THE CRYSTAL STRUCTURE OF NASONITE

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Abstract

Nasonite, $Pb_6Ca_4(Si_2O_7)_3Cl_2$, is hexagonal, $P6_3/m$, a 10.08, c 13.27Å, Z 2. Using the 872 *hkl* intensities measured photometrically from Weissenberg photographs, the structure was determined with the heavy atom method. Least-squares refinement reduced the conventional R factor to 0.054. The crystal structure of nasonite can be derived in a simple way from that of the members of the apatite group. Si_2O_7 groups characterise the structure of nasonite. The Pb atoms have irregular coordination polyhedra; Ca atoms are surrounded by six oxygens at the vertices of trigonal prisms forming columns along the three-fold axis. A partially covalent bonding system involving Pb, Cl, and O is described.

Introduction

Frondel and Bauer (1951) pointed out the morphological and chemical relations between nasonite $Pb_6Ca_4(Si_2O_7)_3Cl_2$ and the members of the apatite group. Owing to the almost certain presence in nasonite of Si_2O_7 groups, Frondel and Bauer supposed that: "The chemical similarity between nasonite and pyromorphite presumably follows from a near equivalence in the geometrical manner of packing of $3(Si_2O_7)^{-6} = 6(PO_4)^{-3}$ with equal number of Cl and (Pb,Ca) ions." The aim of this structural study is to verify this hypothesis.

Experimental

A small sphere (0.19 mm in diameter) of nasonite from Franklin, New Jersey, was used for collecting the X-ray diffraction data. Nine reciprocal lattice layers (rotation axis a) were recorded with an equi-inclinating Weissenberg camera using the multiple film technique (CuKα radiation).

The lattice parameters measured on rotation and Weissenberg photographs are in good agreement with those of nasonite from Franklin published by Frondel and Bauer, so their values were used: $c = 10.08$ Å, $c = 13.27$ Å; space group $P6_3/m$; cell content 2 $Pb_6Ca_4(Si_2O_7)_3Cl_2$ (from the analysis of Frondel and Bauer of nasonite from Franklin).

The photometrically measured intensities were corrected for the Lp factor, α_1-α_2 spot doubling, and absorption (μR 9.1). The measured intensities were reduced to a common relative scale on the basis of the fact that different reciprocal lattice layers of a hexagonal crystal rotated around a contain reflexions equivalent by symmetry. For this purpose the computer program FILTRO, written in this laboratory, was used. The program performs an auto-scaling process according to the method of Hamilton *et al.* (1965) and averages the scaled equivalent intensities in one value. The measured intensities were so reduced to 872 independent values; 382 out of these 872 reflexions were considered unobservably weak.

Determination of the Structure

The crystal structure was determined with the heavy atom method by finding on the three-dimensional Patterson synthesis the positions of

TABLE 1. FINAL ATOMIC PARAMETERS FOR NASONITE[a]

Atom	S	N	x/a	y/b	z/c	B($\overset{o2}{A}$)
Pb	1	12	0.25801(11)	0.26493(11)	0.10862(6)	1.44[b]
Ca(1)	3	4	1/3	2/3	.9936(7)	0.98(11)
Ca(2)	$\bar{6}$	2	1/3	2/3	1/4	0.95(16)
Ca(3)	$\bar{6}$	2	2/3	1/3	1/4	0.77(16)
Cl(1)	$\bar{6}$	1.7	0	0	1/4	2.14(28)
Cl(2)	$\bar{3}$	1.6	0	0	0	2.02(29)
Si	1	12	0.0259(7)	0.4198(7)	0.3644(4)	0.52(8)
O(1)	1	12	.0710(22)	.3291(22)	.4444(13)	2.11(32)
O(2)	1	12	.8588(17)	.3949(17)	.6208(12)	1.08(24)
O(3)	1	12	.8545(20)	.3748(20)	.3725(13)	1.71(30)
O(4)	m	6	.0714(29)	.3830(29)	1/4	1.38(39)

[a]Values in parentheses are standard deviations. S is the point symmetry. N is the number of atoms per unit cell. The standard deviations of the multipliers N which were allowed to vary in the least-squares refinement, affect the second decimal figure.

