Refinement of the Structures of Low and High Hyalophanes

By R. De Pieri and S. Quareni

Istituto di Mineralogia e Petrologia, Università di Padova, Padova, Italy

and K. M. Hall

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

Least-squares methods have been used to refine the crystal structures of natural and heat-treated specimens of a hyalophane, a member of the potassium–barium feldspar series. The composition of the material selected for study corresponds closely to the idealized formula of 0·43 mol% orthoclase ($KAlSi_3O_8$), 0·39 mol% celsian ($BaAl_2Si_2O_8$). For both specimens the space group is $C2/m$, and only slight structural differences between the refined structures are observed. These differences are discussed in relation to the striking differences in optical properties reported by Gay [*Miner. Mag.* (1965), **34**, 204] and Gay & Roy [*Miner. Mag.* (1968), **36**, 914–932].

Introduction

Evidence has been given (Gay, 1965) for the possibility of the existence of different structural states for feldspars in the orthoclase–celsian series. In particular, the treatment of a hyalophane at high temperature has given rise to changes in the intensities of certain reflexions, as well as to variations in d_{132}, the interplanar spacing which Gay uses to construct a variation diagram to give the Ba content of feldspars in the K–Ba series.

Dr Gay very kindly made some of his specimens available for a detailed structural study. The results reported here are those obtained for a hyalophane in the natural, low-temperature state and for the same material after high-temperature treatment.

Material

A small quantity of crystalline fragments of a perfectly transparent hyalophane, free from twinning, was available (Gay's No. 195367 from Bosnia, Yugoslavia). Some of this was the naturally occurring material, and some had been maintained at 1400 °C for 24 h. In this paper the heated material will be called 'high hyalophane' and the unheated 'low hyalophane'.

The crystals were analysed chemically in the Department of Mineralogy and Petrology at the University of Cambridge, and the results of the analysis are given in Table 1. This analysis was used for calculating the mineralogical composition of the material, $K_{0.43}Ba_{0.39}Na_{0.17}Ca_{0.01}Al_{1.42}Si_{2.59}O_8$, and its absorption coefficient for Mo $K\alpha$ radiation.

Table 1. *Chemical composition and crystal data of low and high hyalophanes*

	Wt%
SiO_2	49·54
Al_2O_3	23·14
Fe_2O_3	0·11
MnO	–
MgO	0·04
CaO	0·19
BaO	19·01
Na_2O	1·65
K_2O	6·37
TiO_2	Trace
Total	100·05

Formula: $K_{0.43}Ba_{0.39}Na_{0.17}Ca_{0.01}Al_{1.42}Si_{2.59}O_8$

	Low	High
a_0 (Å)	8·557	8·556
b_0 (Å)	13·040	13·045
c_0 (Å)	7·200	7·189
β (°)	115·69	115·63
V (Å³)	1447·0	1446·8
$2V_\alpha$ (°)	70	62

From Gay & Roy (1968). Average accuracy of cell edge $\pm$ 0·006 Å, $\beta \pm$ 0·08°.

Lattice parameters and space group

The values used for the lattice parameters were those of Gay & Roy (1968), and are given in Table 1.

Systematic absences indicated the space group $C2/m$, a careful check having been made for any type '*b*' reflexions. No significant differences were observed in

the intensities of pairs of reflexions related by mono-clinic symmetry which would have differed from each other if the material had been triclinic.

Intensity data

Three-dimensional intensity data were collected with the multiple-film technique in a Weissenberg camera with the equi-inclination method and filtered Mo $K\alpha$ radiation.

High- and medium-intensity reflexions were measured with a Joyce–Loebl flying-spot integrating microdensitometer. Weak reflexions were measured by visual comparison with scales obtained from each crystal used.

A fragment of low hyalophane, $0\cdot10 \times 0\cdot11 \times 0\cdot14$ mm, was used to collect the layers $hk0–hk8$ about the z axis and $0kl–3kl$ about the x axis.

The crystal of high hyalophane was $0\cdot07 \times 0\cdot06 \times 0\cdot06$ mm, and the layers $h0l–h16l$ about the y axis and $hk0–hk5$ about the z axis were recorded.

Absorption corrections were calculated for each crystal with the method of Wells (1960). Lorentz and polarization corrections were applied.

In each case, intensity measurements from different layers perpendicular to one axis were scaled to each other with measurements from all the layers perpen-dicular to the other axis used.

