# Crystal Structure Refinements of the Lead(II) Oxoarsenates(V) $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}, \mathrm{~Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}, \mathrm{~Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ and $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ from Single-Crystal X-ray Data 

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$\dagger$ Dedicated to the late Ekkehard Tillmanns. He will be remembered as a human and scientific role model.

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#### Abstract

Single-crystals of lead(II) oxoarsenates(V) were grown from the melt $\left(\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}\right)$, from solution $\left(\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}\right.$ and $\left.\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}\right)$, and under hydrothermal conditions $\left(\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}\right)$. Crystal structure refinements from single-crystal X-ray diffraction data revealed isotypism for both $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ and $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ with the corresponding barium and phosphate phases. A quantitative comparison of the crystal structures showed a high similarity for the isotypic $M_{2} X_{2} \mathrm{O}_{7}$ structures $(M=\mathrm{Pb}, \mathrm{Ba} ; X=\mathrm{As}, \mathrm{P})$, whereas for the $M\left(\mathrm{H}_{2} \mathrm{XO}_{4}\right)_{2}$ structures only the pair $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ and $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$ is similar, but not $\mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2} . \mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ adopts the apatite structure type in space group $\mathrm{Pb}_{3} / m$, with the hydroxyl group disordered around Wyckoff position $2 b(0,0,0)$ in the channels of the structure. $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ 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 $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ that reported an apatite-type structure in space group $\mathrm{P}_{3} / m$, the current singlecrystal data clearly revealed a symmetry reduction to space group $P \overline{3}$. Hence, $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ 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 $\mathrm{Pb} / \mathrm{As} / \mathrm{O} /(\mathrm{H})$, two approved and crystallographically fully characterized mineral phases are known to exist, viz. paulmooreite, $\mathrm{Pb}^{\mathrm{II}}{ }_{2} \mathrm{As}^{\mathrm{V}}{ }_{2} \mathrm{O}_{5}$, and schultenite, $\mathrm{Pb}^{\mathrm{II}} \mathrm{HAs}^{V} \mathrm{O}_{4}$. Paulmooreite represents a lead(II) oxoarsenate(III) with a pyroarsenite anion, $\mathrm{As}_{2} \mathrm{O}_{5}{ }^{4-}$ [1], whereas schultenite is a lead(II) oxoarsenate(V) with a hydrogenarsenate anion, $\mathrm{HAsO}_{4}{ }^{2-}$ [2]. Other synthetic phases for which their crystal structures have been determined include lead(II) arsenite, $\mathrm{Pb}^{\mathrm{II}} \mathrm{As}^{\mathrm{III}}{ }_{2} \mathrm{O}_{4}$ [3], the lead(II) oxoarsenates $(V) \mathrm{Pb}_{3}{ }_{3}\left(\mathrm{As}^{\mathrm{V}} \mathrm{O}_{4}\right)_{2}$ [4], $\mathrm{Pb}_{8}{ }^{\mathrm{II}} \mathrm{O}_{5}\left(\mathrm{As}^{\mathrm{V}} \mathrm{O}_{4}\right)_{2}$ [5], and $\mathrm{Pb}^{\mathrm{II}} \mathrm{As}^{\mathrm{V}}{ }_{2} \mathrm{O}_{6}$ [6], as well as the lead(IV) oxoarsenate $(\mathrm{V}) \mathrm{Pb}^{\mathrm{IV}}\left(\mathrm{HAs}^{\mathrm{V}} \mathrm{O}_{4}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)$ [7]. Although other synthetic lead(II) oxoarsenates $(\mathrm{V})$ 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 $\mathrm{Pb}^{\mathrm{II}}{ }_{2} \mathrm{As}^{\mathrm{V}}{ }_{2} \mathrm{O}_{7}, \mathrm{~Pb}^{\mathrm{II}}\left(\mathrm{H}_{2} \mathrm{As}^{V} \mathrm{O}_{4}\right)_{2}, \mathrm{~Pb}^{\mathrm{II}}\left(\mathrm{As}^{V} \mathrm{O}_{4}\right)_{3} \mathrm{OH}$, and $\mathrm{NaPb}^{\mathrm{II}} 4^{( }\left(\mathrm{As}^{\mathrm{V}} \mathrm{O}_{4}\right)_{3}$ 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.
$\mathbf{P b}_{\mathbf{2}} \mathbf{A s}_{\mathbf{2}} \mathbf{O}_{7}$. Single-crystals of lead(II) diarsenate(V) were obtained from the melt, starting with polycrystalline $\mathrm{PbHAsO}_{4}$. The latter was prepared by slow addition of aqueous solutions of $\mathrm{Na}_{2} \mathrm{HAsO}_{4}\left(1.9 \mathrm{~g}\right.$ in 50 mL water) to $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}(3.3 \mathrm{~g}$ in 50 mL water) in a molar ratio of 1:1. The precipitated $\mathrm{PbHAsO}_{4}$ 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 $\mathrm{PbHAsO}_{4}$ was then placed in a platinum crucible covered with a lid. The crucible was heated within 24 h to $850^{\circ} \mathrm{C}$ and then cooled within 99 h to room temperature. Crystals of $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ were present as a minor constituent in the recrystallized melt with $\mathrm{Pb}_{3}\left(\mathrm{AsO}_{4}\right)_{2}$ as the main constituent because $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ melts incongruently [9]. Polycrystalline single-phase $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ was prepared by heating $\mathrm{PbHAsO}_{4}$ at $600^{\circ} \mathrm{C}$ for one day.
$\mathbf{~} \mathbf{P b}\left(\mathbf{H}_{\mathbf{2}} \mathbf{A s O} \mathbf{O}_{\mathbf{4}}\right)_{\mathbf{2}}$. A concentrated $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ solution ( 10 g in 50 mL water) was refluxed for one day with 8 mL concentrated arsenic acid $\left(80 \%_{\mathrm{wt}}\right)$. After cooling to room temperature, plate-like crystals could be isolated next to recrystallized $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ crystals. The latter were easily distinguishable from the bis(dihydrogen)arsenate due to their cubic symmetry.
$\mathrm{Pb}_{5}\left(\mathbf{A s O}_{4}\right)_{3} \mathbf{O H}$. Hydrothermal treatment of $\mathrm{PbHAsO}_{4}$ in $20 \%_{\mathrm{wt}}$ ammonia solution at $210{ }^{\circ} \mathrm{C}$ 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, $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$, 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]. $\mathrm{PbHAsO}_{4}$ (see above) was added to 20 mL of a warm KOH $\left(10 \%_{\mathrm{wt}}\right)$ 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 $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ were manually isolated from this material under a polarizing microscope. Phase analysis of the bulk using the program Highscore [11] revealed $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ as the main phase $\left(80 \%{ }_{\mathrm{wt}}\right)$, and $\mathrm{KPb}_{2}\left(\mathrm{CO}_{3}\right)_{2}(\mathrm{OH})$ [12] and $\mathrm{Pb}_{3}\left(\mathrm{CO}_{3}\right)_{2}(\mathrm{OH})_{2}$ (hydrocerrusite) [13] as minor side products $\left(10 \%_{\text {wt }}\right.$ each).
