 ightarrow 14	$-$ 14 \rightarrow 14	
1	-23 ightarrow 23	-10 ightarrow 10	-10 ightarrow 9	$-10 \rightarrow 10$	
Measured reflections	70,283	24,488	9576	32,342	
Independent reflections	8240	3579	699	1279	
Obs. reflections $[I > 2\sigma(I)]$	6951	3017	482	1207	
R_i	0.074	0.060	0.077	0.063	
Transmis. coeff. T_{min} ; T_{max}	0.1644; 0.5697	0.3792; 0.7472	0.1107; 0.5411	0.2245; 0.6244	
Structure solution and refinement	— SHELXS and SHELXL —				
Absorption correction	— Sadabs —				
Number of parameters	200	114	40	64	
Ext. coef. (SHELXL)	0.00118(8)	0.00095(16)	-	-	
Diff. elec. dens. max; min/e ⁻ Å ⁻³ (dist./Å,	6.23 (0.61, Pb2);	1.47 (0.68, Pb1);	5.60 (0.67, Pb2);	2.61 (0.43, (Pb/Na)3);	
atom)	-5.53 (0.59, Pb1)	– 1.24 (0.71, Pb1)	-3.05 (0.76, Pb2)	- 1.69 (0.57, Pb1)	
$R[F^2 > 2\sigma(F^2)]$	0.0346	0.0237	0.0380	0.0211	
$wR2(F^2 \text{ all})$	0.0848	0.0403	0.0871	0.0452	
Goof	1.098	1.014	1.080	1.096	
CSD number	2099610	2099611	2099612	2099609	

All crystal structures were initially solved with SHELXS (using direct methods) [16] and refined with SHELXL [17] (version 2018/3). For the purpose of better comparison between the isotypic pairs Pb₂As₂O₇/Pb₂P₂O₇ and Pb(H₂AsO₄)₂/Pb(H₂PO₄)₂, respectively, atom labelling, atomic coordinates, and the unit cell settings were adapted from the corresponding phosphate structure [18,19]. This explains why the chosen unit cell of $Pb(H_2AsO_4)_2$ is not reduced [20] (reduced unit cell parameters are: a = 5.9984(8), b = 7.9497(10), c = 8.6137(10) Å, $\alpha = 108.888(5), \beta = 108.449(6), \gamma = 96.128(5)^{\circ}$). The hydrogen atom positions in the crystal structure of Pb(H₂AsO₄)₂ were discernible from difference-Fourier maps and were refined freely for H7 and with a distance constraint of 0.85 Å for all other H atoms; all H atoms in this structure were refined with a common U_{iso} parameter. In the crystal structure of Pb₅(AsO₄)₃OH, the O atom of the hydroxyl group was refined as being disordered over the center of symmetry at (0, 0, 0), leading to two occupied sites with a site occupation factor of 0.5 each. Its H atom could not be located and thus was not included in the model but is considered in the formula and other numerical parameters in the CIF. In the crystal structure of NaPb(AsO₄)₃, two of the Pb sites were found to be statistically occupied with Na. Each of the mixed-occupied sites, M1a and M1b, were refined with the same coordinates and displacement parameters of the two elements under consideration of full occupancies and charge neutrality for the compound. The NaPb $(AsO_4)_3$ crystal under investigation was found to be twinned in a 1:1 ratio by mirroring perpendicular to the *c* axis.

Further details of the crystal structure investigations may be obtained from The Cambridge Crystallographic Data Centre (CCDC) on quoting the depository numbers listed at the end of Table 1. The data can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

2.3. Powder X-ray Powder Diffraction (PXRD)

Powder diffraction data were measured on a recently calibrated (NIST LaB₆ standard) PANalytical X'Pert PRO diffractometer with Cu-K $\overline{\alpha}$ radiation in Bragg-Brentano geometry (X'Celerator multi-channel detector, silicon zero background sample holder, 2.546° scan length, 25 s exposure time per scan length, 20 range 5°–70°; the scans were finally converted into 0.02° step-size bins). Temperature-dependent PXRD data were collected under atmospheric conditions with a HTK1200 Anton-Paar high-temperature oven chamber mounted on the diffractometer. The samples were finely ground and placed on a glass ceramic (MarcorTM) sample holder with 0.5 mm depth. The zero point was automatically adjusted during the measurements with a PC-controllable alignment stage. The samples were heated with 10 °C/h to the respective temperature and kept for 15 min before measurement of each step to ensure temperature-stability. Refinement of unit-cell parameters were performed with the program TOPAS [21].

3. Results and Discussion

Table 2 lists selected interatomic distances for all crystal structures.

Table 2. Selected interatomic distances.

