

Crystal structure and crystal-chemical features of a new Ti-rich member of the eudialyte family

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Abstract. The trigonal structure of a new member of the eudialyte group was established from X-ray single-crystal diffraction, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$; space group $R3m$; $a = 14.153(9) \text{ \AA}$, $c = 60.72(5) \text{ \AA}$, $V = 10546.1 \text{ \AA}^3$; $M = 3050$; $D_x = 2.88 \text{ g/cm}^3$; $Z = 3$; $\mu = 28 \text{ cm}^{-1}$; $R(hkl) = 0.068$ for 3402 reflections. Due to the ordered replacement of Zr with Ti, the new mineral is characterized by a doubling of c and an alternation along [001] of two microdomains, containing (Zr, Ti) or (Ti, Zr)-octahedra, respectively. The key positions on the triad axis are accommodated by Si, Mn and Al atoms. Mn is four-fold coordinated and dominates in one nine-membered ring of the Ti microdomain while Al is six-fold coordinated in the ring of the Zr microdomain. The second key sites are related to Fe atoms which are situated in a slightly aplanar oxygen squares similarly to other relevant examples. These two positions are completed with some neighbour subsites. The axial Al octahedron is connected with three Ti octahedra around the triad axis forming a polyhedral cluster. The splitting and isomorphic substitution of the Na dominant positions are similar to other eudialyte minerals. It was also reported for kentbrooksites. The Na(8b) and Na(9b) atoms are the most disordered around the 18c site with 25% occupancy. The unusual doubling of the structure in the new mineral may be interpreted as a commensurate modulation with wave displacements along the c axis. Other original features of this new representative in the eudialyte family are also discussed.

Introduction

Eudialyte is a very complex cyclosilicate with varying amounts of Na, Ca, Sr, K, REE, Fe, Mn, Zr, Ti, Si, Cl, F and some other elements. It is a typical mineral of apgaitic nepheline syenites. Due to their ability to concentrate Zr, Ti, Nb, REE eudialytes are of interest as potential ore minerals. Since the first structure investigations [1–2] we have studied and summarized in [3] crystal structures of eight eudialyte samples from the Khibina massif with dif-

ferent chemical compositions. Among them are eudialyte and potassium oxonium eudialyte [4–6], so-called eucolite, TR-Fe and TR-Mn eucolites [7, 8], “barsanovite” and “red-brown barsanovite” [9, 10], alluaivite [11] and a new Fe-low analogue of eudialyte [12]. In this paper we describe the crystal structure of a new member from the Lovozero massif (Kola Peninsula) and compare it with earlier published structural data and recently published data on kentbrooksites from East Greenland [13]. The selection of a new representative of this group for the structure investigation is of special interest because of the high content of Ti atoms atypical for the eudialytes. The new mineral^I, studied so far only structurally, was discovered in the Lovozero massif of nepheline syenites in a special type of ultraaluminous pegmatitic rocks, saturated with alkaline, volatile and rare elements [14]. It occurs as yellow transparent grains with a maximal size of up to 0.5–1 mm. The main feature of this mineral is a large amount of Ti accompanied by Zr. In spite of the similar ionic radii and chemical features, these elements have very different crystal-chemical functions in the structures of natural and synthetic compounds [15]. That is why Ti analogues of eudialyte were unknown so far and why the discovery of two Ti-rich eudialyte analogues in the alkaline massif of the Kola Peninsula was unexpected. One of them was named alluaivite [11], and the other one was conventionally called “Ti-rich eudialyte”. Alluaivite is completely lacking Zr while the second member can be regarded as intermediate between titanium and zirconium eudialytes with high ordering of Ti and Zr on structural positions.

Experimental details

The results of electron microprobe analyses showed wide range variations of the chemical composition among grains of Ti-rich eudialyte (in wt%): Na₂O, 16.45–18.53; K₂O, 0.08–0.26; CaO, 7.49–8.81; MnO, 2.43–2.83; SrO, 1.31–2.08; BaO, 0.42–0.74; FeO, 0.64–1.19; REE₂O₃, 3.26–3.94; SiO₂, 44.49–50.46; ZrO₂, 2.00–10.71; TiO₂,

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^I The complete characteristics of the new mineral will be given in a special paper after its approval by the IMA.

Table 1. Crystal data and experimental details of the structure determination for Ti-rich eudialyte.

Chemical formula	Zr _{3.65} Ti _{3.37} Ca _{8.5} Mn _{2.13} Si _{50.68} Al _{0.42} Fe _{0.94} Na _{34.43} Sr _{0.77} Ce _{1.13} O ₁₄₄ Cl _{0.9} (OH) _{5.7} · 1.5 H ₂ O
Formula weight	3050
Crystal system	Trigonal
Space group; <i>Z</i>	<i>R</i> 3 <i>m</i> ; 3
Unit cell dimensions, Å	<i>a</i> = 14.153(9), <i>c</i> = 60.72(5)
Unit cell volume, Å ³	10546.1
Density (calc.), g/cm ³	2.88
Linear absorption coefficient, cm ⁻¹	28
Radiation; λ, Å	MoK _α ; 0.71073
Crystal size (mm)	0.15 × 0.23 × 0.35
Diffractometer	Enraf Nonius CAD4
Scan type	ω/2θ
Maximum sin θ/λ	0.807
Index ranges	-22 < <i>h</i> < 22, 0 < <i>k</i> < 22, 0 < <i>l</i> < 96
Internal <i>R</i>	0.037
Collected reflections (total)	9540
Unique reflections	3402
Criterion for significance	<i>F</i> > 4σ(<i>F</i>)
Absorption correction	Empirical (DIFABS)
Structure refinement	Full-matrix least squares on <i>F</i>
Minimised function	∑ <i>w</i> (Δ <i>F</i>) ²
Number of unique positions	96
<i>R</i> for observed reflections	0.068
<i>wR</i> for observed reflections	0.095
Program	AREN