$\mathrm{NaPb}\left(\mathrm{AsO}_{4}\right)_{3}$. The sodium lead arsenate phase was obtained as a minor by-product during single-crystal growth studies of $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ under hydrothermal conditions. For that purpose, 0.3 g PbHAsO 4 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 $210^{\circ} \mathrm{C}$ for five days. Crystals of $\mathrm{NaPb}\left(\mathrm{AsO}_{4}\right)_{3}$ appeared as block-like crystals next to yet-unidentified polycrystalline material.
$\mathrm{Pb}_{\mathbf{4}} \mathbf{A s}_{\mathbf{2}} \mathbf{O}_{9}$. Attempts to prepare $\mathrm{Pb}_{4} \mathrm{As}_{2} \mathrm{O}_{9}$ were made by heating a mixture of PbO $(0.795 \mathrm{~g})$ and $\mathrm{As}_{2} \mathrm{O}_{5}(0.205 \mathrm{~g})$ in the molar ratio $4: 1$ and a mixture of $\mathrm{PbO}(0.398 \mathrm{~g})$ and $\mathrm{PbHAsO}_{4}(0.618 \mathrm{~g})$ 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 $750^{\circ} \mathrm{C}$ for the first and at $680^{\circ} \mathrm{C}$ for the second batch, followed by intermediate grindings after each day. Phase analysis of the products by PXRD revealed $\mathrm{Pb}_{3}\left(\mathrm{AsO}_{4}\right)_{2}$ and $\mathrm{Pb}_{8}\left(\mathrm{AsO}_{4}\right)_{2} \mathrm{O}_{5}$ 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 MicroLoops ${ }^{\mathrm{TM}}$. The X-ray diffraction studies were conducted at room temperature on a Bruker APEX-II CCD diffractometer (Bruker-AXS, Madison, WI, USA) using MoK $\alpha$ 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 | $\mathrm{Pb}_{2}\left(\mathrm{As}_{2} \mathrm{O}_{7}\right)$ | $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ | $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ | $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ |
| :---: | :---: | :---: | :---: | :---: |
| Temperature $/{ }^{\circ} \mathrm{C}$ |  | $\begin{gathered} -23(1)- \\ — \text { Bruker-AXS APEX-II CCD detector - } \\ - \text { Mo K } \bar{\alpha} ; 0.71073- \end{gathered}$ |  |  |
| Diffractometer |  |  |  |  |
| Radiation; $\lambda / \AA$ |  |  |  |  |
| Space group (\# no.) | $P \overline{1}$ (\# 2) | $P \overline{1}$ (\# 2) | $P 63 / m(\# 176)$ | P $\overline{3}$ (\# 147) |
| Formula units Z | 4 | 2 | 2 | 2 |
| Formula weight | 676.22 | 489.06 | 1469.72 | 1268.51 |
| Crystal dimensions/mm | $0.10 \times 0.03 \times 0.03$ | $0.10 \times 0.06 \times 0.01$ | $0.10 \times 0.01 \times 0.01$ | $0.04 \times 0.04 \times 0.02$ |
| Crystal description | light-yellow fragment | colorless plate | light-yellow needle | colorless block |
| $a / \AA$ | 7.13790(10) | 7.9497(10) | 10.1266(3) | 10.0230(14) |
| $b / \AA$ | 7.14000(10) | 8.6137(10) | 10.1266(3) | 10.0230(14) |
| c/ $\AA$ | 13.0681(3) | 5.9984(8) | 7.5010(2) | 7.3117(15) |
| $\alpha /{ }^{\circ}$ | 83.3602(11) | 108.888(5) | 90 | 90 |
| $\beta /{ }^{\circ}$ | 86.6710(10) | 96.128(5) | 90 | 90 |
| $\gamma /{ }^{\circ}$ | 89.9469(10) | 108.449(6) | 120 | 120 |
| $V / \AA^{3}$ | 660.42(2) | 358.51(8) | 666.16(4) | 636.1(2) |
| $\mu / \mathrm{mm}^{-1}$ | 60.851 | 32.693 | 70.429 | 60.606 |
| X-ray density/g. $\mathrm{cm}^{-3}$ | 6.801 | 4.531 | 7.327 | 6.623 |
| Range $\theta_{\text {min }}-\theta_{\text {max }}$ | 1.57-40.18 | 2.69-36.73 | 2.32-30.00 | 2.35-30.28 |
| Range $h$ | $-12 \rightarrow 12$ | $-13 \rightarrow 13$ | $-14 \rightarrow 14$ | $-14 \rightarrow 14$ |
| $k$ | $-12 \rightarrow 12$ | $-14 \rightarrow 14$ | $-14 \rightarrow 14$ | $-14 \rightarrow 14$ |
| $l$ | $-23 \rightarrow 23$ | $-10 \rightarrow 10$ | $-10 \rightarrow 9$ | $-10 \rightarrow 10$ |
| 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 | HELXL - |  |
| Absorption correction |  | -SAD |  |  |
| Number of parameters | 200 | 114 | 40 | 64 |
| Ext. coef. (SHELXL) | 0.00118(8) | 0.00095(16) | - | - |
| Diff. elec. dens. max; min $/ \mathrm{e}^{-} \AA^{-3}$ (dist./ $\AA$, atom) | $\begin{gathered} 6.23(0.61, \mathrm{~Pb} 2) ; \\ -5.53(0.59, \mathrm{~Pb} 1) \end{gathered}$ | $\begin{gathered} 1.47(0.68, \mathrm{~Pb} 1) \\ -1.24(0.71, \mathrm{~Pb} 1) \end{gathered}$ | $\begin{gathered} 5.60(0.67, \mathrm{~Pb} 2) ; \\ -3.05(0.76, \mathrm{~Pb} 2) \end{gathered}$ | $\begin{gathered} 2.61(0.43,(\mathrm{~Pb} / \mathrm{Na}) 3) ; \\ -1.69(0.57, \mathrm{~Pb} 1) \end{gathered}$ |
| $R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | 0.0346 | 0.0237 | 0.0380 | 0.0211 |
| $w R 2\left(F^{2}\right.$ 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 $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7} / \mathrm{Pb}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ and $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2} / \mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$, 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 $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ is not reduced [20] (reduced unit cell parameters are: $a=5.9984(8), b=7.9497(10), c=8.6137(10) \AA$, $\left.\alpha=108.888(5), \beta=108.449(6), \gamma=96.128(5)^{\circ}\right)$. The hydrogen atom positions in the crystal structure of $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ were discernible from difference-Fourier maps and were refined freely for H 7 and with a distance constraint of $0.85 \AA$ for all other H atoms; all H atoms in this structure were refined with a common $U_{\text {iso }}$ parameter. In the crystal structure of $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$, 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 $\mathrm{NaPb}\left(\mathrm{AsO}_{4}\right)_{3}$, 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 $\mathrm{NaPb}\left(\mathrm{AsO}_{4}\right)_{3}$ 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 $\mathrm{LaB}_{6}$ standard) PANalytical X'Pert PRO diffractometer with $\mathrm{Cu}-\mathrm{K} \bar{\alpha}$ radiation in Bragg-Brentano geometry ( $\mathrm{X}^{\prime}$ Celerator multi-channel detector, silicon zero background sample holder, $2.546^{\circ}$ scan length, 25 s exposure time per scan length, $2 \theta$ range $5^{\circ}-70^{\circ}$; the scans were finally converted into $0.02^{\circ}$ 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 (Marcor ${ }^{\text {TM }}$ ) 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 $10^{\circ} \mathrm{C} / \mathrm{h}$ 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.