$Pb_2As_2O_7$					
Pb1	O6	2.416(5)	Pb4	O7 ^v	2.463(4)
Pb1	O2 ⁱ	2.485(5)	Pb4	O3 ⁱ	2.479(5)
Pb1	O10	2.521(5)	Pb4	07	2.514(5)
Pb1	O3	2.563(5)	Pb4	O5 ^{ix}	2.523(5)
Pb1	O1 ⁱⁱ	2.673(5)	Pb4	O14	2.673(5)
Pb1	O7 ⁱⁱⁱ	2.878(5)	Pb4	O2 ^v	2.695(5)
Pb1	O4 ⁱⁱ	2.965(5)	Pb4	O6	3.140(5)
Pb1	O14 ⁱⁱⁱ	3.319(5)	Pb4	O12	3.226(5)
Pb1	O5 ⁱⁱⁱ	3.464(5)	As1	O1	1.657(4)
Pb2	O13 ^{iv}	2.417(4)	As1	O3	1.669(4)
Pb2	O12 ⁱ	2.484(5)	As1	O2	1.679(5)
Pb2	O8 ⁱⁱ	2.624(5)	As1	O4	1.777(4)
Pb2	O10 ⁱ	2.631(5)	As2	O5	1.649(5)
Pb2	O14 ^v	2.817(5)	As2	O6	1.671(5)
Pb2	O2	2.883(6)	As2	O7	1.679(4)
Pb2	O11 ^v	2.903(4)	As2	O4	1.760(4)
Pb2	O1	2.987(5)	As3	O9	1.649(4)
Pb2	O9 ⁱⁱ	3.369(5)	As3	O10	1.674(4)
Pb3	O9 ^{vi}	2.441(5)	As3	O8	1.683(4)
Pb3	O13	2.546(5)	As3	O11 ^x	1.760(4)
Pb3	O8 ^{vii}	2.555(5)	As4	O14	1.651(4)
Pb3	O12 ^{viii}	2.642(5)	As4	O13	1.669(4)
Pb3	O8	2.753(5)	As4	O12	1.672(4)
Pb3	O5	2.871(6)	As4	O11	1.778(4)
Pb3	O1 ⁱⁱ	2.912(4)			
Pb3	O10	3.021(5)			
Pb3	O6	3.149(6)			
Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $-x$, $-y + 1$, $-z + 1$; (iii) x , $y + 1$, z ; (iv) x , y , $z + 1$;					
(v) - x + 1, -y, -z + 1; (vi) x, y - 1, z; (vii) - x, -y + 1, -z; (viii) x - 1, y, z; (ix) x + 1, y, z;					

Table 2. Cont.

Pb(H ₂	$_2$ AsO ₄) ₂				
Pb1	O5 ⁱ	2.442(2)	As1	O2	1.652(2)
Pb1	O1 ⁱⁱ	2.529(2)	As1	O1	1.657(2)
Pb1	O2	2.559(2)	As1	O4 ^{vi}	1.719(2)
Pb1	O5 ⁱⁱⁱ	2.575(2)	As1	O3 ^{vii}	1.727(2)
Pb1	O1 iv	2.584(2)	As2	O5	1.665(2)
Pb1	O7 ^v	2.701(2)	As2	07	1.673(2)
Pb1	O4	2.944(2)	As2	O8	1.676(2)
Pb1	O6	3.117(3)	As2	O6	1.722(2)
Symmetry	y codes: (i)	-x + 1, -y + 1, -z + 1; (ii)	-x,-y+1,	-z+1; (iii)	x, y + 1, z; (iv) $x, y, z + 1;$
	(1	(x) - x + 1, -y, -z + 1; (vi) x,	y - 1, z; (vi	i) $-x, -y + 1$	1 <i>, -z</i> ;
Pb ₅ (As	O ₄) ₃ (OH)				
Pb1	O2 ⁱ	2.534(8) 2.534	Pb2	O1 ^{vi}	2.355(14) 2.398
Pb1	O2 ⁱⁱ	2.534(8)	Pb2	O3 ^{vii}	2.616(9) 2.618
Pb1	O2 ⁱⁱⁱ	2.534(8)	Pb2	O3 ^{viii}	2.616(9)
Pb1	O1 ^{iv}	2.774(10) 2.754	Pb2	O3 ^{iv}	2.664(11) 2.691
Pb1	O1 ^v	2.774(10)	Pb2	O3 ^v	2.664(11)
Pb1	O1	2.774(10)	Pb2	O4 ^{xi}	2.88(3) 2.693
Pb1	O3 ^v	3.009(13) 2.944	Pb2	O4 ^{xii}	2.88(3)
Pb1	O3 ^{iv}	3.009(13)	Pb2	O2 ^{vi}	2.937(12) 3.058
Pb1	O3	3.009(13)			
As1	O2 ^{vi}	1.655(11) 1.674			
As1	O3 ^{xiii}	1.655(10) 1.691			
As1	O3	1.655(10)			
As1	O1	1.681(13) 1.711			
S	symmetry	codes: (i) $x - y$, x , $-z$; (ii) -	x + 1, -y + 1	1, -z; (iii) $y,$	-x + y + 1, -z;
(iv) –	y + 1, x - 1	y + 1, z; (v) - x + y, -x + 1, z	z; (vi) - y + 1	, $x - y$, z ; (v	ii) $y, -x + y, z + 1/2;$
(v:	iii) <i>y,</i> − <i>x</i> +	y, -z; (xi) $-x, -y, z - 1/2;$	x(xii) - x, -y	$y_{i} - z + 1;$ (xi	ii) $x, y, -z + 1/2$.
	Va	lues in italics are from the p	owder sync	hrotron stuc	iy [22].
NaPb ₄ (AsO ₄) ₃					
(Na/Pb)1a	02 ⁱ	2.428(7)	Pb2	O1 ^{vi}	2.248(7)
(Na/Pb)1a	ı O2 ⁱⁱ	2.428(7)	Pb2	O4 ⁱⁱ	2.433(7)
(Na/Pb)1a	ı O2 ⁱⁱⁱ	2.428(7)	Pb2	O4 ^{viii}	2.509(7)
(Na/Pb)1a	01 ^{iv}	2.564(7)	Pb2	O3 ^{xv}	2.568(7)
(Na/Pb)1a	01 ^v	2.564(7)	Pb2	O2 ^{ix}	2.805(6)
(Na/Pb)1a	o O1 ^{vi}	2.564(7)	Pb2	O3	2.912(8)
(Na/Pb)1a	04 ^{vii}	3.202(8)	As1	O2 ^{ix}	1.673(5)
(Na/Pb)1a	04 ^{viii}	3.202(8)	As1	O3 ^{xvii}	1.675(7)
(Na/Pb)1a	04 ^{ix}	3.202(8)	As1	O1 ^{xviii}	1.689(6)
(Na/Pb)1b	02 ^x	2.435(7)	As1	O4	1.699(7)
(Na/Pb)1b	o O2 ^{xi}	2.435(7)			
(Na/Pb)1b	o O2 ^{xii}	2.435(7)			
(Na/Pb)1t	O3 ^{xiii}	2.773(8)			
(Na/Pb)1b	O3	2.773(8)			
(Na/Pb)1t	O3 xiv	2.773(8)			
(Na/Pb)1b	01 ⁱ	3.070(8)			
(Na/Pb)1t	01 v	3.070(8)			
(Na/Pb)1b	o O1 ^{vi}	3.070(8)			