1.40–5.24; Nb₂O₅, 1.67–3.74; Cl, 0.52–0.97. As was later established by X-ray analysis, the grain content corresponded approximately to the average values.

A single crystal with approximate dimensions (mm) 0.15 × 0.23 × 0.35 was selected for X-ray study. The intensities were collected up to sin θ/λ < 0.807 Å⁻¹ on a Nonius CAD-4 diffractometer with monochromated MoK_α (λ = 0.71073 Å) radiation. The intensity of one standard reflection, measured every 50 observations, did not show any fluctuation larger than 3%. The refined lattice constants of the hexagonal unit cell are: *a* = 14.153(9) Å, *c* = 60.72(5) Å, *V* = 10546.1 Å³. The software package AREN [16] was used for the structure determination which was based on 3402 unique observations with |*F*| > 4σ(*F*) obtained after reflection averaging. The experimental details are given in Table 1.

The framework atoms of alluaivite, a Ti mineral in the eudialyte family with *c'* = 2*c* and a centrosymmetric space group [11] served as a starting model. An attempt to determine non-framework atoms in the space group *R*3*m* failed. The use of the non-centrosymmetric space group *R*3*m* revealed all the framework and most of the non-framework atoms from subsequent *F* syntheses using an automatic structure amplitudes phases refinement procedure [17]. The refinement of their positions in isotropic approximation led to *R*(*hkl*) = 0.10. The atomic scattering factors were corrected for anomalous dispersion. The positions of the remaining atoms with partial occupancy as a result of splitting were determined from difference electron-density syntheses. These peaks were assigned to axial Si atoms with their apical OH vertices and to some axial anions such as Cl, OH and water molecules. All these positions are only statistically occupied.

The formula of the Ti-rich eudialyte has thus been established from the result of its structural investigation and on the basis of the sum of the bond strengths on the anions, which allowed the assignment of O, OH and H₂O to

oxygen positions. The anisotropic least squares refinement using intensities empirically corrected for absorption [18] decreased *R*(*hkl*) to 0.068 with some atoms refined isotropically. The final atomic coordinates and interatomic distances are given in Tables 2, 3 and 4. The chemical composition for the mixed positions is given in Table 5.

