

GEOMETRICAL CRYSTALLOGRAPHY OF PbO_2 AND Pb_5O_8

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ABSTRACT

Large crystals of PbO_2 and Pb_5O_8 have been prepared by heating lead peroxide, sodium hydroxide, and water together in a steel bomb. The PbO_2 crystals so obtained are tetragonal ($c=0.6785$), twinning on (101), and show the forms: $\{101\}$, $\{111\}$, $\{211\}$, and $\{230\}$. Pb_5O_8 crystals are also tetragonal ($c=0.989$), twinning on (101). Crystals exhibit parallel growth on (110) and show the forms: $\{001\}$, $\{111\}$, $\{100\}$, and $\{110\}$. Some of the twin-crystals mimic hexagonal crystals.

During the preparation, for magnetic measurements, of specimens of intermediate oxides of lead by the method of Clark *et al.*,¹ and variants of it, several crystalline products other than those they have reported were obtained. Of particular interest were crossed acicular crystals which proved to be the elusive PbO_2 . Large crystals of Pb_5O_8 , adequate for goniometric study, were also obtained.

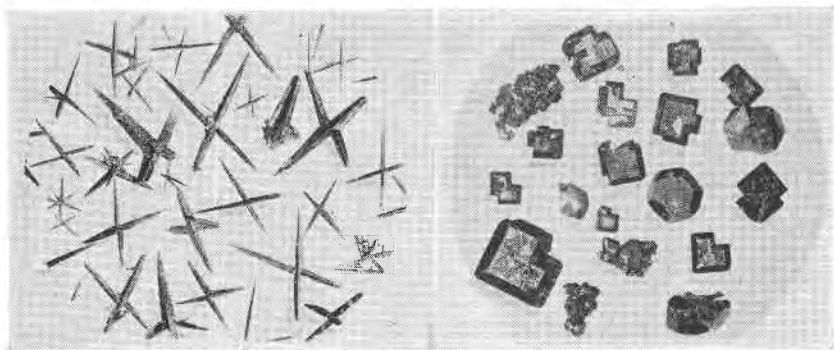


FIG. 1. Crystals of PbO_2 . Magnification 6 diam.

FIG. 2. Crystals of Pb_5O_8 . Magnification 6 diam.

The method employed in the production of these crystals consisted of heating sodium hydroxide, water, and lead peroxide together in a steel bomb which was very heavily gold plated over nickel, in order to prevent ferro-magnetic contamination. Heating was accomplished in an electric furnace whose temperature, determined by a chromel-alumel thermocouple, could be controlled accurately. One part of sodium hydroxide, four parts of water, and three parts of lead peroxide (0.0003% or less Mn) were held from four to six days in the bomb at a steady temperature between 260° and 390°C .

¹ Clark, G. L., Shieltz, N. C., Quirke, T. T., *Jour. Am. Chem. Soc.*, **59**, 2305-2308 (1937).

When the bomb was held at increasingly higher temperatures the degree of "reduction" of the PbO_2 became greater until, at the highest temperatures used, numerous flakes of yellow PbO were found mixed with the larger quantities of the higher oxides. Whether a simple removal of oxygen atoms from the PbO_2 crystal structure constitutes the reduction of PbO_2 , or whether some essential intermediate product occurs is still problematical. Unsettled chemical questions, which need not be considered here, are involved.²

The goniometric measurement of the crystals so obtained presented certain difficulties. In the case of the Pb_3O_8 crystals, striations due to parallel growth caused most of the trouble. Faces of the form $\{001\}$ in particular are so thoroughly striated on all measurable crystals that it was impossible to obtain a sharp signal. The pyramid faces are somewhat better, but none of them reflect a signal which could be measured with the desired precision. The most consistent results were obtained by measuring the angle between the normals to the (111) faces, thereby eliminating the highly striated (001) face.

In measuring the PbO_2 crystals the chief difficulty was caused by the minuteness of the pyramid faces. Although these crystals sometimes grow to a length of nearly 3 mm. their ends are usually mere points, as may be seen in Fig. 1. No normal signal was obtainable on any of the surfaces, but because of the small size of the pyramid faces it was possible to use a "pin-hole" image in measuring the angles.³

² Le Blanc and Eberius (*Zeits. physik. Chem.*, A 160, 69, 1939), have indicated that the tetragonal PbO_2 may be reduced to $PbO_{1.66}$ without the appearance of a lattice different from that of PbO_2 . Furthermore, they point out, the next lattice encountered in the reduction is that of PbO , which may be either orthorhombic or tetragonal. This would seem to indicate that the lattices of the intermediate oxides do not exist, or that they are merely distortions of the PbO_2 and PbO lattices. And yet, if it were possible to start with PbO_2 and reduce it successively through the various intermediate stages to PbO , a triclinic and a monoclinic system of symmetry would be encountered before reaching the end member, PbO . The following list will illustrate the point.

