

The Crystal Structures of Ag_2PbO_2 and $\text{Ag}_5\text{Pb}_2\text{O}_6$

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Ag_2PbO_2 was first synthesized by Bullnheimer¹ in the following way: AgNO_3 is mixed with KOH and enough NH_3 is added to dissolve the precipitate. A small amount of this solution is mixed with about the same amount of a potassium plumbite solution of the same molarity as the silver solution. If a precipitate is formed, more NH_3 is added to the silver solution. When enough NH_3 is present to prevent precipitation, the two main solutions are mixed and warmed on a steambath. If the surplus of NH_3 is not too large, a crust of crystals of Ag_2PbO_2 is formed almost immediately. Ag_2PbO_2 forms brown prismatic crystals with metallic lustre. The density was determined by Bullnheimer to be 8.60.

X-ray investigation with the Laue method showed that the symmetry is monoclinic. Rotation photographs around $[010]$, $[100]$ and $[11\bar{1}]$ and Weissenberg photographs of the reflexions $h0l$, $h1l$, $0kl$, $1kl$ and h , k , $h+k$ (Cu-K radiation) showed that the structure can be described in a body-centered cell with the dimensions: $a = 6.082 \pm 0.003 \text{ \AA}$, $b = 8.715 \pm 0.003 \text{ \AA}$, $c = 6.556 \pm 0.003 \text{ \AA}$, $\beta = 93.69^\circ$. The dimensions are determined from powder photographs, taken with focussing cameras with Cr-K radiation (Table 4).

The following reflexions appeared:

$$\begin{aligned} hkl & \text{ for } h + k + l = 2n \\ h0l & \text{ for } h = 2n \text{ and } l = 2n \\ 0kl & \text{ for } k + l = 2n \\ hk0 & \text{ for } h + k = 2n \end{aligned}$$

If it is assumed that the structure is centro-symmetric, then the space group is $C_{2h}^6 - I^2/c$.

With a cell content of 4 Ag_2PbO_2 the density can be calculated to be 8.72, in satisfying agreement with Bullnheimer's experimental value of 8.60. Thus

there are 8 Ag, 4 Pb, and 8 O atoms in the unit cell. In C_{2h}^6 only the following arrangement of the metal atoms gave calculated intensities in agreement with those observed:

$$\begin{aligned}
 &(000; 1/2 \ 1/2 \ 1/2) + \\
 &4 \text{ Ag}_1 \text{ in } 4 \ (b) : 0 \ 1/2 \ 0; \ 0 \ 1/2 \ 1/2. \\
 &4 \text{ Ag}_2 \text{ in } 4 \ (d) : 1/4 \ 1/4 \ 3/4; \ 3/4 \ 1/4 \ 3/4. \\
 &4 \text{ Pb in } 4(e) : 0 \ \bar{y} \ 1/4; \ 0 \ \bar{y} \ 3/4. \qquad y = 0.125
 \end{aligned}$$

The Weissenberg photographs showed strong absorption effects, especially those with $[010]$ and $[11\bar{1}]$ as rotation axis.

There is, however, one discrepancy among the $h0l$ reflexions which seems difficult to explain, *viz.* that 604 is visible but not $60\bar{4}$. If the small contribution from the oxygen atoms to the intensities is not taken into account, then it follows that $I(hkl) \sim I(hk\bar{l})$. As no deviation from this condition appeared among the $1kl$ reflexions, only those with l positive are listed in the table. However, the difference in intensity between 604 and $60\bar{4}$ might be due to some deviation from the centrosymmetry. As the atomic positions in the yz -plane are ascertained beyond doubt by the Fourier synthesis, this difference might imply that there are some deviations from the suggested coordinates in the x -direction. In the space group C_s^4-I2 , which would then apply, the x -parameter of the lead atoms can be arbitrarily fixed to 0. A variation of the x -parameter of the Ag_1 and Ag_2 atoms shows, however, that these atoms can be moved at the most $\sim \pm 0.03$ from the suggested positions, but that the agreement between observed and calculated intensities is not improved for any combination of the x -parameters within these limits. As there is no structural indication, that these small displacements from the positions in C_{2h}^6 really exist, it seems more probable that the difference in observed intensity between 604 and $60\bar{4}$ has another origin than an error in the suggested atomic positions.

In all the photographs the inner reflexions are considerably weaker than was calculated. Therefore, it could hardly be expected that it would be possible to derive the oxygen atoms from the intensities. A Fourier synthesis using the $0kl$ reflexions (Fig. 1) showed, in addition to the metal atom maxima, several minor peaks, but the number of these peaks is larger than the number of oxygen atoms in the cell. However, a careful inspection of the intensities of the reflexions (Table 2) disclosed a couple of discrepancies which must be due to the fact that the influence of the oxygen atoms is not taken into account. These discrepancies are:

- 1) 020 is visible, although $F_{\text{Met}} = 0$
- 2) 011 is visible but not $\bar{1}10$, although for both reflexions $|F_{\text{Met}}| = 44$.