Symmetry codes: (i) -x + 1, -y + 1, -z; (ii) x - y, x, -z; (iii) y, -x + y + 1, -z; (iv) y, -x + y, -z; (v) -x, -y + 1, -z; (vi) x - y + 1, z; (vii) x, y + 1, z; (viii) -y, x - y, z; (ix) -x + y, -x + 1, -x + 1, z; (x) -x + 1, -y + 1, -z + 1; (xi) x - y, x, -z + 1; (xii) y, -x + y + 1, -z + 1; (xii) -y + 1, x - y + 1, z; (xiv) -x + y, -x + 1, z; (xv) y, -x + y, -z + 1; (xvii) -x + y, -x, z; (xviii) -x, -y, -z.

3.1. $Pb^{II}_2As^V_2O_7$

Pb₂As₂O₇ belongs to the family of diarsenates. In a previous study on this phase [23], isotypism with the diphosphate analogue Pb₂P₂O₇ was suggested, and indexed power diffraction data as well as unit cell parameters for the non-reduced unit cell were given, with *a* = 6.86(2), *b* = 7.13(2), *c* = 12.93(3) Å, *α* = 99.01(10), *β* = 91.10(12), *γ* = 89.48(12)°, *V* = 625 Å³ for room temperature data. However, the reduced unit cell [20] parameters (*a* = 6.86(2), *b* = 7.13(2), *c* = 12.93(3) Å, *α* = 80.99(10), *β* = 88.90(12), *γ* = 89.48(12)°), the unit cell volume, and the calculated density (7.18 g·cm⁻³) based on the powder study differ considerably from those of the current single-crystal study (Table 1).

 $Pb_2As_2O_7$ is in fact isotypic with $Pb_2P_2O_7$ [18] and crystallizes in the triclinic $K_2Cr_2O_7$ structure type that is also referred to as the "dichromate" structure type [24,25] and adopted by many $M_2X_2O_7$ phases where M is a large divalent cation and X is As or P. The asymmetric unit of Pb₂As₂O₇ comprises four Pb, four As, and 14 O sites. The coordination numbers of the lead(II) cations are nine for Pb1, Pb2 and Pb3, and eight for Pb4, with minimum and maximum bond lengths of 2.416(5) and 3.464(5) Å (Table 2). The two As₂O₇⁴⁻ pyroarsenate (or diarsenate) anions are made up from two AsO₄ tetrahedra fused by a bridging O atom. As a characteristic structural feature of inorganic pyrogroups X_2O_7 [25], the X—O bond lengths to the bridging O atom are significantly longer than those to the terminal atoms. The corresponding averaged (av) values of $d(As-O)_{av} = 1.769$ Å for bridging and $d(As-O)_{av} = 1.667$ Å for terminal O atoms are in good agreement with the compiled values for pyroarsenate groups [26–28]. The conformation of the two pyroarsenate anions is ecliptic, with virtually identical As–O–As bridging angles (\angle (As2–O4–As1) = 126.0(3)°, \angle (As3–O11–As4) = 126.3(2)°), and As…As separations (As1...As2 = 3.1518(8) Å; As3...As4 = 3.1575(8) Å). In the crystal structure of Pb₂As₂O₇, the pyroarsenate anions are arranged in layers at $z \approx 0, \frac{1}{2}$, extending parallel to (001) (Figure 1).