Description of the structure

The structures of the eudialyte group minerals are characterized by the presence of the same framework [1, 2] based on both discrete three-membered rings [Si₃O₉] and nine-membered rings [Si₉O₂₇] (Fig. 1) combined with discrete and nearly regular Zr-octahedra and by six-membered rings of distorted [Ca₆O₂₄] octahedra (Fig. 2). In classic eudialytes all these types of polyhedra are sandwiched parallel to (001) in proportion Zr:Si:Ca = 1:2:1. Thus the unit cell contains 12 sheets. In this three-dimensional network the holes are filled mainly with Na and variable amounts of additional atoms with different coordinations. In the Ti-rich eudialyte structure there are two crystallographically independent rings of each sort (Fig. 1, 2) and the structure is characterized by the alternation along [001] of five layer types, formed by Si tetrahedra, *M*(1), *M*(2), *M*(3) and *M*(4) octahedra respectively. As a result, 24 polyhedral sheets are arranged along the *z* axis in the following sequence: *M*(4)–Si–*M*(1)–Si–*M*(3)–Si–*M*(2)–Si–*M*(4) ... (Fig. 3). They are connected along [001] by sharing the common vertices of polyhedra. Four sheets on *z* ~ 0.02–0.18 levels are combined into a packet or microdomain with a thickness of ~10 Å, which corresponds to the classic Zr eudialyte structure, while the next four sheets form another microdomain close to the Ti eudialyte (alluaivite) structure. Six of these microdomains alternate along the *z* axis according to the rule of *R*-centering.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for the framework in the Ti-rich eudialyte structure.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
<i>M</i> (1)	0.1637(1)	0.3274(1)	0.0833(1)	1.21(2)
<i>M</i> (2)	−0.0034(2)	0.4983(1)	0.2496(1)	1.27(3)
<i>M</i> (3)	0.0743(1)	0.6668(2)	0.1662(1)	1.26(3)
<i>M</i> (4)	−0.0007(2)	0.2606(1)	−0.0007(1)	1.24(2)
Si(1)	0.3209(2)	0.0514(2)	0.1183(1)	1.65(5)
Si(2)	0.2464(3)	0.1232(2)	0.2955(1)	1.24(6)
Si(3)	0.0627(3)	0.3446(3)	0.2843(1)	1.37(5)
Si(4)	0.5981(2)	0.4019(2)	0.2924(1)	1.71(7)
Si(5)	0.0717(2)	0.1434(3)	0.0405(1)	1.49(7)
Si(6)	0.4054(2)	0.5946(2)	0.2068(1)	1.44(7)
Si(7)	0.5398(1)	0.4602(1)	0.1269(1)	1.35(6)
Si(8)	0.2632(2)	0.5264(3)	0.1249(1)	1.54(8)
Si(9)	0.0029(2)	0.6064(2)	0.0487(1)	0.97(4)
Si(10)	0.1246(2)	0.2492(3)	0.2042(1)	1.50(7)
Si(11)	0.4172(4)	0.2086(3)	0.0374(1)	1.37(7)
Si(12)	0.3399(3)	0.0651(3)	0.2146(1)	1.33(5)
O(1)	0.3558(8)	0.1779(5)	0.1105(1)	0.9(3)
O(2)	0.3110(8)	0.1555(6)	0.3188(1)	2.2(2)
O(3)	0.5136(3)	0.0272(5)	0.1521(1)	0.8(3)
O(4)	0.3794(9)	0.2783(6)	0.0542(1)	2.1(2)
O(5)	0.0714(5)	0.3715(5)	0.3092(1)	1.0(2)
O(6)	0.0261(6)	0.2478(6)	0.1033(1)	1.6(2)
O(7)	0.3024(11)	0.1512(9)	0.2246(2)	2.5(3)
O(8)	0.1007(6)	0.3969(7)	0.0641(1)	2.5(2)
O(9)	0.0614(5)	0.1228(7)	0.2047(3)	5.3(5)
O(10)	0.5709(8)	0.1418(10)	0.2678(4)	4.6(4)
O(11)	0.2357(6)	0.4714(9)	0.1016(2)	2.5(4)
O(12)	0.2962(7)	0.2533(6)	0.1436(1)	1.3(2)
O(13)	0.5500(4)	0.4500(4)	0.3103(1)	1.5(3)
O(14)	0.2717(5)	0.5434(7)	0.2059(2)	2.1(3)
O(15)	0.0328(9)	0.6219(7)	0.0225(1)	2.6(2)
O(16)	0.3756(11)	0.3026(9)	0.1894(1)	3.2(2)
O(17)	0.1238(8)	0.0619(5)	0.0391(2)	2.4(4)
O(18)	0.5444(11)	0.2722(8)	0.2952(2)	2.1(4)
O(19)	0.0570(4)	0.2981(4)	0.2196(1)	1.0(1)
O(20)	0.5112(3)	0.0224(5)	0.0565(1)	1.1(3)
O(21)	0.3970(6)	0.6030(6)	0.1262(2)	2.6(4)
O(22)	0.0939(3)	0.1878(5)	0.0642(1)	1.1(3)
O(23)	0.0706(6)	0.6357(7)	0.2686(1)	1.6(2)
O(24)	0.1640(6)	0.3280(9)	0.2746(2)	3.0(3)
O(25)	0.4370(9)	0.3596(9)	0.2315(1)	2.9(3)
O(26)	0.5490(13)	0.2745(9)	0.0320(2)	5.8(4)
O(27)	0.1135(6)	0.2270(8)	0.0204(2)	2.8(4)
O(28)	0.2247(6)	0.4494(8)	0.1452(2)	2.4(3)
O(29)	0.1100(13)	0.5550(9)	0.1871(1)	3.2(5)
O(30)	0.2720(9)	0.2235(7)	0.2797(1)	2.6(2)
O(31)	0.6069(5)	0.2137(7)	0.1251(2)	2.5(5)
O(32)	0.4384(9)	0.3856(9)	0.1121(1)	3.4(3)
O(33)	0.1146(14)	0.0573(9)	0.2975(3)	6.0(6)
O(34)	0.1476(5)	0.2952(8)	0.1818(2)	1.8(4)
O(35)	0.4351(6)	0.5649(6)	0.2316(2)	3.5(5)
O(36)	0.3618(9)	0.1809(7)	0.1044(1)	1.6(4)

$$B_{\text{eq}} = 1/3[B_{11}a^{*2}a^2 + \dots + 2B_{23}b^*c^*bc \cos(\alpha) + \dots]$$

The main differences between the two microdomains are associated with the Si₆O₆ rings, *M*(1)–*M*(4) polyhedra and several key sites.

M(1) and *M*(2) sites

Both of these sites (Fig. 3) form nearly regular octahedra combining three and nine-membered rings of two layers. The scattering power of the *M*(1) site is higher than that of the *M*(2) position and we postulated that they must be predominantly accommodated by Zr and Ti, respectively. However, the average distance of 2.05 Å for the *M*(1) octahedron is shorter than the usual 2.06–2.07 Å for Zr oc-

tahedra in classic eudialytes, and 2.02 Å for the *M*(2) octahedron is much larger than 1.94 Å in alluaivite. The site populations of (Zr_{2.33}Ti_{0.67}) and (Ti_{1.7}Zr_{1.3}) fit the scattering values and give reasonable agreement between the average radii and the size of both octahedra. In spite of the fact that chemical analyses show some content of Nb, we could not establish the role of this element in the structure.