| $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Pb 1 | O6 | 2.416 (5) | Pb4 | O7 ${ }^{\text {v }}$ | 2.463(4) |
| Pb1 | O2 ${ }^{\text {i }}$ | $2.485(5)$ | Pb 4 | O3 ${ }^{\text {i }}$ | 2.479(5) |
| Pb 1 | O10 | 2.521(5) | Pb 4 | O7 | 2.514(5) |
| Pb1 | O3 | 2.563(5) | Pb 4 | O5 ${ }^{\text {ix }}$ | 2.523(5) |
| Pb 1 | O1 ${ }^{\text {ii }}$ | 2.673 (5) | Pb 4 | O14 | 2.673 (5) |
| Pb1 | O7 ${ }^{\text {iii }}$ | 2.878(5) | Pb 4 | O2 ${ }^{\mathrm{v}}$ | 2.695(5) |
| Pb1 | $\mathrm{O} 4{ }^{\text {ii }}$ | 2.965(5) | Pb 4 | O6 | 3.140(5) |
| Pb1 | O14 ${ }^{\text {iii }}$ | 3.319(5) | Pb 4 | O12 | $3.226(5)$ |
| Pb 1 | O5 ${ }^{\text {iii }}$ | 3.464(5) | As1 | O1 | 1.657(4) |
| Pb 2 | $\mathrm{O} 13{ }^{\text {iv }}$ | 2.417(4) | As1 | O3 | 1.669(4) |
| Pb 2 | O12 ${ }^{\text {i }}$ | 2.484(5) | As1 | O2 | 1.679(5) |
| Pb2 | $\mathrm{O} 8{ }^{\text {ii }}$ | 2.624(5) | As1 | O4 | 1.777(4) |
| Pb2 | O10 ${ }^{\text {i }}$ | 2.631(5) | As2 | O5 | 1.649(5) |
| Pb2 | O14 ${ }^{\text {v }}$ | 2.817(5) | As2 | O6 | 1.671(5) |
| Pb2 | O2 | 2.883(6) | As2 | O7 | 1.679(4) |
| Pb2 | O11 ${ }^{\text {v }}$ | 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 ${ }^{\text {x }}$ | 1.760(4) |
| Pb3 | O8 ${ }^{\text {vii }}$ | 2.555(5) | As4 | O14 | 1.651(4) |
| Pb3 | O12 ${ }^{\text {viii }}$ | 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 | O1i ${ }^{\text {ii }}$ | 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) $x, y, z+1$; <br> (v) $-x+1,-y,-z+1$; (vi) $x, y-1, z$; (vii) $-x,-y+1,-z$; (viii) $x-1, y, z$; (ix) $x+1, y, z$; <br> (x) $-x+1,-y+1,-z$. |  |  |  |  |  |

Table 2. Cont.

| $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Pb1 | O5 ${ }^{\text {i }}$ | 2.442(2) | As1 | O2 | 1.652(2) |
| Pb 1 | O1 ${ }^{\text {ii }}$ | 2.529(2) | As1 | O1 | 1.657(2) |
| Pb 1 | O2 | 2.559(2) | As1 | O4 ${ }^{\text {vi }}$ | 1.719(2) |
| Pb1 | O5 ${ }^{\text {iii }}$ | 2.575(2) | As1 | O3 ${ }^{\text {vii }}$ | 1.727(2) |
| Pb1 | $\mathrm{O} 1^{\text {iv }}$ | 2.584(2) | As2 | O5 | 1.665(2) |
| Pb 1 | $\mathrm{O} 7^{\mathrm{v}}$ | 2.701(2) | As2 | O7 | 1.673(2) |
| Pb 1 | O4 | 2.944(2) | As2 | O8 | 1.676(2) |
| Pb 1 | O6 | 3.117(3) | As2 | O6 | 1.722(2) |