Figure 1. The crystal structure of $Pb_2As_2O_7$ in a projection along [$\overline{100}$]. Anisotropic displacement parameters are given at the 74% probability level with Pb in blue, O in white, and As in red. AsO4 tetrahedra (red) are given in polyhedral representation, and Pb–O bonds shorter than 2.7 Å as solid bonds, and between 2.7 and 3.5 Å as open bonds.

The metrics of the triclinic unit cell of Pb₂As₂O₇ (Table 1) suggest a possible phase transition to a tetragonal phase crystallizing in the β -Ca₂P₂O₇ structure type [29], with $a_{\text{triclinic}}$, $b_{\text{triclinic}} \approx a_{\text{tetragonal}} \approx 7$ Å and $c_{\text{triclinic}} \approx \frac{1}{2}c_{\text{tetragonal}} \approx 13$ Å. For that purpose, temperature-dependent XRPD measurements were conducted (Figure 2).



Figure 2. Temperature-dependent XRPD of Pb₂As₂O₇.

As a result, $Pb_2As_2O_7$ shows no phase transition into a higher-symmetric phase upon heating until melting of the compound slightly below 800 °C, in good agreement with the reported melting temperature of 800 °C [9]. All unit cell parameters (Figure 3) increase more or less in a linear way with temperature, except the γ angle that shows a slight decrease. The evolution of unit cell parameters with temperature resembles that of isotypic Ba₂As₂O₇ [30].

3.2. $Pb(H_2AsO_4)_2$

Pb(H₂AsO₄)₂ adopts the Ca(H₂PO₄)₂ structure type [31] and crystallizes isotypically with Pb(H₂PO₄)₂ [19,32,33] and Ba(H₂AsO₄)₂ [30]. The triclinic crystal structure of Pb(H₂AsO₄)₂ comprises one Pb, two As, eight O, and five H atom positions. Except one H atom (H7) being located on an inversion center (Wyckoff position 1 *d*, site symmetry $\overline{1}$) and one H atom (H8) showing half-occupancy, all other atoms are located on general sites of space group $P\overline{1}$ with full occupation. The crystal structure of Pb(H₂AsO₄)₂ can be described as being made up from [PbO₈] polyhedra (range of Pb–O distances 2.442(2)—3.117(3) Å) that share common edges O1—O1' and O5—O5' to form chains extending along [001]. These chains are flanked by dihydrogen arsenate anions parallel to the chain direction at shorter Pb–O distances (<2.7 Å) and additionally bonded to dihydrogen arsenate anions that are part of an adjacent chain at longer distances (3.11 Å). In this way, a layered arrangement along (010) is accomplished. An excessive array of hydrogen bonds links two adjacent layers and consolidates the crystal packing.

The As1–O bond lengths appear to be normal for the dihydrogen arsenate group $H_2As(1)O_4$, with two significantly longer As–OH bonds (\approx 1.72 Å; O4, O3) and two shorter As–O bonds (\approx 1.65 Å; O2, O1), whereas the bond lengths of the $H_2As(2)O_4$ tetrahedron are atypical for a dihydrogen arsenate group: one shorter As–O bond of 1.665 Å to O5, two somewhat longer As–OH bonds (\approx 1.67 Å; O7, O8), and one long As–OH bond of 1.72 Å (O8) are observed. The As(2)O4 group shows very short interpolyhedral O···O distances of \approx 2.45 Å between the two pairs of inversion-related OH groups involving atoms O7 and O8. For such very strong hydrogen bonds, an asymmetric O–H···O hydrogen bond with a disordered H atom (50% occupation each), or a symmetric O···H···O hydrogen bond with an ordered H atom located on the inversion center are possible in the present case. On basis of difference–Fourier maps, the first possibility was chosen for the hydrogen bond O8–H···O8' that is located between two layers, and the second possibility for the hydrogen



bond O7–H···O7' that is located within a layer (Figure 4). Table 3 gives numerical details of the hydrogen bonding scheme for $Pb(H_2AsO_4)_2$.

Figure 3. Pb₂As₂O_{7.} Evolution of unit cell parameters with temperature.

The hydrogen bonding situation in Pb(H₂AsO₄)₂ resembles that in the related alkaline earth arsenate Ba(H₂AsO₄)₂ [30] or in the two polymorphs of Na₅H₃(SeO₄)₄(H₂O)₂ [34–37] where interpolyhedral O···O distances in the range 2.44–2.48 Å are observed, and for which either asymmetrical or symmetrical hydrogen bonds were modelled. A special case in this context is Pb(H₂PO₄)₂. The first two structure refinements of Pb(H₂PO₄)₂ did not consider H atom positions in the model [18,32], whereas in the latest refinement of Pb(H₂PO₄)₂ all H atom positions were automatically placed by the refinement program [33]. The resulting hydrogen bonding scheme, however, is highly questionable, with two O–H···O angles less than 130° and an O···O distance of 3.36 Å for one of the reported hydrogen bonds.



Figure 4. The crystal structure of $Pb(H_2AsO_4)_2$ in a projection along $[00\overline{1}]$. Color codes and displacement ellipsoids are as in Figure 1. Ordered H atoms are shown as light-gray spheres, and disordered H atoms as dark-gray spheres; hydrogen bonds are shown as green lines.