[b]Pb was treated anisotropically in the refinement; the value listed in this Table corresponds to the equivalent isotropic temperature factor (Hamilton, 1959).

the Pb atoms and placing the remaining atoms after the inspection of a three-dimensional electron density map based on the Pb signs. The atomic parameters of all the atoms were refined with the least-squares method.

Three least-squares cycles, with isotropic temperature factors, reduced the R value from 0.22 to 0.096. Two cycles, with anisotropic temperature factor for Pb, lowered R to 0.065. In these two cycles the multipliers of Pb, Ca, and Cl were allowed to vary in order to obtain information about occupancy; only the two non-equivalent Cl atoms showed an occupancy significantly lower than 100 percent. The last two least squares cycles

TABLE 2. ANALYSIS OF THE ANISOTROPIC THERMAL PARAMETERS OF Pb.

r.m.s.($\overset{o}{A}$)	B ($\overset{o2}{A}$)	Angles (°) with respect to		
		a	b	c
0.11	0.90	92	114	11
0.12	1.15	167	27	79
0.18	2.64	77	79	86

TABLE 3. INTERATOMIC DISTANCES AND ANGLES
(STANDARD DEVIATIONS IN PARENTHESES)

Atoms	Distance ($\overset{\circ}{A}$)	Atoms	Distance ($\overset{\circ}{A}$)
Si – O(1)	1.61(2)	Pb – O(1)	2.31(2)
Si – O(2)	1.65(2)	Pb – O(1')	2.38(2)
Si – O(3)	1.55(2)	Pb – O(2)	2.37(2)
Si – O(4)	1.68(2)	Pb – O(3)	3.23(2)
Ca(1) – O(2)[a]	2.40(2)	Pb – O(4)	3.27(2)
Ca(1) – O(3)[a]	2.36(2)		
Ca(2) – O(2)[b]	2.42(2)	Atoms	Angle (°)
Ca(2) – O(4)[a]	2.76(3)		
Ca(3) – O(3)[b]	2.37(2)	O(1)–Si–O(2)	109(1)
		O(1)–Si–O(3)	112(1)
Pb – Cl(1)	3.236(3)	O(1)–Si–O(4)	106(1)
Pb – Cl(2)	3.005(4)	O(2)–Si–O(3)	112(1)
		O(2)–Si–O(4)	104(1)
		O(3)–Si–O(4)	113(1)
		Si–O4–Si	129(2)

[a] The distance occurs three times.
[b] The distance occurs six times.

with anisotropic temperature factors for Pb, fixed multipliers, and secondary extinction correction (Zachariasen, 1963) led to the final discrepancy value of 0.054.

In all the least-squares cycles the anomalous dispersion correction for Pb, Ca and Cl was applied using the $\Delta f'$ and Δ'' values given by Cromer (1965).

The positional parameters are listed in Table 1; the anisotropic thermal vibration analysis for Pb is given in Table 2; the interatomic bond distances and angles are listed in Table 3. Observed and calculated structure factors are compared in Table 4.[1]

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of nasonite could be formally derived from that of apatite[2] in the following way: if one imagines two unit cells of apatite

[1] Table 4 may be ordered as NAPS Document No. 01478 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue New York, N.Y. 10022, remitting in advance $2.00 for microfiche or $5.00 for photocopies, payable to CCMIC-NAPS.

