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Neutron diffraction studies of sillimanite

R. C. PETERSON[1]
Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061
R. K. MCMULLAN
Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

ABSTRACT

The crystal structure of sillimanite, refined using single-crystal neutron diffraction data measured at room temperature yielded $a = 7.479(1)$, $b = 7.670(2)$, $c = 5.769(1)$ Å, space group *Pbnm*. The atomic parameters were refined by full-matrix least-squares techniques. The final agreement $R(F^2)$ is 0.037 based on 857 reflections. The Al–O and Si–O bond lengths and O–Si–O and O–Al–O bond angles have estimated standard deviations of ≤0.001 Å and 0.06° and agree well with those based on X-ray diffraction experiments. Refinement of the neutron scattering lengths, *b*, show Al and Si to be ordered within the tetrahedral sites and the minor Fe present in the structure to occupy the octahedral site.

INTRODUCTION

Recent measurements of low-temperature heat capacities of the Al_2SiO_5 polymorphs by Robie and Hemingway (1984) have suggested that Al and Si are ordered in the sillimanite structure to at least 1100 K. Direct evidence of the order in sillimanite at room temperature has been obtained by neutron diffraction experiments (Peterson and McMullen, 1980) and is presented here. Neutron diffraction data were also collected for kyanite and andalusite, and the results are similar to published refinements (Finger and Prince, 1972; Winter and Ghose, 1979; Burnham and Buerger, 1961; Burnham, 1963a, 1963b). Details of the neutron refinements of kyanite and andalusite may be obtained from the authors.

EXPERIMENTAL METHOD

The crystal used in the neutron study was chosen from among the available specimens on the basis of sample homogeneity and purity. These requirements together with the relatively large crystal size needed for neutron diffraction limited the number of suitable crystals. The sillimanite specimen from Norwich, Connecticut (Carnegie Museum of Natural History, #7389) was colorless and displayed many poorly developed faces in the $\{hk0\}$ zone.

The sillimanite chosen was submitted to neutron activation and energy-dispersive microprobe analyses. The trace elements detected by these methods, as well as those reported in aluminosilicate polymorphs (Pearson, 1960; Chinner et al., 1969; Albee and Chodos, 1969) were determined quantitatively by wavelength-dispersive analysis using an Associated Research Laboratory SEMQ microprobe. For analyses of Al_2O_3, TiO_2, MgO, V_2O_3, and Cr_2O_3, 20-kV accelerating voltage and 30-nA sample current were used, and backgrounds were taken from fused silica. The FeO content was determined using 15 kV and 30 nA with background determined by off-peak measurements on either side of the FeK_α emission line. Two standards used for FeO: Rockport fayalite (FeO = 67.9 wt%) and VGl glass (Microbeam Analysis Society, FeO = 0.71 wt%) gave consistent results. The trace-metal oxides detected at the 0.01 wt% level are given in Table 1; the standard deviations in parentheses are based on averages of six points distributed about the grains.

NEUTRON DIFFRACTION

The neutron diffraction data were collected with an automated four-circle diffractometer using a neutron beam obtained by the (002) reflection from a Be crystal monochromator. The neutron wavelength of 1.0024(2) Å was determined by least-squares fit of $\sin^2\theta$ data for the KBr reference crystal ($a_0 = 6.60000(13)$ Å at 25°C). The sillimanite crystal selected for study is described above and in Table 2 together with the crystal data and conditions for the diffraction measurements. The crystal was mounted on a hollow Al pin and centered optically in the neutron beam. The sillimanite crystal was of good diffraction quality, having reflection profiles that were Gaussian in shape with full-width at half-height of ~0.25° in scan angle ω.

