

ALEKSANDROVITE¹, $\text{KLi}_3\text{Ca}_7\text{Sn}_2[\text{Si}_6\text{O}_{18}]_2\text{F}_2$ – A NEW TIN MINERAL

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Aleksandrovite, $\text{KLi}_3\text{Ca}_7\text{Sn}_2[\text{Si}_6\text{O}_{18}]_2\text{F}_2$ is a new mineral, the tin analogue of baratovite. It was discovered in a moraine boulder of microcline-calcite rock, along with quartz, albite, aegirine-hedenbergite pyroxene, in the Darai-Pioz glacier (Tajikistan). The mineral association is represented by baratovite, fluorite, miserite, Sn-bearing titanite, bazirite, pabstite, Sn-bearing sogdianite, sugilite, turkestanite, fluorapatite (apatite-(CaF)). The new mineral occurs in two types: a) minute (up to 50–70 μm) lamellar grains with no zoning visible under BSE, and b) crystals (up to 0.8 mm) and aggregates of zoned and sectorial grains with separate zones of aleksandrovite, and baratovite or katayamalite. The mineral is colourless, transparent, with vitreous lustre and pearl lustre on cleaved surface. Streak colour is white. Cleavage is perfect along (001). Density (measured) = 3.05(2) g/cm^3 , density (calculated) = 3.07(2) g/cm^3 . Microhardness is 300 kg/mm^2 . Mohs hardness is 4–4.5. It fluoresces light-blue under short wave UV (254 nm). The mineral is biaxial, optically negative: $n_p = 1.629(2)$, $n_m = 1.635(4)$, $n_g = 1.638(2)$ (589 nm); $2V$ (calculated) = -70.3° . Dispersion is strong, $r > v$. Elongation is positive, angle of extinction varies from 0° to 22° . Aleksandrovite is monoclinic, $C2/c$, $a = 17.01(2)$, $b = 9.751(6)$, $c = 21.00(2)$ Å, $\beta = 112.45(8)^\circ$, $V = 3219(7)$ Å³, $Z = 4$. The strongest X-Ray lines are as follows: (d in Å (hkl)): 4.86(21)(31–1); 3.712(33)(312); 3.234(100)(006); 3.206(34)(223); 3.039(28)(025); 2.894(42)(314); 2.425(42)(008); 1.950(25)(426). Chemical analysis (EMPA, an average out of 17 analyses; Li_2O – ICP OES, H_2O – calculated; wt.%): SiO_2 – 48.01, Al_2O_3 – 0.07, TiO_2 – 2.86, SnO_2 – 12.84, ZrO_2 – 1.27, Nb_2O_5 – 0.11, Fe_2O_3 – 0.27, Ce_2O_3 – 0.04, MgO – 0.05, CaO – 25.52, SrO – 0.39, Na_2O – 0.20, K_2O – 2.91, Li_2O – 3.01, F – 1.71, H_2O – 0.39, ($-\text{O}=\text{F}_2$) = -0.72 , total 99.12. Empiric formula of aleksandrovite – $(\text{K}_{0.93}\text{Na}_{0.10})_{1.03}\text{Li}_{3.02}(\text{Ca}_{6.82}\text{Sr}_{0.06}\text{Mn}_{0.04}\text{Mg}_{0.02})_{6.94}(\text{Sn}_{1.28}\text{Ti}_{0.54}\text{Zr}_{0.15}\text{Fe}_{0.05}\text{Nb}_{0.01})_{2.03}(\text{Si}_{11.98}\text{Al}_{0.02})_{12}\text{O}_{36.00}[\text{F}_{1.35}(\text{OH})_{0.65}]_{2.00}$.

IR spectrum of aleksandrovite is similar to that of baratovite, the strongest absorption strips are: 1083, 1024, 974, 950, 673, 607, 568, 520, 470, 440 cm^{-1} . Compatibility index is $1 - (K_p/K_c) = -0.005$. The mineral is named to honour of the well-known Russian geochemist, geologist and mineralogist Stanislav Mikhailovich Aleksandrov (born in 1932) for his great contribution in geology, geochemistry and mineralogy of tin. The type specimen is stored in the Fersman Mineralogical Museum RAS in Moscow (registration number 3825/1).

5 tables, 6 figures, 19 references.

Keywords: aleksandrovite, baratovite, katayamalite, Darai-Pioz, tin minerals, alkaline rocks.

During examination of the field materials collected by the authors in 2004 and 2007 in Darai-Pioz alkaline massif (Tajikistan) a new tin mineral was discovered. The chemical composition can be expressed as the simplified formula $\text{KLi}_3\text{Ca}_7\text{Sn}_2[\text{Si}_6\text{O}_{18}]_2\text{F}_2$. It was named aleksandrovite to honour Stanislav Mikhailovich Aleksandrov (born in 1932), the well-known Russian geochemist, geologist and mineralogist, for his great contribution in geology, geochemistry and mineralogy of tin.

Aleksandrovite is the tin analogue of baratovite, $\text{KLi}_3\text{Ca}_7\text{Ti}_2[\text{Si}_6\text{O}_{18}]_2\text{F}_2$ and fluorine-tin analogue of katayamalite, $\text{KLi}_3\text{Ca}_7\text{Ti}_2[\text{Si}_6\text{O}_{18}]_2(\text{OH},\text{F})_2$.