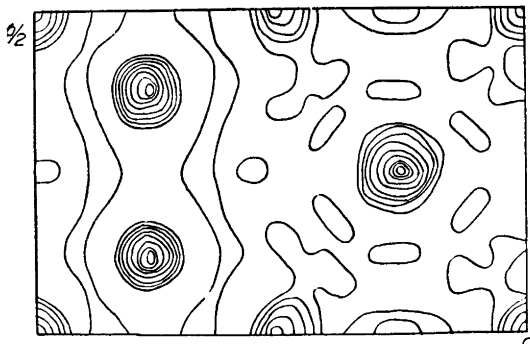


Fig. 1. Ag₂PbO₂. Projection of the electron density on the *yz*-plane. Compare Fig. 2.

Obviously, the oxygen atoms must be placed so that $F_{\text{oxyg}}(020)$ will be large and so that $|F_{\text{Met}}(011) + F_{\text{oxyg}}(011)| > |F_{\text{Met}}(\bar{1}10) + F_{\text{oxyg}}(\bar{1}10)|$. These conditions do not suffice to determine the positions of the oxygen atoms. However, from previous investigations of lead oxides it is known that the distance Pb²⁺—O is 2.15 Å or larger. The distance Ag⁺—O can hardly be shorter than 2.0 Å, as 2.05 Å is found for two-coordinated silver atoms in Ag₂O.

To account for the visibility of 020, the oxygen atoms must be situated approximately at $y = 0$ and $1/2$ or at $y = \pm 1/4$. An inspection of the positions with $y \sim 0$ and $1/2$ shows that no reasonable arrangement of the oxygen atoms can be obtained for these z -values. However, for $y \sim \pm 1/4$, an arrangement of the oxygen atoms can be worked out, which gives reasonable distances to both the Pb and the Ag atoms. The oxygen parameters are:

$$(000; 1/2 \ 1/2 \ 1/2) + 8 \ 0 \ \text{in} \ 8 \ (f); \pm (x, y, z); \pm (x, y, 1/2-z) \text{ with } x = 0.311, y = 0.195 \text{ and } z = 0.446.$$

The following F -values are obtained:

$h \ k \ l$	F_{Met}	F_{oxyg}	ΣF	$ F_{\text{obs}} $
020	0	— 38	— 38	48
011	— 44	— 17	— 61	50
$\bar{1}10$	44	— 7	37	< 50

As will be seen, this arrangement of the oxygen atoms accounts for both the visibility of 020 and the higher intensity of 011 compared with $\bar{1}10$.

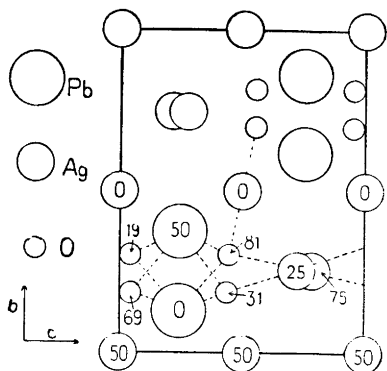


Fig. 2. Ag_2PbO_2 . Projection of the structure on the yz -plane. Large circles denote lead atoms, medium circles silver atoms and small circles oxygen atoms. The figures denote the height of the atoms in percentages of a . The metal-oxygen bonds are shown with dotted lines. Superimposed silver atoms in $a = 1/4$ and $3/4$ are symmetrically displaced.

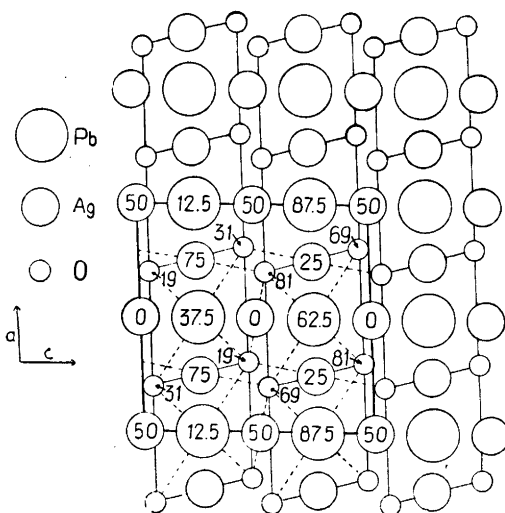


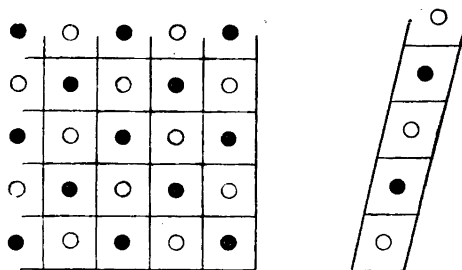
Fig. 3. Ag_2PbO_2 . Projection on the xz -plane. Large circles denote lead atoms, medium circles silver atoms and small circles oxygen atoms. The figures denote the height of the atoms in percentages of b . Compare Fig. 2.