Atomic scattering factors

The atomic scattering factors used were those given by Thomas & Fermi (*International Tables for X-ray Crystallography*, 1962) for Ba, K and Ca, by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenen-daal (*International Tables*, 1962) for Na, Al and Si, and by Tokonami (1965) for O. A weighted mean value was calculated according to the chemical composition of the material for K, Ba, Ca and Na which are structurally indistinguishable from each other, and similarly for Si and Al.

With the scattering factors thus obtained, the method of Forsyth & Wells (1959) was used to calculate the constants of the analytic approximation suggested by these authors. These constants were then used in all successive calculations.

Programs for atomic scattering factors, Lp corrections, absorption corrections and difference-Fourier and least-squares refinements were written by Mrs J. C. Matthewman for the Titan computer.

Structure refinement

The structures were refined by difference-Fourier and full-matrix least-squares methods with the coordinates obtained for sanidinized orthoclase by Ribbe (1963) as starting parameters.

During the refinement a few strong reflexions at low Bragg angles, which appeared to be suffering from extinction, were omitted from the calculations. The number of reflexions used in the refinement was 1311 for low hyalophane and 1122 for high hyalophane.

For the least-squares refinement the observed structure factors were weighted according to the scheme suggested by Cruickshank (1965) by the factor $1/[F_o^2(2/F_{o\max}) + F_o + 2F_{o\min}]$.

The structures were refined first with isotropic and then anisotropic temperature factors for all atoms. The atomic coordinates from the isotropic refinement were not significantly different from those from the aniso-tropic refinement. The final R values (%) in each case are:

	Isotropic	Anisotropic
Low hyalophane	10·7	8·4
High hyalophane	10·2	8·0.

Final coordinates are given in Table 2, interatomic distances in Table 3, bond angles in Table 4 and isotropic temperature factors in Table 5.* Details of anisotropic thermal displacement are in Table 6; these

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32756 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic coordinates, in fractions of the cell edges*

Standard errors in parentheses refer to the last decimal figure.

	Low			High		
	x	y	z	x	y	z
K,Ba	0·28257 (6)	0	0·13252 (8)	0·28321 (9)	0	0·1327 (1)
$T(1)$	0·0085 (1)	0·18319 (6)	0·2243 (1)	0·0088 (1)	0·18313 (9)	0·2244 (1)
$T(2)$	0·7044 (1)	0·11784 (6)	0·3453 (1)	0·7059 (1)	0·11771 (8)	0·3458 (2)
$O(A1)$	0	0·1431 (2)	0	0	0·1424 (4)	0
$O(A2)$	0·6265 (4)	0	0·2854 (5)	0·6278 (6)	0	0·2879 (8)
$O(B)$	0·8255 (3)	0·1406 (2)	0·2253 (4)	0·8275 (5)	0·1412 (3)	0·2250 (6)
$O(C)$	0·0296 (3)	0·3103 (2)	0·2570 (4)	0·0305 (4)	0·3099 (3)	0·2559 (5)
$O(D)$	0·1847 (3)	0·1261 (2)	0·4020 (4)	0·1833 (4)	0·1258 (3)	0·4022 (5)

Table 3. *Interatomic distances* (Å) *with standard deviations* ($\times 10^3$) *in parentheses*

	Low	High		Low	High
T(1)—O(A1)	1·669 (1)	1·669 (2)	O(A1)—O(B)	2·639 (4)	2·620 (5)
—O(B)	1·665 (3)	1·647 (5)	O(A1)—O(C)	2·799 (4)	2·795 (6)
—O(C)	1·673 (3)	1·669 (4)	O(A1)—O(D)	2·638 (4)	2·635 (4)
—O(D)	1·671 (3)	1·663 (4)	O(B)—O(C)	2·767 (4)	2·752 (6)
Mean T(1)—O	1·669 (1)	1·662 (2)	O(B)—O(D)	2·777 (4)	2·751 (5)
			O(C)—O(D)	2·724 (4)	2·719 (5)
T(2)—O(A2)	1·656 (1)	1·654 (2)	Mean O—O,		
—O(B)	1·638 (3)	1·648 (5)	tetrahedron 1	2·724 (2)	2·712 (2)
—O(C)	1·642 (3)	1·649 (4)			
—O(D)	1·650 (3)	1·644 (4)	O(A2)—O(B)	2·662 (4)	2·681 (6)
Mean T(2)—O	1·647 (1)	1·649 (2)	O(A2)—O(C)	2·589 (3)	2·594 (4)
			O(A2)—O(D)	2·688 (4)	2·675 (5)
K,Ba—O(A1)	2·871 (2)	2·869 (4)	O(B)—O(C)	2·716 (4)	2·721 (6)
—O(A2)	2·657 (4)	2·662 (5)	O(B)—O(D)	2·729 (5)	2·729 (6)
—O(B)	2·965 (3)	2·965 (4)	O(C)—O(D)	2·736 (4)	2·742 (6)
—O(C)	3·122 (3)	3·128 (4)	Mean O—O,		
—O(D)	2·929 (3)	2·934 (4)	tetrahedron 2	2·686 (2)	2·690 (2)

