Crystal chemistry of basic lead carbonates.
I. Crystal structure of synthetic shannonite, $Pb_2O(CO_3)$

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ABSTRACT

The crystal structure of synthetic shannonite, $Pb_2O(CO_3)$, orthorhombic, $P2_12_12_1$, a = 5.1465(7), b = 9.014(1), c = 9.315(1) Å, V = 432.12(10) Å^3, Z = 4, has been solved by direct methods and refined to R = 0.054. There are two symmetrically distinct Pb^{2+} cations in irregular coordination polyhedra due to the effect of stereoactive s^2 lone-electron pairs. The structure can be described as composed of chains of $[OPb_2]$ composition running parallel to [100] that are built by corner-sharing of OPb_3 oxocentred triangles. The $[OPb_2]$ chains are surrounded by CO_3 groups to form complex $[OPb_2](CO_3)$ chains that are linked into a 3-dimensional framework by additional Pb—O bonds. The structure has channels that are parallel to [100] in which the lone-electron pairs of the Pb^{2+} cations are probably located.

KEYWORDS: shannonite, lead oxide carbonate, lone-electron pairs.

Introduction

DURING the last decade, low-temperature minerals have received considerable attention because of their importance to the environment. Such minerals are important for the transport of heavy metals from ore bodies as well as mine and mill tailings to the biosphere. The mobility of Pb in the alteration zones of ore deposits is governed largely by the formation of secondary minerals such as lead carbonates, sulfates, chlorides, etc. A knowledge of the crystal chemistry of these minerals is important for understanding transport and re-deposition of Pb during weathering. Basic Pb-carbonates are also well known as intermediate products of thermal decomposition of cerussite to lead oxide (Warne and Bayliss, 1962; Grisafe and White, 1964). The initial stages of this decomposition include the transition $PbCO_3$–$Pb_2O(CO_3)$ (shannonite)–$Pb_3O_2(CO_3)$. In addition

to their geological importance, formation of these and other lead oxide and hydroxide carbonates (e.g. hydrocerussite and 'plumbonacrite') is important for lead acid batteries because their presence in battery plates increases the resistivity of the electrolyte (Steele *et al.*, 1998).

Shannonite, $Pb_2O(CO_3)$, was described as a new mineral species by Roberts *et al.* (1995) from the Grand Reef mine, Graham County, Arizona, USA, in association with other Pb minerals such as plumbojarosite, litharge, massicot, hydrocerussite and unnamed $PbCO_3$·$2PbO$ or $Pb_3O_2(CO_3)$. The mineral occurs as white opaque porcellaneous crusts; no grains appropriate for single-crystal studies were found. Previously, $Pb_2O(CO_3)$ (shannonite) was described by Pring *et al.* (1990) as a mine fire product at Broken Hill, New South Wales, Australia. Pring *et al.* (1990) determined the orthorhombic symmetry of the phase and gave possible space groups $P2_12_12_1$ and $P2_12_12$. The unit-cell and symmetry data were confirmed by Roberts *et al.* (1995) for the natural sample.

Here we report the crystal structure of shannonite carried out on synthetic crystals as part of a wider study of basic Pb carbonates (Krivovichev and Burns, 2000*a,b*).

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TABLE 1. Crystallographic data for synthetic shannonite.

a (Å)	5.1465(7)	Crystal size (mm)	$0.68 \times 0.10 \times 0.03$
b (Å)	9.014(1)	Radiation	Mo-$K\alpha$
c (Å)	9.315(1)	Total refl.	2552
V (Å^3)	432.1(1)	Unique refl.	996
Space group	$P2_12_12_1$	Unique $|F_o| = 4\sigma_F$	915
F_{000}	808	R	0.054
μ (cm^{-1})	777.02	wR	0.155
D_{calc} (g/cm^3)	7.54	S	1.066
Unit-cell contents	4{Pb$_2$O(CO$_3$)}		

Note: $R = \Sigma(F_o - F_c)/\Sigma F_o$; $S = [\Sigma w(F_o - F_c)^2/(m - n)]^{\acute{Y}}$, for m observations and n parameters
$w = 1/[\sigma^2(F_o^2) + (0.1170P)^2 + 3.6042P]$ where $P = (F_o^2 + 2F_c^2)/3$