Table 3. $Pb(H_2AsO_4)_2$. Hydrogen-bond geometry/Å.

<i>D</i> –H···A	D-H	H···A	$D \cdots A$	$D-H\cdots A$	
O3–H3…O8 ^{vi}	0.85 (1)	1.81 (1)	2.660 (3)	176 (3)	
O4−H4…O2 ^{ix}	0.85 (1)	1.87 (2)	2.685 (3)	160 (4)	
O6-H6…O3	0.85 (1)	1.96 (1)	2.805 (3)	170 (5)	
07–H7…O7 ^v	1.23 (1)	1.23 (1)	2.450 (4)	180 (1)	
O8–H8…O8 ^x	0.85 (1)	1.63 (2)	2.458 (5)	165 (7)	
Symmetry codes: (v) $-x + 1$, $-y$, $-z$; (vi) x , y , $z + 1$; (ix) $-x + 1$, $-y + 1$, $-z + 1$;					
(x) - x + 2, -y + 1, -z + 1.					

It has to be stressed that modelling of H atom positions based on conventional X-ray diffraction measurements is ambiguous, in particular under consideration of the presence of heavy atoms in the structure (here Pb, As). Although in many cases, high-quality X-ray data have allowed the determination of H atoms for such or similar structures, only much more reliable neutron diffraction data will prove satisfactory whether the chosen model is correct or not.

3.3. Structural Comparison of $Pb_2As_2O_7$ and $Pb(H_2AsO_4)_2$ with Their Isotypic Ba and as Analogues

For a structural comparison of the isotypic structures of $M_2X_2O_7$ and $M(H_2XO_4)_2$ (M = Pb, Ba; X = P, As), respectively, the program *compstru* [38], available at the Bilbao Crystallographic Server [39], was used. The comparison allows for the quantification of the influence caused by the exchange of the anion (phosphate versus arsenate) and the cation (barium versus lead(II)). Atomic displacements for the atom pairs in the two sets of isotypic structures as well as numerical values for the degree of lattice distortion (S), the maximum distance between the atomic positions of paired atoms, the arithmetic mean of all distances (d_{av}), and the measure of similarity (Δ) are compiled in Table 4, with the respective lead arsenate as the reference structure.

Ph. Ac. O	Ph. P. O. [19]	••	$P_{2} = A_{2} = O_{2} = [201, (1)]$	
T 02A52O7	r 02r 207 [10]	i u i	Ba ₂ AS ₂ O ₇ [50]	i u i
a = 7.13790, b = 7.14000,		٥		٥
c = 13.06810 A,	a = 6.9140, b = 6.966	0, c = 12.7510 A,	a = 7.3996, b = 7.3812	2, <i>c</i> = 13.3261 A,
$\alpha = 83.3602, \beta = 86.6710,$	$\alpha = 83.180, \beta = 88.8$	860, $\gamma = 89.640^{\circ}$	$\alpha = 83.116, \beta = 86.4$	46, $\gamma = 89.792^{\circ}$
$\gamma = 89.9469^{\circ}$				
Pb1	Pb1	0.0609	Ba2	0.2396
O10	O10	0.0699	07	0.1127
Pb2	Pb2	0.0709	Ba3	0.0571
As2	P2	0.0751	As2	0.0562
O8	O8	0.0792	O5	0.0653
As3	P3	0.0845	As4	0.0447
O12	O12	0.1220	O14	0.2650
O2	O2	0.1266	O3	0.0404
O4	O4	0.1332	O4	0.0907
Pb4	Pb4	0.1367	Ba1	0.1397
As1	P1	0.1390	As1	0.0735
O5	O5	0.1459	O2	0.0537
07	07	0.1561	O11	0.1227
As4	P4	0.1721	As3	0.1624
O11	O11	0.1756	O13	0.1020
Pb3	Pb3	0.1780	Ba4	0.1873
O3	O3	0.1803	O9	0.1343
O13	O13	0.1873	O6	0.2288
O6	O6	0.1977	O8	0.1125
O9	O9	0.2333	O12	0.1897
O1	O1	0.2390	O10	0.0968
O14	O14	0.2918	O1	0.1930
S		0.0189		0.0170
$d_{\rm max.}$ (Å)		0.2918		0.2650
d _{av.} (Å)		0.1480		0.1258
Δ		0.041		0.043
$Pb(H_2AsO_4)_2$	Pb(H ₂ PO ₄) ₂ [19]	lul	Ba(H ₂ AsO ₄) ₂ [30] ⁽¹⁾	lul
a = 7.9497, b = 8.6137,				
c = 5.9984 Å,	a = 7.823, b = 8.31	5, c = 5.856 Å,	a = 7.2453, b = 7.4341, c = 8.1890 Å,	
$\alpha = 108.888, \beta = 96.128,$	$\alpha = 108.24, \beta = 96.9$	90, $\gamma = 108.61^{\circ}$	$\alpha = 104.685, \beta = 96.210, \gamma = 110.276^{\circ}$	
$\gamma = 108.449^{\circ}$				
Pb1	Pb1	0.0082	Ba1	0.9896
As2	P2	0.0125	As2	0.5838
As1	P1	0.0226	As1	0.4551
O3	O3	0.0767	O3	0.7901
O8	O8	0.0795	O8	0.9794
07	07	0.1049	07	1.9663
O4	O4	0.1160	O2	0.7304
O1	O1	0.1284	O4	0.8412
O6	O6	0.1309	O5	1.7444
O2	O2	0.1328	O1	0.4070
O5	O5	0.1340	O6	0.6014
C		0.0151		0 1107
		0.0151		0.110/
$u_{\text{max.}}(\mathbf{A})$		0.1340		1.9003
$u_{\rm av.}(A)$		0.0860		0.91/2
Δ		0.047		0.705

