

Synthetic hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, by X-ray powder diffraction

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Received 13 March 2002

Accepted 16 April 2002

Online 21 May 2002

Synthetic hydrocerussite [trilead dihydroxide dicarbonate, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] can be easily obtained, as a white powder, by the action of carbon dioxide and water on either lead or litharge at pH 4–5. This compound is also found in lead corrosion technological products as a fine-grained phase. *Ab initio* crystal structure determination was carried out on X-ray powder diffraction data. The heavy-atom method and the Patterson function helped determine the crystallographic model and the atom locations. The Rietveld fitting procedure was used for the final refinement. The atomic arrangement is closely related to the structures of other lead hydroxide carbonates. The hydrocerussite structure can be viewed as a sequence of two types of layers stacked along [001]. Layer A is composed of Pb and CO_3 , and layer B is composed of Pb and OH. The stacking sequence is ...BAABAA...

Comment

Although basic lead carbonate occurs naturally as the rare mineral hydrocerussite, it has been synthesized since early historical times and has been used extensively for artistic and cosmetic purposes ('lead white' pigment). Theophrastus, Pliny and Vitruvius all described its preparation from metallic lead and vinegar. In addition to its artistic importance, lead hydroxide carbonates play a significant role in geology (Krivovichev & Burns, 2000a) and in lead acid battery chemistry (Steele *et al.*, 1998), and they have attracted much attention in recent years. We report here the crystal structure of hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, carried out on a commercially available synthetic powder.

In 1966, Olby published a review on the basic lead carbonates. He showed that the existence of two closely related basic lead carbonates was the reason for the publication of a large range of values for the unit-cell constants of hydrocerussite (Kokkoros & Vassiliadis, 1953; Cowley, 1956;

Voronova & Vainshtein, 1964). The action of carbon dioxide and water on either lead or litharge produces the hydrocerussite $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ [or $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] and the plumbonacrite $6\text{PbCO}_3 \cdot 3\text{Pb}(\text{OH})_2 \cdot \text{PbO}$ [or $\text{Pb}_{10}(\text{CO}_3)_6\text{PbO}(\text{OH})_6$]. This latter compound was recently revised by Krivovichev & Burns (2000b), who suggested a slightly different chemical formula, *i.e.* $\text{Pb}_5\text{O}(\text{OH})_2(\text{CO}_3)_3$. In 1964, Voronova & Vainshtein presented an electron-diffraction

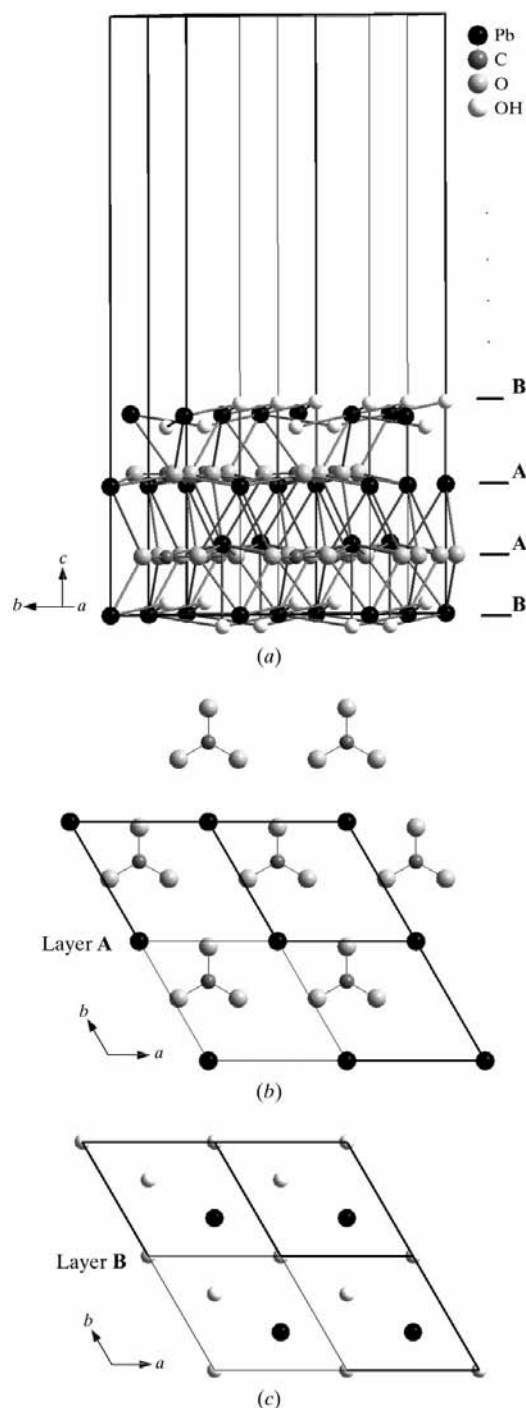


Figure 1
(a) The crystal structure of $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, (b) projection of the A layers along [001] and (c) projection of the B layers along [001].