Experimental

Single crystals of synthetic shannonite were obtained by hydrothermal methods from a mixture of 0.10 g of PbO, 0.06 g of K$_2$CO$_3$ with 5 ml of H$_2$O. The pH of the solution was adjusted to ~11 using aqueous NaOH. The reactants were placed in a Teflon-lined Parr bomb and were heated to 230°C for ~36 h. The products were filtered and washed with ultrapure water. Crystals of Pb$_2$O(CO$_3$) (shannonite), Pb$_3$O$_2$(CO$_3$) and 'plumbonacrite', Pb$_5$O(OH)$_2$(CO$_3$)$_3$, were obtained. The crystals of shannonite occur as colourless plates up to 0.8 mm in length and 0.2 mm across.

A suitable crystal was mounted on a Bruker three-circle CCD-based X-ray diffractometer operated at 50 kV and 40 mA. More than a hemisphere of 3-dimensional data was collected using monochromatic Mo-$K\alpha$ radiation, with frame widths of 0.3° in ω, and with 10 s spent counting for each frame. The unit-cell parameters (Table 1) were refined with 1787 reflections using least-squares techniques. The intensity data were reduced and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. An empirical absorption-correction was based upon 1452 intense reflections. The crystal was modelled as a (010) plate; reflections with plate-glancing angle of <3° were discarded from the data set, which lowered the $R_{azimuthal}$ from 23.9 to 9.0%.

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. Systematic absences of reflections indicated space group $P2_12_12_1$, which was suggested by Pring *et al.* (1990) and Roberts *et al.* (1995). The structure was solved by direct methods and was successfully refined in this space group. The final model included all atomic positional parameters, anisotropic displacement parameters for Pb and O, an isotropic displacement parameter for C, and a refinable weighting scheme of the structure
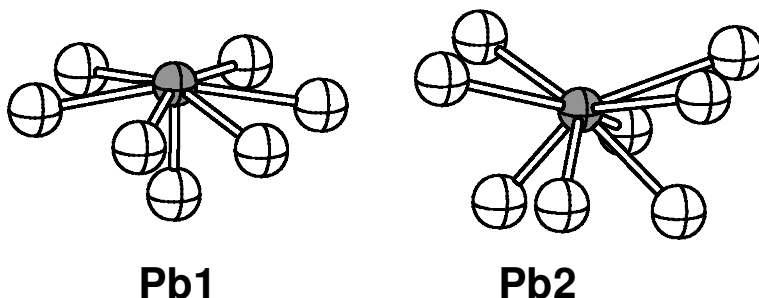

Pb1   **Pb2**

FIG. 1. Pb coordination polyhedra in the structure of shannonite.

TABLE 2. Atomic coordinates and displacement parameters ($\mathring{A}^2$) for synthetic shannonite.