Before concentration on the description of the new mineral we shall dwell on the history of the investigation of baratovite and katayamalite, because the view of their chemical

composition and nomenclature differed over many years.

Baratovite was described as a new mineral discovered within quartz-albite-aegirine rocks with miserite from Darai-Pioz massif in 1975 by Vyacheslav D. Dusmatov with co-authors. According to the wet chemical analysis (Table 1, an. 1) the suggested formula was $\text{KLi}_2\text{Ca}_8\text{Ti}_2\text{Si}_2\text{O}_{37}\text{F}$ (Dusmatov *et al.*, 1975). That differs by the number of atoms per formula unit from the one approved at present: Ca (8 *apfu* instead of 7 *apfu*), Li (2 *apfu* instead of 3 *apfu*) and F (1 *apfu* instead of 2 *apfu* in the extreme fluorine end member). Unfortunately, in this paper there is no data on the sample preparation for chemical analysis, on the methods of determination of the chemical compounds, or on whether the water content was measured. Absence of these data makes

¹ – the mineral was considered and recommended for publication by the Commission on New minerals and mineral names of Russian mineralogical society and approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA on 4th of May 2009.

Table 1. Chemical composition of baratovite, katayamalite and aleksandrovite (wt.%)

Comp.	Baratovite	Katayamalite	Aleksandrovite	
	1	2	3 average variation limits	
SiO ₂	50.46	52.31	48.01	47.32–48.79
Al ₂ O ₃			0.07	0.01–0.27
TiO ₂	9.55	10.99	2.86	0.88–3.89
SnO ₂			12.84	10.73–16.03
ZrO ₂	2.28		1.27	0.18–3.01
Nb ₂ O ₃	0.72		0.11	0.00–0.28
Fe ₂ O ₃	0.50	0.29	0.27	0.01–0.74
Ce ₂ O ₃			0.04	0.00–0.23
MgO			0.05	0.01–0.25
MnO	0.12	0.22	0.17	0.10–0.25
CaO	30.36	28.25	25.52	24.98–25.87
SrO			0.39	0.01–1.48
Na ₂ O	0.70	0.22	0.20	0.01–0.56
K ₂ O	2.96	2.89	2.91	2.76–3.06
Li ₂ O	2.05	3.25	3.01*	
F	1.05	0.34	1.71	1.10–2.01
H ₂ O		1.21	0.39**	
-O=F ₂	-0.44	-0.14	-0.72	
Total	100.31	99.83	99.12	

Note: calculated for (Si + Al) = 12 atoms

1 – baratovite, Darai-Pioz, Tajikistan. Analyst A.V. Bykova (Dusmatov *et al.*, 1975) (K_{0.90}Na_{0.28})_{1.18}Li_{1.96}(Ca_{7.75}Mn_{0.03})_{1.78}(Ti_{1.71}Zr_{0.26}Fe_{0.09}Nb_{0.08})_{2.14}Si₁₂O_{37.23}F_{0.79}
 2 – katayamalite, Iwaki, Japan. EMPA. Li₂O – flame photometry, H₂O – thermal-gravimetry, Fe₂O₃ – titrimetry (Murakami *et al.*, 1983) (K_{0.85}Na_{0.10})_{0.93}Li_{3.00}(Ca_{6.94}Mn_{0.04})_{6.98}(Ti_{1.90}Fe_{0.05})_{1.95}Si₁₂O_{35.78}(OH)_{1.85}F_{0.25}
 3 – aleksandrovite, EMPA, average from 17 analyses. Li₂O – ICP OES, H₂O – calculated. Analyst L.A. Pautov, (K_{0.93}Na_{0.10})_{1.03}Li_{3.02}(Ca_{6.82}Sr_{0.06}Mn_{0.04}Mg_{0.02})_{6.94}(Sn_{1.28}Ti_{0.54}Zr_{0.15}Fe_{0.05}Nb_{0.01})_{2.03}(Si_{11.98}Al_{0.02})₁₂O_{36.00}(F_{1.35}(OH)_{0.65})_{2.00}

evaluation of correctness of the original baratovite formula difficult.

The crystal structure of baratovite was studied (R = 5.6%) by P.A. Sandomirskiy with co-authors on the sample from Darai-Pioz kept in the Fersman Mineralogical Museum RAS (Sandomirskiy *et al.*, 1976). The picturesque description of baratovite crystal structure is given in the famous "Essays on structural mineralogy" by Nikolay V. Belov and Elizaveta N. Belova (1978). Later, the baratovite structure was refined (R = 3.4%) by Silvio Menchetti and Cesare Sabelli (Menchetti, Sabelli, 1979), also on the sample from Darai-Pioz obtained from Alexander S. Povarennykh. The study of the structure in both works was not accompanied by the