Table 4. *Interatomic angles* (°) *with standard errors* ($\times 10$) *in parentheses*

	Low	High
O(A1)—T(1)—O(B)	104·7 (1)	104·4 (2)
O(A1)—T(1)—O(C)	113·8 (1)	113·7 (2)
O(A1)—T(1)—O(D)	104·4 (1)	104·5 (2)
O(B)—T(1)—O(C)	112·0 (2)	112·2 (2)
O(B)—T(1)—O(D)	112·7 (1)	112·4 (2)
O(C)—T(1)—O(D)	109·1 (1)	109·4 (2)
Mean O—T(1)—O	109·4 (1)	109·4 (1)
O(A2)—T(2)—O(B)	107·8 (2)	108·6 (3)
O(A2)—T(2)—O(C)	103·4 (1)	103·5 (2)
O(A2)—T(2)—O(D)	108·8 (2)	108·3 (2)
O(B)—T(2)—O(C)	111·8 (1)	111·2 (2)
O(B)—T(2)—O(D)	112·1 (1)	112·0 (2)
O(C)—T(2)—O(D)	112·4 (2)	112·8 (2)
Mean O—T(2)—O	109·4 (1)	109·4 (1)
T(1)—O(A1)—T(1)	143·5 (2)	142·9 (4)
T(2)—O(A2)—T(2)	136·2 (2)	136·3 (3)
T(1)—O(B)—T(2)	150·9 (2)	150·9 (3)
T(1)—O(C)—T(2)	130·1 (2)	130·5 (2)
T(1)—O(D)—T(2)	140·3 (2)	140·6 (3)
Mean T—O—T	140·2 (1)	140·2 (1)

Table 6. *R.m.s. components of thermal displacement along the axes of the vibration ellipsoids* (Å) *and their directions relative to the crystallographic axes* (°)

		Low				High			
		R.m.s.	a	b	c	R.m.s.	a	b	c
K,Ba	1	0·155	124	90	8	0·161	90	0	90
	2	0·135	90	0	90	0·142	68	90	177
	3	0·104	34	90	82	0·114	157	90	86
T(1)	1	0·109	62	102	167	0·109	107	19	91
	2	0·102	132	57	99	0·065	36	71	85
	3	0·069	125	144	81	0·049	121	91	5
T(2)	1	0·107	51	91	166	0·095	84	16	79
	2	0·088	40	82	77	0·073	93	75	148
	3	0·073	96	8	92	0·066	6	95	120
O(A1)	1	0·133	154	90	90	0·152	90	0	90
	2	0·123	116	90	0	0·151	159	90	85
	3	0·108	90	0	90	0·073	69	90	175
O(A2)	1	0·178	122	90	6	0·172	133	90	17
	2	0·124	148	90	96	0·102	137	90	107
	3	0·086	90	0	90	0·101	90	0	90
O(B)	1	0·157	83	73	37	0·177	87	176	92
	2	0·151	56	144	95	0·157	65	89	51
	3	0·106	145	120	54	0·080	155	93	39
O(C)	1	0·140	97	56	133	0·156	113	37	103
	2	0·132	32	112	136	0·126	141	92	26
	3	0·115	59	42	81	0·113	61	53	69
O(D)	1	0·166	32	98	146	0·147	52	136	123
	2	0·133	96	172	82	0·143	134	133	59
	3	0·118	59	88	57	0·097	113	86	132

Table 5. *Isotropic temperature factors* [B (Å²)]

	Low	High
K,Ba	1·35 (1)	1·52 (1)
T(1)	0·67 (1)	0·48 (1)
T(2)	0·60 (1)	0·46 (1)
O(A1)	1·08 (5)	1·32 (7)
O(A2)	1·26 (5)	1·31 (7)
O(B)	1·58 (4)	1·61 (6)
O(C)	1·32 (4)	1·39 (5)
O(D)	1·52 (4)	1·31 (5)

were calculated from the anisotropic temperature factors with a program written by J. K. Brandon.