PbO_2	Tetragonal
$PbO_{1.66}$, (Pb_3O_8)	Tetragonal
$PbO_{1.50}$, (Pb_2O_3)	Triclinic
$PbO_{1.33}$, (Pb_3O_4)	Monoclinic
PbO	Dimorphous

³ This method consists of placing the focusing lens in front of the telescope and then moving the telescope ocular so that the crystal is somewhat out of focus. If the reflecting surfaces are small enough, a pinhole image of the slit will appear in the spot of light reflected from the surface. Upon rotation of the crystal this image moves in and out of the spot of light just as the signal image in the orthodox arrangement moves in and out of the telescope field. The telescope cross-hairs do not, in this case, offer a reference point for the measurements, but consistent results may be obtained by centering the image in the spot of light. Reference to Table 1 will show that the maximum deviation in using this "pinhole" method on the PbO_2 crystals was 4'.

Pb_5O_8

Pb_5O_8 crystals were first identified by Clark *et al.*,⁴ who reported them as having a density of 9.514 and as showing tetragonal symmetry with an axial ratio very nearly equal to 1. Their crystals were too small,—judging from their photomicrograph,—to allow goniometric measurements. Those obtained in this laboratory are evidently considerably larger, some of them being more than one mm. on a side. Although the choice of an axial ratio for Pb_5O_8 based on goniometric measurement alone is rather arbitrary, preliminary investigation of the *x*-ray powder pattern appearing in Fig. 6 indicates the value given in Table 1.

The crystals of this oxide are jet black, very good reflectors of light, exhibit various interference colors, particularly orange, yellow, and blue,

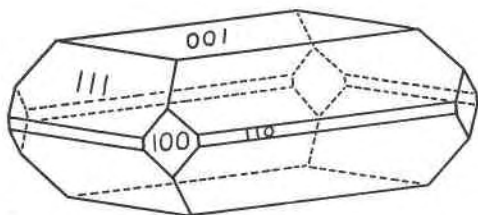


FIG. 3. Typical crystal of Pb_5O_8 .

and are often iridescent. This is due to striations caused by a highly characteristic twinning of the crystals parallel to the first order prism face. This parallel growth is also responsible for the 90° re-entrant angles which may be seen in Fig. 2. First order pyramids and basal pinacoids account for nearly all of the area on these crystals, but fragments of both the first and second order prisms may frequently be found. These forms are drawn approximately in their relative sizes in Fig. 3.

Generally speaking, four types of Pb_5O_8 crystals appear. Large crystals showing only parallel growth are most numerous; such is the one in the lower left-hand corner of Fig. 2. Double crystals like that in the upper right-hand corner of the same figure, and triplets such as that shown in the center are fairly abundant. The aggregates similar to that in the upper left-hand corner of the photomicrograph are less numerous.

Especially interesting is the twinning of the Pb_5O_8 crystals. It occurs on the (101) plane and frequently repeats to form triplets. When either a double or a triple crystal of this oxide forms, it usually grows in such a manner that the faces which are common become considerably larger

⁴ Clark, G. L., *et al.*, *loc. cit.*

than any of the others. Thus this common (111) face becomes the natural base of the composite crystal. When the triplet is set upon this base and viewed from above, the normals to the other faces apparently lie so that their projections on the base plane are 60° apart. In other words, the triplet mimics hexagonal symmetry; it appears as though the common face, $(\bar{1}\bar{1}1)$ in the drawing, were a (0001) plane and the others were of the form $\{10\bar{1}1\}$. The twinned nature of the crystal is, however, quite obvious from the re-entrant angles caused by the failure of the various faces of the form $\{111\}$ to coincide. Figure 4 is a stereographic projection of such a triplet.