chemical composition determination, and there is no evidence of correlation between the specimens of baratovite studied and the type material. In both cases the authors suggest the formula KLi₃Ca₇Ti₂[Si₆O₁₈]₂F₂. According to the structural data, the mineral does not contain hydroxyl-groups. However, Werner H. Bauer and Dethard Kassner (Baur, Kassner, 1992) doubted this and suggested the formula KLi₃Ca₇Ti₂[Si₆O₁₈]₂(F,OH)₂. They concluded this on the basis of comparison of the structures of baratovite and similar to it katayamalite KLi₃Ca₇Ti₂[Si₆O₁₈]₂(OH,F)₂. Our study established that the hydroxyl-groups are present in baratovite, at least in some specimens from Darai-Pioz. The content of H₂O⁺, determined by the Penfield method, varies from 0.44 to 1.02 wt.% in the studied samples. The presence of hydroxyl-groups is also confirmed by the IR-spectroscopy data. For the hypothetical mineral the water and fluorine contents with intermediate composition KLi₃Ca₇Ti₂[Si₆O₁₈]₂F_{1.00}(OH)_{1.00} would be 0.65 and 1.37 wt.% respectively. Thus, samples of the mineral with H₂O content over 0.65 wt.% should formally be attributed to katayamalite. It is possible that the difference in fluorine content according to the chemical analysis by A.V. Bykova (Dusmatov *et al.*, 1975) and to the structural research of baratovite (Sandomirskiy *et al.*, 1976; Menchetti, Sabelli, 1979) is related to variations in the fluorine-hydroxyl ratio in different samples of this mineral from Darai-Pioz.

Ekaterina Reguir with co-authors (1999) performed over 30 analyses of baratovite from quartz-albite-aegirine rocks from the Darai-Pioz complex (in the paper there are only 2 analyses of baratovite with no data on fluorine- and water content) and indicate that the new analytical data correlated well with the structural formula suggested by Pavel A. Sandomirskiy with co-authors (1976) and almost identical to katayamalite analyses.

Katayamalite was discovered and described by Nobuhide Murakami with co-authors in 1983 in aegirine syenite from Iwaki island, Ehime Pref., on the South-West of Japan (Murakami *et al.*, 1983), and its structure was interpreted by Toshio Kato and Nobuhide Murakami (Kato, Murakami, 1985). Katayamalite differs from baratovite by triclinic symmetry and by predominance of OH over F (water content was determined using thermogravimetric analysis). Werner H. Bauer

and Dethard Kassner indicated that triclinic value of katayamalite is extremely low, and the α and γ angles deviation from 90° is within the experimental error limits (Baur, Kassner, 1992). On this basis they conclude the identity of baratovite and katayamalite structures. Thus, at present katayamalite is recognised as a hydroxyl-dominant mineral, and baratovite, according to the structural study – as fluorine-dominant, although it is in contradiction with the results of the first chemical analysis (Dusmatov *et al.*, 1975).

We draw your attention to the history of the study of fluorine and hydroxyl ratio in baratovite and katayamalite because aleksandrovite has wide variations of fluorine concentration. After calculating some of aleksandrovite analyses (for 12 Si atoms), the fluorine coefficient appeared to be less than one, and therefore the mineral of such a chemical composition is formally not aleksandrovite but its hydroxyl analogue. Unfortunately until now we could not find sufficient quantity of such a material for the detail study.

The variations of cations composition in the minerals of baratovite group have been studied to a lesser degree. In this paper we tried to fill this gap up by presenting the characteristics of isomorphism in the octahedral position, predominantly occupied by titanium in baratovite and by tin in aleksandrovite.

Type locality

The alkaline massif Darai-Pioz is located on the joint of three sub-latitudinal ridges – Turkestanskiy, Alaiskiy and Zeravshanskiy in the upper reaches of the Darai-Pioz river, the left tributary of the Obi-Kabud (Yarkhych) river which belong to the Surkhob river basin. The first data on this massif were obtained by Alexander V. Moskvin during Tajik-Pamirs expedition in 1932–1936 (Moskvin, 1937). During 1946–1947 the specific works on rare-metal mineralization in alkaline rocks in the Alai and Turkestan ridges were held under the leadership of Yuriy A. Arapov. Since 1960 detailed mineralogical research of the Darai-Pioz massif, mostly by Vyacheslav D. Dusmatov, lead to the revelation of unique mineralization of lithium, boron, zirconium and *REE* (Dusmatov, 1968; 1971 etc.). The extremely complex high-mountainous relief and overlapping of considerable parts of the outcrops by glaciers and moraines make geological rese-

arch difficult. The total area of the outcrops are nearly 16 sq. km. On the north the massif intrudes through Silurian limestone strata, and on the south – through terrigene-schistose strata with limestones and Middle-Upper Carboniferous effusion interlayers. The external part of the massif consists of sub-alkaline biotite granites of the 2nd phase of the Turkestan complex (300–290 Ma) and their tourmalinized and greisenized varieties. Further towards the centre there are interrupted rings of biotite granites changing in some areas to granosyenites and alkaline granites. The core of the massif is composed of quartz- and aegirine syenites. In the north-eastern part of the massif there are outcrops of cancrinite foyaites (247 ± 6 Ma). All the intrusive rocks are crossed by the dykes of fine-grained biotite granites with tourmaline. The fenitized varieties of the rocks, sometimes with bafertsite, calcybeborosilite-(Y) and thorite are widespread. In the moraine of the Darai-Pioz glacier blocks of rather peculiar aegirine-microcline-quartz-albite rocks with miserite, baratovite occur; these rocks are described by Reguir *et al.* (1999). The massif is locally albitized (203 ± 8 Ma), carbonatized and graphitized. The vein rocks are various. Amongst them there are several types: muscovite-microcline-quartz pegmatites with schorl (limited occurrence); aegirine-microcline-quartz pegmatites with polyolithionite, leucosphenite, stillwellite-(Ce), pyrochlore, sogdianite etc. (286 ± 7 Ma); aegirine-microcline-sogdianite pegmatites with stillwellite-(Ce), titanite, danburite, rarely – with quartz; aegirine-microcline-quartz pegmatites with neptunite, eudialyte, titanite; aegirine-microcline-reedmergnerite pegmatites with pectolite, eudialyte, leucosphenite; syenite pegmatites with turkestanite; microcline-calcite-pectolite veins with turkestanite. The petrology and mineralogy of the massif is described in detail in a number of publications (Dusmatov, 1968, 1971; Belakovskiy, 1991; Grew *et al.*, 1993 etc.). It is significant that carbonatites – essentially calcite rocks, sometimes with quartz (Dusmatov, 1971; Mayorov, Gavrilin, 1971) are widespread in the massif, and aleksandrovite is related exactly with them. It is possible that these rocks are not genetically similar, and are under intensive research at present (Faiziev *et al.*, 2008; Gafurov, 2008).

