Short Communication

Further refinement of the goyazite structure

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Abstract

The crystal structure of goyazite has been re-refined using the counter data, giving $R=0.039$ for 417 reflections. Formula: $SrAl_3(OH)_6[PO_3(O_{1/2}(OH)_{1/2})]_2$. Cell dimensions: $a=7.015(3)$, $c=16.558(6)$Å, space group $R\bar{3}m$, $Z=3$. Goyazite has a structure analogous with that of alunite and/or crandallite. Either apical O of a pair of P tetrahedra is replaced by OH. Mean distances of M–(O, OH) are as follows: P–(O, OH) 1.535Å, Al–(O, OH) 1.896Å, Sr–(O, OH) 2.748Å.

Introduction

The formula of goyazite was supposed to be $SrAl_3H[(OH)_6(PO_4)_2]$. Once, Kato (1971) refined the structure of this mineral using the film data. It was revealed that goyazite belongs to the alunite-type structure. However, the extra hydrogen could not be located because of low precision of the structure analysis ($R=12.9\%$).

Recently, Radoslovich and Slade (1980) and Radoslovich (1982) refined the gorceixite structure and found that its true space group is Cm rather than $R\bar{3}m$. Radoslovich (1982) also suggested that careful refinement of goyazite might produce a structure closely comparable to that of gorceixite.

To make clear these problems, I have re-refined the goyazite structure using the counter data, and obtained the conclusion that (1) true space group of goyazite is $R\bar{3}m$ and (2) the structure formula of goyazite should be written as $SrAl_3(OH)_6$ $[PO_3O_{1/2}(OH)_{1/2}]_2$ like crandallite. Here, the detail of the obtained results will be described.

Experimental

Crystals of goyazite from Palesmo mine, North Groton, New Hampshire, U.S.A. (NMNH #141049) were provided by Dr. P. J. Dunn, Smithsonian Institution. This locality is the same as that of the sample previously studied. A crystal of the size of $0.02 \times 0.016 \times 0.008$ cm was selected for this work. Cell dimensions were determined using 25 reflections measured on a Philips PW-1100 single crystal diffractometer.

TABLE 1. Crystal data

Formula		$SrAl_3(OH)_6[PO_3(O_{1/2}(OH)_{1/2})]_2$
	KATO (1971)	This study
Cell dimensions		
a	7.021(3) Å	7.015(3) Å
c	16.505(15)	16.558(6)
Space group		R3̄m
Z		3

Crystal data are given in Table 1 with those obtained in the previous work. The cell dimensions are in good agreement with the reported ones. Intensity data were collected on the same computer-controlled diffractometer with graphite-monochromated MoKα (λ=0.71069Å). The $\theta-2\theta$ scan mode was applied. The rhombohedral cell was selected and intensity data were collected on the triclinic condition. The theta range was $1° < \theta < 30°$. The reflections of I $> 3\sigma_{(I)}$ were considered to be observed. Absorption correction was made using a program ACACA written by Prewitt (Wuensch and Prewitt, 1965). Equivalent reflections were averaged. The number of independent reflections was 417. Wilson test showed that the structure would be probably centrosymmetric.

The atomic parameters reported by Kato (1971) were used as starting parameters. The refinement was carried out using a block diagnoal least-squares program, BDLS-60 in the UNICS system (Sakurai ed., 1974). Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (Vol. IV). The final atomic parameters are listed in Table 2 and bond distances and angles are given in Table 3 with those for the previous work.

Discussion

The goyazite structure belongs to the rhombohedral space group R3̄m, but is more easily described in terms of the larger equivalent hexagonal cell in which a=7Å, c=17Å approx. Goyazite consists of sheets of Al octahedra each of which shares four corners with four other octahedra to form large hexagonal and small trigonal rings. The sheets are perpendicular to the c axis, and Sr cations lie between the sheets in large cavities surrounded by twelve oxygen and hydroxyl ions. Each phosphate tetrahedron shares three corners with the three Al octahedra common to a trigonal ring. The remaining unshared corner points away from the trigonal hole towards the adjacent sheet and is hydrogen bonded thereto (Fig. 1).