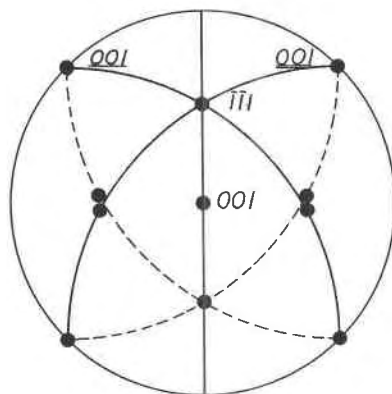


FIG. 4. Stereographic projection of a triplet of Pb_3O_8 . Twin-plane = (101). One zone of each of the three crystals is shown. Each zone contains the following faces: (001), $(\bar{1}\bar{1}1)$, (111), (001), (111), (111); and the face common to the three crystals is $(\bar{1}\bar{1}1)$.

PbO_2

Lead peroxide is found in various parts of the United States and of Europe as a mineral named plattnerite. It is secondary and usually occurs in nodular or botryoidal masses. Specific gravity determinations give values ranging from 8.5 to 9.45, the lower values being due to porosity and to various impurities, especially limonite. The mineral is coal-black and shows no signs of cleavage or twinning.⁵

Plattnerite was first described as rhombohedral, but the crystals so described were apparently pseudomorphous after pyromorphite.⁶ Later investigation by A. F. Ayres showed the mineral to be tetragonal with an axial ratio of 0.67643.⁷ But since Ayres' measurements were made on

⁵ Dana, E. S., *System of Mineralogy*, Wiley, New York (1920), p. 239.

⁶ Greg and Lettsom, *Mineralogy of Scotland* (1858), p. 389.

⁷ Yeates and Ayres, *Am. Jour. Sci.*, **43**, 407 (1892).

minute crystals, and since he did not indicate the probable error of his measurements, no particular significance can be given to the discrepancy between the ratio indicated by Ayres and that given in Table 1.

TABLE 1. ONE-CIRCLE MEASUREMENTS OF PbO_2 AND Pb_3O_8 CRYSTALS

	Angle	No. of meas.	Arith. mean	Max. devia.	Axial ratio
PbO_2	$101 \wedge \bar{1}01$	24	$68^\circ 19'$	4'	0.6785
Pb_3O_8	$111 \wedge \bar{1}\bar{1}1$	24	54 26	5	0.989

TABLE 2. TWO-CIRCLE MEASUREMENTS OF PbO_2 CRYSTALS

Form	No. of faces	No. of meas.	Measured (arith. mean)		Computed	
			ϕ	ρ		
101	4	24	$90^\circ 00'$	$34^\circ 9.5'$	$90^\circ 00'$	$34^\circ 9.5'$
111	4	2	44 30	43 30	45	43 49
211	8	20	63 30	56 30	63 26	56 38
230	8	20	32 32	85	33 40	90

Lead peroxide is also well known as a brown powder⁸ used for various industrial and laboratory purposes, but it has never been described in the artificially crystalline state. Indeed, it is evident that lead peroxide has not been recognized as an artificial crystal prior to this study.

M. L. Michel,⁹ in 1890, reported having obtained lead peroxide crystals by fusing lead oxide with a certain quantity of potash. In describing the crystals so obtained he relates,

Ces cristaux sont très brillants, d'un brun foncé; ils affectent la forme de prismes très allongés, suivant l'axe principal; on observe sur la base des lignes de clivage croisées à angle droit; . . .

This description applies to the crystals exhibited in Fig. 1 in so far as the prismatic habit goes, but the crystals presently to be described are jet black, and show no signs of cleavage. As was mentioned above, the natural mineral, plattnerite, is also black, and in contradistinction to Michel's crystals shows no traces of cleavage.

A. Simon¹⁰ reported obtaining lead peroxide crystals in 1930, but it is

⁸ X-ray diffraction patterns of this powder give the PbO_2 lattice as tetragonal, body centered, with $a=4.96$ to 4.98 , $c=3.39$ to 3.40 . (*Str. Ber.*, **1**, p. 211; and *Int. Crit. Tab.*, **1**, p. 342.)

⁹ Michel, M. L., *Bull. Soc. Min.*, **13**, 56 (1890).

¹⁰ Simon, A., *Zeits. anorg. allgem. Chem.*, **185**, 300 (1930).

now apparent that the crystals he pictured in Fig. 1 of his article and designated as PbO_2 were not tetragonal PbO_2 , but triclinic Pb_2O_3 .