The nine-membered silicate rings

Among the nine tetrahedra of the large Si-rings (Fig. 1) there are three tetrahedra with free oxygen vertices. In the central area of the ring these three inner oxygens form a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>N</i>	<i>q</i>	<i>B</i> _{eq} (Å ²)
T(1a)	2/3	1/3	0.0195(8)	3	0.20(4)	1.7(9)
T(1b)	2/3	1/3	0.0438(1)	3	0.80(4)	0.8(7)
T(2a)	2/3	1/3	0.1165(1)	3	0.16(4)	3.0(9)
TM	2/3	1/3	0.1366(1)	3	0.84(3)	1.8(1)
T(3a)	0	0	0.1861(1)	3	0.90(2)	2.6(1)
T(3b)	0	0	0.2160(1)	3	0.10(3)	2.9(9)
T(4a)	0	0	0.2884(1)	3	0.80(4)	0.6(1)
T(4b)	0	0	0.3051(4)	3	0.20(4)	1.0(8)
Ti	0.3734(9)	0.1867(6)	0.1641(1)	9	0.38(1)	2.1(1)
Fe(1)	0.3142(5)	0.1571(4)	0.1674(1)	9	0.23(1)	1.5(1)
Fe(2)	-0.0136(20)	0.4932(16)	0.0005(4)	9	0.08(2)	1.1(4)
M(5)	0.2228(7)	0.4456(9)	0.3348(2)	9	0.30(1)	2.3(2)
M(6)	0.0973(2)	0.1946(3)	0.1429(1)	9	1	3.3(1)
M(7)	0.2227(4)	0.4454(5)	0.2434(1)	9	0.70(2)	4.9(1)
M(8)	0.4459(9)	0.2228(7)	0.2573(1)	9	0.42(1)	3.3(2)
M(9)	0.4416(6)	0.5584(6)	-0.0019(2)	9	0.62(3)	2.1(2)
Na(1)	0.1032(8)	0.5516(6)	0.3039(1)	9	1	2.9(2)
Na(2)	0.2176(9)	0.1088(6)	0.0768(1)	9	1	3.1(3)
Na(3)	0.2132(3)	0.4264(5)	0.0280(2)	9	1	3.8(2)
Na(4)	0.4450(5)	0.5550(5)	0.0898(1)	9	1	4.7(3)
Na(5a)	0.5731(3)	0.1462(4)	0.1878(2)	9	0.83(3)	2.4(2)
Na(5b)	0.5395(11)	0.4605(11)	0.1939(15)	9	0.19(3)	2(1) ^a
Na(6)	0.2634(25)	0.5268(36)	0.2499(6)	9	0.30(3)	4(1) ^a
Na(7)	0.5072(20)	0.2536(15)	0.2476(3)	9	0.58(4)	4.9(2)
Na(8a)	0.1478(10)	0.0739(7)	0.2403(3)	9	0.58(5)	5.0(3)
Na(8b)	0.1115(40)	0.1616(50)	0.2528(9)	18	0.22(2)	7.4(9) ^a
Na(9a)	0.5040(15)	0.2520(9)	0.0865(3)	9	0.53(4)	3.7(3)
Na(9b)	0.5087(30)	0.2078(30)	0.0863(5)	18	0.23(4)	3.7(5) ^a
Na(10)	0.2002(47)	0.1001(33)	0.1721(8)	9	0.80(4)	3.1(9)
Cl(1)	1/3	2/3	0.3131(1)	3	0.80(3)	0.9(2)
Cl(2)	0	0	0.1165(9)	3	0.20(3)	2.7(7)
OH(1)	1/3	2/3	0.3250(9)	3	0.11(9)	3(2) ^a
OH(2)	2/3	1/3	0.0678(2)	3	0.83(9)	1.0(4)
OH(3)	2/3	1/3	0.0928(50)	3	0.16(9)	5(4) ^a
OH(4)	0.5462(47)	0.2731(33)	0.1721(11)	9	0.70(7)	4.9(9)
OH(5)	2/3	1/3	0.1637(9)	3	0.52(9)	1.0(7)
OH(6)	0	0	0.1463(12)	3	0.90(9)	7.8(7)
OH(7)	0	0	0.2410(11)	3	0.16(5)	2.1(5) ^a
OH(8)	0	0	0.2597(12)	3	0.80(6)	0.4(4)
OH(9)	0	0	0.3333(11)	3	0.20(3)	3.4(4) ^a
H ₂ O(1)	1/3	2/3	0.2683(15)	3	0.29(9)	3(2) ^a
H ₂ O(2)	2/3	1/3	0.2241(15)	3	0.29(9)	7(4) ^a
H ₂ O(3)	1/3	2/3	0.0228(2)	3	0.80(3)	2.8(1)
H ₂ O(4)	0	0	0.0026(9)	3	0.19(3)	7(1) ^a

a: isotropic thermal parameters $B_{\text{eq}} = 1/3[B_{11}a^{*2}a^2 + \dots + 2B_{23}b^*c^*bc \cos(\alpha) + \dots]$