The interatomic distances are:

Pb — 2 O = 2.28 Å	Ag ₁ — 2 O = 2.08 Å	O — O = 2.79 Å
Pb — 2 O = 2.37 Å	Ag ₂ — 2 O = 2.10 Å	(shortest distance)
Pb — 2 Pb = 3.74 Å	Ag ₁ — 2 Ag ₁ = 3.28 Å	
Pb — 2 Pb = 3.94 Å	Ag ₂ — 2 Ag ₂ = 3.04 Å	
Pb — 2 Ag ₁ = 3.65 Å	Ag ₁ — 2 Ag ₂ = 3.07 Å	
Pb — 2 Ag ₂ = 3.61 Å	Ag ₂ — 2 Ag ₁ = 3.18 Å	

The structure is given in Figs. 2 and 3. The coordination figure of the lead atom is of the same type as in tetragonal PbO (Dickinson and Friauf², Moore and Pauling³, Byström⁴) but here the oxygen atoms are displaced a little from the corners of a square, so that they form a very distorted tetrahedron with the lead atom outside the tetrahedron. The mean distance Pb—O, which is 2.32 Å is very close to the value in tetragonal PbO (2.30 Å). The low oxygen tetrahedra form chains in the a -direction with lead atoms alternately above and below the chains. Thus every chain forms a one-dimensional complex of the formula $(\text{PbO}_2^{2-})_\infty$ (Fig. 4), whereas in tetragonal PbO there are two-dimensional layers of the formula $(\text{PbO})_\infty$ (Fig. 4). These $(\text{PbO}_2^{2-})_\infty$ -

Fig. 4. A two-dimensional layer of the composition $(\text{PbO})_\infty$ in tetragonal PbO and a one-dimensional chain of the composition $(\text{PbO}_2^{2-})_\infty$ in Ag_2PbO_2 . Filled circles denote lead atoms below the layer or chain respectively and open circles lead atoms above the layer or chain.



chains are linked together by the Ag-atoms, each silver atom forming two linear bonds of the length 2.08 Å (Ag_1) or 2.10 Å (Ag_2) with two oxygen atoms belonging to different chains. Thus the Ag-atoms knit the chains together to a three-dimensional framework.

It is also of interest to note that the prism axis of the crystals and the direction of the $(\text{PbO}_2^{2-})_\infty$ -chains coincide, *i. e.* the crystals grow fastest in the chain direction.

2. $\text{Ag}_5\text{Pb}_2\text{O}_6$

In the course of the attempts to produce single crystals of lead oxides hydrothermally (Byström⁵) a substance was obtained in the form of large hexagonal plates or hexagonal prisms. These crystals were first assumed to belong to a new lead oxide and gave beautiful X-ray photographs. The unit cell is hexagonal with $a = 5.939 \pm 0.003$ Å and $c = 6.428 \pm 0.003$ Å. The structure could not, however, be solved assuming only lead atoms (and oxygen atoms) in the unit cell. As the syntheses were carried out in silver crucibles, the only possible metal constituent besides lead in the substance is silver. As the yield of the phase by these first syntheses was only some ten mg, an analysis without a micro balance was not possible. However, by assuming five silver atoms and two lead atoms in the unit cell, a reasonable agreement between observed and calculated intensities was obtained.

As the substance was of considerable interest for the crystal chemistry of both silver and lead, an attempt has been made to solve the structure completely. Obviously the first step was to establish the formula. A series of hydrothermal syntheses were carried out in the temperature range 250°—300° C. Mixtures of Ag_2O and PbO_2 in various proportions were heated either with H_2O only or with a 5% NaOH solution for about seven days. Mostly only a few crystals of the hexagonal phase were obtained, and as the crystals grew from the silver oxide (or silver) powder, a separation of the phases was

Table 1. Ag_2PbO_2 . Powder photographs. Cr-K radiation. β -reflexions are omitted.

<i>I</i>	$\sin^2\Theta_{obs}$	<i>h k l</i>	$\sin^2\Theta_{calc}$	<i>I</i>	$\sin^2\Theta_{obs}$	<i>h k l</i>	$\sin^2\Theta_{calc}$
m	0.1226	002	0.1226	m	0.4675	150	0.4671
st	0.1312	12 $\bar{1}$	0.1309	m	0.4760	330	0.4757
st	0.1392	121	0.1394	w	0.4855	312	0.4858
w	0.1425	200	0.1424	st	0.4905	004	0.4904
st	0.1677	11 $\bar{2}$	0.1669	st	0.5245	24 $\bar{2}$	0.5242
st	0.1820	21 $\bar{1}$	0.1818			30 $\bar{3}$	0.5581
m	0.1843	112	0.1839	m	0.5583	242	0.5582
st	0.1861	031	0.1859	w	0.5702	400	0.5696
v st	0.1911	{130 022}	{0.1909 0.1916}	v w	0.5792	15 $\bar{2}$	0.5812
m	0.1989	211	0.1988			41 $\bar{1}$	0.6004
m	0.2116	220	0.2114	v w	0.5997	20 $\bar{4}$	0.5988
st	0.3682	12 $\bar{3}$	0.3676			143	0.6004
m	0.3931	123	0.3932			152	0.5982
m	0.3990	042	0.3939	w	0.6279	23 $\bar{3}$	0.5990
st	0.4108	21 $\bar{3}$	0.4100	v w	0.6593	32 $\bar{3}$	0.6271
m	0.4187	240	0.4186			40 $\bar{2}$	0.6582
st	0.4315	{321 033}	{0.4328 0.4312}	m	0.6663	204	0.6668
st $^-$	0.4355	31 $\bar{2}$	0.4348	w	0.6846	134	0.6643
st	0.4620	{213 051}	{0.4610 0.4622}	v w	0.6921	224	0.6678
				w	0.6985	161	0.6833
						134	0.6917
							0.6983

impossible. However, a reasonable amount of the substance could be separated from a sample with a large surplus of lead (Pb:Ag 2 : 1) and analyses could be made on 50 mg samples. The following percentages were obtained:

Ag (as AgCl)	: 51.0 \pm 0.5 %	Ag:	51.39 %
Pb (as PbSO ₄)	: 39.0 \pm 0.5	Calculated for Ag ₅ Pb ₂ O ₆ :	Pb: 39.44
O (peroxide)	: 2.32 \pm 0.02	O:	2.29

The peroxide oxygen was determined by dissolving the substance in a measured amount of oxalic acid and by titrating the excess of oxalic acid with KMnO₄.

Because of the limited amount of material a reliable determination of water could not be carried out. However, the only possible modification of the formula would be Ag₅Pb₂O₆ · H₂O (calculated percentages: Ag: 50.51, Pb: 38.81, O: 2.25), but as the structure determination will show, this formula is very improbable for space and symmetry reasons.

The Weissenberg photographs showed that the Laue symmetry was D_{6h} — $6/mmm$ (at least for the arrangement of the metal atoms). As no systematic extinctions appeared, the possible space groups are D_{6h}^1 , D_6^1 , C_{6v}^1 , D_{3h}^1 , D_{3h}^3 .

Table 2. Ag_2PbO_2 . Comparison between observed and calculated intensities. The influence of the oxygen atoms on the intensities is not taken into account. Cu-K radiation. Observed intensities from Weissenberg photographs.

hkl	$ F_{\text{obs}} $	F_{Met}	hkl	$ F_{\text{obs}} $	F_{Met}
	0 kl reflexions				
002	160	- 287	190	< 120	34
004	300	484	1110	190	- 195
006	210	- 193	121	140	- 283
008	300	332	141	< 80	0
020	48	0	161	190	219
040	< 60	26	181	< 120	0
060	< 80	0	1101	180	- 168
080	210	392	132	80	51
0100	< 70	0	152	< 100	41
011	30	44	172	240	- 243
013	< 60	40	192	180	- 214
015	< 80	- 39	123	270	257
017	< 80	33	143	< 100	0
022	240	300	163	240	- 202
024	< 80	0	183	< 110	0
026	210	196	1103	130	162
028	< 60	0	114	< 100	39
031	250	- 355	134	340	- 267
033	320	298	154	330	- 246
035	232	- 249	174	< 120	33
037	220	210		$h0l$ reflexions	
042	236	246	200	230	280
044	< 80	9	400	320	470
046	180	180	600	220	184
051	280	315	202	-	26
053	290	- 268	402	280	- 222
055	270	242	602	-	8
057	190	- 200	20 $\bar{2}$	-	22
062	140	224	40 $\bar{2}$	320	- 216
064	< 75	0	60 $\bar{2}$	-	- 18
066	140	174	204	220	252
071	< 75	37	404	320	408
073	< 75	- 36	604	-	185
075	< 75	34	20 $\bar{4}$	330	240
082	170	- 186	40 $\bar{4}$	260	392
084	290	352	60 $\bar{4}$	300	162
091	< 75	- 30	206	-	8
093	100	34	406	480	- 176
	1 kl reflexions		20 $\bar{6}$	-	3
130	300	- 338	40 $\bar{6}$	450	- 168
150	230	- 294	208	420	162
170	< 120	37			