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) $-x,-y+1,-z$;

| $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3}(\mathrm{OH})$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Pb1 | $\mathrm{O} 2{ }^{\text {i }}$ | 2.534(8) 2.534 | Pb2 | O1 vi | 2.355 (14) 2.398 |
| Pb1 | $\mathrm{O} 2{ }^{\text {ii }}$ | 2.534(8) | Pb2 | O3 vii | 2.616 (9) 2.618 |
| Pb1 | $\mathrm{O} 2{ }^{\text {iii }}$ | 2.534(8) | Pb2 | O3 ${ }^{\text {viii }}$ | 2.616 (9) |
| Pb1 | O1 ${ }^{\text {iv }}$ | 2.774(10) 2.754 | Pb2 | O3 ${ }^{\text {iv }}$ | 2.664 (11) 2.691 |
| Pb1 | O1 ${ }^{\mathrm{v}}$ | 2.774 (10) | Pb2 | O3 ${ }^{\mathrm{v}}$ | 2.664(11) |
| Pb1 | O1 | 2.774(10) | Pb2 | $\mathrm{O} 4{ }^{\text {xi }}$ | 2.88(3) 2.693 |
| Pb1 | O3 ${ }^{\mathrm{v}}$ | 3.009(13) 2.944 | Pb2 | $\mathrm{O} 4{ }^{\text {xii }}$ | 2.88(3) |
| Pb1 | O3 ${ }^{\text {iv }}$ | 3.009(13) | Pb 2 | $\mathrm{O} 2{ }^{\text {vi }}$ | 2.937(12) 3.058 |
| Pb1 | O3 | 3.009(13) |  |  |  |
| As1 | $\mathrm{O} 2{ }^{\text {vi }}$ | 1.655(11) 1.674 |  |  |  |
| As1 | O3 ${ }^{\text {xiii }}$ | 1.655(10) 1.691 |  |  |  |
| As1 | O3 | 1.655(10) |  |  |  |
| As1 | O1 | 1.681(13) 1.711 |  |  |  |
| (iv) | $\begin{aligned} & \text { mmetry } \\ & +1, x- \\ & \text { i) } y,-x+ \\ & \text { Va } \end{aligned}$ | $\begin{aligned} & \text { es: (i) } x-y, x,-z \\ & z ;(\mathrm{v})-x+y, \\ & z ;(\text { (xi) }-x,-y, z \\ & \text { in italics are fron } \end{aligned}$ | $1,-y$ ) $-y$ der | $\begin{aligned} & -z ; \text { (iii) } \\ & x-y, z ; \\ & -z+1 ; \\ & \text { rotron st } \end{aligned}$ | $\begin{aligned} & x+y+1,-z \\ & y,-x+y, z+1 / 2 \\ & x, y,-z+1 / 2 \end{aligned}$ [22]. |


| $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \quad \mathrm{O}^{2}{ }^{\text {i }}$ | 2.428(7) | Pb 2 | O1 ${ }^{\text {vi }}$ | 2.248(7) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \quad \mathrm{O} 2{ }^{\text {ii }}$ | 2.428 (7) | Pb 2 | $\mathrm{O} 4{ }^{\text {ii }}$ | 2.433(7) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \quad \mathrm{O} 2{ }^{\text {iii }}$ | $2.428(7)$ | Pb 2 | $\mathrm{O} 4^{\text {viii }}$ | 2.509(7) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \mathrm{O}^{\text {iv }}$ | $2.564(7)$ | Pb 2 | $\mathrm{O}^{\text {xv }}$ | 2.568(7) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \mathrm{O}^{\text {v }}$ | $2.564(7)$ | Pb 2 | O2 ${ }^{\text {ix }}$ | 2.805(6) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \quad \mathrm{O} 1^{\text {vi }}$ | $2.564(7)$ | Pb 2 | O3 | 2.912(8) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \quad \mathrm{O} 4{ }^{\text {vii }}$ | 3.202(8) | As1 | $\mathrm{O} 2^{\text {ix }}$ | 1.673(5) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \quad \mathrm{O} 4{ }^{\text {viii }}$ | $3.202(8)$ | As1 | $\mathrm{O}^{\text {xvii }}$ | 1.675(7) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{a} \quad \mathrm{O}^{\text {ix }}$ | $3.202(8)$ | As1 | O1 ${ }^{\text {xviii }}$ | 1.689(6) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b} \quad \mathrm{O} 2{ }^{\text {x }}$ | $2.435(7)$ | As1 | O4 | 1.699(7) |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b} \quad \mathrm{O} 2{ }^{\text {xi }}$ | 2.435 (7) |  |  |  |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b} \quad \mathrm{O} 2{ }^{\text {xii }}$ | 2.435(7) |  |  |  |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b} \quad \mathrm{O} 3{ }^{\text {xiii }}$ | 2.773(8) |  |  |  |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b}$ O3 | 2.773(8) |  |  |  |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b} \quad \mathrm{O} 3{ }^{\text {xiv }}$ | 2.773(8) |  |  |  |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b} \mathrm{O}^{\text {i }}{ }^{\text {i }}$ | 3.070 (8) |  |  |  |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b} \mathrm{O}^{\mathrm{v}}$ | 3.070 (8) |  |  |  |
| $(\mathrm{Na} / \mathrm{Pb}) 1 \mathrm{~b}$ O1 ${ }^{\text {vi }}$ | 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) $x-y+1, x+1,-z$; (vii) $x, y+1, z$; (viii) $-y, x-y, z$; (ix) $-x+y+1$,
$-x+1, z ;(\mathrm{x})-x+1,-y+1,-z+1$; (xi) $x-y, x,-z+1$; (xii) $y,-x+y+1,-z+1$; (xiii) $-y+1$,
$x-y+1, z$; (xiv) $-x+y,-x+1, z ;(\mathrm{xv}) y,-x+y,-z+1$; (xvii) $-x+y,-x, z$; (xviii) $-x,-y,-z$.
3.1. $\mathrm{PbII}_{2} \mathrm{As}^{\mathrm{V}}{ }_{2} \mathrm{O}_{7}$
$\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ belongs to the family of diarsenates. In a previous study on this phase [23], isotypism with the diphosphate analogue $\mathrm{Pb}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ was suggested, and indexed power diffraction data as well as unit cell parameters for the non-reduced unit cell were given, with $a=6.86(2), b=7.13(2), c=12.93(3) \AA, \alpha=99.01(10), \beta=91.10(12), \gamma=89.48(12)^{\circ}$, $V=625 \AA^{3}$ for room temperature data. However, the reduced unit cell [20] parameters $\left(a=6.86(2), b=7.13(2), c=12.93(3) \AA, \alpha=80.99(10), \beta=88.90(12), \gamma=89.48(12)^{\circ}\right)$, the unit cell volume, and the calculated density $\left(7.18 \mathrm{~g} \cdot \mathrm{~cm}^{-3}\right)$ based on the powder study differ considerably from those of the current single-crystal study (Table 1).
$\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ is in fact isotypic with $\mathrm{Pb}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ [18] and crystallizes in the triclinic $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ structure type that is also referred to as the "dichromate" structure type [24,25] and adopted by many $M_{2} X_{2} \mathrm{O}_{7}$ phases where $M$ is a large divalent cation and $X$ is As or P . The asymmetric unit of $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ comprises four Pb , four As , and 14 O sites. The coordination numbers of the lead(II) cations are nine for $\mathrm{Pb} 1, \mathrm{~Pb} 2$ and Pb 3 , and eight for Pb 4 , with minimum and maximum bond lengths of $2.416(5)$ and $3.464(5) \AA$ (Table 2). The two $\mathrm{As}_{2} \mathrm{O}_{7}{ }^{4-}$ pyroarsenate (or diarsenate) anions are made up from two $\mathrm{AsO}_{4}$ tetrahedra fused by a bridging O atom. As a characteristic structural feature of inorganic pyrogroups $X_{2} \mathrm{O}_{7}$ [25], the $X-\mathrm{O}$ bond lengths to the bridging O atom are significantly longer than those to the terminal atoms. The corresponding averaged (av) values of $d(\mathrm{As}-\mathrm{O})_{\mathrm{av}}=1.769 \AA$ for bridging and $d(\mathrm{As}-\mathrm{O})_{\mathrm{av}}=1.667 \AA$ 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 $\left(\angle(\right.$ As2-O4-As1 $)=126.0(3)^{\circ}, \angle($ As3-O11-As4 $\left.)=126.3(2)^{\circ}\right)$, and As $\cdots$ As separations (As1 $\cdots$ As2 $=3.1518(8) \AA$; As3 $\cdots$ As4 $=3.1575(8) \AA$ ). In the crystal structure of $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$, 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 $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ in a projection along [ $\overline{1} 00$ ]. Anisotropic displacement parameters are given at the $74 \%$ probability level with Pb in blue, O in white, and As in red. AsO 4 tetrahedra (red) are given in polyhedral representation, and $\mathrm{Pb}-\mathrm{O}$ bonds shorter than $2.7 \AA$ as solid bonds, and between 2.7 and $3.5 \AA$ as open bonds.

