ZUNYITE FROM POSTMASBURG, SOUTH AFRICA

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Abstract

New determinations of the cube edge, refractive index, dispersion and disintegration on heat treatment combined with existing chemical analysis of zunyite are given. This mineral has a face-centered cubic lattice and a cube edge of 14.034 (0.003) Å. The refractive index for Na-light is 1.600 ($\pm$0.001) and dispersion $n_F - n_C = 0.009$ ($\pm$0.001). Its determined specific gravity of 2.87 is in good agreement with the calculated value of 2.85. On heating zunyite to 1100° C. the structure breaks down to form mullite, indicating a Si:Al ratio of 1:3 in the zunyite itself. The mineral contains less fluorine but more chlorine than the American variety from Zuni-mine.

Introduction

The occurrence of the very rare aluminum silicate, zunyite, in the highly aluminous shales and flagstones at Postmasburg, was first described by Nel (1, pp. 207–216). The zunyite crystals vary in size from about 3 mm. to less than 1 mm. (measured along the edges). They are usually perfectly crystallized octahedrons which often show twinning. The crystals have a flesh color, some having reddish nuclei. The latter type was never used for examination. Pure material was obtained by hand picking from the soft country rock in which it occurs.

As described by Nel (1, p. 211), zunyite occurs in two ways; "either it forms curious patches in the coarse diaspore-rock or its crystals are roughly arranged in layers or disseminated through a rock in which diaspore is only of microscopic dimensions." The zunyite occurring in the latter manner is also larger and only these have been used for the investigations. The matrix of this rock was identified as consisting of intimately intergrown pyrophyllite and kaolinite.

Specific Gravity

The specific gravity was determined in two ways: (*a*) according to the method of Jahns (2, pp. 216–222) in which fragments are suspended in Clerici solution. The mean of three determinations yielded G_4^{16} 2.87^1 ($\pm$0.005), and (*b*) by the pyknometer method. The results obtained by this method were corrected for the difference in the displacement of air by the volume of the contents of the bottle and the volume of the weights used with the balance. For this correction the density of air was calculated as 0.0010296 gr./cc. at Pretoria where the atmospheric pressure is 65 cms. Hg at a temperature of 25° C. (3. p. 1694). The mean of three

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determinations was found to be G_4^{25} 2.877 (± 0.005). The final specific gravity was taken as 2.874 (± 0.005). Taking the molecular weight of zunyite as 4736 (i.e. when the unit-cell contains the following atoms, 19 Si, 53 Al, 1 Fe, 2 Na, 64 OH, 7 Cl, 1 F and 82 oxygen) its specific gravity can be calculated as 2.845 (4, pp. 109–110), which is in good agreement with the experimental value.

Optical Properties

Zunyite is optically isotropic and its refractive index and dispersion were determined according to a single variation method at room temperature (20° C.) using a monochromator. Its index of refraction was found to be:

$$n_{Na} = 1.600\ (\pm 0.001)$$

Dispersion: $n_F - n_C = 0.009\ (\pm 0.001)$.

Table 1. Qualitative Spectrographic Analysis of Zunyite

Present:	Si, Al, Fe, Na.
Trace:	Mg, Ca, K, Ti, Cr, V.
Absent:	Be, Sr, Bb, Cs, Li, Mn, Mo, Ba.

Table 2. Chemical Analysis

a		*b*	*c*		*d*		
SiO_2	24.10	0.4016	Si	0.4016	19.18	Si	(19)
Al_2O_3	56.85	0.5573	Al	1.1146	53.23	Al	(54)
Fe_2O_3	1.45	0.0091	Fe	0.0182	0.87		
MgO	0.30	0.0075	Mg	0.0075	0.35		
CaO	0.20	0.0036	Ca	0.0036	0.17		
Na_2O	1.45	0.0232	Na	0.0464	2.24	Na	(2)
K_2O	tr.	tr.	P	0.0036	0.17		
Cl_2	4.80	0.1352	Cl	0.1352	6.56	Cl, F+OH	(72)
F_2	0.40	0.0211	F	0.0211	1.01		
P_2O_5	0.25	0.0018	H	1.3334	63.73		
H_2O	11.65	0.6667	O−(F+Cl)	3.0563	146.00*	O	(82)
H_2O	0.35						
Less O for F, Cl	1.30						
	100.50						

* After an equivalent amount of O has been subtracted for (F+Cl).
a. Chemical analysis by H. G. Weall.
b. Molecular proportions.
c. Atomic ratios.
d. Unit-cell contents.