hkl	$ F_{\text{obs}} $	F_{Met}	hkl	$ F_{\text{obs}} $	F_{Met}
	hkl reflexions				
110	—	44	217	470	213
310	—	40	417	—	32
510	—	40	21 $\bar{7}$	450	208
710	—	33	41 $\bar{7}$	—	32
011	80	— 44	$\bar{1}76$	280	— 196
211	170	— 344	$\bar{2}75$	320	206
411	—	— 42	$\bar{3}74$	80	35
611	140	— 221	$\bar{4}73$	—	— 35
21 $\bar{1}$	220	337	$\bar{5}72$	180	— 206
41 $\bar{1}$	—	40	$\bar{6}71$	160	196
61 $\bar{1}$	200	221	066	270	176
112	160	— 347	$\bar{1}65$	330	180
312	220	— 298	$\bar{2}64$	350	196
512	140	— 245	$\bar{3}63$	250	— 188
712	100	— 205	$\bar{4}62$	125	192
11 $\bar{2}$	130	— 347	$\bar{5}61$	110	178
31 $\bar{2}$	160	— 293	$\bar{6}60$	150	176
51 $\bar{2}$	100	— 239	257	75	— 32
71 $\bar{2}$	90	— 200	156	—	36
013	—	41	055	500	232
213	130	303	$\bar{1}54$	380	— 250
413	—	38	$\bar{2}53$	—	— 39
613	100	214	$\bar{3}52$	—	39
21 $\bar{3}$	130	296	$\bar{4}51$	190	— 178
41 $\bar{3}$	—	38	$\bar{5}50$	160	— 223
61 $\bar{3}$	80	210	$\bar{6}5\bar{1}$	—	— 36
114	—	42	246	530	356
314	—	38	145	—	0
514	—	35	044	—	10
11 $\bar{4}$	—	37	$\bar{1}43$	—	0
31 $\bar{4}$	—	35	$\bar{2}42$	450	478
51 $\bar{4}$	—	33	$\bar{3}41$	—	0
015	55	— 38	$\bar{4}40$	—	10
215	450	— 250	$\bar{5}4\bar{1}$	—	0
415	—	— 34	$\bar{6}4\bar{2}$	410	350
615	280	— 199	336	100	34
21 $\bar{5}$	500	— 244	235	—	— 36
41 $\bar{5}$	—	— 32	134	350	— 263
116	550	— 236	033	470	307
316	420	— 221	$\bar{1}32$	—	42
516	320	— 200	231	—	— 42
11 $\bar{6}$	550	229	$\bar{3}30$	300	— 292
31 $\bar{6}$	400	— 214	$\bar{4}3\bar{1}$	180	263
51 $\bar{6}$	300	— 197	$\bar{5}3\bar{2}$	—	34
017	—	34	$\bar{6}3\bar{3}$	—	— 29

<i>h k l</i>	$ F_{\text{obs}} $	F_{Met}	<i>h k l</i>	$ F_{\text{obs}} $	F_{Met}
426	310	172	516	270	- 195
325	270	- 186	415	-	- 37
224	210	224	314	-	38
123	220	246	213	280	296
022	360	314	112	180	- 338
$\bar{1}21$	260	- 284	011	50	- 44
$\bar{2}20$	300	296	$\bar{1}10$	-	- 44
$\bar{3}2\bar{1}$	170	262	$\bar{2}1\bar{1}$	200	338
$\bar{4}2\bar{2}$	210	216	$\bar{3}1\bar{2}$	250	- 292
$\bar{5}2\bar{3}$	190	- 184	$\bar{4}1\bar{3}$	-	- 38
$\bar{6}2\bar{4}$	180	168	$\bar{5}1\bar{4}$	-	37

Only one arrangement of the metal atoms in the *xy*-plane was found which agreed with the observed intensities. This can be described in any of the above-mentioned space groups with the following *x y* coordinates:

- 2 Ag in 0 0 and 0 0
- 3 Ag in 1/2 0; 0 1/2; 1/2 1/2
- 2 Pb in 1/3 2/3; 2/3 1/3

The lead atom position and the three-fold silver atom position are parameter-free in the *c*-direction in D_{6h}^1 , D_6^1 , D_{3h}^3 and D_{3h}^1 . However, agreement between observed and calculated intensities could not be obtained by varying the *z*-parameters of the silver atoms in 0 0 and thus the space group for the metal atoms must be C_{6v}^1 — $C6mm$. In C_{6v}^1 the metal atoms occupy the following positions:

- 1 Ag₁ in 1 (*a*): 0 0 z_1
- 1 Ag₂ in 1 (*a*): 0 0 z_2
- 3 Ag₃ in 3 (*c*): 1/2 0 z_3 ; 0 1/2 z_3 ; 1/2 1/2 z_3
- 2 Pb in 2 (*b*): 1/3 2/3 z_4 ; 2/3 1/3 z_4

Because of the symmetry, the *z*-parameters can be arbitrarily chosen so that $z_1 = -z_2$. The intensity of the reflexions 00*l* showed that z_3 and z_4 must be close to the parameter-free values of the positions 2 (*c*) and 3 (*g*) in the space group D_{6h}^1 and that z_1 must be approximately 1/4. In the Weissenberg photograph the reflexions 00*l*, because of the habit of the crystal (a hexagonal plate), showed up very strong, as also the *h* 0 *l* reflexions with *l* high. This influence of the crystal habit on the intensity could be easily traced in the photographs from the variation in the general blackening. By the final adjuste-

Table 3. $Ag_5Pb_2O_6$. Powder photographs. Cr-K radiation. The influence of the oxygen atoms on the intensities is not taken into account. β -reflexions are omitted.

