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Crystal Structure of High-Silica K,Na-Ordered Acentric Eudialyte Analogue

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The zirconosilicate eudialyte is the parent of a mineral group differing in the structural chemical features [1, 2]. In this work, we studied by X-ray diffraction a new representative of the group with an individual chemical composition in the species-forming positions. The sample, which we designated conventionally as potassium eudialyte (no. 3545) was found in the Khibiny alkaline massif. The mineral is confined to the central parts of Rastsvetaevite exposures $Na_{27}K_8Ca_{12}Fe_3Zr_6Si_{52}O_{144}(O,OH,H_2O)_6Cl_2$ [3] and presumably could serve as a precursor or seed for its crystallization. Therefore, determination of the structure of this mineral is also of interest for elucidating the genesis of high-potassium minerals of the eudialyte group.

The chemical composition of the sample was determined by electron probe microanalysis and corresponded to the empirical formula (calculated for the sum of Zr, Hf, Si, Al, Nb, and Ti cations equal to 29 at $Z = 3$):

$$(Na_{12.42}K_{2.26}Sr_{0.29}Ba_{0.03})_{\Sigma 15}Ca_6(Fe^{2+}_{2.26}Mn_{0.16}Na_{0.58})_{\Sigma 3}$$

$$\times (Zr_{2.80}Hf_{0.03}Ti_{0.15}Nb_{0.02})_{\Sigma 3}(Si_{25.96}Al_{0.04})_{\Sigma 26}O_{72}$$

$$\times (O_{1.10}OH_{0.90})_{\Sigma 2}(Cl_{1.62}H_2O_{0.38})_{\Sigma 2},$$

which is close to idealized $Na_{12}K_3Ca_6Fe_3Zr_3Si_{26}O_{72}(O,OH)_2Cl_2$.

The unit cell parameters are $a = 14.2956(2)$ Å, $c = 30.0228(5)$ Å, $V = 5314$ Å^3, $MW = 3041.42$, $Z = 3$, d(calc) = 2.85 g/cm^3. The diffraction data were collected from a dark lilac isometrically shaped single crystal. The crystal data and X-ray experiment details are summarized in Table 1.

According to [5, 6], all minerals containing more than 25 silicon atoms per asymmetric unit are a priori centrosymmetric. Therefore, the crystal structure of a high-silica sample was first refined within space group $R\text{-}3m$. However, due to high R values (~7%) and the difficulties with distribution of the chemical composition, we switched to acentric group $R3m$; as a result, a low R value (3.9%) and adequate thermal parameters of atoms were attained. The main structural features of the mineral are reflected in its crystal-chemical formula ($Z = 3$):

$$Na_9[K_{2.3}Na_{0.7}][Na_{2.7}Sr_{0.3}][Ca_6][Zr_{2.8}Ti_{0.2}]$$

$$\times [\overset{IV}{Fe}_{2.25}\overset{VI}{Mn}_{0.15}][Si_1(OH)_1][Si_1(OH)_1][Si_3O_9]_2$$

$$\times [Si_9O_{27}]_2Cl_{1.1}(OH)_{0.3}\ \ 0.9H_2O,$$

Table 1. Crystal data and experiment details

Characteristics	Value
System, space group, Z	Rhombohedral, $R3m$, 3
a, Å	14.2956(1)
c, Å	30.0228(5)
V, Å^3	5313.6
Radiation; λ, Å	MoK_α; 0.71073
d_{exp}, g/cm^3	2.812
Crystal size, mm	0.2 × 0.25 × 0.2
Diffractometer	Bruker SMART CCD
Scan range	$-19 < h < 20$; $-20 < k < 20$; $-38 < l < 42$
sinθ/λ	<0.714
The number of measured reflections	
The number of independent reflections	8414/1427 $F > 3\sigma(F)$
R_{int}	0.012
R	0.039
Refinement software	AREN [4]
Absorption correction software	SADABS