Chemical Composition

The chemical analysis listed is the one given by Nel (1, p. 216) and the spectrographic analysis was carried out on a large Hilger Littrow-type spectrograph; samples were arced in hollowed copper anodes (the cathodes were slightly pointed) for 20 seconds at 5 amps.

The unit-cell contents were determined by the following equation:

$$\text{Number of ions of each element in the unit-cell} = \frac{\text{Unit-cell volume} \times \text{Avogadro's number} \times \text{atomic ratio} \times \text{density}}{\text{Sum total of the chemical analysis}}$$

where $a = 14.03$ Å and Avogadro's number $= (6.0597 \pm 0.0016)\ 10^{23}$ (4, p. 110).

X-Ray Examination

X-ray powder diffraction patterns were obtained by using 114 cms. diameter cameras in which the film is mounted according to the Straumanis method (5, p. 726). The temperature during the exposures remained reasonably constant and did not vary more than 1° C. above room temperature of 20° C. The time of exposure was $2\frac{1}{4}$ hours using unfiltered Cu-radiation at 35 K.V. and 20 ma. Shrinkage correction factors were determined and the measuring carried out as described by Wasserstein (6, p. 106).

The final value for a_0 was determined using Bradley and Jay's graphical extrapolation method (7, p. 563) and represents the mean of three determinations. *X*-ray diffraction angles were converted to interplanar spacings by using suitable tables. The wavelengths used were:

$CuK\alpha_1$ 1.537395 KXu. or 1.540501 Å
$CuK\alpha_2$ 1.541232 KXu. or 1.544345 Å

Pauling (9, pp. 442–452) determined the cube edge of zunyite from Zuni-mine, Colorado, U.S.A., as 13.830 ($\pm$0.005)Å. He suggested that it has a face-centered lattice and a space-group symmetry T_d^2. The powder photographs of the Postmasburg zunyite also indicate a face-centered cubic lattice.

The South African variety contains more chlorine and less fluorine than that from the Zuni-mine. As the water content is more or less the same in the two samples, chlorine replaces fluorine in the Postmasburg zunyite. The ionic radius of chlorine is much larger than that of fluorine viz: Cl^- 1.81 Å and F^- 1.33 Å (10, p. 1314) and this causes an expansion of the unit-cell.

Pauling also suggested that the unit-cell contains four molecules of composition $Al_{13}Si_5O_{20}(OH, F)_{18}Cl$. If the unit-cell contents as calculated in Table 2 (*d*) are divided by 4 the results shown in Table 4 are obtained.

TABLE 3. *X*-RAY DATA FOR POSTMASBURG ZUNYITE

$\alpha_o = 14.034\ (\pm 0.003)$ Å

No.	Int(obs.)	2θ (Cu)	d Å	(*hkl*)
1	2	9.98	β-line	
2	10	11.08	7.99	(111)
3	3	19.19	β-line	
4	10	21.24	4.18	(311)
5	8	22.23	4.00	(222)
6	1	25.25	β-line	
7	4	28.02	3.18	(331)
8	6	30.26	β-line	
9	7	31.63	2.83	(422)
10	10	33.59	2.67	(333) (511)
11	5	36.61	2.45	(440)
12	5	38.41	2.34	(531)
13	4	40.72	2.22	(620)
14	7	42.75	2.12	(622)
15	8	45.32	2.00	(444)
16	4	46.77	1.942	(711) (551)
17	6	49.14	1.854	(642)
18	6	50.47	1.808	(731) (553)
19	5	54.55	1.682	(820) (644)
20	9	56.23	1.636	(555)
21	4	57.76	1.600	(662)
22	2	59.80	1.547	(840)
23	5	60.87	1.522	(842)
24	1	62.62	1.484	(664)
25	4	64.00	1.455	(931)
26	4	65.89	1.418	(844)
27	6	67.16	1.394	(933)
28	2	68.96	1.362	(10, 2, 0) (862)
29	5	70.17	1.341	(666), (10, 2, 2)
30	5	74.94	1.267	(10, 42)
31	2	76.15	1.251	(11, 1, 1) (775)
32	5	77.85	1.227	(880)
33	3	79.18	1.210	(10, 4, 4) (882)
34	6	81.91	1.176	(10, 6, 2)
35	5	93.16	1.0606	(12, 4, 4)
36	6	96.19	1.0347	(12, 6, 2)
37	2	98.84	1.0149	(888)
38	1	101.64	0.9937	(14, 2, 0)
39	4	105.01	0.9708	(12, 8, 0)
40	1	107.76	0.9535	(14, 4, 2) (12, 6, 6)
41	7	109.29	0.9444	(12, 8, 4)
42	2	112.55	0.9261	(14, 4, 4)
43	2	113.94	0.9187	(14, 6, 0)
44	1	116.81	0.9043	(999) (13, 7, 5) (11, 11, 1)
45	3	120.08	0.8891	(12, 10, 2)
46	3	123.22	0.8756	(16, 0, 0)
47	4	126.89	0.8611	(13, 7, 7)
48	4	128.75	0.8543	
49	4	130.18	0.8493	(15, 5, 5)
50	6	133.99	0.8368	(12, 10, 6)
51	2	140.60	0.8181	(16, 4, 2)
52	3	145.27	0.8093	(16, 8, 2)
53	1	152.79	0.7925	(17, 5, 1)
54	1	157.07	0.7858	(16, 8, 4)
55	6	159.76	0.7824	(17, 5, 3)

