CRYSTAL STRUCTURE OF K,Y-TRIORTHOSILICATE

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Abstract

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CRYSTAL STRUCTURE OF K,Y-TRIORTHOSILICATE

$K_3Y[Si_3O_8(OH)_2]$

Transparent, well-faceted single crystals of a K–Y silicate, isolated among the products of hydrothermal crystallization in the system K_2O—Y_2O_3—SiO_2—H_2O (450°, ~ 1500 atm), served as the object of the X-ray structural investigation.

Qualitative (spectral and X-ray spectral) chemical analysis of carefully selected single crystals revealed in this phase Y, Si, H_2O, and alkalis; however, the minimum portion of material did not make it possible to obtain a reliable quantitative result, especially with respect to K and, in part, Y. Possible variants of the formula were: from $KYSiO_4$ through $KYSi_2O_6$ to $K_5YSi_3O_{10} \cdot nH_2O$—and the structural analysis was begun without knowledge of the chemical formula. From a single crystal of dimensions $0.10 \times 0.20 \times 0.30$ mm, Weissenberg layer photographs $h0l$, $h1l$, $0kl$, $hk0$—$hk5$ were obtained ($\max \sin\theta/\lambda \leq 1.0$ Å^{-1}, MoK_α radiation). The parameters of the rhombic cell after refinement on a DRON-1 diffractometer (CuK_α radiation) are: $a = 13.536 \pm 0.005$, $b = 13.17 \pm 0.001$, $c = 5.867 \pm 0.002$ Å. The two space groups $Pmnb$ and $P2_1nb$ correspond to the X-ray group $mmmP$—nb following from the systematic extinctions.

From 1500 nonzero intensities, estimated from blackening marks with a step of $\sqrt[4]{2}$ and reduced to a common scale,* the three-dimensional Patterson function $P(uvw)$ was constructed.

The structure determination was carried out in parallel within both of the indicated groups. The conclusion in favor of the very frequent holohedral $D_{2h}^{16} = Pmnb$ was made first of all on the basis of the statistical test from integral curves ([2]) for the intensities $hk0$ and $hk3$, was then confirmed by analysis of interaction peaks ([3]), and finally at the last stage of the analysis by comparison of the two coordinate variants. However, it would have been incorrect to discard the lower group at once because of the absence of a chemical formula, especially since in the process of structure determination it was necessary not only, and not so much, to find the atomic coordinates as to determine the number of atoms of each kind in the unit cell.

At the first stage the contents of the cell were divided into three groups in accordance with atomic factors: A–Y ($Z = 39$), B–K ($Z = 19$) and Si ($Z = 14$),

X–O ($Z = 8$). Initially, for atoms of the second group the f-curve of the Si atom was used.

Analysis of the linkage and interaction peaks according to ([3]) indicated the presence in the cell of one complex of heavy atoms in a position with multiplicity 4. In analogous fourfold complexes two quartets of "medium"atoms from group B were fixed. The remaining medium atoms occupied general positions: eightfold ones within the group $Pmnb$ (2 octets), or fourfold ones in the case of the acentric group (4 quartets). The final variant of the model, which formed the basis of the subsequent calculations, was that with heavy atoms and two kinds of medium atoms in the planes m and with two more kinds of medium atoms in general positions, i.e. $A^4 + 2B^4 + 2B^8$, and, correspondingly, for the acentric variant $A^4 + 6B^4$.

* According to programs by B. L. Tarnopol' skii and V. I. Andrianov ([1]).

The separation of the atoms of group B into Si and K became possible at the second stage of the structure determination from interatomic distances, and also upon refinement of the multiplicity of the atomic positions and their isotropic quasi-temperature factors according to ([4]). Refinement of the coordinates of the atoms of all three groups of the structure led (with an overall thermal correction $B = 0.9$ Å^{-2}) to discrepancy factors $R_{h\bar{k}l} = 12.7\%$ and 13.56% for the groups $P2_1nb$ and $Pmnb$, respectively.

Table 1

	x/a	y/b	z/c	U_j
Y	−0.250	0.041	0.089	0.792
Si_1	0.396	0.401	0.089	0.394
Si_2	−0.250	0.252	0.418	0.330
K_1	0.250	0.129	0.412	1.652
K_2	0.485	0.139	0.091	1.744
O_1	−0.131	0.031	0.368	0.934
O_2	−0.131	0.045	0.832	0.932
O_3	0.017	0.129	0.581	1.019
O_4	−0.156	0.212	0.570	0.894
O_5	−0.250	0.205	0.164	1.120
O_6	−0.250	0.375	0.434	1.216

Better interatomic distances and a more regular trend in the individual thermal factors at nearly equal R were a sufficient argument in favor of holohedry, i.e., a centrosymmetric structure. The final coordinates of the 11 basis atoms are given in Table 1 (centrosymmetric variant $R = 13.56$).