The lattice parameters in Table 2 were determined by a least-squares fit of $\sin^2\theta$ data for 32 reflections. Reflection-intensity data were measured by a $\theta/2\theta$ step-scan procedure in which counts at each step were accumulated for a preset monitor count of the direct beam. Fixed scan widths in 2θ were used below $\sin\theta/\lambda = 0.42$ Å^{-1}; variable scan widths computed from empirical dispersion relationships were used above $\sin\theta/\lambda = 0.42$ Å^{-1}. Intensities of two reflections were monitored at regular intervals (ca. 3 h) as a check on experimental stability; these measurements showed no variation with time. The integrated intensity (I) and background (B) were determined for each reflection by summing counts over the central 80% of the scans and over the outer two 10% portions, respectively. The variance in an intensity was derived from the relationship $\sigma^2(I) = C + kB$, where C is the total accumulated

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[1] Present address: Department of Geological Sciences, Queen's University, Kingston, Ontario K7L 3N6, Canada.

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Table 1. Electron-microprobe analysis of sillimanite

	Oxide Wt%	Atomic Proportions*
MgO	n.d.	
Al_2O_3	62.20(11)	1.99
SiO_2	36.32(8)	0.99
TiO_2	n.d.	--
V_2O_3	0.02(1)	0.000
Cr_2O_3	0.01(1)	0.000
FeO	0.93(4)	0.021
Total	99.48	

*Based on five oxygens
n.d. not detected

Table 2. Crystallographic data

	PM*	B**
A. Unit-cell data		
λ(A)	1.0024(2)	CuKα
a	7.479(1)	7.4856(6)
b	7.670(1)	7.6738(3)
c	5.769(1)	5.7698(8)
B. Description of crystal faces (best approximation)	$(\bar{1}02),(00\bar{1}),(\bar{3}20),(\bar{3}\bar{2}0)$ $(110),(1\bar{1}0),\{150\}$	
Max. dimensions (mm)	1.4 x 1.0 x 1.8	
Volume (mm^3) from face measurements	1.172	
Absorption coefficients (cm^{-1})	0.0042	
C. Intensity data measurements		
Temperature (°C)	24	
$(\sin\theta/\lambda)$ max (A^{-1})	0.807	
Scan width (°in 2θ)	3.0 - 5.0	
Ave. No. of steps/scan	50 - 75	
Counting time/step (sec.)	2.5	
No. of observations	1709	
No. of unique observations	857	
Agreement factor $R=\Sigma\|F_o{}^2-\bar{F}_o{}^2\|/\Sigma F_o{}^2$	0.026	
D. Refinement		
No. of observations (NO)	857	
No. of paramenters (NP)	50	
$R(F^2) = \Sigma\Delta/\Sigma F^2$	0.037	
$R_w(F^2) = [\Sigma w\Delta^2/\Sigma(wF^2)]^{1/2}$	0.046	
$S = [\Sigma w\Delta^2/(NO-NP)]^{1/2}$	1.513	
Final difference map		
largest residual $\|\Delta\rho\|$ %ρ at oxygen site	1.56	
Scale factor K $(KF_c)^2$	5.24(2)	
Smallest extinction factor Y $(YF_c)^2$	0.88	
Extinction parameters $x10^{-4}$ isotropic r	0.142(8)	

*present work
**Burnham (1963)

count in the scan and k is the ratio of peak to background count times. Neutron absorption corrections were applied, and weighted-mean crystal beam path lengths were calculated using an analytical procedure (de Meulenaer and Tompa, 1965; Templeton and Templeton, 1973). The linear absorption coefficient, μ, was evaluated from tabulated values of the mass absorption coefficients of Al, Si, and O (MacGillavry and Rieck, 1968). The squared amplitudes F_o^2 and its variance were computed for each observation from the relationships $F_o^2 = (I) \sin 2\theta$ and $\sigma^2(F_o^2) = \sigma^2(I) \sin 2\theta$.