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


Figure 2. Temperature-dependent XRPD of $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$.
As a result, $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ shows no phase transition into a higher-symmetric phase upon heating until melting of the compound slightly below $800^{\circ} \mathrm{C}$, in good agreement with the reported melting temperature of $800^{\circ} \mathrm{C}$ [9]. All unit cell parameters (Figure 3) increase more or less in a linear way with temperature, except the $\gamma$ angle that shows a slight decrease. The evolution of unit cell parameters with temperature resembles that of isotypic $\mathrm{Ba}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ [30].

## 3.2. $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$

$\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ adopts the $\mathrm{Ca}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$ structure type [31] and crystallizes isotypically with $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}[19,32,33]$ and $\mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}[30]$. The triclinic crystal structure of $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ 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 $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ can be described as being made up from $\left[\mathrm{PbO}_{8}\right]$ polyhedra (range of $\mathrm{Pb}-\mathrm{O}$ distances 2.442(2)-3.117(3) $\AA$ ) that share common edges $\mathrm{O} 1-\mathrm{O}^{\prime}$ and $\mathrm{O} 5-\mathrm{O} 5^{\prime}$ to form chains extending along [001]. These chains are flanked by dihydrogen arsenate anions parallel to the chain direction at shorter $\mathrm{Pb}-\mathrm{O}$ distances ( $<2.7 \AA$ ) and additionally bonded to dihydrogen arsenate anions that are part of an adjacent chain at longer distances ( $3.11 \AA$ ). 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 $\mathrm{H}_{2} \mathrm{As}(1) \mathrm{O}_{4}$, with two significantly longer As-OH bonds ( $\approx 1.72 \AA ; \mathrm{O} 4, \mathrm{O} 3$ ) and two shorter As-O bonds ( $\approx 1.65 \AA$; O2, O1), whereas the bond lengths of the $\mathrm{H}_{2} \mathrm{As}(2) \mathrm{O}_{4}$ tetrahedron are atypical for a dihydrogen arsenate group: one shorter As-O bond of $1.665 \AA$ to O 5 , two somewhat longer As-OH bonds ( $\approx 1.67 \AA ; \mathrm{O} 7, \mathrm{O} 8$ ), and one long As-OH bond of $1.72 \AA$ (O8) are observed. The $\mathrm{As}(2) \mathrm{O} 4$ group shows very short interpolyhedral $\mathrm{O} \cdots \mathrm{O}$ distances of $\approx 2.45 \AA$ between the two pairs of inversion-related OH groups involving atoms O 7 and O8. For such very strong hydrogen bonds, an asymmetric $\mathrm{O}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bond with a disordered H atom ( $50 \%$ occupation each), or a symmetric $\mathrm{O} \cdots \mathrm{H} \cdots \mathrm{O}$ 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 $\mathrm{O} 8-\mathrm{H} \cdots \mathrm{O}^{\prime}$ that is located between two layers, and the second possibility for the hydrogen
bond $\mathrm{O} 7-\mathrm{H} \cdots \mathrm{O}^{\prime}$ that is located within a layer (Figure 4). Table 3 gives numerical details of the hydrogen bonding scheme for $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$.