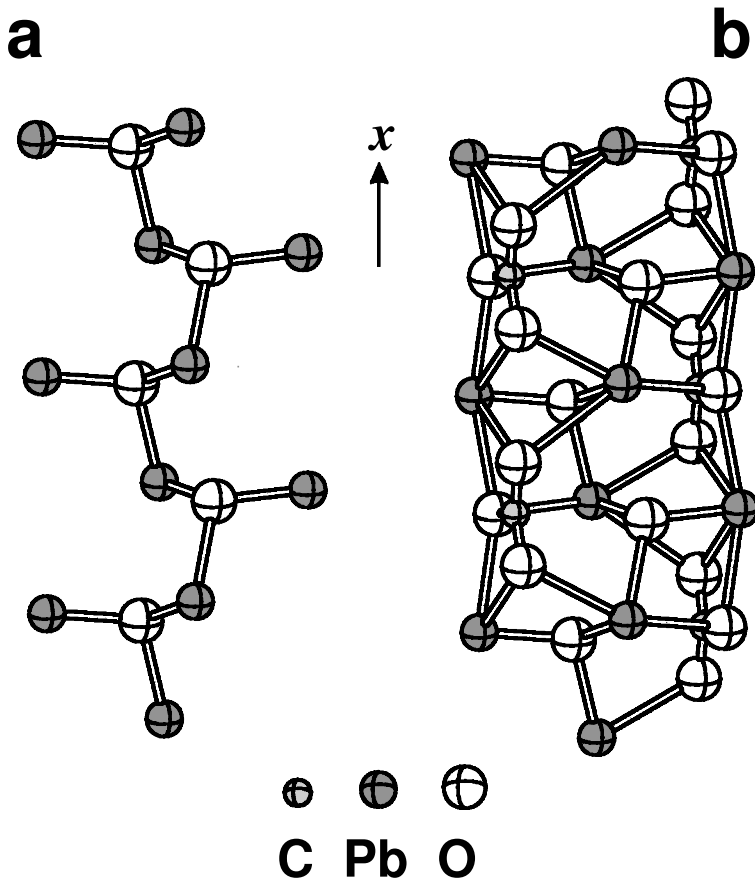| Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	0.0101(2)	0.5556(1)	0.58425(9)	0.0185(4)	0.0188(5)	0.0163(6)	0.0204(5)	−0.0012(4)	0.0004(4)	−0.0003(4)
Pb(2)	0.9673(2)	0.2439(1)	0.34664(9)	0.0219(4)	0.0336(7)	0.0190(5)	0.0129(5)	0.0001(4)	0.0014(3)	0.0013(4)
C	0.991(5)	0.492(3)	0.898(3)	0.018(5)	—	—	—	—	—	—
O(1)	0.214(3)	0.485(3)	0.838(2)	0.032(5)	0.010(7)	0.055(15)	0.031(10)	−0.018(11)	0.010(8)	0.000(8)
O(2)	0.722(3)	0.502(2)	0.336(2)	0.022(4)	0.014(8)	0.021(9)	0.031(9)	−0.006(9)	0.009(8)	0.005(7)
O(3)	0.016(3)	−0.020(2)	0.455(2)	0.018(3)	0.015(8)	0.025(9)	0.015(7)	0.003(7)	0.009(6)	−0.008(8)
O(4)	0.043(4)	0.321(2)	0.572(2)	0.019(4)	0.028(9)	0.021(8)	0.008(6)	0.000(7)	0.005(7)	0.005(8)

a

b

x

C Pb O

Fig. 2. [OPb$_2$] chain of corner-sharing OPb$_3$ triangles (*a*) and complex chains of composition [OPb$_2$](CO$_3$) built by addition of CO$_3$ groups to the [OPb$_2$] chain (*b*).

factors. The final refinement converged to an agreement index (*R*) of 0.054 for 915 unique observed ($Fo \geqslant 4\sigma_F$) reflections. The final atomic coordinates and anisotropic displacement parameters are given in Table 2, selected interatomic distances are in Table 3. Lists of calculated and observed structure factors have been deposited with the editor of *Mineralogical Magazine* and are available upon request.

Results

Cation coordination

There are two symmetrically independent Pb^{2+} cations in the structure of shannonite (Fig. 1). The Pb(1) and Pb(2) cations are coordinated by seven and eight atoms of O, respectively. The coordination polyhedra are strongly distorted due to the

effect of s^2 lone electron pairs on the Pb^{2+} cations. In both Pb coordination polyhedra the location of the lone electron pair is apparent from the asymmetry of the polyhedra (Fig. 1).

The carbonate triangle shows typical bond-lengths, with a <C—O> of 1.30 Å. The bond valence sums for atoms calculated using the bond-valence parameters given by Brese and O'Keeffe (1991) are equal to 2.25, 2.00, 3.91, 1.99, 2.16, 1.80 and 2.14 for Pb(1), Pb(2), C, O(1), O(2), O(3) and O(4), respectively, which are in agreement with their formal valences expected from the chemical formula.

Structure description

Description of the structure of shannonite in terms of Pb^{2+} coordination polyhedra and carbonate

TABLE 3. Selected interatomic distances (Å) in the structure of synthetic shannonite.

Pb(1)—O(4)	2.13(2)	Pb(2)—O(4)f	2.24(2)
—O(3)a	2.59(2)	—O(4)b	2.38(2)
—O(3)b	2.65(2)	—O(3)f	2.60(2)
—O(1)	2.66(2)	—O(2)	2.65(2)
—O(2)c	2.68(2)	—O(1)g	2.95(2)
—O(1)d	2.72(2)	—O(1)b	2.99(2)
—O(2)e	2.79(2)	—O(4)h	3.12(2)
C —O(2)j	1.24(3)	—O(2)i	3.20(2)
—O(1)f	1.27(3)	O(4)—Pb(1)	2.13(2)
—O(3)k	1.38(3)	—Pb(2)e	2.24(2)
<C—O>	1.30	—Pb(2)a	2.38(2)
		<O(4)—Pb>	2.25