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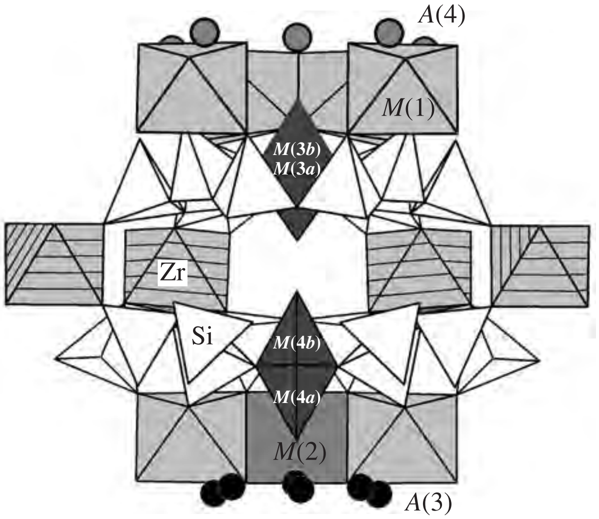

Fragment of the crystal structure of the high-silica potassium eudialyte 3545. Dark gray color marks the Si tetrahedra incorporated into the nine-membered rings; dark circles stand for K atoms with Na impurity; and gray circles denote Na atoms with Sr impurity.

where square brackets distinguish the compositions of key positions of the structure and Roman numerals designate the coordination numbers of cations in the *M*(2) position. The split and partly filled positions of the extraframework cations and anions were found from difference electron density syntheses. Some positions were refined using mixed atomic scattering curves. The atomic coordinates and characteristics of the coordination polyhedra for the mineral are summarized in Tables 2 and 3, respectively.

Most minerals of the eudialyte group with *R*3*m* space group contain considerable amounts of Nb (more than 0.5 f.u., $Z = 3$), which is located most often in the *M*(3) position, whereas *M*(4) is occupied by silicon. Potassium-enriched mineral 3545 does not contain octahedral cations on a threefold axis and a slight amount of Nb occupies Zr positions with Ti impurity. In this mineral, for the maximum silicon content (26 atoms per formula unit), positions *M*(3) and *M*(4) are occupied by silicon. Each position is split into two statistically occupied subpositions with the distances *M*(3a)–*M*(3b) = 0.93(1) Å and *M*(4a)–*M*(4b) = 1.11(2) Å. The apical vertices of the additional Si tetrahedra are rotated in pairs to opposite sides from the plane of the rings, the inversion center being statistically retained. The Al atoms are locating apparently in one Si tetrahedron. Presumably, minor impurity of Al is present in the *M*(4b) tetrahedron having the greatest size of 1.63(1)–1.64(1) Å.

The presence of Fe at the center of a square with distances to oxygen atoms of 2.010(5)–2.058(6) Å and a minor amount of Mn in the same position completed to an octahedron by two OH groups with distances of 2.010(5)–2.199(4) Å is also consistent with a local center of symmetry. The breakdown of structure centrosymmetry is mainly due to the different compositions of the *A*(3) and *A*(4) positions, which are predominantly potassium and sodium, respectively (figure). The predominance of potassium in the *A*(3) position, which is occupied by sodium in most eudialyte type minerals, sometimes by calcium (feklichevite and mogovidite), and by oxonium in some hydrated eudialytes, is a distinguishing feature of rastsvetaevite with a doubled period *c* [3], and in the andrianovite structure [7], potassium predominates over sodium in position *A*(4).

In view of the problem of existence of acentric typical eudialyte in nature discussed in the literature, the mineral studied here can be regarded as a model one. Although the structures of zircono- and titanosilicates of the eudialyte group are based on centrosymmetric mixed frameworks of Si tetrahedra, Zr(Ti) octahedra, and Ca octahedra, filling of the framework cavities results most often in the loss of symmetry center. A composition complicated by impurities is formed, as a rule, in acentric structures in which the extraframework cations are ordered over positions *M*(3), *M*(4), *A*(3), and *A*(4) and additional anions are ordered over *X*(1) and *X*(2). In addition, for most of acentric eudialytes, position *M*(2) is displaced from the center of the “square” and filled by cations with coordination numbers 5 or 6.