Figure 3. $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$. Evolution of unit cell parameters with temperature.
The hydrogen bonding situation in $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ resembles that in the related alkaline earth arsenate $\mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ [30] or in the two polymorphs of $\mathrm{Na}_{5} \mathrm{H}_{3}\left(\mathrm{SeO}_{4}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ [34-37] where interpolyhedral $\mathrm{O} \cdots \mathrm{O}$ distances in the range 2.44-2.48 $\AA$ are observed, and for which either asymmetrical or symmetrical hydrogen bonds were modelled. A special case in this context is $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$. The first two structure refinements of $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$ did not consider H atom positions in the model $[18,32]$, whereas in the latest refinement of $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$ all H atom positions were automatically placed by the refinement program [33]. The resulting hydrogen bonding scheme, however, is highly questionable, with two $\mathrm{O}-\mathrm{H} \cdots \mathrm{O}$ angles less than $130^{\circ}$ and an $\mathrm{O} \cdots \mathrm{O}$ distance of $3.36 \AA$ for one of the reported hydrogen bonds.


Figure 4. The crystal structure of $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ in a projection along [001̄]. 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. $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$. Hydrogen-bond geometry/ $\AA$.


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 $\mathrm{Pb}, \mathrm{As}$ ). 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 $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ and $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ with Their Isotypic Ba and as Analogues

For a structural comparison of the isotypic structures of $M_{2} X_{2} \mathrm{O}_{7}$ and $M\left(\mathrm{H}_{2} \mathrm{XO}_{4}\right)_{2}$ ( $M=\mathrm{Pb}, \mathrm{Ba} ; X=\mathrm{P}, \mathrm{As}$ ), 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 $\left(\mathrm{d}_{\mathrm{av}}\right)$, and the measure of similarity $(\Delta)$ are compiled in Table 4, with the respective lead arsenate as the reference structure.

Table 4. Atom pairs and their absolute distances $|\mathrm{u}| / \AA$ in the isotypic structures of $M_{2} X_{2} \mathrm{O}_{7}$ and $M\left(\mathrm{H}_{2} \mathrm{XO}_{4}\right)_{2}(M=\mathrm{Pb}$, Ba; $X=P, A s)$, as well as degree of lattice distortion (S), arithmetic mean of the distances ( $d_{\mathrm{av}} / \AA$ ), and measure of similarity ( $\Delta$ ). H atoms were not considered for the comparison.

| $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ | $\mathrm{Pb}_{2} \mathbf{P}_{2} \mathrm{O}_{7}$ [18] | \|u| | $\mathrm{Ba}_{2} \mathrm{As}_{2} \mathrm{O}_{7}\left[30{ }^{\text {(1) }}\right.$ | \|u| |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} a=7.13790, b=7.14000, \\ c=13.06810 \AA, \\ \alpha=83.3602, \beta=86.6710, \\ \gamma=89.9469^{\circ} \end{gathered}$ | $\begin{gathered} a=6.9140, b=6.9660, c=12.7510 \AA, ~ \\ \alpha=83.180, \beta=88.860, \gamma=89.640^{\circ} \end{gathered}$ |  | $\begin{gathered} a=7.3996, b=7.3812, c=13.3261 \AA, \\ \alpha=83.116, \beta=86.446, \gamma=89.792^{\circ} \end{gathered}$ |  |
| Pb1 | Pb1 | 0.0609 | Ba2 | 0.2396 |
| O10 | O10 | 0.0699 | O7 | 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 |
| O7 | O7 | 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 |
| $d_{\text {max. }}(\mathrm{A}$ ) |  | 0.2918 |  | 0.2650 |
| $d_{\text {av. }}(\AA)$ |  | 0.1480 |  | 0.1258 |
| $\Delta$ |  | 0.041 |  | 0.043 |
| $\mathbf{~ P b}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ | $\mathbf{P b}\left(\mathbf{H}_{\mathbf{2}} \mathrm{PO}_{4}\right)_{2}$ [19] | \|u| | $\mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}[30]{ }^{(1)}$ | $\|u\|$ |
| $\begin{gathered} a=7.9497, b=8.6137, \\ c=5.9984 \AA, \\ \alpha=108.888, \beta=96.128, \\ \gamma=108.449^{\circ} \end{gathered}$ | $\begin{gathered} a=7.823, \\ \alpha=108.24, \end{gathered}$ | $\begin{aligned} & .856 \AA, \\ & 108.61^{\circ} \end{aligned}$ | $\begin{gathered} a=7.2453, b=7.4341, c=8.1890 \AA \\ \alpha=104.685, \beta=96.210, \gamma=110.276^{\circ} \end{gathered}$ |  |
| 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 |
| O7 | O7 | 0.1049 | O7 | 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 |
| S |  | 0.0151 |  | 0.1107 |
| $d_{\text {max. }}$ ( $\AA$ ) |  | 0.1340 |  | 1.9663 |
| $d_{\text {av. }}(\AA)$ |  | 0.0860 |  | 0.9172 |
| $\Delta$ |  | 0.047 |  | 0.703 |