(a) $x - ½, -y + ½, -z + 1$;
(b) $x + ½, -y + ½, -z + 1$;
(c) $-x + ½, -y + 1, z + ½$;
(d) $-x + ½, -y + 1, z - ½$;
(e) $x - 1, y, z$;
(f) $x + 1, y, z$;
(g) $-x + ¾, -y + 1, z - ½$;
(h) $x + ¾, -y + ½, -z + 1$;
(i) $-x + 2, y - ½, -z + ½$;
(j) $-x + ¾, -y + 1, z + ½$;
(k) $-x + 1, y + ½, -z + ¾$

groups is complicated by the non-regular Pb^{2+} polyhedra. A more elegant description may be given in terms of anion-centred polyhedra. The description of crystal structures of minerals and inorganic compounds on the basis of coordination polyhedra around specific anions (O,F) has recently been proposed (Krivovichev *et al.*, 1998*a,b*; Krivovichev and Filatov, 1999), although its utility has long been recognized (e.g. O'Keeffe and Hyde, 1985; Hyde and Andersson, 1989).

The Pb—O(4) distances [the O(4) atom is not bonded to C] are considerably shorter (2.13–2.38 Å) than the Pb—O distances associated with O atoms that belong to the CO_3 groups (>2.59 Å). Thus, the O(4)-centred polyhedron may be considered as an independent structural subunit in the structure of shannonite. The O(4) atom is coordinated by three Pb^{2+} cations, forming an approximately planar $OPb(1)Pb(2)_2$ triangular group. These groups are linked through the Pb(2) cations to form $[OPb_2]$ infinite chains that are parallel to the *a* axis (Fig. 2*a*). The carbonate groups are linked to these chains via
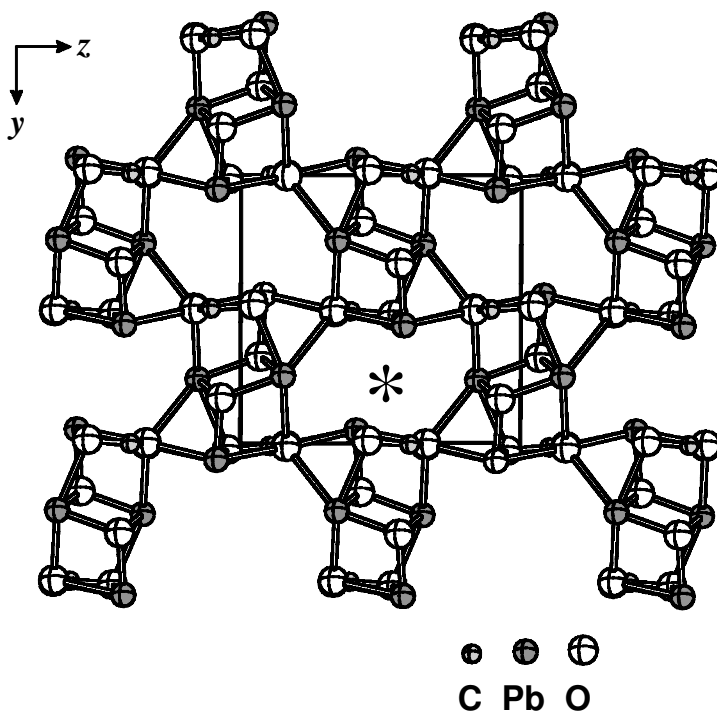

FIG. 3. The structure of shannonite viewed along the *a*-axis. Asterisk shows channels that contain the s^2 lone-electron pair on the Pb^{2+} cations.

Pb—O bonds, giving complex chains with the chemical formula $[OPb_2](CO_3)$ (Fig. 2b). These chains are arranged in a checker-board fashion and are connected with each other via additional Pb—O bonds to form a 3-dimensional framework (Fig. 3). The framework has channels (one of which is marked in Fig. 3 by an asterisk) which contain the lone-electron pairs of the Pb^{2+} cations. It is common for electron lone pairs to be located in structural cavities in minerals and inorganic compounds with such cations as Se^{4+}, Bi^{3+} or Pb^{2+}. The structure of shannonite is considerably influenced by the existence of lone-electron pairs on Pb^{2+}.

Acknowledgements

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