TABLE 4. COMPARISON OF EMPERICAL FORMULA OF THE SOUTH AFRICAN AND AMERICAN ZUNYITES

Atom	S.A. Zunyite	American Zunyite (9, p. 445)
Si	4.80	4.63
Al	13.31	13.17
Fe	0.22	0.03
P	0.04	0.09
Ca	0.04	—
Mg	0.09	—
Na	0.56	0.12
K	—	0.04
Cl	1.64	0.96
F	0.20	3.17
OH	15.94	14.37
O	20.50	20.08
(OH+F+Cl)	17.78	18.50

TABLE 5. *X*-RAY DIFFRACTION DATA FOR MULLITE EX. ZUNYITE COMPARED TO THAT FOR MULLITE EX. KAOLINITE AND NATURAL MULLITE

Mullite ex. zunyite			Mullite ex. Kaolinite[1]		Natural mullite[2]	
No.	Int(*est*)	*d* Å	Int(*est*)	*d* Å	Int(*est*)	*d* Å
1	8	5.40	7	5.40		
2	4	3.77	3	3.76		
3	10	3.41	10	3.39	10	3.44
4	1	2.87	3	2.88	4	2.90
5	7	2.70	6	2.70	5	2.70
6	7	2.54	7	2.54	6	2.56
7	3	2.43	4	2.42	3	2.43
8	3	2.29	3	2.28	4	2.30
9	8	2.20	7	2.20	7	2.21
10	3	2.12	5	2.11	5	2.13
11	3	2.03	2	2.00		
12	4	1.694	5	1.699	6	1.70
13	4	1.595	5	1.600	4	1.60
14	7	1.524	7	1.520	7	1.53
15	4	1.436	5	1.444	4	1.45

[1] McVay and Thompson, *Jour. Am. Cer. Soc.*, **11,** 834 (1928).
[2] Norton, *Jour. Am. Cer. Soc.*, **8,** 637 (1925).

There is a close agreement in Si, Al, oxygen, and the minor constituents. The Cl, F and OH values vary antipathetically but the (Cl+F+OH) totals for both are about the same, and its emperical formula can therefore be written as: $Al_{13}Si_5O_{20}(OH, F, Cl)_{19}$. The Postmasburg zunyite also contains more sodium.

Packing Index

The packing index of zunyite calculated from the formula

$$P.I. = \frac{\text{volume of ions}}{\text{volume of cell}} \times 10$$ (10, p. 1310) is *6.4*.

For this calculation the volumes of the ions given by Fairbairn (10, p. 1314) were used.

Heat Treatment

Grosner and Musgnug (11, p. 153) published data on the dehydration of zunyite for temperatures ranging from 300° C. to 810° C. When the Postmasburg zunyite, pulverized to −200 mesh, was heated in an electric furnace to 1100° C., mullite was formed. No fluorine could be detected spectrographically in this mullite and all the volatile constituents OH, F and Cl, were probably completely driven off below 1100° C.

Mullite, with a chemical formula of $3Al_2O_3 \cdot 2SiO_2$ (orthorhombic) reveals the primary Al:Si ratio of 3:1 in the zunyite as suggested by Grosner and Musgnug (11, p. 154). This 3:1 ratio is also indicated in Table 4. The Postmasburg zunyite has (Al, Fe):Si=2.82:1 and the American zunyite Al:Si=2.82:1.

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