STRUCTURE REFINEMENTS

The atomic parameters reported by Burnham (1963a) were taken as starting values in the refinements. The neutron scattering lengths used were 5.803 b (= barn) for O, 3.449 b for Al, 4.149 b for Si, and 9.54 b for Fe; these were taken from Koester and Steyerl (1977). The parameters were refined by full-matrix least-squares procedures (Busing et al., 1962) in which the quantity minimized was $\Sigma\, w[F_o^2 - (KF_c)^2]^2$ where w is the observation weight and K the scale factor. The weights were taken to be equal to $[\sigma_c^2 + (C_iF_o^2)^2]^{-1}$, where C_i are instability constants with $C_i = 0.01$. Reflections observed with $F_o^2 < 0.0$ were included in the refinements (Hirschfeld and Rabinovich, 1973). All positional and anisotropic thermal parameters not constrained by symmetry were varied, together with the scale factor for the data set. Secondary extinction parameters (Becker and Coppens, 1974) and scattering lengths at the Al and Si sites were also varied in the final refinement cycles. Anisotropic extinction parameters (type I crystal with Lorentzian mosaic distribution) did not significantly improve the least-squares fit of the sillimanite data. The isotropic model was retained for the description of extinction effects in the sillimanite crystal. The final fit indices at convergence are listed in Table 2.

The atomic parameters from the final cycle of refinement are reported in Table 3. Listings of the observed and calculated squared structure factor amplitudes are given in Table 4.[2]

RESULTS AND DISCUSSION

The positional parameters given in Table 3 are within 2σ of those reported by Finger and Prince (1972) and within 3σ of those reported by Winter and Ghose (1979) for their room-temperature refinements.

Table 5 lists the bond lengths and angles for sillimanite that are obtained from the present neutron refinement. In all cases they are within 3σ of those published by Burnham (1963a) and Winter and Ghose (1979).

SITE OCCUPANCY

Table 6 summarizes the least-squares refinement results of the scattering amplitudes of the cation sites in silli-

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[2] To obtain a copy of Table 4, order Document AM-86-301 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit $5.00 in advance for the microfiche.

Table 3. Positional and thermal parameters

Atom	x/a	y/b	z/c	U11	U22	U33	U12	U13	U23
Sillimanite									
Al1	0000	0000	0000	31(4)	47(4)	34(4)	1(3)	-3(3)	1(5)
Al2	1418(2)	3449(2)	2500	39(5)	58(5)	43(5)	-2(4)	0	0
Si	1535(1)	3402(1)	7500	30(4)	49(4)	37(4)	-4(3)	0	0
OA	3600(1)	4088(1)	7500	35(3)	72(3)	58(3)	-16(2)	0	0
OB	3563(1)	4340(1)	2500	38(3)	72(3)	53(3)	-13(2)	0	0
OC	4765(1)	0017(1)	7500	90(3)	100(3)	111(4)	-50(3)	0	0
OD	1256(1)	2232(1)	5144(1)	61(2)	56(2)	45(2)	-15(1)	-2(2)	-2(2)

All parameters have been multiplied by 10^4. The temperature factor has the form $\exp - [2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2\,a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$.

