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Study of morphology of α -PbO₂ and determination of elementary cell constants

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ABSTRACT

A laboratory prepared compound lead oxide α -PbO₂ was used for XRD and electron microscopic investigation. Using B.E.T. Method, the measurement of the particle size turned out to be 2.40 m²/g. A series of calculations was made to refine the cell constants. Then a frequently-used computer program (LSUCRIPC) was run to compute the cell constants more precisely. The received values were a=4.95048, b=5.93631, c=5.47491.

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KEYWORDS

Lead (IV) oxide;
XRD;
Cell constants;
Crystallite size.

INTRODUCTION

α -PbO₂ has an orthorhombic system with space group Pbcn-D₂h, Z=4. In the α -PbO₂ lattice with its distorted hexagonal closest O²⁻ packing is occupied half of the octahedron situations by Pb⁴⁺ (Pb \leftrightarrow O:2.16Å). Each O²⁻ ion is to three Pb⁴⁺ ions neighboring^[1]. α -PbO₂ can be understood on the one hand as Halbbrookite (TiO₂) type, and on the other as a ground structure of the types of the Wolframits (FeWO₄) and Columbits (FeNb₂O₆). The latter one can be understood as order structure of the α -PbO₂ type. Debye-Scherrer-diagram with schematic representation of the intensities is shown in the following TABLE^[1-5].

a	b	c	Lit.
4.938	5.939	5.486	1
4.938	5.939	5.486	2
4.954	5.954	5.477	3
4.938	5.939	5.486	4
4.977	5.94	5.444	5

The work aimed to determine cell constants and crystallite sizes.

EXPERIMENTAL

Materials and equipment

The preparation of α -PbO₂ as described in the next section; The utilization of α -SiO₂, made by Merck Co.Darmstadt, Germany; The use of XRD: X-Ray diffractometer D 5000, Siemens, Kristalloflex; SEM: Scanning Electron Microscope, REM-JEOL (GSM-840); TEM: Transition Electron Microscope, Hitachi (H600).

Preparation of α -PbO₂

A (NH₄)₂S₂O₈ solution (25 g solved in 25 ml H₂O) was added to 100 ml saturated CH₃COONH₄ solution (solved in H₂O). To this mixture was added gradually 32.5 g Pb(CH₃COO)₂ (PbAc₂)(solved in 30 ml H₂O). At the same time 70 ml 25% NH₃ solution was added to the mixture. This solution turned yellow and then dark-brown and finally reddish. After approximately 6 hours stirring, 5 g (NH₄)₂S₂O₈ was added to it. This mixture was further-stirred about 38 hours at

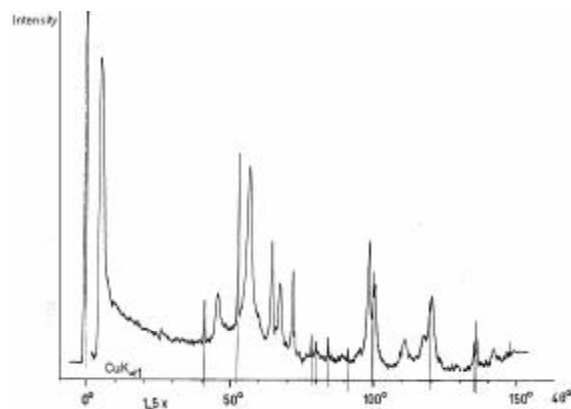


Figure 1: XRD diagram of α -PbO₂

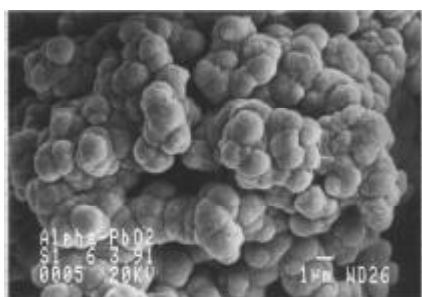


Figure 2: SEM electron microscopic photograph of α -PbO₂, enlargement is 5000X

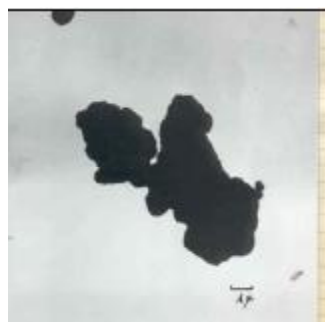


Figure 2: SEM electron microscopic photograph of α -PbO₂, enlargement is 5000X

25°C. In order to remove excess of NH₃ and to bring unwanted lead compound in solution, it was warmed up to 70°C, This mixture was cooled down and the supernatant (jut out) solution with white crystals of PbAc₂ was removed temporarily. The black precipitation consisted of fine-grained, water insoluble of α -PbO₂. In order to clean the product, it was transferred into some centrifuge container and was washed for several times with diluted CH₃COONH₄ solution. Afterwards it was dried in a desiccators over silica gel at 25°C.