study of the crystal structure of $\text{PbCO}_3 \cdot \text{PbO} \cdot \text{H}_2\text{O}$. The phase is trigonal (space group $R\bar{3}m$) and was indexed on the basis of an hexagonal unit cell, with cell parameters $a = 5.23 \text{ \AA}$ and $c = 23.82 \text{ \AA}$. However, their method of preparation produces a mixture of litharge and plumbonacrite in addition to the trigonal phase; hence, the composition of the trigonal phase could not be established by analysis. Therefore, they attempted to resolve the structure with an incorrect chemical formula. Later on, Olby (1966) proved that the phase of interest was, in fact, the hydrocerussite compound.

The structure of hydrocerussite is layered and based on hexagonal sheets of Pb atoms (labelled *A* and *B* in Fig. 1). These two distinct types of layers are stacked along [001] as ...BAABAA... Layer *A* is composed of Pb (Pb1 site) and CO_3 (C1 and O1 sites), and layer *B* is composed of Pb (Pb2 site) and OH (O2 site). The five atoms in the asymmetric unit all lie on special positions; Pb1 and C1 have $3m$ symmetry, while Pb2, O1 and O2 have m symmetry. Layer *A* can be considered as interpenetrating hexagonal nets of Pb and CO_3 groups. Pb atoms (Pb1) lie on the 3-axis and are surrounded by six O atoms [2.674 (6) \AA] belonging to CO_3 groups in the plane of this layer. Furthermore, they are coordinated to one OH [2.36 (2) \AA] and to three O1 [3.261 (10) \AA], above and below this layer. The Pb–OH bond length is in agreement with the usually accepted average value (2.3 \AA ; Steele *et al.*, 1998). In the *B* layer, the Pb atoms (Pb2) are split on the 18*h* sites, with occupation factors of $\frac{1}{6}$. The splitting of the Pb atoms reveals some static disorder which also occurs for the six (OH) groups (O2 sites) surrounding the Pb2 site. These groups are bonded to the Pb2 atoms, forming a thick layer of approximately 1 \AA . The Pb–OH bond lengths are presumably equal to 2.43 and 2.51 \AA ; the two other values (1.95 and 2.90 \AA) obtained for this disordered structural model are not realistic. Above and below this layer, the Pb2 atoms are coordinated to three O1 atoms [2.558 (12) and 2.740 (11) \AA]. The disorder observed in the *B* layer is probably due to the long-range order built from the two somewhat similar layers *A* and *B*, but of different density (Pb/3O per unit cell in *A* and Pb/2O in *B*). The double-layer AA forms a structural backbone, which basically reproduces a slab of the cerussite structure. This

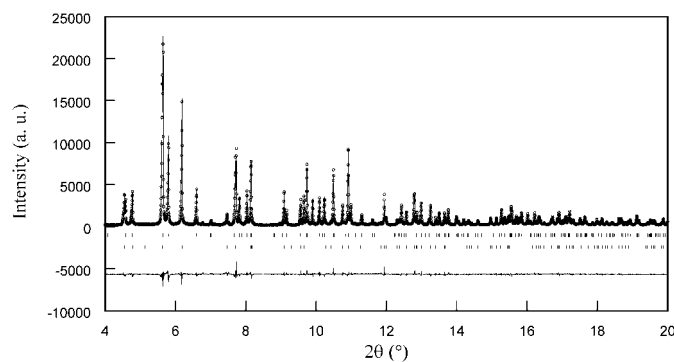


Figure 2
The Rietveld plot for $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$. Comparison of observed (circles) and calculated (solid line) profiles; the bottom curve is the difference pattern. The markers indicate reflection positions for the cerussite and hydrocerussite phases.

grouping, which might be considered as an 'anchor unit', is also found in other lead hydroxide carbonate structures, *viz.* $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$, macphersonite, plumbonacrite, leadhillite, susannite, *etc.* (Krivovichev & Burns, 2000*a,b,c*; Steele *et al.*, 1998). This layered crystal structure could explain some physical properties of the 'lead white' pigment, *viz.* the easy spreading and high covering power much appreciated by painters.

Experimental

Synthetic basic lead carbonate is commercially available from Merck Eurolab SAS, KgaA, Darmstadt, Germany. The powder was used as received.