[2] The term "apatite" is used in this work to indicate a compound of chemical formula M_{10} $(TO_4)_6Cl_2$ having the crystal structure of chloroapatite.

superposed in the c direction (Fig. 1 left) and rotates one of them of 60° around the 6_3 axis, one obtains the unit cell of nasonite. This operation leads two oxygens of two PO_4 tetrahedra to be nearly superposed (Fig. 1 center); in this way a T_2O_7 group could be formed corresponding to the Si_2O_7 group of nasonite. The cell of nasonite (Fig. 1 right) has the same space group of that of apatite and its projection along c is very similar to the corresponding projection of the two superposed cells of apatite (Fig. 2).

The hypothesis of Frondel and Bauer can be considered correct if these considerations are taken into account.

A more detailed inspection of the crystal structure reveals some inter-esting features that are peculiar of nasonite.

Silicon. As said above, nasonite is a sorosilicate with Si_2O_7 groups. The two tetrahedra are related by the mirror plane passing through the shared oxygen $O(4)$. The Si-O bond lengths range from 1.56 to 1.68 Å; this last figure is referred to the distance between Si and the shared oxygen $O(4)$.

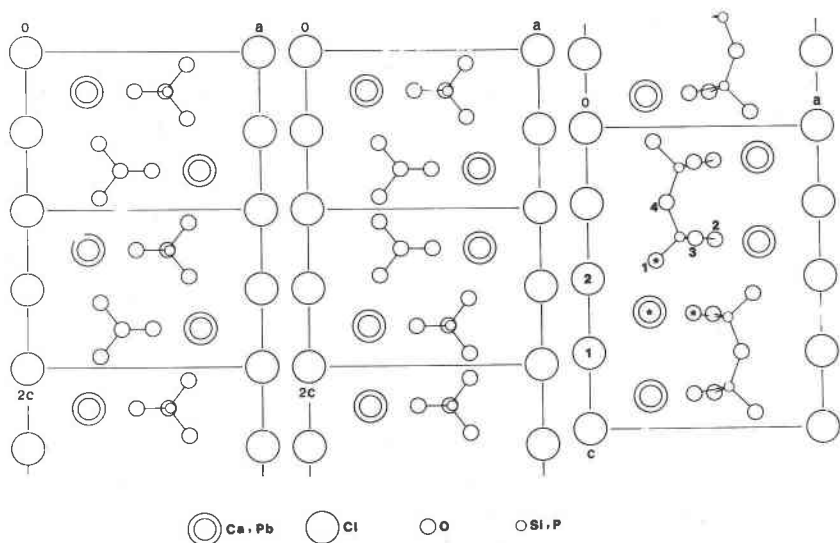$\bigcirc$ Ca, Pb $\quad$ $\bigcirc$ Cl $\quad$ $\bigcirc$ O $\quad$ $\bigcirc$ Si, P

FIG. 1. Left: schematic projection along the normal to the plane ac, onto the same plane, of a slab of the crystal structure of apatite 4 Å thick, This slab contains the atoms which have the y coordinate in the range ±0.15. Center: the same after rotation of 60° around the hexagonal screw axis of the part belonging to the lower cell. Right: partial schematic projection of the crystal structure of nasonite obtained in the same way of the left part of this figure. Pb marked with a star is bonded to the oxygens marked in the same manner. The third Pb-O bond is directed along the normal to the plane of the figure.
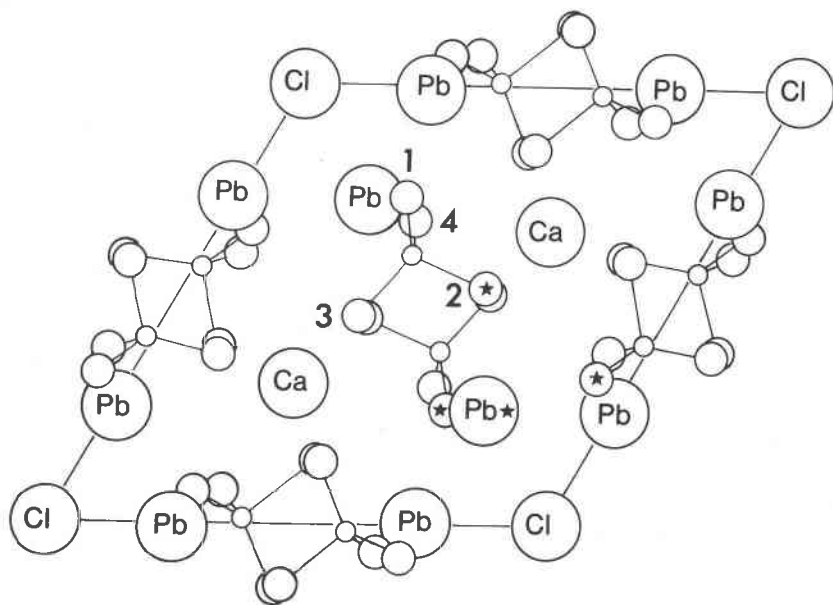
Fig. 2. The crystal structure of nasonite projected along *c*. The circles of Ca and Cl represent four superposed atoms; the circles of the remaining atoms but O(4) represent two superposed atoms. The Pb atom marked with a star is bonded to the oxygens marked by stars.