Table 3. Atomic coordinates, number of equivalent sites (*N*), site-occupancy factor (*q*) and equivalent isotropic displacement parameters (*B*_{eq}) for extraframework positions in the Ti-rich eudialyte structure.

triangle, which can be used for the construction of additional polyhedra (tetrahedra or octahedra). If the sites on the triad axes accommodate Si atoms, the additional tetrahedra may have two orientations with the apexes pointing towards or away from the hole between two rings. If other octahedra forming elements are present, the orientation is only away from the hole. Both of these variants of population exist for the axial positions in the Ti-rich eudialyte structure. In one crystallographically independent pair of rings, combined with (Ti, Zr) octahedra, all the additional atoms form tetrahedra with two statistical orientations and shorted distances 0.99(2) Å and 1.81(1) Å between them. The mean bond length of the T(3b), T(4a) and T(4b) have reasonable values for Si tetrahedra 1.62 Å, 1.56 Å and 1.54 Å while the T(3a) is characterized by the mean value 2.0 Å and corresponds to Mn–O bond. Recently Mn tetrahedron with a mean bond distance of 1.97 Å was discovered in Fe-low eudialyte [12]. The other pair of rings combined with Zr octahedra also contains Si tetrahedra with

mean bond lengths 1.64 Å, 1.57 Å, 1.56 Å and 1.62 Å for T(1a), T(1b), T(2a) and TM, respectively. They also have two orientations along the triad axis with distances 1.47(5) Å and 1.22(1) Å. There is an additional polyhedron around the TM site, which statistically accommodates Al_{1.25} atoms per unit cell. Similar to Zr(2) [2] this axial M position is occupied by Al_{0.9} in eudialyte-817 [4], Ti_{0.5} and (Nb, Al)_{2.2} in “eucolite-638” [7], Ti_{0.2} and [(Zr, Nb)_{1.8}Al_{0.4}] in “red-brown barsanovite” [10], Nb_{1.8}Zr_{0.8} and Nb_{1.7}Zr_{0.4} in “TR-Fe eucolite” and “TR-Mn eucolite” respectively [8], Nb_{2.0}Zr_{0.9} in barsanovite [9] and Nb_{1.65}Ti_{0.3}Zr_{0.36} in kentbrooksite [13]. The TM position is coordinated by six anions, including three inner oxygens O(31) from the nine-membered ring and three OH(4) shared with the Ti octahedra. The bond-valence sum on this anion point to an OH group. This key position, like O(19) in kentbrooksite, well known in above mentioned eudialytes especially in barsanovite with full occupation, participates in two octahedra (Al and Ti) and the Na(5) polyhedron.

Table 4. Selected interatomic distances (Å) in the structure of Ti-rich eudialyte.

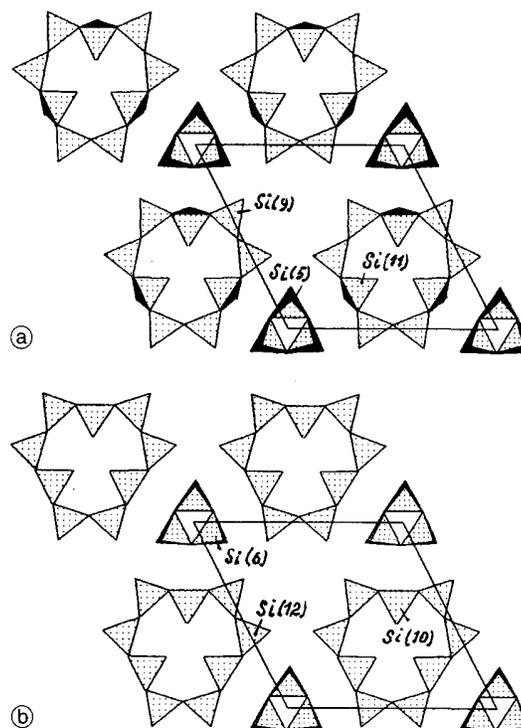
Bonds	Multiplicity	Distance		
		min.	max.	aver.
<i>M</i> (1)	6	2.00	2.08	2.05
<i>M</i> (2)	6	1.96	2.04	2.02
<i>M</i> (3)	6	2.26	2.48	2.35
<i>M</i> (4)	6	2.29	2.39	2.34
Si(1)	4	1.57	1.69	1.62
Si(2)	4	1.59	1.62	1.60
Si(3)	4	1.55	1.67	1.61
Si(4)	4	1.60	1.63	1.61
Si(5)	4	1.54	1.65	1.61
Si(6)	4	1.54	1.66	1.62
Si(7)	4	1.57	1.66	1.61
Si(8)	4	1.55	1.65	1.60
Si(9)	4	1.59	1.66	1.63
Si(10)	4	1.47	1.71	1.61
Si(11)	4	1.55	1.68	1.64
Si(12)	4	1.59	1.67	1.63
<i>T</i> (1a)	4	1.62	1.69	1.64
<i>T</i> (1b)	4	1.46	1.61	1.57
<i>T</i> (2a)	4	1.44	1.60	1.56
<i>TM</i>	4	1.62	1.64	1.62
<i>TM</i>	6	1.62	2.17	1.89
<i>T</i> (3a)	4	1.87	2.41	2.00
<i>T</i> (3b)	4	1.52	1.65	1.62
<i>T</i> (4a)	4	1.53	1.74	1.56
<i>T</i> (4b)	4	1.47	1.71	1.54
Ti	6	2.12	2.23	2.18
Fe(1)	4	2.08	2.23	2.15
Fe(2)	4	2.08	2.22	2.15
<i>M</i> (5)	9	2.41	3.01	2.75
<i>M</i> (6)	7	2.39	2.87	2.66
<i>M</i> (7)	9	2.38	3.10	2.66
<i>M</i> (8)	8	2.53	2.81	2.64
<i>M</i> (9)	8	2.34	3.09	2.77
Na(1)	7	2.37	2.87	2.59
Na(2)	8	2.51	2.71	2.61
Na(3)	7	2.47	2.96	2.62
Na(4)	8	2.50	2.71	2.65
Na(5a)	10	2.44	3.18	2.78
Na(5b)	6	2.29	2.69	2.48
Na(6)	9	2.04	2.97	2.63
Na(7)	7	2.38	2.92	2.57
Na(8a)	8	2.12	3.09	2.75
Na(8b)	7	2.07	2.98	2.43
Na(9a)	9	2.10	2.94	2.67
Na(9b)	6	2.10	2.71	2.44
Na(10)	7	2.56	2.92	2.80