hkl	$\sin\Theta_{\text{obs}}^2$	$\sin\Theta_{\text{calc}}^2$	I_{obs}	I_{calc}	hkl	$\sin\Theta_{\text{obs}}^2$	$\sin\Theta_{\text{calc}}^2$	I_{obs}	I_{calc}
011	0.0808	0.0814	w^-	3.9	004	0.5082	0.5082	m^-	3.8
002	0.1268	0.1270	w^+	9.1	014	0.5573	0.5578	$v\ w$	0.8
110	0.1489	0.1488	st	21	032	—	0.5734	—	0.3
012	0.1764	0.1766	st	34	220	0.5957	0.5952	st	11
111	0.1804	0.1806	st^-	29	221	—	0.6270	—	0.1
020	0.1985	0.1984	w	6.7	213	—	0.6330	—	0.1
021	0.2302	0.2302	st	25	310	—	0.6448	—	0.2
112	0.2745	0.2758	$v\ w$	0.7	114	0.6568	0.6580	w	6.0
003	—	0.2858	—	0.2	311	—	0.6765	—	0.7
022	0.3253	0.3254	$v\ w$	0.8	024	0.7070	0.7066	$v\ w$	2.4
013	—	0.3354	—	0.1	222	0.7231	0.7222	w	8.1
210	0.3474	0.3472	$v\ w$	0.4	033	0.7314	0.7322	w	8.8
211	0.3799	0.3790	w	1.0	312	0.7720	0.7718	m	15
113	0.4349	0.4346	st	10	040	—	0.7936	—	1.6
030	0.4462	0.4464	m	4.2	005	—	0.7940	—	0.0
212	0.4737	0.4752	st	16	041	0.8245	0.8254	m^-	9.5
031	0.4782	0.4782	m	7.2	015	—	0.8436	—	0.9
023	0.4837	0.4842	m	6.6	214	—	0.8554	—	2.2
					223	—	0.8810	—	0.8

ment of the z -parameters only reflexions from those parts of photographs were compared, where no noticeable changes in the general blackening occurred, *i. e.* the reflexions with $l = 5, 6, 7$ and 8. The following values of the z -parameters were obtained:

$$\begin{array}{ll}
 2\pi z_1 = 95^\circ & z_1 = 0.264 \\
 2\pi z_2 = -95^\circ & z_2 = -0.264 \\
 2\pi z_3 = 188^\circ & z_3 = 0.522 \\
 2\pi z_4 = 8^\circ & z_4 = 0.022
 \end{array}$$

As will be seen (Table 4), the agreement between observed and calculated F -values is very good for these reflexions with high l -indices.

The positions of the oxygen atoms cannot be deduced directly from the intensities, as they have only very little influence on the intensity of these high-angle reflexions, the F -values of which can be estimated with the best accuracy. However, a consideration of the positions in C_{6h}^1 shows that the one-fold positions cannot possibly be occupied by oxygen atoms, because in that case Ag—O distances of 1.7 Å or less would result. For the same reason the formula cannot be $Ag_5Pb_2O_6 \cdot H_2O$. The six-fold positions lead to unacceptable O—O distances ~ 2 Å. A combination of three two-fold positions

Table 4. Ag₅Pb₂O₆. Comparison between observed and calculated intensities. Observed intensities from Weissenberg photographs. The influence of the oxygen atoms on the intensities is not taken into account. Cu—K radiation.

<i>h k l</i>	$ F_{\text{obs}} $	$ F_{\text{calc}} $	<i>h k l</i>	$ F_{\text{obs}} $	$ F_{\text{calc}} $
100	30	34	055	30	38
200	120	118	016	120	100
300	160	152	026	< 24	30
400	100	85	036	50	48
500	< 30	22	017	28	37
600	180	193	027	90	94
110	80	180	037	100	120
210	20	28	018	55	55
310	50	27	011	14	41
410	150	124	021	64	180
510	40	21	031	57	140
610	40	20	041	50	140
220	170	262	051	< 24	18
320	< 30	24	061	< 24	16
420	70	71	012	43	180
520	150	103	022	17	31
330	150	114	032	< 24	30
430	20	20	042	< 24	27
001	14	15	052	40	110
002	90	180	062	38	100
003	< 14	40	013	< 17	14
004	190	260	023	52	140
005	31	16	033	38	140
006	150	140	043	38	110
007	40	48	053	24	12
008	140	160	063	38	29
015	45	45	014	38	49
025	120	140	024	43	110
035	90	105	034	52	120
045	110	130	044	24	67
			054	19	36

is also impossible for space reasons and also 6 O in 2 · 2 (b) + 3 (c). Then the only possibility which remains is that the six oxygen atoms are placed in two three-fold positions: 1/2 0 z; 0 1/2 z; 1/2 1/2 z. However, if the distance between superimposed oxygen atoms is assumed to be 2.6 Å, which is reasonable, then the two Ag₃—O distances will be only 1.91 Å (*cf.* 2.05 Å in Ag₂O), and if the Ag₃—O distances are increased to 2.05 Å then the O—O distances will be only 2.3 Å. Further, this alternative would imply six lead bonds, directed to the corners of a trigonal prism: a rather unlikely configuration.

