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STRUCTURE OF INORGANIC COMPOUNDS

Crystal Structure of a New Mn, Na-Ordered Analogue of Eudialyte with the Symmetry *R*3

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Abstract—The crystal structure of a new representative of the eudialyte family was studied. This mineral is characterized by a low calcium content and by ordering the elements that isomorphically replace calcium, which lowers the symmetry from *R*3*m* to *R*3. The structure of the sample under study consists of the six-membered rings with two octahedra of substantially different volumes, one occupied mainly by manganese and the other, mainly by sodium and characterized by the average distances of 2.22 and 2.45 Å, respectively. The formation of such octahedra is the most characteristic structural feature of the third low-symmetry mineral of the eudialyte family. © *2000 MAIK "Nauka/Interperiodica".*

In recent years, the eudialyte family has been complemented with several new representatives, including minerals with an unusually low symmetry, *R*3 [1, 2]. Such a low symmetry of the eudialyte structural type is explained by the deficiency of calcium and a differentiation of the elements isomorphically replacing calcium in the octahedra entering six-membered rings. In this work, the crystal structure of a new mineral of the eudialyte family with an anomalously low calcium content was studied. This mineral was found in alkaline-, volatile-, and rare-element supersaturated pegmatites at the Alluaiv mountain of the Lovozero alkaline massif (the Kola Peninsula). The mineral occurs as pinkish-yellow grains of sizes ranging from 3 to 5 mm. The grains are optically uniaxial positive crystals with *No* = 1.610 and *Ne* = 1.619; ρ_{calcd} = 2.8 g/cm^3. The major structural

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Table 1. Structural data and details of X-ray diffraction study

Characteristic	Value
Unit-cell parameters, Å	a = 14.205(7), c = 30.265(15)
Unit-cell volume, Å^3	V = 5288.8
Sp. gr., Z	*R*3; 3
Radiation, λ, Å	MoK_α; 0.71073
Crystal dimensions, mm	0.15 × 0.20 × 0.28
Diffractometer	Syntex $P2_1$
Scanning mode	ω/2θ
sinθ/λ, Å^{-1}	<0.77
Range of data collection	$-21 < h < 21$, $-21 < k < 21$, $0 < l < 46$
R_{int} for equivalent reflections	0.014
Total number of reflections	6788 $I > 2\sigma(I)$
Number of independent reflections	4004 $\|F\| > 4\sigma(F)$
Program used for calculations	AREN [3]
Absorption correction	DIFABS [4]
Number of independent positions	69
R factor for anisotropic refinement	0.036

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Table 2. Atomic coordinates, equivalent thermal parameters, multiplicities (Q), and occupancies (q) of the positions