There is only fragmentary data on the geochemistry and mineralogy of tin in the Darai-

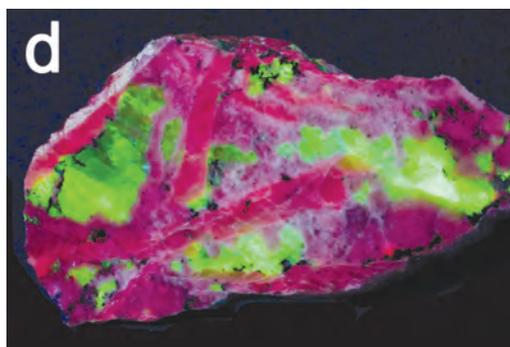
Pioz massif. Certain speciality was mentioned by V.V. Mogarovsky (1987). The average content of tin in the rocks of the massif is 8–12 ppm according to his data. The enrichment in tin was observed in titanite – 0.13 wt.% SnO₂ (Dusmatov, 1971), up to 8.1 wt.% SnO₂ (Reguir *et al.*, 1999); in bazirite 2.9 wt.% SnO₂ (Reguir *et al.*, 1999), in sogdianite up to 1.4 wt.% SnO₂ (Pautov *et al.*, 2000). The only proper tin mineral in the Darai-Pioz massif before aleksandrovite discovery was pabstite (Pautov, 2003).

Aleksandrovite was found in a large boulder (Fig. 1) in a vein within microcline-calcite rock with pyroxene and quartz from the Darai-Pioz glacier moraine. The vein has complex zoned structure. It is composed of (from periphery towards the centre): 1 – leucocratic medium-grained pyroxene-microcline rock, 2 – inequigranular quartz-pyroxene-microcline rock with large segregations (ovoids) of calcite, 3 – coarse-grained microcline-calcite rock with aegirine, quartz, albite. The host rock is an intensively altered clay

slate. Microcline-calcite rock (Fig. 1 a–d) is composed of disorderly located coarse (10–15 × 8–15 × 0.5–1.5 cm) grains of white calcite flattened along (001). Calcite comprises the framework of the rock, and interstitions are filled with aggregates of pale-grey oval zoned microcline crystals (1–2 cm across) and fine-grained aggregates of albite, quartz, calcite, apatite. Pyroxene is represented by columnar grains up to 1 cm long, often associated with the boundary between large plates of calcite and feldspar aggregate. Some interstitions between calcite plates are filled with translucent colourless quartz with irregular but very bright yellowish-green fluorescence under short wave UV (254 nm). Some areas of such a rock (on the border with the Zone 2) consist predominantly of fine-grained quartz-albite aggregates with miserite. In one of these areas aleksandrovite was found.

The predominant minerals in association with aleksandrovite are calcite, microcline and quartz, the minor phases are albite, pyroxene, the accessory phases – baratovite, fluo-

Fig. 1. The rock and specimens with aleksandrovite: a – the general view of the boulder of microcline-calcite rock with pyroxene and quartz, size 2 × 2 × 3.5 m (1 – syenite zone, 2 – transition zone from syenite to quartz-microcline-calcite rock (large oval segregation of calcite are visible), 3 – quartz-microcline-calcite rock zone); b – the fragment of the previous image (zone 3) – quartz-microcline-calcite rock; c & d – rock sample from the zone 3, under incandescent light (c) and SW UV illumination (d). Quartz fluoresces bright-green, platy calcite – pinkish-red, microcline – pinkish-purple. Black grains – aegirine-hedenbergite. Size 6 × 14 cm.