On the basis of the completed X-ray structure investigation, the formula of the synthesized crystalline compound is $K_3Y[Si_3O_8(OH)_2]$; the cell contains 4 formula units. The participation of hydroxyl groups, required for valence

balance, is confirmed by IR spectra.* The X-ray density is 2.81, compared with a pycnometric density of 2.72.

Table 2

Si_1-tetrahedron	Si_2-tetrahedron	Y-octahedron
Si_1—O_1 = 1.61	Si_2—O_4 = 1.65	Y—O_1 = 2.30 = Y—O_1'
—O_2 = 1.63	—O_4' = 1.65	—O_2 = 2.21 = Y—O_2'
—O_3 = 1.68	—O_5 = 1.61	—O_5 = 2.22
—O_4 = 1.64	—O_6 = 1.61	—O_6 = 2.18
O_1—O_2 = 2.72	O_4—O_5 = 2.70	O_1—O_2 = 3.22 = O_1'—O_2'
—O_3 = 2.69	O_4'—O_5 = 2.70	O_1—O_5 = 3.03 = O_1'—O_5
—O_4 = 2.65	O_4—O_6 = 2.67	O_1—O_6 = 3.17 = O_1'—O_6
O_2—O_3 = 2.72	O_4'—O_6 = 2.67	O_1—O_1' = 3.22
—O_4 = 2.70	O_4—O_4' = 2.58	O_2—O_2' = 3.34
O_3—O_4 = 2.54	O_5—O_6 = 2.68	O_2—O_6 = 3.08

K_1-polyhedron	K_{11}-polyhedron
K_1—O_1 = 2.94	K_{11}—O_1 = 2.93
—O_1' = 2.94*	—O_2 = 2.91
—O_5 = 2.62	—O_2' = 2.77
—O_6 = 2.96	—O_3 = 3.06
—O_2' = 3.14	—O_3' = 2.87
—O_2 = 3.14	—O_3'' = 2.99
—O_4 = 3.10	—O_4 = 2.73
—O_4' = 3.10	
—O_6' = 2.91	

* Primes denote atoms obtained from the basis by symmetry operations.

The interatomic distances calculated from the coordinates of Table 1 are presented in Table 2.

The rare-earth cation Y is located in a fairly regular octahedron: 4 Y—O distances are almost equal, 2.18-2.22 Å, and 2 are very close to them, 2.30 Å. The same applies to the edges of the Y-octahedron, with lengths in the narrow interval 3.03-3.34 Å. Similar sixfold coordination of the Y cation (with its moderately "large" radius of 0.92 Å) was noted in an earlier work ([5]) and by other authors ([5]). The two crystallographically non-equivalent

* The investigations were kindly carried out in the laboratory of Prof. V. M. Tatevskii, Faculty of Chemistry, Moscow University.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

large cations K occupy different polyhedra: K_1 (on the planes m) in nine-vertex polyhedra with 8 close distances K—O = 2.94—3.14 Å (average 3.04_5 Å) and one sharply protruding distance of 2.62 Å, equal to the sum of the ionic radii. Similar anisotropy has already been noted for the loose cation K ([7,8]). The polyhedron around the K_2 seven-vertex polyhedron is more compact (K—O = 2.73—3.06 Å, with an average of 2.90 Å), but two distances are shorter and only slightly exceed the sum of the ionic radii (2.73 and 2.77 Å).

In the Si tetrahedra the distances are Si—O = 1.59—1.69 Å (1) and 1.54–1.66 Å (2), with edges of 2.58–2.70 Å and 2.55–2.73 Å, respectively. In the tetrahedra, along with O atoms, hydroxyl groups OH take part, as was the case in ([9—11]) and others.

Fig. 1. Structure of $K_3Y[Si_3O_8(OH)_2]$ in polyhedra. Projection xy. Alternation of yttrium-silicate layers along the $x(a)$ axis with layers of K atoms. Light octahedra and circles are atoms at level ~ 0, dark ones at level $\sim 1/2$.

The architectural motif of the structure $K_3Y[Si_3O_8(OH)_2]$ is demonstrated by the xy projection (Fig. 1). The basic building detail may be considered a complex of a YO_6 octahedron and a cluster group (sorogroup according to Strunz) of 3 Si tetrahedra $[Si_3O_{10}]$ ($Si_3O_8(OH)_2$). A similar triorthogroup has already been recorded twice ([12,13]) in synthetic Cd silicates, but in a rare-earth silicate it is encountered for the first time. A "bracket" of 3 tetrahedra connects (by vertices) two Y octahedra, separated along the $c(z)$ axis by the short translation 5.86 Å, in such a way that the outer tetrahedra of the bracket (its wings) with their edges simply continue the "vertical" (parallel to the c axis) edges of the Y octahedra, while the middle tetrahedron of the bracket fixes the tilt of the octahedron, linking to it by an O atom lying in the plane of symmetry. With its fourth vertex this tetrahedron* connects with the overlying (along c) Y octahedron (shifted by the $(b + c)/2$ plane b), as a result of which one may speak of the merging of increments $[(Y + 3Si)O_{10}]$ into layers parallel to the yz plane and having the gross formula $[M_2X_5]_{\infty,\infty}$.