Atom	x/a	y/b	z/c	B_{eq}, Å^2	Q	q
Zr(1)	0.3334(1)	0.1582(1)	0.1666(1)	1.89(1)	9	1
M(1)*	−0.0001(1)	0.2726(1)	−0.0002(1)	1.41(1)	9	1
M(1)'*	0.2435(1)	0.2435(1)	−0.0003(1)	1.52(1)	9	1
Si(1)	−0.0108(2)	0.6090(1)	0.0965(1)	1.47(3)	9	1
Si(1)'	−0.0050(1)	0.3968(1)	0.0963(1)	1.40(3)	9	1
Si(2)	0.1403(1)	0.0571(1)	0.0811(1)	1.60(5)	9	1
Si(3)	0.0634(1)	0.3285(1)	0.2374(1)	1.42(4)	9	1
Si(3)'	0.2754(1)	0.3223(1)	0.2373(1)	1.46(4)	9	1
Si(4)	0.2085(1)	0.4170(1)	0.0750(1)	1.77(4)	9	1
Si(5)	0.5264(1)	0.2499(1)	0.2528(1)	1.61(4)	9	1
Si(6)	0.4581(1)	0.5419(1)	0.2586(1)	1.81(4)	9	1
O(1)	0.1709(3)	0.3593(3)	0.0288(1)	2.3(2)	9	1
O(2)	0.1840(3)	0.3537(3)	0.2210(1)	2.3(1)	9	1
O(3)	0.6259(3)	0.5837(3)	0.0446(1)	3.2(5)	9	1
O(3)'	0.6367(4)	0.0407(3)	0.0452(1)	2.2(2)	9	1
O(4)	0.2557(4)	0.0224(3)	0.2071(1)	2.6(1)	9	1
O(4)'	0.2630(3)	0.2269(3)	0.2060(1)	3.3(5)	9	1
O(5)	0.4758(4)	0.2220(4)	0.2042(1)	4.3(3)	9	1
O(6)	0.2250(4)	0.0918(4)	0.0417(1)	3.2(3)	9	1
O(7)	0.1914(3)	0.0797(4)	0.1293(1)	2.8(3)	9	1
O(8)	0.1070(4)	0.3937(5)	0.1076(1)	3.5(3)	9	1
O(8)'	0.2726(3)	0.3708(3)	0.1058(1)	2.1(2)	9	1
O(9)	0.4423(4)	0.1996(4)	0.2922(1)	2.8(3)	9	1
O(10)	0.6167(3)	0.2104(3)	0.2569(1)	3.0(3)	9	1
O(11)	0.0729(3)	0.1233(3)	0.0772(1)	3.2(4)	9	1
O(12)	0.0579(5)	0.4379(4)	0.2261(1)	3.1(4)	9	1
O(12)'	0.3948(3)	0.4310(3)	0.2282(1)	2.1(2)	9	1
O(13)	0.0255(3)	0.5045(3)	0.3053(1)	2.4(1)	9	1
O(14)	0.4048(4)	0.2978(4)	0.1280(1)	3.2(5)	9	1
O(14)'	0.4115(4)	0.1011(4)	0.1267(1)	2.5(2)	9	1
O(15)	0.0454(3)	0.3002(3)	0.2895(1)	2.3(4)	9	1
O(15)'	0.2625(3)	0.2926(3)	0.2885(1)	1.9(2)	9	1
O(16)	0.0210(3)	0.5175(3)	0.1125(1)	2.3(2)	9	1
O(17)	0.2861(5)	0.5465(4)	0.0714(2)	5.9(4)	9	1
O(18*a*)	0.2095(6)	0.610(1)	0.2534(4)	2.9(2)	9	0.41(1)
O(18*b*)	0.374(1)	0.590(1)	0.2669(3)	3.5(2)	9	0.59(1)
Si(7*a*)	0.3333	0.6667	0.0435(1)	2.1(1)	3	0.64(1)
Si(7*b*)	0.3333	0.6667	0.0882(3)	2.7(2)	3	0.36(1)
Si(8*a*)	0.3333	0.6667	0.2458(3)	1.9(1)	3	0.25(1)
Si(8*b*)*	0.3333	0.6667	0.2897(1)	2.19(5)	3	0.75(1)
M(2*a*)*	0.1842(2)	0.3526(2)	0.3315(1)	2.27(5)	9	0.40(1)
M(2*b*)*	0.460(1)	0.528(1)	0.0035(3)	2.7(1)	9	0.10(1)
Fe	0.0162(1)	0.5163(1)	0.0013(1)	3.1(1)	9	0.50(1)

Table 2. (Contd.)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2	*Q*	*q*
Na(1*a*)	0.189(2)	0.621(2)	0.1601(7)	8.1(4)	9	0.20(1)
Na(1*b*)	0.186(1)	0.577(1)	0.1499(5)	5.3(3)	9	0.25(1)
Na(1*c*)	0.245(1)	0.515(1)	0.1819(6)	5.0(3)	9	0.25(1)
Na(1*d*)	0.227(2)	0.573(2)	0.1647(7)	6.1(3)	9	0.20(1)
Na(2*a*)*	0.1201(3)	0.2300(4)	0.1521(1)	2.5(1)	9	0.46(1)
Na(2*b*)	0.092(2)	0.177(2)	0.1668(5)	5.3(5)	9	0.22(1)
Na(2*c*)	0.105(1)	0.206(1)	0.1552(4)	4.9(3)	9	0.32(1)
Sr	0.2346(7)	0.1127(7)	0.2820(3)	4.1(1)	9	0.10(1)
Na(3)	0.1988(3)	0.0966(2)	0.2883(1)	3.2(1)	9	0.90(1)
Na(5*a*)	0.4411(5)	0.2165(4)	0.0510(2)	3.1(1)	9	0.52(1)
Na(5*b*)*	0.4722(3)	0.2334(3)	0.0420(1)	2.7(1)	9	0.48(1)
Na(6*a*)	0.5607(3)	0.1081(3)	0.1806(1)	2.7(1)	9	0.67(1)
Na(6*b*)	0.5729(8)	0.4128(9)	0.1689(5)	2.5(4)	9	0.14(1)
Na(6*c*)	0.605(2)	0.431(2)	0.166(1)	7(5)	9	0.19(1)
OH(1)	0.0	0.0	0.3304(8)	5.8(4)	3	0.52(3)
OH(2)	0.3333	0.6667	0.1390(7)	3.2(5)	3	0.37(3)
OH(3)	0.3333	0.6667	0.1889(7)	3.2(3)	3	0.39(2)
OH(4*a*)	0.609(3)	0.387(3)	–0.0064(8)	6.9(4)	9	0.40(1)
OH(4*b*)	0.6667	0.3333	0.007(2)	7.3(6)	3	0.70(1)
OH(5)	0.408(2)	0.603(2)	0.0029(8)	4.9(7)	9	0.30(3)
H_2O(1*a*)	0.0	0.0	0.2348(8)	3.6(5)	3	0.47(3)
H_2O(1*b*)	0.0	0.0	0.268(3)	9(1)	3	0.25(4)
H_2O(3*a*)	0.6667	0.3333	0.1033(7)	4.2(6)	3	0.50(3)
H_2O(3*b*)	0.6667	0.3333	0.141(2)	8(1)	3	0.20(2)
Cl(1*a*)*	0.6667	0.3333	0.0437(7)	3.7(3)	3	0.30(2)
Cl(1*b*)	0.6667	0.3333	0.080(1)	3.7(3)	3	0.10(2)

Note: The notation of the atomic positions correspond to that used in [1]; the positions crystallographically independent in the sp. gr. *R*3 are primed.