A far more satisfying distribution of the oxygen atoms is obtained if the symmetry is lowered to C_{3v}^2-C31m . Then the two oxygen triangles can be moved around the three-fold axis, so that the lead atom is linked to six oxygen atoms, situated at the corners of a distorted octahedron. The parameters of the oxygen atoms are:

$$C_{3v}^2 - C31m$$

$$3 \text{ O in } 3 (c): x_5 \ 0 \ z_5; 0 \ x_5 \ z_5; \bar{x}_5 \ \bar{x}_5 \ z_5; \quad x_5 = 0.603, z_5 = 0.205$$

$$3 \text{ O in } 3 (c): x_6 \ 0 \ z_6; 0 \ x_6 \ z_6; x_6 \ x_6 \ z_6; \quad x_6 = 0.397, z_6 = -0.171$$

The influence of the oxygen atoms on the intensities is in most cases too small to be observed. However, a recalculation of the $00l$ reflexions shows that the incorporation of the scattering of the oxygen atoms in the F -values leads to a still better agreement between observed and calculated intensities. The observed F -values have been multiplied with a factor, to allow for the stronger influence of the absorption on the inner reflexions. This factor is taken as $A = \left| \frac{F_{\text{calc}}}{F_{\text{obs}}} \right|$ for the reflexions with h even. On these reflexions the oxygen atom has only a negligible influence. The values for l odd are then extrapolated (for 001) or interpolated. The values of $|F_{\text{obs}}| \cdot A$ are compared below with the calculated F values:

$h \ k \ l$	001	002	003	004	005	006	007	008
$ F_{\text{obs}} \cdot A$	40	180	<25	260	37	150	40	140
$ F_{\text{calc}} $ (only metal atoms)	15	180	40	260	16	140	48	160
$ F_{\text{calc}} $ (metal + oxygen)	31	160	14	260	28	150	42	150

As will be seen, the agreement for the reflexions with l odd is much improved when allowing for the influence of the oxygen atoms, and thus the arrangement of the oxygen atoms in the z -direction is substantiated.

The following interatomic distances are obtained:

Pb — 6 O	= 2.19 Å	Ag ₁ — 3 O	= 2.39 Å	O ₁ — O ₂	= 2.75 Å
Pb — 3 Pb	= 3.43 Å	Ag ₂ — 3 O	= 2.44 Å	O ₁ — O ₁	= 3.15 Å
Pb — 3 Ag ₁	= 3.76 Å	Ag ₁ — Ag ₂	= 3.04 Å	O ₂ — O ₂	= 3.15 Å
Pb — 3 Ag ₂	= 3.89 Å	Ag ₁ — 6 Ag ₃	= 3.40 Å	Ag ₃ — 2O	= 2.07 Å
Pb — 6 Ag ₃	= 3.64 Å	Ag ₂ — 6 Ag ₃	= 3.27 Å		

The distance Pb—6 O is very close to the corresponding value in PbO₂ (2.15 Å) and must imply that the Pb atoms are in a tetravalent state. The

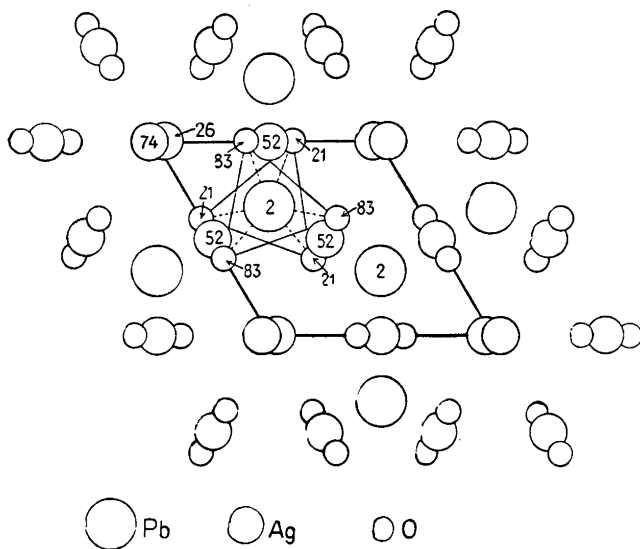
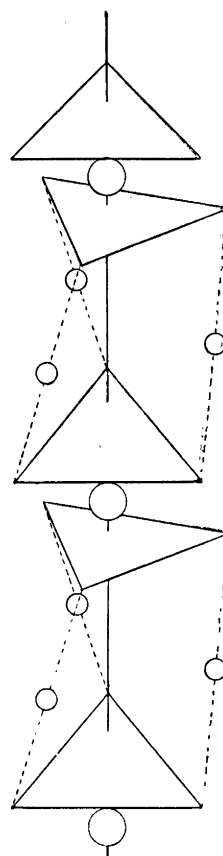


Fig. 5. $\text{Ag}_5\text{Pb}_2\text{O}_6$. Projection of the structure on the xy -plane. Large circles denote lead atoms, medium circles silver atoms and small circles oxygen atoms. The figures denote the height of the atoms in percentages of c . The dotted lines show the $\text{Pb}-\text{O}$ bonds.