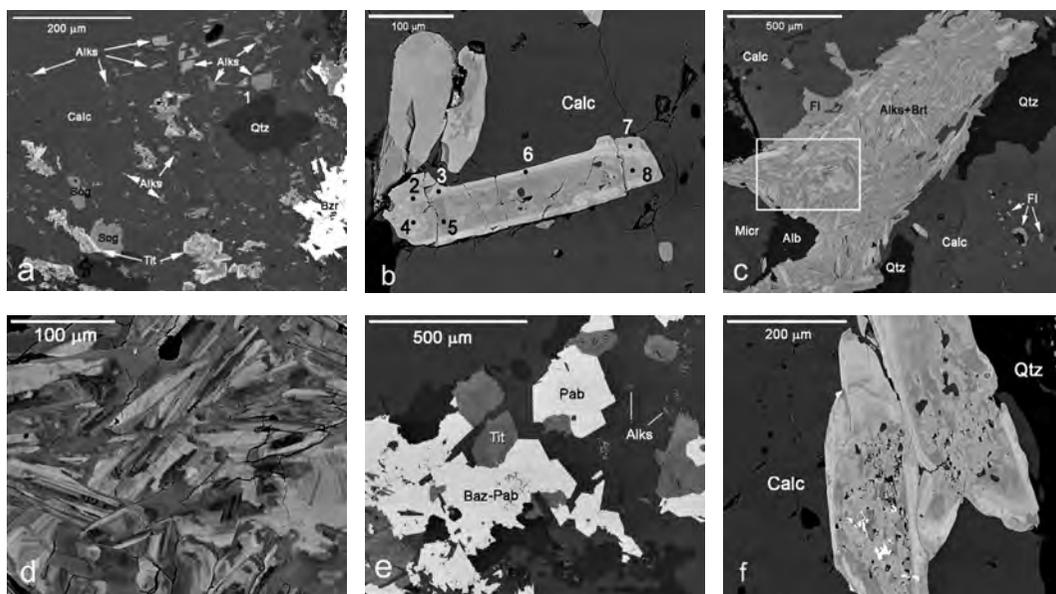


Fig. 2. Aleksandrovite grains in quartz-aegirine-albite-microcline-calcite rock. BSE images of polished thin sections. Labelled points – analysed minerals using EMPA (the numbers correspond to the ones in the Table 3). Alks – aleksandrovite, Brt – baratovite or katayamalite, Tit – titanite, Bzr – bazirite, Sog – sogdianite, Calc – calcite, Qtz – quartz, Micr – microcline, Alb – albite, Fl – fluorite.

a – small (5–60 μm) and relatively homogeneous grains of aleksandrovite with no visible zonation, in calcite. This was the source of aleksandrovite for obtaining physical properties, X-ray data and determination of Li content. Aggregates of distinctly zoned and sectorial Sn-bearing titanite (the paler areas are enriched in tin) and Sn-bearing sogdianite are located in the lower part of the image; b – zoned crystal, its central part corresponds to baratovite-katayamalite and periphery paler part – to aleksandrovite; c – an aggregate of sectorial-zoned grains of the minerals of aleksandrovite-baratovite series in quartz-albite-microcline-calcite rock; d – the fragment of the previous image (marked with white frame), with details of the complex sectorial-zoned structure of the grains; e – aggregates of crystals of the minerals of bazirite-pabstite series (Baz-Pab) with tin-bearing titanite in quartz-calcite aggregate; aleksandrovite is represented by thin platy grains; f – an aggregate of relatively large crystals with complex layout pale areas are corresponded to aleksandrovite, grey – to baratovite or katayamalite. White ingrowths in the crystals – are tin-bearing bazirite. Small isometric crystals in the upper right corner of the image belong to fluorite. Images are obtained using SEM CamScan-4D.

rite, miserite, titanite, bazirite, pabstite, sogdianite, sugilite, turkestanite and fluorapatite. Calcite is characterized by the relatively high content of barium and strontium, and by enrichment in light REE (according to ICP-MS analysis: Ba – 1030, Sr – 4530, Mn – 1010, Ce – 165, Y – 38 ppm) which is typical for calcite from carbonatites. Microcline is represented by the zoned crystals enriched in barium (separate crystals contain up to 2.0 wt.% BaO). Pyroxene crystals in the rock are poorly terminated. Their chemical composition corresponds to aegirine-hedenbergite. A typical mineral in the above-described association is tin-bearing titanite, that occurs in zoned-sectorial, blocked and split crystals. The constant companion of aleksandrovite is bazirite which forms a continuous solid solutions series with pabstite (Fig. 2e). Selective chemical compositions of the minerals from the association

with aleksandrovite are presented in the Table 2.

Aleksandrovite occurs in different shapes and forms. For convenience one can assign two "extreme" types: minute (up to 50–70 μm) lamellar grains with no zoning visible under BSE, separate grains (Fig. 2a) and larger (up to 0.8 mm) crystals and aggregates of zoned and sectorial grains with separate zones of aleksandrovite (paler colour under BSE) and baratovite or katayamalite (Fig. 2b – d, f, Fig. 3).