For dozens of structurally studied eudialyte group minerals [1, 2], space groups *R*-3*m*, *R*3*m*, and *R*3 were established. Of 66 structures, 53 structures have *R*3*m* and *R*3 groups and only 13 minerals are characterized by centrosymmetric space group *R*-3*m*. The eudialytes we studied with the typical unit cell ($c \sim 30$ Å) are characterized by acentric symmetry groups, while centrosymmetric groups were encountered only among eudialytes with a doubled unit cell [1]. As regards samples studied by foreign researchers in the centrosymmetric version, Johnsen and Grice [5, 6] noted slight deviations from centrosymmetry in their refinement but still insisted that the high-silica samples fit better the *R*-3*m* symmetry.

Thus, the title mineral is similar in composition and structure to the proper eudialyte described by Golyshev et al. [8], differing in the replacement of Na by K in one of the key *A* positions. As can be seen from [8] and from this study, an eudialyte structure should not be a priori considered centrosymmetric on the basis of high silica content alone. Even the greatest number (26 atoms) of silicon does not ensure a centrosymmetric structure, it is also necessary that the orientation of Si tetrahedra incorporated into nine-membered rings be the same as the orientation of the tetrahedra of both nine-membered rings. In addition, significant are other factors such as the lack of ordering of elements that cause non-identity of pseudocentric positions. However, there are structures containing less that 26 silicon atoms and having additional Nb, Zr, and Ti octahedra on the threefold axis in which the center of symmetry is nevertheless

Table 2. Atomic coordinates and equivalent (*U*) thermal parameters, position multiplicity (*Q*) and population (*q*) for the high-silica eudialyte structure

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*Q*	*q*	U_{eq}, Å^2
Zr	0.3328(2)	0.1664(1)	0.1668(1)	9	1	0.015(1)
M(1)	0.9999(3)	0.2600(1)	0.9998(1)	18	1	0.006(1)
Si(1)	0.5273(2)	0.2636(1)	0.2510(1)	9	1	0.006(1)
Si(2)	0.9946(1)	0.6028(1)	0.0976(1)	18	1	0.006(1)
Si(3)	0.2093(1)	0.4186(1)	0.0751(1)	9	1	0.011(1)
Si(4)	0.0856(2)	0.5428(1)	0.2578(1)	9	1	0.012(1)
Si(5)	0.0582(1)	0.3290(1)	0.2364(1)	18	1	0.010(1)
Si(6)	0.1414(2)	0.0707(1)	0.0832(1)	9	1	0.011(1)
O(1)	0.4747(6)	0.2373(4)	0.2005(2)	9	1	0.018(3)
O(2)	0.2625(5)	0.0284(5)	0.2063(1)	18	1	0.018(2)
O(3)	0.4019(5)	0.2971(4)	0.1243(1)	18	1	0.018(2)
O(4)	0.6055(3)	0.3945(3)	0.2540(2)	9	1	0.017(3)
O(5)	0.4428(5)	0.2210(4)	0.2879(2)	9	1	0.008(3)
O(6)	0.4121(4)	0.0287(4)	0.0445(1)	18	1	0.009(2)
O(7)	0.1070(4)	0.3913(5)	0.1064(1)	18	1	0.020(2)
O(8)	0.0109(7)	0.5055(5)	0.1173(2)	9	1	0.019(3)
O(9)	0.2737(3)	0.5475(5)	0.0621(4)	9	1	0.044(3)
O(10)	0.1770(3)	0.3540(5)	0.0290(2)	9	1	0.014(3)
O(11)	0.0298(6)	0.5149(4)	0.3038(2)	9	1	0.011(3)
O(12)	0.1766(3)	0.3543(4)	0.2179(2)	9	1	0.012(3)
O(13)	0.0449(4)	0.3005(4)	0.2886(1)	18	1	0.014(2)
O(14)	0.3873(5)	0.4361(5)	0.2239(1)	18	1	0.021(2)
O(15)	0.3931(4)	0.6069(4)	0.2545(3)	9	1	0.036(3)
O(16)	0.0615(3)	0.1231(4)	0.0771(2)	9	1	0.011(3)
O(17)	0.1821(6)	0.0910(4)	0.1328(2)	9	1	0.016(3)
O(18)	0.2336(6)	0.1168(4)	0.0439(2)	9	1	0.015(3)
M(2)	0.4987(2)	0.5012(2)	0.0003(1)	9	0.81(1)	0.011(1)
M(3a)	0.3333	0.6667	0.2473(3)	3	0.50(2)	0.012(3)
M(3b)	0.3333	0.6667	0.2786(4)	3	0.49(2)	0.025(2)
M(4a)	0.3333	0.6667	0.0485(6)	3	0.41(2)	0.026(4)
M(4b)	0.3333	0.6667	0.0856(3)	3	0.57(2)	0.015(3)
A(1)	0.1083(2)	0.2165(3)	0.1542(1)	9	1	0.036(2)
A(2)	0.5812(2)	0.4188(2)	0.1650(1)	9	1	0.033(2)
A(3a)	0.2404(1)	0.4806(2)	–0.0464(1)	9	0.53(2)	0.013(1)
A(3b)	0.2328(6)	0.1159(4)	0.2769(2)	9	0.47(1)	0.024(1)
A(4a)	0.4613(4)	0.2307(2)	0.0499(1)	9	0.93(1)	0.018(1)
A(4b)	0.493(1)	0.2466(8)	0.0445(5)	9	0.06(1)	0.010(3)
A(5a)	0.2548(4)	0.5096(6)	0.1743(4)	9	0.58(3)	0.082(3)
A(5b)	0.4193(6)	0.5807(6)	0.1638(4)	9	0.42(2)	0.056(3)
Cl(1)	0	0	0.2424(4)	3	0.54(1)	0.036(2)
Cl(2)*	0.6667	0.3333	0.1026(4)	3	0.70(2)	0.036(2)
OH(1)	0.410(1)	0.591(1)	0.004(7)	9	0.05(1)	0.045(3)
OH(2)	0.582(1)	0.421(1)	–0.002(6)	9	0.05(2)	0.023(2)
OH(3)	0.3333	0.6667	0.140(1)	3	0.57(2)	0.02(1)
OH(4)	0.3333	0.6667	0.1967(7)	3	0.50(3)	0.013(9)
OH(5)	0.3333	0.6667	0.995(7)	3	0.41(3)	0.057(7)
OH(6)	0.3333	0.6667	0.330(8)	3	0.50(4)	0.076(8)
H_2O(1)*	0	0	0.2194(9)	3	0.46(3)	0.039(4)
H_2O(2)*	0.6667	0.3334	0.049(1)	3	0.30(4)	0.029(7)