X-ray diffraction

The α -PbO₂ sample was prepared in Bedacryl and it was exposed to CuK α 1 radiation for two hours (see figure 1).

Initial materials as well as products were finely ground and prepared on a sample holder using a Scotch tape and Bedacryl I.C.I. They were X-rayed with CuK α 1 radiation using a Guinier Camera with focusing quartz Monochromator. The exposure time varied from 8 to 16 hours (mostly 10 h.). For precise d spacing, an internal standard was used: α -SiO₂ proved unsatisfactory because of insufficient reflections in the higher d range.

Electron microscopy

The first series of the morphologic investigation of α -PbO₂ was accomplished with a SEM electron microscope (REM-JEOL-JSM-840). The preparation of the sample was also accomplished by coating of the surface with gold (3-4 min). The reasonable enlargement was 5000 times. The second series of electron microscopic investigation with TEM equipment was accomplished (EM-Hitachi, H-600). The sample was prepared in the following way. The white powdery sample was first coated with carbon. This carbon film was then treated with HF acid on the surface and was investigated by means of TEM equipment. The reasonable enlargement was 5000 times (see figures 2 and 3)^[6-15].

RESULTS AND DISCUSSION

The XRD results show a good agreement with standard diagram of α -PbO₂ (Figure 1)(ASTM 21-474). The analysis of the product showed that the sample was stable. Making use of this method, we managed to produce pure α -PbO₂ for the first time.

SEM photograph of the produced α -PbO₂ is shown in Figure 2. Crystals are round with a diameter of 1 μ m, they have a good arrangement to each other forming large round crystals.

TEM photograph of the produced α -PbO₂ is shown in Figure 3. The crystals are somehow larger, yet they are round. The reasonable enlargement in TEM photograph was 5000 times.

Specific surface, particles size and crystal size of α -PbO₂: BET method was used to measure particle

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size of α - PbO_2 . The received result was $2.40 \text{ m}^2/\text{g}$.

Calculation of cell factor

A mixture of two powder α - PbO_2 and α - SiO_2 was prepared in the ratio of 3:1 which made its grinding easy. Now an X-ray diffraction was made. The goal was to obtain a precision of the line situation. It is often quoted in references that α - SiO_2 supplies sharp lines.

TABLE 1: line of the α - SiO_2 (ASTM-33-1161), Hex. $a_0=4.9133$, $c_0=5.4053$, $z=3$, $D_x=2.649 \text{ g/cm}$, $D_m=2.656$.

No.	4θ CuK α 1 Lit.	4θ FeK α 1 Lit.	D (\AA)	I	h.k.l.
1	41.69	52.58	4.257	2.2	100
2	33.30	67.35	3.342	1.0	101
3	73.08	92.81	2.457	0.8	110
4	78.91	100.40	2.282	0.8	102
5	80.56	102.56	2.237	0.4	111
6	84.93	108.29	2.127	0.6	200
7	91.62	117.12	1.9792	0.4	201
8	100.28	128.70	1.8179	1.4	112
9	101.22	129.96	1.8021	0.1	003
10	109.73	141.52	1.6719	0.4	202
11	110.65	142.78	1.6591	0.2	103
12	114.47	148.03	1.6082	0.1	210
13	119.89	155.97	1.5418	0.9	211
14	127.99	167.02	1.4536	0.1	113
15	131.52	172.07	1.4189	0.1	300
16	135.50	177.85	1.3820	0.6	212
17	136.26	178.97	1.3752	0.7	203
18	136.64	179.53	1.3718	0.8	301
19	146.92	194.91	1.2880	0.2	104
20	151.34	201.72	1.2558	0.2	302
21	155.32	207.98	1.2285	0.1	220
22	159.75	215.12	1.1999	0.2	213
23	160.09	215.67	1.1978	0.1	221
24	162.29	219.29	1.1843	0.3	114
25	163.94	220.37	1.1804	0.3	310

TABLE 3: The measured and calculated data of $\text{Sin}^2 \theta \cdot 10^4$ for α - PbO_2

No.	α - SiO_2				α - PbO_2		$4\theta_{\text{corr.}}$	$\text{Sin}^2 \theta \cdot 10^4$ (meas.)	$\text{Sin}^2 \theta \cdot 10^4$ (cal.)	PbO_2 hkl
	hkl	$4\theta_{\text{meas.}}$	$4\theta_{\text{ref.}}$	Δ	$4\theta_{\text{meas.}}$	$\Delta_{\text{rec.}}$				
1	100	41.33	41.69	0.36	46.46	0.677	47.137	405.35	389.1	110
2	101	53.33	53.30	0.97	56.66	0.92	57.58	598.85	604.66	111
3	102	78.66	78.91	0.25	-	-	-	-	671.18	020
4	111	80.33	80.56	0.23	65	0.56	65.65	783.04	794.33	002
5	200	84.66	84.93	0.27	68.2	0.47	68.67	859.70	869.5	021
6	201	91.33	91.62	0.29	72.4	0.37	72.77	965.2	953.37	200
7	112	100.33	100.28	-0.05	81	0.24	81.24	1197.97	1200.8	112
8	211	120	119.89	-0.11	-	-	-	-	1465.7	022
9	212	135.33	135.50	0.17	-	-	-	-	1623.6	220
10	203	136.2	136.26	0.06	99.3	0	99.3	1762.72	1748.1	202,130
11	-	-	-	-	101.2	-0.02	101.18	1826.3	1822.9	221
12	-	-	-	-	111.6	-0.073	111.53	2189.58	2193.9	113
13	-	-	-	-	118	-0.101	117.89	2424.8	2418.8	222
14	-	-	-	-	121	-0.101	120.89	2537.88	2445.8	023