All the data of the physical properties of aleksandrovite were obtained from grains of type I. In order to separate the grains we dissolve the second half of the polished section with non-zoned aleksandrovite, in 5% HNO_3 at room temperature. The insoluble residue was thoroughly washed with deionized water, rinsed with acetone and dried at room temperature. Several transparent, non-included

Table 2. Chemical composition of the minerals from association with aleksandrovite, EPMA data (wt.%)

Comp.	titanite		sogdianite		bazirite	pabstite		pyroxene
	1	2	3	4	5	6	7	8
SiO ₂	26.68	28.11	29.45	65.77	39.37	37.10	38.69	50.16
Al ₂ O ₃	0.15*	0.61	0.89	0.01	—	—	—	0.13
TiO ₂	21.78	24.94	30.82	0.03	—	—	1.89	0.16
Nb ₂ O ₅	1.09	1.04	1.05	—	—	—	—	—
ZrO ₂	1.96	0.76	0.99	15.08	25.29	1.17	3.41	—
SnO ₂	21.08	14.63	7.36	9.07	1.90	28.76	24.20	—
FeO	0.92	2.02	2.35	—	0.19*	—	—	24.38
MnO	0.04*	0.04*	0.08*	—	—	—	—	2.50
MgO	0.06*	0.27*	0.00	—	—	—	—	1.65
BaO	—	—	—	—	33.26	32.41	32.37	—
CaO	24.42	25.70	26.86	0.06	—	—	—	13.81
Na ₂ O	0.14*	0.00	0.21*	0.09	—	—	—	5.81
K ₂ O	—	—	—	4.10	—	—	—	—
Li ₂ O	—	—	—	4.09**	—	—	—	—
Total	98.32	98.11	100.06	98.30	100.01	99.44	100.56	98.60

Note: obtained using SEM CamScan 4D with energy dispersive spectrometer Link ISIS, U = 20 kV, I = 4 nA. * = <2 sigma. ** calculated content. "—" component content is under limits of EDS analysis. Analyst L.A. Pautov.

Titanite (calculated for O = 5): 1) Ca_{0.98}Na_{0.01}(Ti_{0.61}Sn_{0.31}Zr_{0.04}Fe_{0.03}Nb_{0.02})_{1.01}Al_{0.01}Si_{1.00}O₅,

2) Ca_{1.00}(Ti_{0.60}Sn_{0.21}Zr_{0.01}Fe_{0.06}Nb_{0.02})_{0.98}Al_{0.03}Si_{1.02}O₅,

3) Ca_{0.99}Na_{0.01}(Ti_{0.79}Sn_{0.10}Zr_{0.02}Fe_{0.07}Nb_{0.02})_{1.00}Al_{0.04}Si_{1.01}O₅.

Sogdianite (calculated for Si = 12): 4) K_{0.93}Na_{0.03}Ca_{0.01}Li_{3.00}(Zr_{1.34}Sn_{0.66})_{2.00}Si₁₂O_{30.02}.

Bazirite (calculated for O = 9): 5) Ba_{0.99}(Zr_{0.94}Sn_{0.06}Fe_{0.01})_{1.01}Si_{3.00}O₉.

Pabstite (calculated for O = 9): 6) Ba_{1.03}(Sn_{0.93}Zr_{0.05})_{0.98}Si_{3.01}O₉, 7) Ba_{0.99}(Sn_{0.75}Zr_{0.13}Ti_{0.11})_{0.99}Si_{3.01}O₉.

Pyroxene (aegirine-hedenbergite) (calculated for O = 6): 8) Ca_{0.38}Na_{0.44}Mg_{0.10}Mn_{0.08}Fe_{0.33}⁺²Fe_{0.47}⁺³(Si_{1.98}Al_{0.01})_{1.99}O₆.

grains of the new mineral were separated under binocular microscope with UV short-wave control, and put onto electroconductive carbonic tape. The chemical composition of the separated grains was obtained from many spots using EMPA JXA-50A with energy dispersive spectrometer. Afterwards the grains were used for measurements of density, optical properties, obtaining X-ray data and for lithium content determination.

Chemical composition

The chemical composition of aleksandrovite was studied for non-zoned fine grains, due to the small amount of material from the zoned crystals for lithium detection. The composition of the mineral was measured using CamScan 4D SEM scanning electron microscope with EDS energy dispersive spectrometer Link ISIS, operated at 20 kV, absorbed current on metallic cobalt at 4nA and beam diameter of 1 μm, and also using X-ray microanalyser Camebax-microbeam with four WDS wave spectrometers at 20 kV (10 kV for F), beam current at 20 nA and beam diameter of 1 μm. Standards we used are as follows: microcline

USNM 143966 (K, Al), jadeite STD 048 (Na), wollastonite STD 097 (Si, Ca), diopside USNM 117733 (Mg), SrSO₄ (Sr), MnTiO₃ (Mn), CePO₄ USNM 168484 (Ce), SnO₂ (Sn), ZrO₂ (Zr), LiNbO₃ (Nb), ilmenite USNM 96189 (Ti, Fe), MgF₂ (F). Calculation of concentrations for EDS analysis was made by Phi-Rho-Z method, for WDS — by ZAF-correction (PAP-correction for F). The average composition on the basis of analyses of 17 grains is presented in the Table 1.