Fe microregion sites

Another key site is a microregion with several subsites between two edges of the *M*(3, 4) octahedra from neighbouring six-membered [*M*₆O₂₄] rings. These subsites can be competitors for some elements. In Fe-rich eudialytes the position in the centre of an almost planar oxygen square is dominated by Fe. If Fe atoms are lacking, this site can be occupied by Na atoms, as in the alluaivite structure [11] or in the structure of Fe-low eudialyte [12]. As evidenced from the chemical composition there are no sufficient Fe atoms to dominate this position even in one microdomain of the Ti-rich eudialyte structure. In the “Zr part” of the structure, the *F* synthesis allowed to localize the Fe(1) and Ti positions based on the short distance between them 0.74(1) Å. The similar splitting of the two

Table 5. The chemical composition for the selected sites in the Ti-rich eudialyte structure (*Z* = 3).

Site	Chemical composition
<i>M</i> (1)	2.33 Zr + 0.67 Ti
<i>M</i> (2)	1.7 Ti + 1.3 Zr
<i>M</i> (3)	4.77 Ca + 1.23 Mn
<i>M</i> (4)	3.73 Ca + 1.87 Na + 0.4 Ce
<i>M</i> (5)	0.67 Na + 0.23 Ce
<i>M</i> (6)	2.6 Na + 0.4 Sr
<i>M</i> (7)	1.83 Na + 0.27 Ce
<i>M</i> (8)	0.94 Na + 0.23 Ce
<i>M</i> (9)	1.46 Na + 0.37 Sr
<i>T</i> (1a)	0.2 Si
<i>T</i> (1b)	0.8 Si
<i>T</i> (2a)	0.16 Si
<i>TM</i>	0.42 Si + 0.42 Al
<i>T</i> (3a)	0.9 Mn
<i>T</i> (3b)	0.1 Si
<i>T</i> (4a)	0.8 Si
<i>T</i> (4b)	0.2 Si
Na(10)	1.33 Na + 1.0 OH

**Fig. 1.** Sections of the Ti-rich eudialyte structure showing three-membered [*Si*₃O₉] and nine-membered [*Si*₉O₂₇] rings at *z* ~ 0.05 (a) and 0.55 (b).

positions with 0.65 Å between them was recently reported for kentbrooksit. Moreover the Fe(1) position is accompanied with Na(10) position on the other side of square at a distance of 1.42 Å. All these three positions can only be statistically occupied. Ti is six-fold coordinated in a rather distorted octahedron with a mean distance 2.18 Å. This distance is larger than the standard value for Ti⁴⁺ which hints for the presence of Ti³⁺ atoms in the position. Four of the oxygens O(12) × 2 and O(16) × 2 belong to the edges of adjacent *M*(3) octahedra while the fifth OH(4) is shared with the axial octahedron in the joint *TM* position containing 1.25 Al atoms. The position of the remaining