In this new refinement, two hydrogens could be located form three-dimensional

TABLE 2. Atomic coordinates and thermal factors

Atom	Sr	P	Al	O(1)	O(2)	O(3)	H(1)	H(3)
KATO (1971)								
x	0	0	1/2	0	0.2158(16)	0.1262(15)		
y	0	0	1/2	0	-0.2158	-0.1262		
z	0	0.3083(5)	1/2	0.4017(16)	-0.0566(8)	0.1366(8)		
B	0.56	0.61	0.56	1.71	1.39	1.16		
This study								
x	0	0	1/2	0	0.2142(4)	0.1247(5)	0	0.194*
y	0	0	1/2	0	-0.2142	-0.1247	0	0.806
z	0	0.3075(1)	1/2	0.4003(3)	-0.0567(2)	0.1371(2)	0.463*	0.110
B(eq)**	1.00	0.52	0.66	0.68	0.66	0.72		
β_{11}***	883(21)	300(31)	353(363)	556(100)	618(96)	313(84)		
β_{22}	883	300	470(384)	556	618	313		
β_{33}	35(3)	63(6)	74(6)	37(17)	48(10)	94(11)		
β_{12}	442	150	235	278	495(58)	58(50)		
β_{13}	0	0	146	0	7(21)	55(22)		
β_{23}	0	0	73(12)	0	7	-55		

*Determined from the three-dimensional difference Fourier map.

**B(eq) = $8\pi^2 \ u^2$

***Anisotropic temperature factor ($\times 10^5$) are of the form: exp. $\left\{ -\sum\limits_{i=1}^{3} \sum\limits_{j=1}^{3} h_i h_j \beta_{ij} \right\}$

TABLE 3. Bond distances(Å) and angles(°)

	KATO (1971)	This study
P O(1)	1.551(28)	1.536(5)
P O(2)	1.522(11)	1.535(3)
O(1) O(2)	2.519(25)	2.508(5)
O(2) O(2')	2.476(18)	2.507(3)
Al O(2)	1.907(13)	1.910(3)
Al O(3)	1.896(11)	1.889(4)
O(2') O(3)	2.741(17)	2.745(5)
O(2") O(3)	2.635(17)	2.626(5)
O(3) O(3')	2.706(18)	2.718(6)
O(3') O(3")	2.658(11)	2.624(4)
Sr O(2)	2.788(14)	2.767(4)
O(2) O(2')	4.454(14)	4.507(5)
Sr O(3)	2.729(12)	2.729(4)
O(3) O(3')	2.706(18)	2.624(6)
Al P	3.091(6)	3.089(2)
Al-Sr	3.418(2)	3.423(1)
O(2) P-O(2')	110.11 (61)	109.45 (0)
O(2) P-O(1)	110.10 (56)	109.48 (0)
O(2)-Al-O(3)	92.24 (52)	92.54 (55)
O(2')-Al-O(3)	87.71 (48)	87.46 (0)
O(3)-Al-O(3')	91.00 (45)	92.05 (55)
O(3')-Al-O(3")	89.00 (45)	87.98 (0)
P-O(2)-Al	128.38 (87)	127.07 (0)
O(1) H(1)		1.05
H(1)---O(1')		2.25
O(3)-H(3)		0.95
H(3)---O(1)		1.84
O(1)-H(3)-O(3)		175.6

difference Fourier map. The hydrogen atoms have two situations. The first ones are designated as H(1) because these are statistically bonded to one half of O(1) atoms and are comprised in $PO_3(OH)$. The second ones are designated as H(3) because these are bonded to O(3) and form (OH). Thus, H(2) does not exist.

First, it was found that H(1) is statistically distributed in two positions between the apical oxygens O(1) of two phosphate tetrahedra along the c axis. This means that a pair of PO_4 and $PO_3(OH)$ are statistically distributed. That is, in a pair of opposed
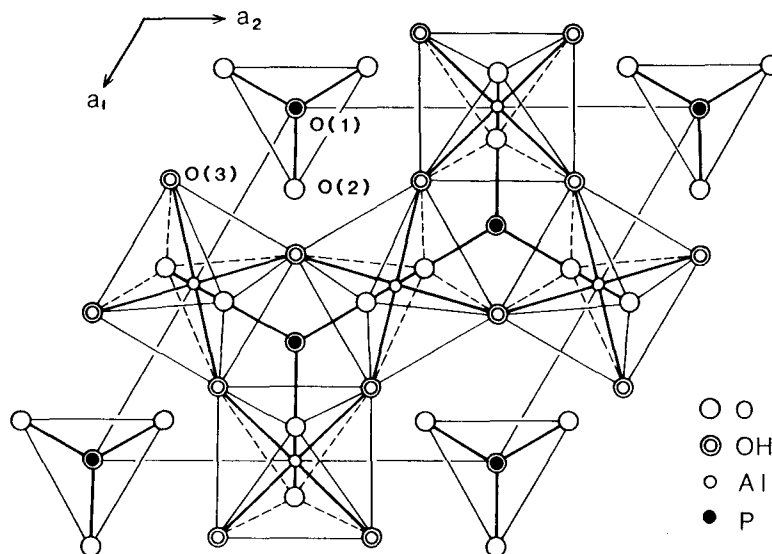
FIG. 1.   The c-axis projection of goyazite structure. Only polyhedral contacts betwen
$z = 1/3$ and $z = 2/3$ and the positions of tetrahedra near the origin are shown.

