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The unit cell and space group of basic lead carbonate.

By GERALD KATZ, *Signal Corps Engineering Laboratories, Fort Monmouth, N.J., U.S.A.*, and LEONARD REED,* *Rutgers University, New Brunswick, N.J., U.S.A.*

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Bourgeois (1888) reported the presence of hexagonal plates of basic lead carbonate when white lead was observed under high magnification. However, the crystals were too small for crystallographic measurement with the existing optical techniques. Recently, Cowley (1956) has described the structure of basic lead carbonate, as determined by electron-diffraction techniques. The crystals used were grown *in situ* in the electron microscope as hexagonal platelets of approximately 6μ. The present investigation, concerned with the hydrothermal system PbO–H_2O, has resulted in the growth of single crystals of basic lead carbonate suitable for optical and X-ray studies.

The hydrothermal system employed was similar to that used by Morey (1953). A platinum crucible containing red tetragonal PbO was placed at the bottom of an 8 inch bomb, and a spiral of platinum wire and gauze was set in the crucible, extending upwards, the length of the chamber. The bomb was then filled with distilled water, sealed, and heated in a furnace containing an upper and lower heating element which was used to provide a decreasing thermal gradient of 60° C. from the bottom to the top of the chamber. The crystals were found to deposit on the platinum mesh during the runs. Various combinations of temperature and pressure in the range 370–440° C. and 7,000–18,000 p.s.i. were used for crystal formation.

The crystals were clear transparent platelets with hexagonal morphology; the average platelet was under 0·5 mm. diameter, although crystals as large as 1 mm. were formed. Examination with a polarizing microscope demonstrated a uniaxial negative optic character, with the optic or *c* axis normal to the platelet; ω was found to be greater than 1·75; owing to the morphology, ε was not observed.

Although the exact ratio of lead carbonate to lead hydroxide may vary, basic lead carbonate, in the ideal case, may be represented by $2PbCO_3.Pb(OH)_2$ or $3PbO.2CO_2.H_2O$ (Mellor, 1941). A microchemical analysis† performed on a 30 mg. sample gave a formulation in good agreement with the ideal 2:1 ratio of carbonate to hydroxide:

	Analysis wt.%	Calculated wt.%	Formula
Pb	79·7	80·1	3.Pb
CO_2	12·0	11·4	2.CO_2
H_2O	2·7	2·3	1.H_2O
O	6·1‡	6·2	3.O
	100·5%	100·0%	

Successful crystal growth of basic lead carbonate was obtained only when a finely divided form of the red tetragonal polymorph of PbO was used. The use of a comparatively coarse crystalline lead oxide resulted in the growth of yellow crystals of the orthorhombic polymorph of PbO. This indicates that only the larger surface area of the finely powdered material contained sufficient adsorbed CO_2 to form basic lead carbonate.

Rotation and equi-inclination Weissenberg photographs were obtained, using Ni-filtered Cu radiation; precession photographs were taken using unfiltered Mo radiation. A hexagonal unit cell was established with dimensions in good agreement with those determined by Cowley (1956) by electron diffraction:

	K. & R.	Cowley
a_0 (Å)	9·09±0·01	9·06
c_0 (Å)	24·89±0·05	24·8
c/a	2·74	2·74

The unit-cell dimensions were determined from the spacings of high-order reflections; a_0 from the ninth order of ($h0.0$) on a Weissenberg photograph, using Cu $K\alpha_1$ = 1·54050 Å, and c_0 from the sixteenth order of ($00.l$) on a precession photograph, using Mo $K\alpha_1$ = 0·70926 Å. Correction for film shrinkage was made for each measurement.

Direct density measurements of the crystals were not feasible, owing to the micaceous nature of the crystals and the small mass available. The density of basic lead carbonate is reported in the literature as ranging from 6·14 to 6·81 g.cm.$^{-3}$. Using Cowley's cell dimensions and his value of $Z = 9$, the X-ray density is calculated to be 6·57 g.cm.$^{-3}$, as compared to 6·51 g.cm.$^{-3}$ obtained in this study.

No evidence was found on the Weissenberg photographs of ($hk.n$), for $n = 0, 1, 2$, to indicate a rhombohedral arrangement; the photographs of adjacent levels could be directly superimposed. The only observed systematic absence is ($h\bar{h}0l$) with $l = 2n+1$; thus basic lead carbonate belongs to one of three possible space groups $P6_3/mcm$, $P6_3cm$, $P\bar{6}c2$.

The observed intensities on the ($hk.0$) precession photograph were in good agreement with the observed structure factors reported by Cowley for the equivalent electron diffraction pattern. Since Cowley has based his structure in terms of a substructure and has not actually determined a most probable space group, a more detailed X-ray analysis is planned.

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* Presently in British military service.
† Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.
‡ By difference.