${ }^{(1)}$ Original unit cell of $\mathrm{Ba}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$ was transformed by $-\mathrm{b},-\mathrm{a},-\mathrm{c}$ to have the same setting as $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$.
$\boldsymbol{M}_{\mathbf{2}} \boldsymbol{X}_{\mathbf{2}} \mathrm{O}_{7}$. The unit cell parameters are similar for the three structures. The highest absolute displacement in the pair $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7} / \mathrm{Pb}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ is observed for one of the terminal O atoms of the $\mathrm{XO}_{4}$ tetrahedra ( $\mathrm{O} 14,0.2918 \AA$ ); in the pair $\mathrm{Pb}_{2} \mathrm{As}_{2} \mathrm{O}_{7} / \mathrm{Ba}_{2} \mathrm{As}_{2} \mathrm{O}_{7}$, the maximum displacement applies to the atom pair O12 (lead compound) and O14 (barium compound) of the same $\mathrm{XO}_{4}$ tetrahedron. Overall, numerical values show a high similarity of the three structures, revealing that the stereochemical influence of the $6 s^{2}$ electron lone pair at the $\mathrm{Pb}^{\mathrm{II}}$ cations is not pronounced in this case.
$M\left(\mathrm{H}_{\mathbf{2}} \mathrm{XO}_{4}\right)_{2}$. The unit cell parameters were very similar for the pair $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2} /$ $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$. The highest absolute displacement relates to O 5 , which is not bonded to a hydrogen atom and is associated with the shortest $\mathrm{Pb}-\mathrm{O}$ 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 $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2} / \mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$. In this case, the unit cell parameters of $\mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ 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 $\S 1.3$ in [40]) for the pair $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2} / \mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ (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 $2 \AA$ for O7 that is involved in formation of the symmetrical hydrogen bond in $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ and in an ordered asymmetric hydrogen bond in $\mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$, respectively. This is an indication that the dissimilarity in the crystal structures of $\mathrm{Pb}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ and $\mathrm{Ba}\left(\mathrm{H}_{2} \mathrm{AsO}_{4}\right)_{2}$ is not primarily associated with the substitution $\mathrm{Pb} \rightarrow \mathrm{As}$ or $\mathrm{As} \rightarrow \mathrm{P}$ but with a change in the hydrogen-bonding system.

## 3.4. $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$

$\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ is a member of the vast family of the apatite $\left[M(1)_{2}\right]\left[M(2)_{3}\right]\left(\mathrm{XO}_{4}\right)_{3} Y$ supergroup $[41,42]$ and belongs to the apatite group, subgroup mimetites- H (mimetite is the Cl -endmember $\left.\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{Cl}[43,44]\right)$. Although a possible mineral phase "mimetite$\mathrm{OH}^{\prime \prime}$ with composition $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ 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 " $\mathrm{Pb}_{4}(\mathrm{PbOH})\left(\mathrm{AsO}_{4}\right)_{3} \cdot \mathrm{H}_{2} \mathrm{O}$ " $\left(=\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3}(\mathrm{OH}) \cdot \mathrm{H}_{2} \mathrm{O}\right)$ [47]] has previously been reported, but its composition was later questioned and revised to $\mathrm{Pb}_{4}(\mathrm{PbOH})\left(\mathrm{AsO}_{4}\right)_{3}\left(=\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3}(\mathrm{OH})\right)$ [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 $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3}(\mathrm{OH})_{0.87}\left(\mathrm{CO}_{3}\right)_{0.04}$ [22]. The current refinement of $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3}(\mathrm{OH})$ 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): $a=10.154, c=7.515 \AA, V=671.02 \AA^{3}$ [49]; $a=10.187$, $c=7.523 \AA, V=676.303(13) \AA^{3}$ [22]; $a=10.14(8), c=7.50(1) \AA, V=669 \AA^{3}$ [50]. Unit cell parameters predicted from elemental radii using pattern recognition and artificial intelligence methods, $a=9.8939, c=7.6039 \AA, V=644.617 \AA^{3}$ [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 $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3}(\mathrm{OH})$, 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. Pb 1 is located on Wyckoff position $4 f$ (site symmetry 3) and has a trigonalprismatic environment if $\mathrm{Pb}-\mathrm{O}$ distances less than $2.8 \AA$ are considered (three more O
atoms cap the lateral faces of the trigonal prism at distances of $3.0 \AA$ ). As a quantitative measure for the reliability of the structure model of apatites, the metaprism twist angle $(\varphi)$, i.e., the $\mathrm{O}(1)-M(1)-\mathrm{O}(2)$ twist angle projected on $(001)$ of the $\left[M(1) \mathrm{O}_{6}\right]$ 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 $P 6_{3} / m$ [52]. From the current refinement of $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}, \varphi$ amounts to $21.9^{\circ}$. This value matches with the metaprism angle of $21.6^{\circ}$ in the analogous crystal structure of the mineral hydroxylpyromorphite, $\mathrm{Pb}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}$, from single-crystal data [53]. The trigonal $\left[\mathrm{Pb}_{6} \mathrm{O}_{6}\right.$ ] metaprism in $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ 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]. Pb 2 (Wyckoff position $6 h, m$..) is surrounded by one arsenate O atom (O1) at a short distance of $2.36 \AA$, and four arsenate O atoms (O3) at longer distances of $\approx 2.62 \AA$. The next nearest O atoms are the hydroxyl O atom O 4 at $2.88 \AA$, followed by O 3 at $3.06 \AA$. 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 $5.071 \AA$ ) formed by the surrounding Pb 2 atoms. The As atom is situated on Wyckoff position $6 h$ and exhibits three equal bond lengths of $1.655 \AA$ to O3 (2x) and O2, and a slightly longer bond length to O1 ( $1.681 \AA$ ). The average As-O bond length of $1.662 \AA$ 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 $1.689 \AA[56])$. The crystal structure of $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ is depicted in Figure 5.


Figure 5. The crystal structure of $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ in a projection along [00 $\left.\overline{1}\right]$. Color codes and displacement ellipsoids are as in Figure 1. The O atom of the hydroxyl group is given in yellow, and the [ Pb 1 O 6$]$ 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 $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}$ from powder synchrotron X-ray data [22], the $\mathrm{Pb}-\mathrm{O}$ and $\mathrm{As}-\mathrm{O}$ bond lengths are the same within the $3 \sigma$ range, with the exception of the $\mathrm{Pb}-\mathrm{O} 4$ bond involving the hydroxyl group (Table 2). The latter bond is by $0.2 \AA$ 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, O 4 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
$\mathrm{Pb}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}$ (space group $\mathrm{Pb}_{3} / m$ ) was modelled in different ways. Whereas for natural hydroxylpyromorphite (containing small amounts of fluorine; single-crystal data; [53]) and synthetic $\mathrm{Pb}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}$ (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 $\mathrm{Pb}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}$ (neutron data from polycrystalline material) with $\mathrm{z}=0.3565$ [58]. All other structurally determined $M_{5}\left(\mathrm{XO}_{4}\right)_{3} \mathrm{OH}$ apatite phases reported up to date were modelled with a disordered hydroxyl group, viz. $\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}$ $\left(P 6_{3} / m ; z=0.195\right)$ [59], $\mathrm{Ca}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}\left(P 6_{3} / m ; z=0.1919\right)$ [60], $\mathrm{Sr}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}\left(P 6_{3} / m ;\right.$ $z=0.1856)$ [61], $\mathrm{Sr}_{5}\left(\mathrm{AsO}_{4}\right)_{3} \mathrm{OH}\left(\mathrm{Pb}_{3} / m ; z=0.1919\right)$ [62], $\mathrm{Ba}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}\left(\mathrm{Pb}_{3} ; z=0.148\right)$ [63], and $\mathrm{Cd}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}(z=0.1880)$ [64].