phosphate tetrahedra, if the apex of the lower tetrahedron, O(1), is occupied by O,
the apex of the upper tetrahedron, O(1'), must be occupied by OH, and vice versa
(Fig. 2). The distances O(1)–H(1) and H(1)–O(1') are 1.05 and 2.25Å, respectively.
The distance O(1)–O(1') is 3.30Å. Blount (1974) deduced the same mechanism,
statistical distribution of a pair of PO_4 and $PO_3(OH)$, in the crandallite structure. She
could not locate the hydrogen atoms during the X-ray structure determination. She
deduced such mechanism by IR data and the results of the total valence of the bonds
reaching the anions. In this case, O(1)–O(1') distance is 2.992Å.

Secondly, the position of H(3) belonging to OH(=O(3)) coordinated to Al and Sr
could be determined. The distances O(3)–H(3), H(3)–O(1) are 0.95 and 1.84Å, re-
spectively, and the angle O(3)–H(3)–O(1) is $175.6°$ These values are comparable with
the results of the alunite and synthetic jarosite structures obtained by Menchetti and
Sabelli (1976).

The most unique feature in such $PO_3(O_{1/2}(OH)_{1/2})$ is that P–O(1), 1.536Å is
nearly the same as that of P–O(2), 1.535Å. This makes a good contrast to the results
of other minerals (For instance, in the florencite structure P–O(1), 1.512Å, is shorter
than P–O(2), 1.543Å. (Kato, in preparation)).

Al ion is coordinated in a slight distorted octahedron formed by four OH groups
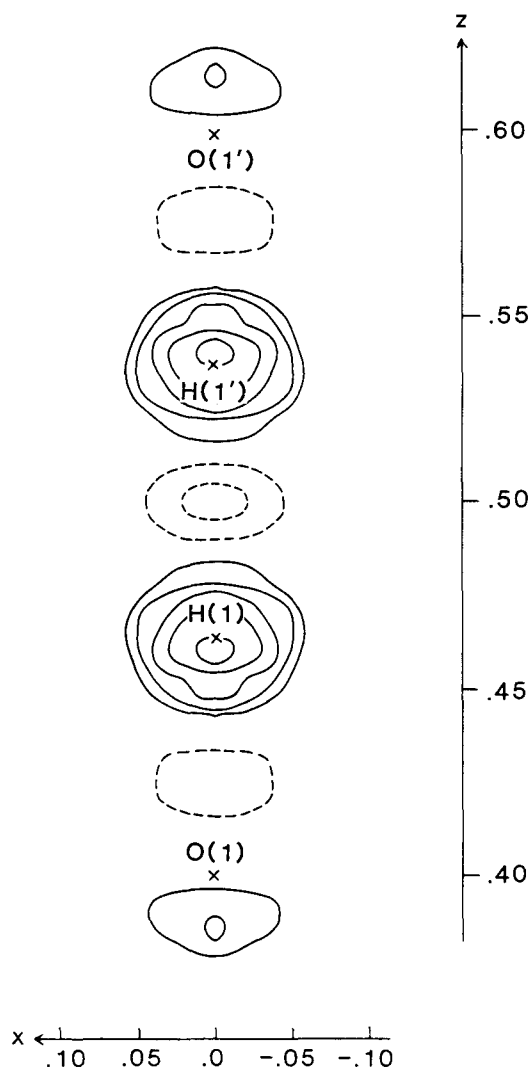and two oxygen atoms from two separate phosphate tetrahedra. The distances Al–

FIG. 2.   Portion of the difference Fourier section, y = 0.00. Contours are drawn at interval of 0.1 e/A^3, zero contours being omitted, and negative contours broken.

O(2) and Al—O(3) are 1.910 and 1.889Å, respectively. The O(3)—O(3) edge distances of the octahedron are 2.627 and 2.718Å; O(2)—O(3) edge distances are 2.626 and 2.714Å.

Sr ion is considered as twelve coordinated. Six oxygen neighbors from six phosphase groups afford a flattened octahedron about each Sr with a bond length of

2.767Å (2.757Å in svanbergite) (Kato and Miúra, 1977), while the six O(3)(=OH) neighbors of Al octahedra in the elongated octahedral arrangement about each Sr are at the distance of 2.729Å (2.710Å in svanbergite).

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