Table 5. Bond lengths and angles based on neutron refinement of sillimanite

Octahedral Aluminum	mult.	d(M-O)A	<(O-M-O)
Al1-OD^{ii}	x2	1.9540(5)	
-OA^{i}	x2	1.9143(5)	
-OB^{i}	x2	1.8683(5)	
OA^{i}-OB^{i}		2.8908(2)	99.67°(2)
OA^{i}-OD^{iv}		2.7695(9)	91.43°(3)
OB^{i}-OD^{ii}		2.7119(8)	90.36°(3)
OA^{i}-OD^{ii}		2.7011(8)	88.57°(3)
OB^{i}-OD^{iv}		2.6950(8)	89.64°(3)
OA^{v}-OB^{i}		2.440(1)	80.33°(2)
Tetrahedral Aluminum			
Al2-OD	x2	1.7925(8)	
-OB		1.744(1)	
-OC^{v}		1.707(2)	
OD -OD^{iv}		3.051(1)	116.63°(7)
OB -OC^{v}		2.883(1)	113.35°(8)
OC^{v}-OD		2.8323(4)	108.06°(5)
OB -OD		2.8142(8)	105.46°(5)
Tetrahedral Silicon			
Si -OD	x2	1.6421(8)	
-OA		1.632(1)	
-OC^{vi}		1.574(1)	
OD -OD		2.718(1)	111.70°(7)
OC^{vi}-OD		2.645(1)	110.60°(5)
OA -OD		2.6360(8)	107.24°(5)
OA -OC		2.616(1)	109.32°(7)
O-M-O Angles			
Si^{xii} -OC-Al2^{xi}		3.272(1)	171.71°(9)
Al1 -OB-Al2^{viii}		3.267(1)	129.44°(2)
Al1^{viii}-OA-Si		3.209(1)	129.45°(2)
Al1^{viii}-OD-Si		3.195(1)	125.11°(4)
Al1^{viii}-OD-Al2		3.194(1)	116.91°(4)
Al2 -OD-Si		2.8858(2)	114.26°(4)
Al1^{viii}-OA-Al1^{ix}		2.8843(1)	97.78°(1)
Al1^{viii}-OB-Al1^{x}		2.8343(1)	101.05°(4)

Symmetry Operations

i 1/2-x, y-1/2, 1/2-z
ii -x, -y, z-1/2
iii 1/2+x, -y-1/2, 1/2+z
iv y, x, 1/2-z
v x-1/2, 1/2-y, z-1/2
vi 1/2-x, 1/2+y, (1 1/2)-z
vii x, y, (1 1/2)-z
viii 1/2-x, 1/2+y, 1/2-z
ix 1/2+x, 1/2-y, 1-z
x 1/2+x, 1/2-y, -z
xi 1/2+x, 1/2-y, 1/2+z
xii 1/2-x, y-1/2, (1 1/2)-z
xiii -x, -y, 1/2+z

manite. The scattering amplitude at the four-coordinated Si site is within 1σ of that expected for Si. A difference of 3σ would indicate a substitution of 8% Al into the tetrahedral site.

The scattering amplitude at the six-coordinated site is significantly greater than expected for occupancy by Al alone. The increased scattering amplitude is consistent with 0.013(3) atoms of Fe at this octahedral site (Table 6). The scattering amplitude at the tetrahedrally coordinated Al site is slightly larger than that expected for occupancy by Al alone. The agreement of the chemical analysis predicted by the site refinement and that obtained by microprobe analysis is improved if this additional scattering amplitude is attributed to Fe at this tetrahedral site (Table 5). Hålenius (1979) also reported Fe^{+3} and Fe^{+2} to be in the octahedral site but did not rule out small amounts of Fe in the tetrahedral sites. The increased scattering amplitude at the tetrahedral Al site in sillimanite could also be due to a substitution of Si. However, if the sillimanite (Al_2SiO_5) is stoichiometric, this would require Al substitution at the Si site and cause a decrease in scattering amplitude at this site that is not observed.

CONCLUSIONS

From the site occupancies obtained by neutron diffraction experiments on a sillimanite crystal from Norwich, Connecticut, there is no evidence of Al occupation of the

Table 6. Site refinement results

Site	b_{obs} (barns)	Δ/σ	Fe atom per site	wt % FeO based on diffraction data
Al1	3.53(3)	2.7	0.013(3)	0.67(25)
Al2	3.49(3)	1.36	.007(3)	.36(25)
Si	4.15(3)	---		--------
			Total FeO	1.03(30)
			microprobe results	0.93

$\Delta = b_{(obs)} - b_{(Si\ or\ Al)}$*

Si site. There is some evidence for minor substitution of Fe in both the octahedrally coordinated Al site and the tetrahedrally coordinated Al site.

The large crystal size required for the neutron experiment precludes the investigation of Al-Si ordering in more common sillimanite occurrences, and care should be taken in applying these results to different conditions of formation.

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