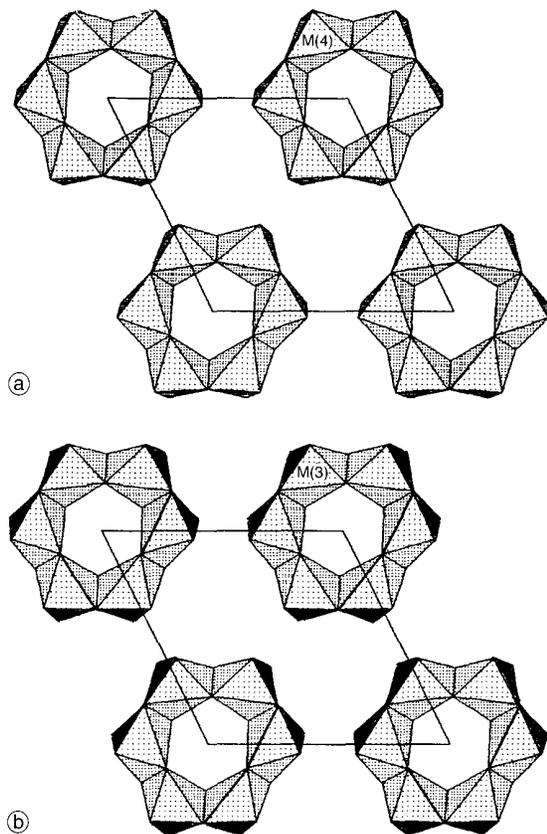


Fig. 2. Sections of the Ti-rich eudialyte structure showing six-membered $[M_6O_{24}]$ rings at $z \sim 0$ (a) and 0.5 (b).

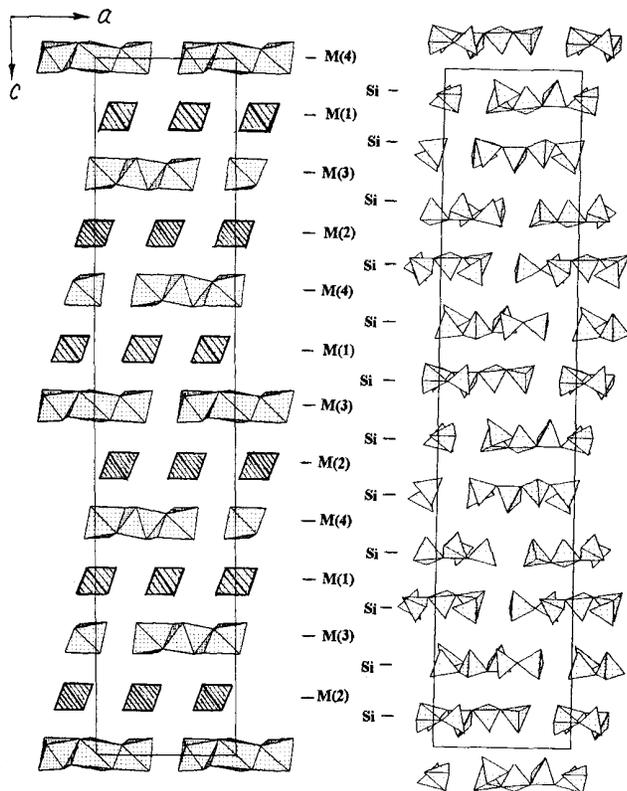


Fig. 3. The arrangement of Si and $M(1)$ – $M(4)$ polyhedra along the c axis.

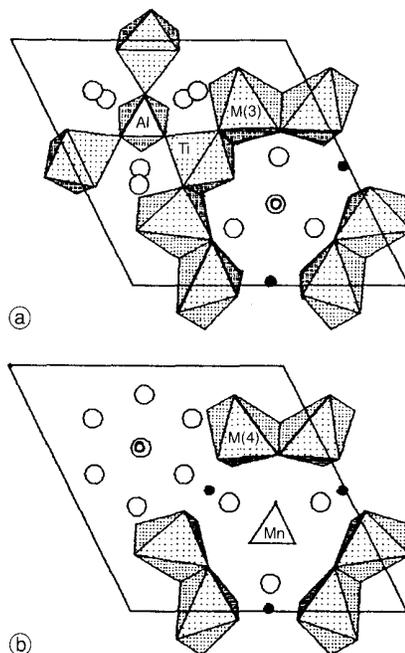


Fig. 4. Fragments of the Ti-rich eudialyte structure of two different sections along c : Al, Ti cluster (a) and Mn tetrahedron (b). Black circles: Fe, open circles: Na, double circles: H_2O .

sixth vertex coincides with the position of Na(10). Such a Na–OH substitution was established in some other eudialytes [4].

As shown earlier [19], the five-fold coordination in a distorted square pyramid is also common in eudialyte structures. A square pyramid of Fe with an almost full occupation of its position was found in barsanovite [11] whereas the corresponding pyramid accommodates mainly Mn atoms in kentbrooksit [13]. Similar to some other relevant minerals, the octahedron on the triad axis and three octahedra (or square pyramids) around it link to form a cluster. Such clusters are the main reason for the strong deviation from centrosymmetry which causes the piezoelectric effect in eucolites [7, 8], especially barsanovites [9, 10]. In the kentbrooksit structure [13], three Mn pentagonal groups are linked together by the (Nb, Ti, Zr) octahedron into a similar cluster. As mentioned above, in Ti-rich eudialyte the Ti, Al-cluster appears only in the “Zr part” (Fig. 4a) of the structure while the “Ti part” accommodates mainly Na atoms in a similar microregion (Fig. 4b).