* Position composition: Cl(2)=$Cl_{0.5}(H_2O)_{0.5}$; H_2O(1), H_2O(2)=$(H_2O)_{0.7}Cl_{0.3}$.

Table 3. Characteristics of the coordination polyhedra

Position	Composition ($Z = 3$)	C.N.	Cation–anion distance, Å		
			min	max	average
Zr	2.80Zr + 0.15Ti + 0.03Hf + 0.02Nb	6	2.027(8)	2.127(8)	2.072
M(1)	6Ca	6	2.304(5)	2.419(7)	2.369
M(2)	2.15Fe	4	2.010(5)	2.058(6)	2.034
	0.15Mn	6	2.010(5)	2.212(4)	2.06
M(3a)	0.50Si	4	1.494(2)	1.52(2)	1.50
M(3b)	0.49Si	4	1.54(1)	1.65(1)	1.62
M(4a)	0.41Si	4	1.53(2)	1.60(1)	1.55
M(4b)	0.53Si + 0.04Al	4	1.63(1)	1.64(3)	1.64
A(1)	3Na	8	2.56(1)	2.88(1)	2.66
A(2)	3Na	7	2.50(1)	2.82(1)	2.61
A(3a)	1.60K	7	2.614(7)	3.178(7)	2.88
A(3b)	0.7Na + 0.7K	6	2.50(1)	2.74(1)	2.60
A(4a)	2.66Na + 0.16Sr	8	2.54(1)	2.99(1)	2.71
A(4b)	0.18Sr	7	2.58(1)	2.98(1)	2.78
A(5a)	1.74Na	7	2.32(1)	2.98(1)	2.84
A(5b)	1.26Na	7	2.32(1)	2.96(1)	2.65

retained. An example is provided by the centrosymmetric eudialyte studied by Giuseppetti [9] in which the additional Si atoms are replaced by additional Zr atoms. The formation of structures in which the impurity is either concentrated in one position or distributed over several positions depends on particular conditions of mineral formation (or transformation).

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