On the PbO_2 crystals recently obtained two crystallographic forms are preponderant. Second order pyramids account for most of the area at the ends, while the lateral area is made up by the ditetragonal prism $\{230\}$. Other forms which occur,— $\{111\}$ and $\{211\}$,—are usually so small as to give mere points of reflected light. Figure 5 is a clinographic

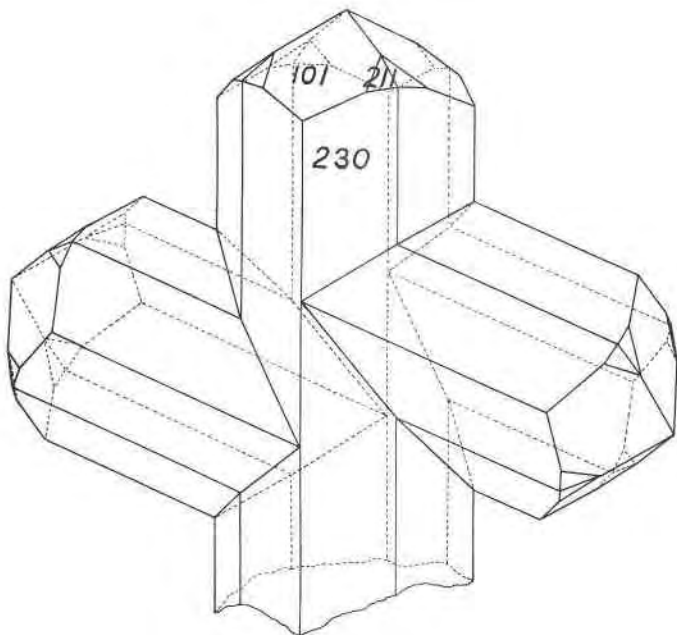


FIG. 5. Twin-crystal of PbO_2 ; twin-plane = $\{101\}$.

projection of the twinned PbO_2 showing the forms $\{101\}$, $\{211\}$, and $\{230\}$. The $\{211\}$ faces are relatively larger in the drawing than on the actual crystals. Of the forms mentioned by Ayres as appearing on plattnerite, only the $\{101\}$ appears on the artificial crystals measured.

Figure 1 shows that the prism faces of the PbO_2 taper toward the extremities of the crystals. Although this taper is fairly constant at 85° on the crystals measured, it has no simple index and must therefore be ascribed to oscillatory growth. The measured angle of the prism also diverges from the computed angle, but this is due to the difficulties of measurement. No signal was obtainable from the face, and it was too large to give a pinhole image.

In common with many other tetragonal minerals, PbO_2 twins on the plane (101), (see Fig. 5); and this particular habit of growth,—not described in plattnerite,—is the only one observed on the many crystals examined. Nearly all are crosses of the type shown in Fig. 1. Some few specimens such as the one shown in the upper right-hand part of that figure, and a fair number of interlaced crosses in clusters were found. But the great mass of the crystals are simple, slender needles crossing at an angle of 68° . In size they range from microscopic dimensions up to nearly 3 mm.

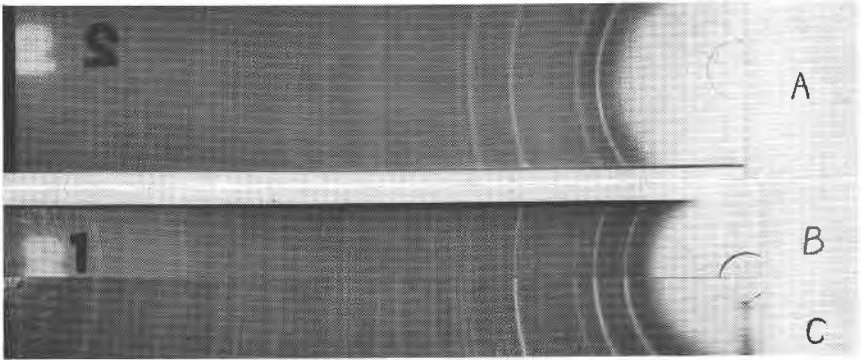


FIG. 6.

- A. . . . Pb_3O_8
 B. . . . PbO_2 crystals
 C. . . . PbO_2 c.p. powder

In Fig. 6 will be found three *x*-ray powder patterns. One is of the Pb_3O_8 crystals; the other two are of PbO_2 crystals and c. p. powder. Those lines which appear on the c. p. lead peroxide pattern but not on that of the crystals of PbO_2 are due to impurities,—especially lead monoxide,—in the powder.

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