Fig. 6. The arrangement of the atoms in the vicinity of one of the three-fold axes. Large circles denote lead atoms and small circles silver atoms. The oxygen atoms are situated at the corners of the equilateral triangles.



two Ag_3 bonds are of practically the same length as the $\text{Ag}-\text{O}$ bonds in Ag_2O (2.05 Å) and, as in Ag_2O , they are linear. Thus it is reasonable to assume that the Ag_3 atoms are in a monovalent state. Then it follows from the formula that the mean valency of the Ag_1 and Ag_2 atoms must be $+1/2$. The coordination figure of these oxygen atoms is a triangle with the Ag atom a little displaced from the triangle plane and the three $\text{Ag}-\text{O}$ bond angles are close to 120° (114° and 117°). As will be seen from the interatomic distances the Ag_1-Ag_2 distance is the shortest metal distance in the structure, being only 3.04 Å. It seems, that there might be covalent bonds also between the Ag_1 and Ag_2 atoms, and that thus there are four bonds from each Ag_1 and Ag_2 atom, three to oxygen atoms and one to a silver atom. Thus a binuclear complex Ag_2O_6 is formed. A similar coordination has been found for silver atoms in Ag_2F (Ott and Seyfarth⁶) with a distance $\text{Ag}-3\text{F} = 2.4$ Å, but in that compound

every silver atom is also in contact with three other silver atoms and the distance Ag—3 Ag is 2.9 Å.

The structure is given in Fig. 5. As will be seen from the figure, the octahedra around the lead atoms are linked together in layers, perpendicular to [001], by sharing edges. These layers form two-dimensional complexes of the composition $(\text{Pb}_2\text{O}_6^{4-})_\infty$. Octahedra from different layers are linked together by the Ag_3 atoms (Fig. 6). Around the origins of the unit cells, there are wide channels in the structure, running in the *c*-direction, and in these channels the Ag_1 and Ag_2 atoms are situated.

3. On the existence of other compounds in the system Ag—Pb—O

A number of compounds have been described in the system Ag—Pb—O, obtained by precipitating a solution containing both lead ions and silver ions with KOH or by precipitating a solution of $\text{Pb}(\text{NO}_3)_2$ in NaOH with AgNO_3 (Aston ⁷). However, we have repeated these syntheses and the only crystalline Ag—Pb—O compound which is obtained is Ag_2PbO_2 . It seems that the other compounds which have been described ($\text{Ag}_4\text{Pb}_7\text{O}_{11}$, $\text{Ag}_4\text{Pb}_3\text{O}_5$, Ag_4PbO_3) are in reality mixtures of Ag_2PbO_2 and PbO or Ag_2O .

SUMMARY

The crystal structures of Ag_2PbO_2 and $\text{Ag}_5\text{Pb}_2\text{O}_6$ have been determined. Ag_2PbO_2 is monoclinic, with $a = 6.082 \pm 0.003$ Å, $b = 8.715 \pm 0.004$ Å, $c = 6.556 \pm 0.003$ Å and $\beta = 93.69^\circ$. There are 4 Ag_2PbO_2 in the unit cell. The space group is C_{2h}^6 —*I* 2/*c* and the atomic positions are:

(000; 1/2 1/2 1/2) +
 4 Ag in 4 (*b*): 0 1/2 0; 0 1/2 1/2
 4 Ag in 4 (*d*): 1/4 1/4 3/4; 3/4 1/4 3/4
 4 Pb in 4 (*e*): 0 *y* 1/4; 0 \bar{y} 3/4 with $y = 0.125$
 8 O in 8 (*f*): $\pm (x, y, z)$; $\pm (\bar{x}, y, 1/2 - z)$ » $x = 0.311$, $y = 0.129$ and $z = 0.446$.

The Pb atoms are bonded to four oxygen atoms, situated at the corners of a distorted square with a mean distance Pb—O of 2.32 Å. The Ag atoms form two linear bonds with a mean distance Ag—O of 2.09 Å.

$\text{Ag}_5\text{Pb}_2\text{O}_6$ is trigonal with $a = 5.939 \pm 0.003$ Å and $c = 6.428 \pm 0.003$ Å. There is one formula unit in the cell. The space group is C_{3v}^2 —*C*3*m*. The atomic positions are:

1 Ag ₁ in 1 (a): 0 0 z ₁	with z ₁ = 0.264
1 Ag ₂ in 1 (a): 0 0 z ₂	» z ₂ = - 0.264
3 Ag ₃ in 3 (c): x ₃ 0 z ₃ ; 0 x ₃ z ₃ ; x ₃ x̄ ₃ z ₃	» x ₃ = 1/2 and z ₃ = 0.522
2 Pb in 2 (b): 1/3 2/3 z ₄ ; 2/3 1/3 z ₄	» z ₄ = 0.022
3 O in 3 (c): x ₅ 0 z ₅	» x ₅ = 0.603 and z ₅ = 0.215
3 O in 3 (c): x ₆ 0 z ₆	» x ₆ = 0.397 and z ₆ = -0.171

As will be seen, the metal atom positions have a higher symmetry than the oxygen positions and can be described in the space group $C_{6v}^1-C 6/mm$. The Pb atoms are surrounded by six oxygen atoms with Pb—O = 2.19 Å. The Ag₃ atoms form two linear bonds with Ag—O = 2.07 Å. The Ag₁ and Ag₂ atoms form three oxygen bonds with Ag—O = 2.39 and 2.44 Å respectively and probably one Ag—Ag bond with the distance Ag—Ag = 3.04 Å.

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