## 3.5. $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$

$\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ 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 $\mathrm{Pb}^{\text {II }}$ that occupies a volume close to that of oxygen allows lacunar apatite structures to be stable [65]. In contrast to a previous refinement of $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ (polycrystalline material prepared by a ceramic route) based on laboratory powder X-ray data and performed in space group $\mathrm{Pb}_{3} / m$ [66], the current single-crystal X-ray data for hydrothermally grown crystals clearly revealed a lower symmetry in space group $P \overline{3}$ due to the violation of reflection condition $l=2 n$ for $00 l$ reflections. For example, reflection 003 has an average $F_{\text {obs }}{ }^{2}$ 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 $\mathrm{NaPb}_{4}\left(\mathrm{PO}_{4}\right)_{3}$ (single-crystal X-ray data) has also been reported to crystallize in space group $P 6_{3} / m$ in the apatite-type of structure $[67,68]$. The question of whether the lower space group symmetry of $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ 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 $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ in a projection along [00 $\left.\overline{1}\right]$. Color codes and displacement ellipsoids are as in Figure 1. The [M1aO6] metaprism is displayed as a turquoise polyhedron and the [M1bO6] metaprism as a blue polyhedron.

According to space group symmetry $P \overline{3}, \mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ belongs to the belovite group within the apatite supergroup [41]. To the best of the author's knowledge, $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ is the first representative of a lacunar apatite comprising solely of $\mathrm{XO}_{4}$ groups as anions, adopting the belovite structure type. In comparison with $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3}(\mathrm{OH})$, the unit cell
volume is reduced by about $4.5 \%$ due to incorporation of smaller $\mathrm{Na}^{\mathrm{I}}$ (ionic radii: $\mathrm{Na}^{\mathrm{I}}$ [IX] $=1.24 \AA$ versus $\mathrm{Pb}^{\mathrm{II}}$ [IX] = $\left.1.35 \AA[69]\right)$. In comparison with the apatite structure type in space group $P 6_{3} / m$, the $M 1$ position related with the metaprism is split into two positions in the belovite structure type (M1a, M1b) that each are located on Wyckoff position $2 d$ (site symmetry 3). Both positions show occupational disorder of $\mathrm{Na} / \mathrm{Pb}$, however, with different absolute ratios. Whereas M1a shows a minor fraction of lead(II) (Pb1a: site occupancy 0.15), the situation for M 1 b is reversed ( Pb 1 b : 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 $\left[\mathrm{M1aO}_{6}\right]$ and a greater volume of $19.04 \AA^{3}$ for Pb -rich $\left[\mathrm{M1bO} \mathrm{O}_{6}\right]$. The angles $\varphi$ for the corresponding metaprisms amount to $24.5^{\circ}$ for O1-(M1a)-O2 and to $45.6^{\circ}$ for O2-(M1b)O3. The latter value is the highest observed for any apatite structure [52] and reflects the high distortion of the $\left[M 1 \mathrm{bO}_{6}\right]$ 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) $\AA$ for $\left[M 1 \mathrm{aO}_{6}\right]$ and 3.070 for $\AA$ for $\left[M 1 \mathrm{bO}_{6}\right]$. The $M 2$ site of $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ is located on a general position $(6 \mathrm{~g})$ of space group $P \overline{3}$. According to refinements of the s.o.f. for this site, significant amounts of $\mathrm{Na}^{\mathrm{I}}$ are not incorporated, and consequently only $\mathrm{Pb}^{\mathrm{II}}$ is situated on this position. The channel diameter for the empty channel defined by Pb 2 atoms is $5.150 \AA$. In comparison with $\mathrm{Pb}_{5}\left(\mathrm{AsO}_{4}\right)_{3}(\mathrm{OH})$, the $\mathrm{As}-\mathrm{O}$ bond lengths of the $\mathrm{AsO}_{4}$ tetrahedron in the crystal structure of $\mathrm{NaPb}_{4}\left(\mathrm{AsO}_{4}\right)_{3}$ are slightly enlarged $\left(d(\mathrm{As}-\mathrm{O})_{\text {av }}=1.684 \AA\right)$.

## 3.6. $\mathrm{Pb}_{4} \mathrm{As}_{2} \mathrm{O}_{9}$

From an investigation of the $\mathrm{PbO} / \mathrm{As}_{2} \mathrm{O}_{5}$ phase diagram, the phase $\mathrm{Pb}_{4} \mathrm{As}_{2} \mathrm{O}_{9}$ was reported to exist up to a temperature of $740{ }^{\circ} \mathrm{C}$ when decomposition through a peritectoid is observed [9]. In the present study, annealing temperatures above ( $750{ }^{\circ} \mathrm{C}$ ) and below $\left(680{ }^{\circ} \mathrm{C}\right)$ the peritectoid were chosen for phase mixtures with a molar ratio of $\mathrm{PbO}: \mathrm{As}_{2} \mathrm{O}_{5}=4: 1$. However, in both cases, only the phases $\mathrm{Pb}_{3}\left(\mathrm{AsO}_{4}\right)_{2}$ and $\mathrm{Pb}_{8}\left(\mathrm{AsO}_{4}\right)_{2} \mathrm{O}_{5}$ were observed as reaction products. Therefore, different molar ratios and/or annealing temperatures might be necessary to reproduce the reported formation of $\mathrm{Pb}_{4} \mathrm{As}_{2} \mathrm{O}_{9}$ [9].

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