Fig. 2. Structure of orthoclase in polyhedra. Alternation in one layer of vlasovite (koesite) chains and corrugated layers of K atoms.

The voids within the layers themselves, i.e., on the planes m, are occupied by the loose K_1 nine-vertex polyhedra. The yttrium-silicate layers as a whole along the axis

* In the triorthogroup, only in the middle tetrahedron are all 4 vertices O atoms.

In the tetrahedra on the wings of the bracket, one ("free") vertex each is occupied by OH groups (with Pauling balance $1^3/_7$).

$x(a)$ are interleaved with layers containing twice the number of K_2 atoms in seven-vertex polyhedra. Such a mica-like alternation of packets and large K cations determines the pronounced cleavage of the specimen.*

In the solved structure, the smaller rare-earth cation Y participates in the construction of the layer in the same way as the Ti atom (in the octahedron) in the titanosilicate nets of astrophyllite ([14]), bafertisite ([15]), lamprophyllite ([16]), and other titanosilicates. This makes it possible to call the solved Y-triorthosilicate an yttrium silicate, in a certain analogy with zinc silicates ([17]) and even aluminosilicates. The analogy may be extended by comparing the projection of the structure of K,Y-triorthosilicate with its pseudoring increment (YSi_3O_{10}) and the corresponding projection of the structure of orthoclase $KAlSi_3O_8$, in which chain-like—more precisely, coesite-like—chains composed of Si_3, Al-squares are especially clearly distinguished; these chains are likewise combined into layers, between which pseudohexagonal layers of large K are situated (Fig. 2). Moreover, in K,Y-triorthosilicate one can distinguish even more clearly expressed chains along the c axis with a pseudosquare cross-section, i.e., very similar to the pseudosquare chains distinguished in orthoclase parallel to the axis of the prism that determines its name. Here, however, the analogy ends, since in orthoclase-coesite the chain-like chains are rectilinear, whereas in the Y-silicate they oscillate between two sublevels along the c axis and are interleaved by large K cations (of another kind) within the layer itself. More significant is the fact that in orthoclase-coesite the (alumino)silico-oxygen layers are linked into a framework with the usual formula $[ZO_2]_{\infty,\infty,\infty}$, whereas Y-triorthosilicate is a distinctly layered structure with the specific dimetaphormula $[Z_2O_5]_{\infty,\infty}$.

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REFERENCES

1. B. L. Tarnopol' skii, V. I. Andrianov, *ZhSKh*, **4**, 434 (1963).
2. E. R. Howells, D. C. Phillips, D. Rogers, *Acta crystallogr.*, **3**, 210 (1950).
3. S. V. Borisov, *Kristallografiya*, **9**, 603 (1964).
4. F. A. Brusentsev, Dissertation, Moscow, 1965.
5. B. A. Maksimov, V. V. Ilyukhin, N. V. Belov, *Kristallografiya*, **11**, 4, 681 (1966).

6. N. G. Batalieva, Yu. A. Pyatenko, *ZhSKh*, **8**, 548 (1967).

7. N. N. Mustafaeva, V. V. Ilyukhin, N. V. Belov, *Kristallografiya*, **10**, 805 (1965).

8. E. A. Kuz' min, V. V. Ilyukhin, N. V. Belov, *DAN*, **173**, 1068 (1967).

9. Helen D. Megaw, *Acta crystallogr.*, **5**, 477 (1952).

10. V. V. Ilyukhin, N. V. Belov, *Kristallografiya*, **5**, 200 (1960).

11. E. A. Pobedimskaya, N. V. Belov, *ZhSKh*, **1**, 51 (1960).

12. M. A. Simonov, Yu. K. Egorov-Tismenko, N. V. Belov, *DAN*, **179**, No. 6 (1968).

13. M. A. Simonov, Yu. K. Egorov-Tismenko, N. V. Belov, *DAN*, **181**, No. 1 (1968).

14. Pu Chze-chzhun, Ma Chzhe-pen, *Sci. Sinica*, **12**, 272 (1963).

15. Guan Ya-syan, V. I. Simonov, N. V. Belov, *DAN*, **149**, No. 6 (1963).

16. P. G. Woodrow, *Nature*, **204**, 375 (1964).

17. V. I. Ilyukhin, A. V. Nikitin, N. V. Belov, *DAN*, **171**, 1326 (1966).

* If, as is customary for layered silicates, the c axis is directed perpendicular to the cleavage plane, the group symbol D_{2h}^{16} becomes the "mineralogical" one: *Pbnm*.

Note: Figure translations are in progress. See original paper for figures.