Lead. The Pb atoms are situated near the hexagonal screw axis. Each of them is bonded to three oxygens belonging to three different Si_2O_7 groups. The Pb-O distances range from 2.31 to 2.38 Å. Pb is also bonded to two chlorine atoms with distances of 3.0 and 3.24 Å. The coordination polyhedron of lead is rather irregular like in other Pb oxygenated compounds. With respect to the oxygens, lead is at the apex of a trigonal pyramid and, considering also the shortest bond length with Cl(2), it lies on the vertex of an irregular square pyramid as in PbO (McKay, 1961). The mean Pb-O distance 2.35 Å, is midway between the sum of the covalent radii (2.2 Å) and that of the ionic radii (2.5 Å) of Pb and O (McKay, 1961). The Pb-Pb shortest distances are 3.75 and 3.91 Å. These distances fall in the range of Pb^{2+}-Pb^{2+} distances (3.60 to 3.95 Å) found by Bouvaist and Weigel (1970) for Pb_2O_3. These authors consider these short distances as a proof of the partial covalent character of the Pb^{2+}-O bond in Pb_2O_3. The same considerations could be applicable to Pb in nasonite. On the other hand the thermal vibration ellipsoid of Pb in nasonite has its shortest axis nearly parallel to *c*, that is to the Pb-Pb vector corresponding to the distance of 3.75 Å, and this fact could be in

favor of some repulsion between the two Pb atoms related by the mirror plane, *i.e.*, in favor of a partial ionic character of these atoms.

Calcium. There are three non-equivalent Ca atoms (8 in the unit cell) situated on the three-fold axis. The coordination polyhedra of these atoms are trigonal prisms which form a sort of column along the three-fold axis by sharing their basal faces. The Ca-O bond lengths range from 2.35 to 2.43 Å (mean value 2.39 Å); in apatite the mean Ca-O distance is 2.43. In apatite (Posner *et al.*, 1958) there are also three oxygens at a distance of 2.80 Å. In nasonite only Ca(2) has these long additional distances (2.75 Å). It must be said that the oxygens involved are screened for a great part by the oxygens of the trigonal prism.

Chlorine. The two non-equivalent Cl atoms are located on the hexagonal screw axis. Each chlorine is surrounded by six Pb atoms; according to the Pauling's rules, if the Pb-O and Pb-Cl bonds were completely ionic each Cl atom, would be reached by a sum of positive charges, greatly exceeding the value of its valence. This fact could be a further argument in favor of the partially covalent bonding system described above. In the mineral ganomalite $Pb_6Ca_4(Si_2O_7)_3(OH)_2$ the chlorine atoms are replaced by hydroxyl groups. This mineral should have with nasonite the same relation existing between hydroxyapatite and chloroapatite.

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