Na and other elements' sites

There are 17 Na positions in the Ti-rich eudialyte structure. Five of them, $M(5)$ – $M(9)$ (Table 5) are dominated by Na atoms and nine positions are occupied by Na only. Moreover Na participates also in the $M(4)$ position together with Ca and in Na(10) together with OH. Most of these positions are splitted, statistically occupied with short distances 0.66(5) Å–1.73(8) Å between them. They are characterized by different coordination numbers and distances (Table 4). All the Na atoms are placed in the 9 site with point symmetry m except Na(8b) and Na(9b), which are disordered and distributed over $18c$ sites with 25% occu-

pancy. Such disordering of Na atoms in the cavity between two nine-membered rings is a remarkable feature of some eudialytes [7–9]. As a whole, there are 15.93 and 18.5 Na atoms in the Zr and Ti parts, respectively.

Mn atoms occupy two different positions: in six-membered rings with Ca and in the center of nine-membered ring in tetrahedron. REE atoms participate in the other six-membered ring. Moreover, REE and Sr atoms are distributed over Na positions, and REE only in the “Ti part”.

Cl and H₂O molecules are localized on triad axes with statistical occupation of their sites and distances to OH 0.72(1) Å–1.81(9) Å. Predominance of Cl and H₂O in the “Ti part” is remarkable feature of the structure. In addition, H₂O(4) molecule occupies one of the compact holes between two three-membered Si-rings inside the six-membered *M*(4)-ring. As a rule, these cavities remain empty in the eudialyte structures. Water molecules were detected in one of them but only in the alluaivite structure. The fact that H₂O molecules occupy only one hole further stresses the asymmetry of the structure.

Modulation features

So far there are only two known eudialyte minerals with 2c: alluaivite and Ti-rich eudialyte. Due to centrosymmetry the alluaivite structure is nonmodulated. In contrast, the non-centrosymmetrical Ti-rich eudialyte structure may be regarded as commensurately modulated, with the modulation vector equal to *c*. The partial substitution of smaller Ti cations for larger Zr cations leads to structural modulation. The oxygen atoms forming Ti and Zr octahedra participate in Si tetrahedra which are modulated with keeping of triad axes in the rings [Si₉O₂₇] and [Si₃O₉]. Atomic displacements in the rings are primarily connected to tilt angle changes between these tetrahedra. As one can see in Fig. 1, the two nine-membered rings, related by the translation $1/2c = \sim 30 \text{ \AA}$, are significantly rotated from their average positions in opposite directions. Such a rotation is also observed in the six-membered *M*(3) and *M*(4) rings (Fig. 2). As a result, some structural positions are connected with displacement and occupational modulation. This consideration makes it possible to interpret the non-splitting of the inner Si(2, 7, 10, 11) atoms and their oxygen O(9, 26, 31, 33) positions in nine membered rings because in eudialytes, as a rule, these positions are splitted or characterized by enlarged thermal parameters.

Conclusion

1. The new mineral represents the most complex eudialyte structure known so far. The Ti-rich eudialyte comprises the unusual framework with the predominance of Zr in one octahedron and Ti in the other which determines the existence of two individual parts within the same structure. Each part is a microdomain with a distinctive distribution of impurities over positions, and the two-stored cell contains six microdomains alternating along the *c* axis in accordance with the *R* centering. Thus it is convenient to represent the crystal-chemical formula of the mineral as consisting of two parts: $\{(Zr_{2.33}Ti_{0.67})(Ca_{4.77}Mn_{1.23}) \times$

$[(Si_3O_9)_2(Si_9O_{27})_2(Si_{1.58}Al_{0.42}^{VI})](Na_{1.33}TiFe_{0.67})(Na_{14.6}Sr_{0.4}) \times Cl_{0.2}OH_{3.7}\}(Ti_{1.7}Zr_{1.3})(Ca_{3.73}Na_{1.87}Ce_{0.4})[(Si_3O_9)_2(Si_9O_{27})_2 \times (Si_{1.1}Mn_{0.9})](Na_{2.13}Sr_{0.37}Fe_{0.27}Ce_{0.23})(Na_{14.5}Ce_{0.5})Cl_{0.7}(OH)_2 \cdot 1.5 H_2O\}$.

2. As can be inferred from the crystal-chemical formula, Ti-rich eudialyte is an intermediate member between classic eudialytes, i.e. Zr, Ca and Fe-rich eudialytes and alluaivite, i.e. Ti, Na, REE-rich eudialyte characterized by an intermediate value of the *a* parameter. The replacement of one independent Zr with Ti leads to the REE elements concentrating in only one part of the structure. Other remarkable features are the presence of H₂O molecules in the small cavity and the increasing in Cl anions in the “Ti part” as in alluaivite.

3. The partial substitution of Zr for smaller Ti is the main reason for the modulation of the framework atoms. The description of the Ti-rich eudialyte superstructure in terms of commensurate modulation allowed us to explain an increase of the *c* parameter and the lowering of its symmetry in comparison with the symmetry of alluaivite and also the absence of splitting for Si and O framework atoms which characterizes the structure of some eudialytes.

4. As a whole, the new member demonstrates all the features of most other representatives of the family and some original features, which allow us to predict the existence of many new members on the basis of chemical composition. As it is impossible to be sure of any new member without structural analysis, they should be studied as part of future experiments.

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