For lithium determination, two grains about 50 μm were extracted from the carbonic conductive tape (after EDS analysis composition control) and decomposed with HF + H₂SO₄ in a glass-carbonic crucible. After evaporation of the solution, the residue was dissolved in HNO₃ and then diluted with water until 5% nitric acid. The solution obtained was analysed using ICP-OES Vista MPX by VARIAN. For calculation of the lithium content in aleksandrovite we used the method of lithium concentration in solution, by the ratio of another elements concentration in the mineral (which was determined by microprobe analysis). As such an elements we chose potassium and calcium, which concen-

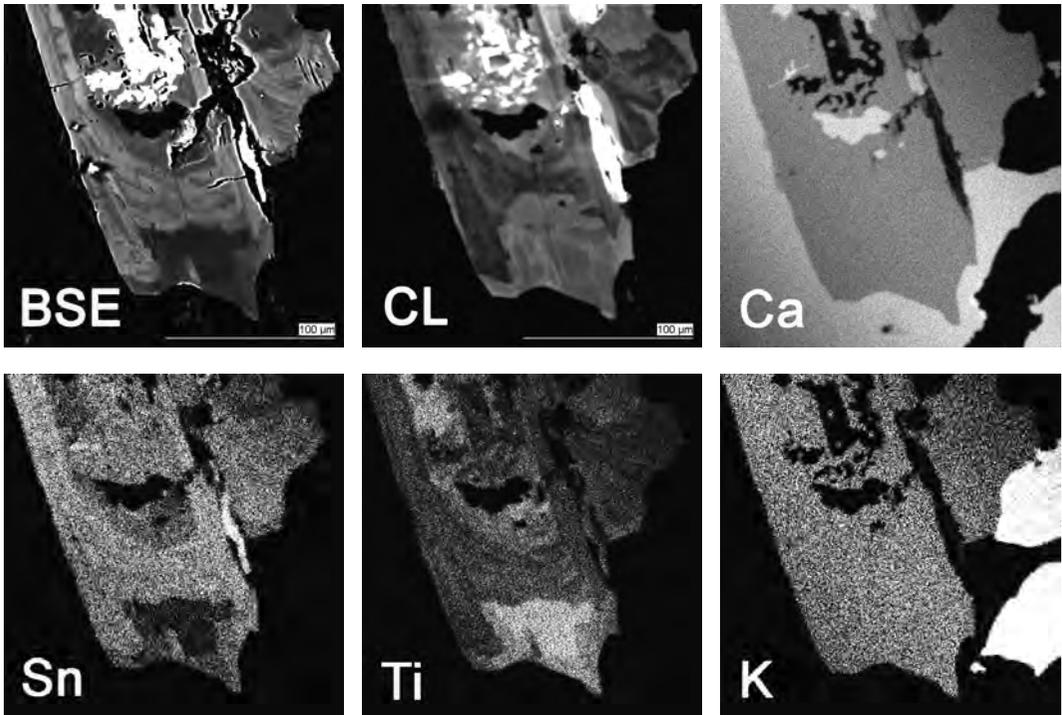


Fig. 3. Twinned zoned-sectorial crystal with grey areas (under BSE) corresponded to aleksandrovite and dark-grey – to baratovite. The crystal is in an aggregate with calcite, microcline and quartz. White grains – the minerals of bazirite-pabstite series. CL – cathodoluminescent image, Ca – characteristic X-ray images in $\text{CaK}\alpha$, Sn – $\text{SnL}\alpha$, Ti – $\text{TiK}\alpha$, K – $\text{KK}\alpha$. Images are obtained using Camebax-microbeam microanalyser.

trations are less inconstant according to microprobe analyses and to scanning of the mineral grains along profiles (Fig. 4). The lithium content calculated according to Li/K and Li/Ca ratios, appeared to be quite similar (divergence in Li content after normalization to K and Ca is 0.03%).

The water content was not determined due to the small amount of the new mineral available for this.

The empirical formula of aleksandrovite (calculated for 38 anions): $(\text{K}_{0.93}\text{Na}_{0.10})_{\Sigma 1.03}\text{Li}_{3.02}(\text{Ca}_{6.82}\text{Sr}_{0.06}\text{Mn}_{0.04}\text{Mg}_{0.02})_{\Sigma 6.94}(\text{Sn}_{1.28}\text{Ti}_{0.54}\text{Zr}_{0.15}\text{Fe}_{0.05}\text{Nb}_{0.01})_{\Sigma 2.03}(\text{Si}_{11.98}\text{Al}_{0.02})_{\Sigma 12.00}\text{O}_{36}[\text{F}_{1.35}(\text{OH})_{0.65}]_{\Sigma 2.00}$.

Idealised formula of aleksandrovite is $\text{KLi}_3\text{Ca}_7\text{Sn}_2\text{Si}_{12}\text{O}_{36}\text{F}_2$.

During the study of the zoned crystals of the mineral the wide variations of octahedral cations (Ti, Sn, Zr etc.) and additional anions (F, OH) were revealed. The typical images of the zoned crystals are shown on the Figure 2 (b – d, f) and Figure 3, the results of microprobe analyses – in the Table 2. Figure 5 shows the triangular diagram Ti-Sn-Zr (at.%), with the analyses obtained and represented in

this paper, and also analyses of the minerals similar to baratovite from quartz-albite-pyroxene-microcline-calcite rocks of Darai-Pioz, both from our and literature data. It is evident that by the octahedral site predominant occupation one can distinguish the following minerals: baratovite and katayamalite – prevalence of titanium, aleksandrovite – tin, and an unnamed zirconium analogue. As was mentioned above, we suggest to combine all these minerals into the baratovite group.