* The position compositions are as follows: *M*(1) = 0.7Mn + 0.24Ca + 0.06Ce; *M*(1)' = 0.45Na + 0.35Ca + 0.15Ce + 0.05Sr; *M*(2*a*) = 0.21Zr + 0.19Na; *M*(2*b*) = 0.056Ti + 0.044Nb; Si(8*b*) = 0.65Si + 0.1Al; Na(2*a*) = 0.4Na + 0.06K; Na(5*b*) = 0.43Na + 0.05Sr; Cl(1*a*) = 0.2Cl + 0.1H_2O.

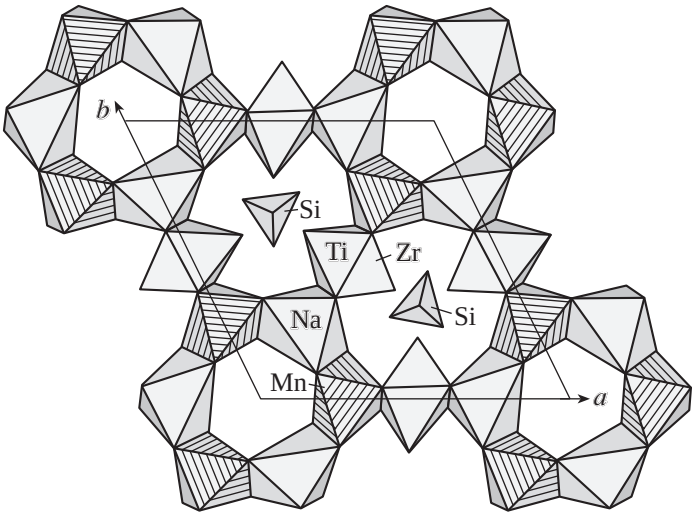
characteristics and the details of single-crystal X-ray diffraction study are summarized in Table 1. The atomic coordinates are listed in Table 2.

The preliminary data on the chemical composition of the mineral (the microprobe analysis) correspond to the empirical formula (with respect to 26(Si + Al)) $Zr_{3.63}Ti_{0.12}Nb_{0.34}Hf_{0.04}Ca_{1.75}Mn_{1.91}Si_{25.91}Al_{0.09}Fe_{1.55}K_{0.12} \cdot Na_{16.34}Sr_{0.53}Ce_{0.63}$.

The crystallochemical formula of the sample (*Z* = 3),

$$Zr_3[(Mn_{2.1}Ca_{0.72}Ce_{0.18})(Na_{1.35}Ca_{1.05}Ce_{0.45}Sr_{0.15})] \times [Si_3O_9]_2[Si_9O_{27}]_2[Fe^{[IV]}_{1.55}(Zr^{[V]}_{0.6}Na^{[VI]}_{0.58})(Ti_{0.15}Nb_{0.12})^{[V]}] \times [Si_{1.9}Al^{[VI]}_{0.1}](Na_{14}Sr_{0.4}K_{0.2})(OH, O)_4(F, Cl)_{0.7} \cdot 1.1H_2O,$$

reflects the ordered distribution of Mn and Na atoms over two crystallographically independent sites of the six-membered ring (the first square brackets). The average cation–anion distances in the Ca-octahedra of eudialytes are in the range of 2.32–2.37 Å, whereas the replacement of Ca cations by smaller Mn cations reduces this distance to 2.26 Å [1]. On the contrary, the presence of larger cations, along with Ca cations, results in an increase of the octahedron dimensions. For example, the corresponding distance in the structure studied in [1] is 2.41 Å. The sample studied consists of six-membered rings built by octahedra of considerably



Fragment of the crystal structure projected onto the (001) plane. The octahedra occupied mainly by manganese atoms entering six-membered rings are hatched with solid lines. The Si(7,8)-tetrahedra are located on threefold axes.

different volumes. These octahedra are occupied mainly by manganese and sodium atoms and are characterized by the average distances of 2.22 and 2.45 Å, respectively. The presence of such octahedra is the most characteristic structural feature of the third representative of the eudialyte family with the symmetry *R*3 (figure). The sample under study is also characterized by a high silica content, which favors the transformation of the nine-membered Si-rings into ten-membered planar radicals containing statistically disordered additional Si-tetrahedra.

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