Table 4. Atom pairs and their absolute distances |u| / Å in the isotypic structures of $M_2 X_2 O_7$ and $M(H_2 X O_4)_2$ (M = Pb, Ba; X = P, As), as well as degree of lattice distortion (S), arithmetic mean of the distances ($d_{av} / Å$), and measure of similarity (Δ). H atoms were not considered for the comparison.

⁽¹⁾ Original unit cell of $Ba_2As_2O_7$ was transformed by -b,-a,-c to have the same setting as $Pb_2As_2O_7$.

 $M_2X_2O_7$. The unit cell parameters are similar for the three structures. The highest absolute displacement in the pair Pb₂As₂O₇/Pb₂P₂O₇ is observed for one of the terminal O atoms of the XO₄ tetrahedra (O14, 0.2918 Å); in the pair Pb₂As₂O₇/Ba₂As₂O₇, the maximum displacement applies to the atom pair O12 (lead compound) and O14 (barium compound) of the same XO₄ tetrahedron. Overall, numerical values show a high similarity of the three structures, revealing that the stereochemical influence of the 6s² electron lone pair at the Pb^{II} cations is not pronounced in this case.

 $M(H_2XO_4)_2$. The unit cell parameters were very similar for the pair Pb(H₂AsO₄)₂/ $Pb(H_2PO_4)_2$. The highest absolute displacement relates to O5, which is not bonded to a hydrogen atom and is associated with the shortest Pb–O bond in the structure. The low degree of lattice distortion (S = 0.0151) and the low value for the measure of similarity $(\Delta = 0.047)$ indicate a high similarity of the two lead structures, in contrast to the pair $Pb(H_2AsO_4)_2/Ba(H_2AsO_4)_2$. In this case, the unit cell parameters of $Ba(H_2AsO_4)_2$ differ considerably from those of the lead structures, in particular for the *b* and *c* axes, which lead to a high degree of lattice distortion (S = 0.1107). Although the definition of isotypism according to the Commission on Crystallographic Nomenclature is formally fulfilled (§1.2 and §1.3 in [40]) for the pair $Pb(H_2AsO_4)_2/Ba(H_2AsO_4)_2$ (neglecting H atoms), the great difference in the metrics alone has an impact on the structural similarity that appears to be low ($\Delta = 0.703$). The highest absolute atomic displacement was nearly 2 A for O7 that is involved in formation of the symmetrical hydrogen bond in Pb(H₂AsO₄)₂ and in an ordered asymmetric hydrogen bond in Ba(H₂AsO₄)₂, respectively. This is an indication that the dissimilarity in the crystal structures of $Pb(H_2AsO_4)_2$ and $Ba(H_2AsO_4)_2$ is not primarily associated with the substitution $Pb \rightarrow As$ or $As \rightarrow P$ but with a change in the hydrogen-bonding system.

3.4. Pb₅(AsO₄)₃OH

 $Pb_5(AsO_4)_3OH$ is a member of the vast family of the apatite $[M(1)_2][M(2)_3](XO_4)_3Y$ supergroup [41,42] and belongs to the apatite group, subgroup mimetites-H (mimetite is the Cl-endmember $Pb_5(AsO_4)_3Cl[43,44]$). Although a possible mineral phase "mimetite-OH'' with composition $Pb_5(AsO_4)_3OH$ has not yet been approved, SEM-EDS analyses of specimen from Styria (Austria) and the Blackforest (Germany) support the existence of such a mineral species [45,46]. A synthetic hydrous phase "Pb₄(PbOH)(AsO₄)₃·H₂O" $(=Pb_5(AsO_4)_3(OH) \cdot H_2O)$ [47]] has previously been reported, but its composition was later questioned and revised to Pb₄(PbOH)(AsO₄)₃ (=Pb₅(AsO₄)₃(OH)) [48]. Subsequent structural studies of this phase were limited to a qualitative assessment to the apatite structure type and unit cell parameters from powder X-ray data [49] until the crystal structure was fully refined from synchrotron powder data under consideration of small amounts of incorporated carbonate, leading to a refined composition of $Pb_5(AsO_4)_3(OH)_{0.87}(CO_3)_{0.04}$ [22]. The current refinement of $Pb_5(AsO_4)_3(OH)$ is based on the first single-crystal study and reports all atoms with anisotropic displacement parameters. The previously given unit cell parameters from room-temperature powder data are slightly larger than those of the current single-crystal study (Table 1): *a* = 10.154, *c* = 7.515 Å, *V* = 671.02 Å³ [49]; *a* = 10.187, c = 7.523 Å, V = 676.303(13) Å³ [22]; a = 10.14(8), c = 7.50(1) Å, V = 669 Å³ [50]. Unit cell parameters predicted from elemental radii using pattern recognition and artificial intelligence methods, a = 9.8939, c = 7.6039 Å, V = 644.617 Å³ [51], are much smaller than all experimentally determined values. As emphasized by White and ZhiLi [42], it seems likely that most of the reported apatites are in fact somewhat non-stoichiometric, particularly with respect to X anions; furthermore, it is difficult to determine such compositional variations directly. For the final crystal structure model of Pb₅(AsO₄)₃(OH), full occupation of the Y site with OH was considered, and without any incorporation of carbonate.