Crystal data

$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$
 $M_r = 775.6$
Trigonal, $R\bar{3}m$
 $a = 5.2465$ (6) \AA
 $c = 23.702$ (3) \AA
 $V = 565.000$ (4) \AA^3
 $Z = 3$
 $D_x = 6.84 \text{ Mg m}^{-3}$
 $D_m = 6.82 \text{ Mg m}^{-3}$

D_m , measured according to Olby (1966)
Synchrotron radiation
 $T = 295 \text{ K}$
White
Specimen shape: cylinder
 $50 \times 0.4 \times 0.4 \text{ mm}$
Particle morphology: thin powder

Data collection

Two-circle diffractometer
BM16 ESRF (Grenoble)
Specimen mounting: glass capillary

Specimen mounted in transmission mode
 $2\theta_{\min} = 3.05$, $2\theta_{\max} = 38^\circ$
Increment in $2\theta = 0.005^\circ$

Refinement

Refinement on I_{net}
 $R_p = 0.0718$
 $R_{\text{wp}} = 0.0906$
 $R_{\text{exp}} = 0.0546$
 $S = 1.66$
 $2\theta_{\min} = 3.05$, $2\theta_{\max} = 38^\circ$
Increment in $2\theta = 0.005^\circ$
Wavelength of incident radiation: 0.35324 \AA
Excluded region(s): none

Pseudo-Voigt convoluted with axial divergence asymmetry (Finger *et al.*, 1994)
517 reflections
23 parameters
H atoms not located
Preferred orientation correction: March–Dollase correction (Dollase, 1986)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Pb1–O1 ⁱ	2.674 (6)	Pb2–O2 ^{vi}	2.51 (2)
Pb1–O1 ⁱⁱ	3.261 (10)	Pb2–O2 ^{vii}	2.430 (17)
Pb1–O2 ⁱⁱⁱ	2.36 (2)	Pb2–O2 ^{viii}	1.95 (2)
Pb2–O1 ^{iv}	2.558 (12)	Pb2–O2 ^{ix}	2.90 (2)
Pb2–O1 ^v	2.740 (11)	C1–O1 ^x	1.302 (6)
O1 ^x –C1–O1 ^{xi}		119.9 (7)	

Symmetry codes: (i) $\frac{1}{3} + y, \frac{5}{3} - x + y, \frac{2}{3} - z$; (ii) $x - \frac{2}{3}, \frac{2}{3} + y, z - \frac{1}{3}$; (iii) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{2}{3} - z$; (iv) $\frac{5}{3} - x, -\frac{5}{3} - y, \frac{1}{3} - z$; (v) $\frac{7}{3} - x + y, -\frac{1}{3} - x, z - \frac{1}{3}$; (vi) $1 - y, x - y, z$; (vii) $1 + y, -1 - x + y, -z$; (viii) $1 + x, y - 1, z$; (ix) $-x, -1 - y, -z$; (x) $x - 1, 1 + y, z$; (xi) $-1 - y, x - y - 2, z$.

In order to perform the structure determination, we used the synchrotron X-ray diffraction data set of a synthetic compound which corresponds to a mixture of 48% hydrocerussite and 52% cerussite (mass fractions deduced afterwards from our Rietveld refinements). The structure of cerussite is known and has not been refined (Sahl, 1974; Chevrier *et al.*, 1992). The two phases were fed into the refinement process, *i.e.* the already known full atomic structure of

cerussite, along with the unknown hydrocerussite phase, which was introduced by a full-profile cell-constrained refinement procedure (Rodríguez-Carjaval, 1990) in order to extract observed integrated Bragg intensities for direct-methods and Patterson-function purposes. The starting cell parameters of hydrocerussite were those suggested by Voronova & Vainshtein (1964). The systematic absences of some reflections confirmed the trigonal symmetry. The structure solution was carried out in parallel for the several different plausible space groups and the centrosymmetric space group $R\bar{3}m$ was eventually retained. This stage was also used to check the cell correctness and the proposed space group. The obtained structure factors were then used to generate a Patterson map, where the positions of the Pb atoms were clearly visible. After Rietveld refinements of the positions of the found Pb atoms and comparison with parent structures, a difference Fourier synthesis revealed the positions of the remaining O and C atoms in the asymmetric unit, which were subsequently introduced into the refinements. We imposed the same isotropic atomic displacement parameter on all the atoms of the CO_3 group.

Data collection: ESRF *SPEC* package; cell refinement: *FULLPROF* (Rodríguez-Carjaval, 1990); data reduction: ESRF *BINIT* BM16 software; program(s) used to solve structure: *Gfourier* (Gonzalez-Platas & Rodríguez-Carvajal, 2002); program(s) used to refine structure: *FULLPROF*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *FULLPROF*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1365). Services for accessing these data are described at the back of the journal.

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