In order to compute the correction factor by measuring the X-ray film, some α - SiO_2 was added to the α - PbO_2 powder. TABLE 1 shows the XRD lines of the compound α - SiO_2 .

Now the two density diagram were compared with each other and the sharp lines were picket out, the results did not belong to α - PbO_2 . The sharp lines belong to α - PbO_2 , the lines of α - SiO_2 were measured and the following TABLE was set up. In this TABLE, Δ shows the difference between reference and experimental values.

Now having Δ and 4θ values, the Δ values were laid on against $4\theta_{\text{meas.}}$ values and the received points were used to calculate the curve. Now on the received curve was read off for each $4\theta_{\text{meas.}}$ values a new Δ value i.e. $\Delta_{\text{rec.}}$. Thus TABLE 3 was set up.

Then there was $4\theta_{\text{corr.}}$ according to the following formula:

$$4\theta_{\text{corr.}} = 4\theta_{\text{meas.}} + \Delta_{\text{rec.}}$$

TABLE 2: The comparison of the lines of α - SiO_2 , the experimentally and those from the references

No.	α - SiO_2			
	hkl	$4\theta_{\text{meas.}}$	$4\theta_{\text{ref.}}$	Δ
1	100	41.33	41.69	0.36
2	101	53.33	53.30	0.97
3	102	78.66	78.91	0.25
4	111	80.33	80.56	0.23
5	200	84.66	84.93	0.27
6	201	91.33	91.62	0.29
7	112	100.33	100.28	-0.05
8	211	120	119.89	-0.01
9	212	135.33	135.50	0.17
10	203	136.2	136.26	0.06

TABLE 4: Calculated $\text{Sin}^2 \theta \cdot 10^4$ -values, 4θ -values are used from TABLE 3

No.	$4\theta_{\text{corr.}}$	I	$\text{Sin}^2 \theta \cdot 10^4$ (corr.)	hkl
1	47.14	1	417.08	110
2	57.56	10	618.06	111
3	-	2	-	020
4	65.65	7	798.35	002
5	68.67	7	871.23	021
6	72.77	2	974.75	200
7	81.24	1	1204.78	112
8	-	1	-	022
9	-	3	-	220
10	99.30	4	1762.7	130,202
11	101.18	3	1825.6	221
12	111.53	2	2186.9	113
13	117.9	2	2420.7	222
14	120.9	3	2533.7	023

Now using the following formula, a TABLE was set up, with the measured $\text{Sin}^2 \theta \cdot 10^4$ values as can be seen in TABLE 3:

$$\text{Sin} \theta = \frac{n \cdot \lambda}{2d}$$

$\lambda = 1.5405$ (CuK α 1), $n=1$, d (from TABLE).

Now we are able to compute on the basis of $\text{Sin}^2 \theta_{\text{corr.}} \cdot 10^4$ the cell constants.

$$\text{Sin}^2 \theta \cdot 10^4 = A \cdot h^2 + B \cdot k^2 + C \cdot l^2$$

At first those lines which possess only a run number of hkl, different of zero were picket out.

Thus the first series of A, B, C values were obtained. These values were registered into the so-called atomic position x-ray diagram. At the beginning one selected: $h=0$; $k=1,2,3,4$; $l=1,2,3,4$ and then calculated the lines (the values larger than 26000 were rejected as insignificant). Next it was selected: $h=1$; $k=1,2,3$; $l=1,2,3$ and then calculated the lines.

Like above: $h=2$; $k=1,2,3$; $l=1,2,3$ etc.

Now the received lines values were compared with measured values. If they correlated well, then the A, B, C values would be selected, otherwise one had to vary A, B, C values (cell constants) till they become optimal. This is known as the refinement of the cell constant. Now these data were computed with a computer program called LSUCRIPC. The input A, B, C values were used 3 times for computations (though not yet optimal). The structure, name, angles (value of θ) and experimentally received lines ($4\theta_{\text{corr.}}$) were also entered into the program. At first the calculated values of A, B, C were compared with LSUCRIPC and Reference

values.

The optimization was accomplished over 40 times. The following values were received $a=4.95048$, $b=5.93631$, $c=5.47491$. This values show good agreement with those from references.

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