The apatite structure is well known and has been reviewed some time ago in a crystal-chemical context [42]. Therefore, only the most important structural features are discussed here. Pb1 is located on Wyckoff position 4f (site symmetry 3) and has a trigonal-prismatic environment if Pb–O distances less than 2.8 Å are considered (three more O

atoms cap the lateral faces of the trigonal prism at distances of 3.0 Å). As a quantitative measure for the reliability of the structure model of apatites, the metaprism twist angle (φ) , i.e., the O(1)–M(1)–O(2) twist angle projected on (001) of the $[M(1)O_6]$ metaprism was introduced with a usual variation of $5^{\circ} \leq \varphi \leq 25^{\circ}$ for inconspicuous structure refinements for apatites crystallizing in space group type $P6_3/m$ [52]. From the current refinement of Pb₅(AsO₄)₃OH, φ amounts to 21.9°. This value matches with the metaprism angle of 21.6° in the analogous crystal structure of the mineral hydroxylpyromorphite, Pb₅(PO₄)₃OH, from single-crystal data [53]. The trigonal [Pb1O₆] metaprism in $Pb_5(AsO_4)_3OH$ has a polyhedral volume of 20.46 \AA^3 (calculated with the VOLCAL option in PLATON [54] and shares faces to build up chains running parallel to [001]. Pb2 (Wyckoff position 6 h, m..) is surrounded by one arsenate O atom (O1) at a short distance of 2.36 Å, and four arsenate O atoms (O3) at longer distances of \approx 2.62 Å. The next nearest O atoms are the hydroxyl O atom O4 at 2.88 Å, followed by O3 at 3.06 Å. The hydroxyl group is disordered around the Wyckoff 2 *b* position (0, 0, 0), with a value for the *z* coordinate of 0.568 and located in channels (diameter 5.071 Å) formed by the surrounding Pb2 atoms. The As atom is situated on Wyckoff position 6 h and exhibits three equal bond lengths of 1.655 Å to O3 (2x) and O2, and a slightly longer bond length to O1 (1.681 Å). The average As–O bond length of 1.662 Å is in very good agreement with literature data of 1.667 (18) for As–O bonds to nonprotonated O atoms [55] (the calculated overall mean As-O bond length including also As–O(H) groups is 1.689 Å [56]). The crystal structure of Pb₅(AsO₄)₃OH is depicted in Figure 5.



Figure 5. The crystal structure of $Pb_5(AsO_4)_3OH$ in a projection along $[00\overline{1}]$. Color codes and displacement ellipsoids are as in Figure 1. The O atom of the hydroxyl group is given in yellow, and the [Pb1O6] metaprism as a blue polyhedron. In the inset, the center of symmetry is indicated by a black dot, and the disordered positions of the hydroxyl O atom (half occupation) by yellow and white ellipsoids.

In comparison with the previous refinement of $Pb_5(AsO_4)_3OH$ from powder synchrotron X-ray data [22], the Pb–O and As–O bond lengths are the same within the 3σ range, with the exception of the Pb–O4 bond involving the hydroxyl group (Table 2). The latter bond is by 0.2 Å shorter in the model refined from powder data with an isotropic refinement of all atoms and the hydroxyl O atom at z = 0.3743 showing the same type of disorder than modelled for the current single-crystal X-ray data (anisotropic refinement of all atoms with the hydroxyl O atom). In the model from single-crystal X-ray data, O4 shows a strong motion along the channel direction as indicated by its unilateral anisotropic displacement parameter (Figure 5, inset). On the other hand, the hydroxyl group of analogous

Pb₅(PO₄)₃OH (space group $P6_3/m$) was modelled in different ways. Whereas for natural hydroxylpyromorphite (containing small amounts of fluorine; single-crystal data; [53]) and synthetic Pb₅(PO₄)₃OH (single-crystal data; [57]) the hydroxyl O atom was not disordered and found to be situated at the 2 *b* Wyckoff position (*z* = 0); it was treated as disordered in another refinement of synthetic Pb₅(PO₄)₃OH (neutron data from polycrystalline material) with *z* = 0.3565 [58]. All other structurally determined $M_5(XO_4)_3$ OH apatite phases reported up to date were modelled with a disordered hydroxyl group, *viz*. Ca₅(PO₄)₃OH ($P6_3/m$; *z* = 0.195) [59], Ca₅(AsO₄)₃OH ($P6_3/m$; *z* = 0.1919) [60], Sr₅(PO₄)₃OH ($P6_3/m$; *z* = 0.1856) [61], Sr₅(AsO₄)₃OH ($P6_3/m$; *z* = 0.1919) [62], Ba₅(PO₄)₃OH ($P6_3; z = 0.148$) [63], and Cd₅(PO₄)₃OH (*z* = 0.1880) [64].