Discussion

As was stated in the *Introduction*, the work of Gay (1965) suggests structural differences between low and

high states in this hyalophane. Subsequently Gay & Roy (1968) studied another hyalophane (32·3 mol% celsian), and found large changes in the optic axial angle after heating. They also estimated the activation energy for the low–high transformation in this material.

In spite of these remarkable differences in optical angles of high and low hyalophanes, which have also been measured in the crystalline material used in this study, only slight structural differences can be observed in the refined structures. In low hyalophane the average dimensions of the tetrahedra and the corresponding Al content, calculated with the equation of Ribbe & Gibbs (1969), show that there is partial order in the Al–Si distribution, with 0·43 Al in $T(1)$ and 0·28 Al in $T(2)$ (Table 7). This partial order seems to be very little affected by the heating; the values for high hyalophane are 0·40 and 0·31 respectively. The interatomic T–O and O–O distances, as well as the individual bond angles within and between tetrahedra (Tables 3 and 4), differ from the average values in the same way as do those in all other feldspar structures. The K,Ba–O bond lengths are also very similar to those of sanidine (Ribbe, 1963) and adularia and orthoclase (Colville & Ribbe, 1968).

The above discussion of evidence for partial ordering of Al and Si in the feldspar structure is on routine familiar lines. In view of the apparent contradiction between the conclusions thus derived from the X-ray observations and those based on the optical properties, the following further studies of the Al–Si ordering are of interest.

First, in an attempt to confirm directly the partial order in Al–Si distributions derived from tetrahedral dimensions, complete refinements including the tetrahedral site occupancies as variable parameters were carried out for both low and high forms but gave no evidence for ordering on those sites for either of these structures. This disappointing outcome may perhaps be a result of extinction effects in low-angle reflexions, but remains in fact unexplained.

Further *indirect* evidence of appreciable partial Al–Si order in low hyalophane is supplied by the significant difference between the isotropic temperature factors for $T(1)$ and $T(2)$ (Table 5), in contrast to the nearly identical and much lower values for high hyalophane. On carrying out a refinement for low hyalophane with scattering factors for sites $T(1)$ and $T(2)$ corresponding to the partial order derived from the T–O bond lengths (Table 7), the new isotropic temperature factors derived were 0·36 for $T(1)$ and 0·38 for $T(2)$, values effectively identical, as in the case of high hyalophane for the disordered Al,Si occupancy assumed in the calculations summarized in Table 5.

The anisotropy of T and O atoms shown in Table 6 is compatible with the existence of small positional differences of similar atoms in subcells of a larger body-centred unit cell in antiphase domains related by the $C2/m$ space group. If this were the case, it might account for the somewhat inconclusive nature of the discussion of differences in the Al/Si distributions in the two forms, which is the most probable cause of the striking differences in the optical properties.

Table 7. Al–Si *distribution in low and high hyalophane*

	Mean T–O (Å)		Average Al content*	
	Low	High	Low	High
$T(1)$	1·669	1·662	0·43	0·40
$T(2)$	1·647	1·649	0·28	0·31

* Calculated from the equation given by Ribbe & Gibbs (1969) and normalized to total 1·42 in accordance with the chemical formula.

References

Colville, A. A. & Ribbe, P. H. (1968). *Amer. Min.* **53**, 25–37.

Cruickshank, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. Rollett. Oxford: Pergamon Press.

Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412–415.

Gay, P. (1965). *Miner. Mag.* **34**, 204.

Gay, P. & Roy, N. N. (1968). *Miner. Mag.* **36**, 914–932.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Ribbe, P. H. (1963). *Acta Cryst.* **16**, 426–427.

Ribbe, P. H. & Gibbs, G. V. (1969). *Amer. Min.* **54**, 85–94.

Tokonami, M. (1965). *Acta Cryst.* **19**, 486.

Wells, M. (1960). *Acta Cryst.* **13**, 722–726.