3.5. NaPb₄(AsO₄)₃

 $NaPb_4(AsO_4)_3$ is also a member of the apatite supergroup [41], but represents a lacunar apatite where the Y position, i.e., the anion located in the channels formed by M2 cations, remains empty (Figure 6). It has been suggested that the stereochemically active lone pair of PbII that occupies a volume close to that of oxygen allows lacunar apatite structures to be stable [65]. In contrast to a previous refinement of $NaPb_4(AsO_4)_3$ (polycrystalline material prepared by a ceramic route) based on laboratory powder X-ray data and performed in space group $P6_3/m$ [66], the current single-crystal X-ray data for hydrothermally grown crystals clearly revealed a lower symmetry in space group P3 due to the violation of reflection condition l = 2n for 00*l* reflections. For example, reflection 003 has an average F_{obs}^2 value of 1040(33). A check for a possibly missed higher symmetry using the ADDSYM feature in PLATON [54] gave no indication for a higher spacer group symmetry on basis of the current X-ray data. However, the corresponding phosphate phase NaPb₄(PO₄)₃ (single-crystal X-ray data) has also been reported to crystallize in space group $P6_3/m$ in the apatite-type of structure [67,68]. The question of whether the lower space group symmetry of $NaPb_4(AsO_4)_3$ is a systematic feature or is related with different preparation conditions (hydrothermal versus ceramic route) and associated polymorphism must remain unanswered for the time being. Future studies on basis of single-phase material from different preparation routes, high-resolution diffraction data, and complementary techniques are definitely needed to achieve a deeper insight.



Figure 6. The crystal structure of NaPb₄(AsO₄)₃ in a projection along $[00\overline{1}]$. Color codes and displacement ellipsoids are as in Figure 1. The [*M*1aO6] metaprism is displayed as a turquoise polyhedron and the [*M*1bO6] metaprism as a blue polyhedron.

According to space group symmetry $P\overline{3}$, NaPb₄(AsO₄)₃ belongs to the belovite group within the apatite supergroup [41]. To the best of the author's knowledge, NaPb₄(AsO₄)₃ is the first representative of a lacunar apatite comprising solely of XO₄ groups as anions, adopting the belovite structure type. In comparison with Pb₅(AsO₄)₃(OH), the unit cell

volume is reduced by about 4.5% due to incorporation of smaller Na^I (ionic radii: Na^I [IX] = 1.24 Å versus Pb^{II} [IX] = 1.35 Å [69]). In comparison with the apatite structure type in space group $P6_3/m$, the M1 position related with the metaprism is split into two positions in the belovite structure type (*M*1a, *M*1b) that each are located on Wyckoff position 2 d (site symmetry 3). Both positions show occupational disorder of Na/Pb, however, with different absolute ratios. Whereas M1a shows a minor fraction of lead(II) (Pb1a: site occupancy 0.15), the situation for M1b is reversed (Pb1b: site occupancy 0.85). The polyhedral volumes of the metaprisms reflect this behavior, with a smaller volume of 18.07 \AA^3 for Na-rich [*M*1aO₆] and a greater volume of 19.04 Å³ for Pb-rich [*M*1bO₆]. The angles φ for the corresponding metaprisms amount to 24.5° for O1–(M1a)–O2 and to 45.6° for O2–(M1b)– O3. The latter value is the highest observed for any apatite structure [52] and reflects the high distortion of the $[M1bO_6]$ polyhedron due to a considerable twist of the opposite trigonal faces. Like in the higher-symmetric apatite structure, the two different trigonal prisms are capped by three additional O atoms at the lateral faces, with distances of 3.202(8) Å for $[M1aO_6]$ and 3.070 for Å for $[M1bO_6]$. The M2 site of $NaPb_4(AsO_4)_3$ is located on a general position (6 g) of space group $P\overline{3}$. According to refinements of the s.o.f. for this site, significant amounts of Na^I are not incorporated, and consequently only Pb^{II} is situated on this position. The channel diameter for the empty channel defined by Pb2 atoms is 5.150 Å. In comparison with Pb₅(AsO₄)₃(OH), the As–O bond lengths of the AsO₄ tetrahedron in the crystal structure of NaPb₄(AsO₄)₃ are slightly enlarged (d(As–O)_{av} = 1.684 Å).

$3.6. Pb_4As_2O_9$

From an investigation of the PbO/As₂O₅ phase diagram, the phase Pb₄As₂O₉ was reported to exist up to a temperature of 740 °C when decomposition through a peritectoid is observed [9]. In the present study, annealing temperatures above (750 °C) and below (680 °C) the peritectoid were chosen for phase mixtures with a molar ratio of PbO:As₂O₅ = 4:1. However, in both cases, only the phases Pb₃(AsO₄)₂ and Pb₈(AsO₄)₂O₅ were observed as reaction products. Therefore, different molar ratios and/or annealing temperatures might be necessary to reproduce the reported formation of Pb₄As₂O₉ [9].

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