X-ray data

The X-ray data for aleksandrovite were obtained using diffractometer DRON-2, the results calculated are presented in the Table 4. Due to the rather limited quantity of material available for investigation, the sample was prepared by putting the mineral powder onto the oriented monocrystal plate of "non-diffractive" silicon in order to obtain a satisfactory X-Ray powder-diffraction pattern. Using the Debye-Scherrer method quite a strong veil due to intensive X-Ray luminescence was ob-

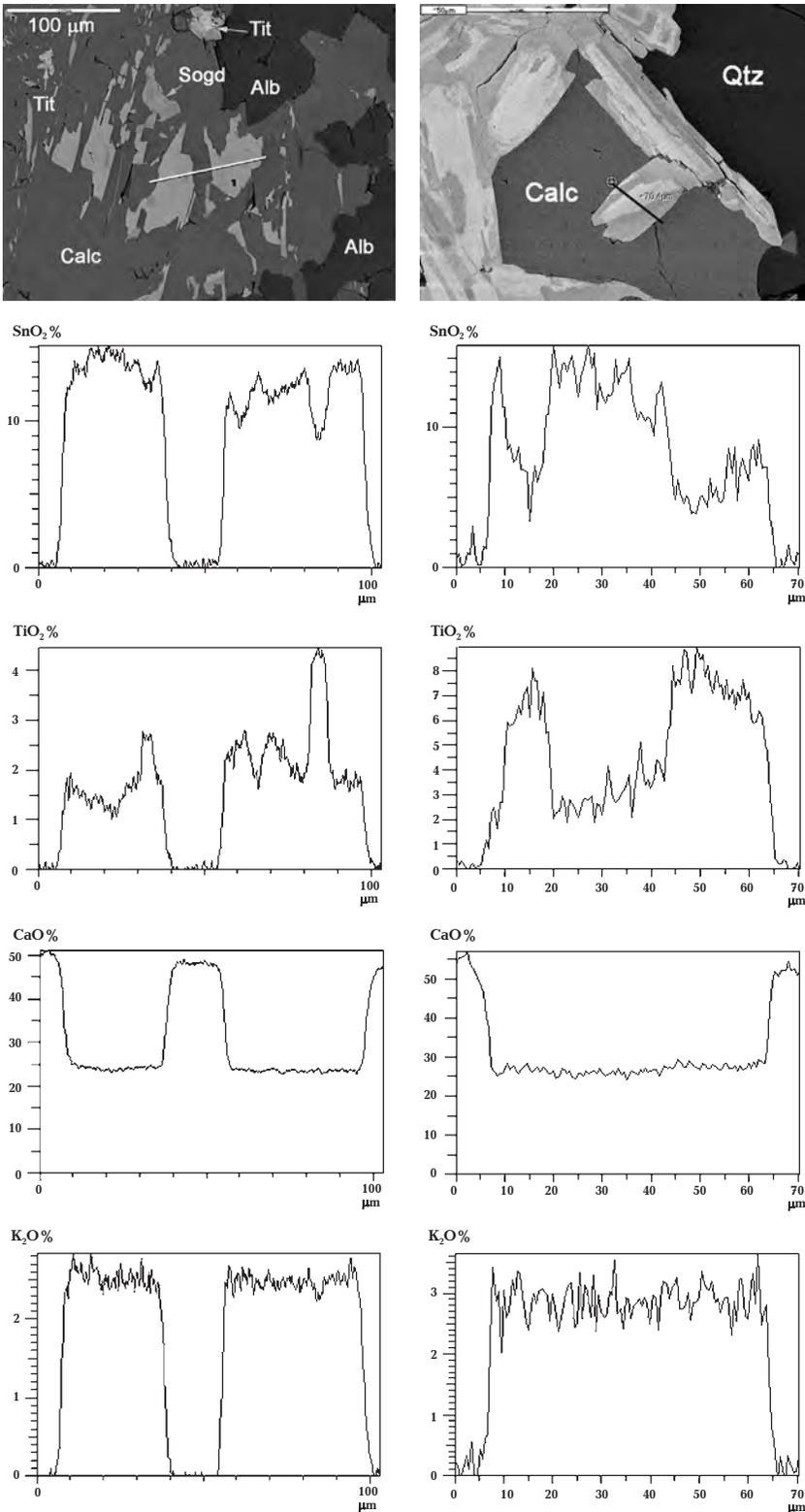


Fig. 4. Elements distribution along the scanning profiles in characteristic X-ray radiation, in alexandrovite grain and in the zoned grain, where paler areas under BSE correspond to alexandrovite and the darker – to barotvite. Vertical scales show wt. %. Images and profiles are obtained using CamScan 4D with energy dispersive spectrometer Link ISIS.

Table 3. Chemical composition of the minerals of baratovite group shown on Fig. 2a, 2b, EMPA data (wt.%)

Comp.	1	2	3	4	5	6	7	8
SiO_2	48.35	48.08	48.24	48.56	49.63	48.86	48.46	48.66
Al_2O_3	0.01	0.20	0.19	0.19	0.07	0.13	0.16	0.11
TiO_2	3.43	2.93	2.90	2.26	6.01	3.97	3.52	4.23
Fe_2O_3	0.21	0.31	0.26	0.41	0.29	0.27	0.31	0.31
CaO	26.39	26.26	26.34	26.14	26.67	26.43	26.70	26.75
MnO	0.16	0.23	0.16	0.20	0.15	0.11	0.14	0.15
SnO_2	11.49	12.43	12.99	11.38	2.04	9.06	11.74	7.53
ZrO_2	1.10	1.01	0.71	3.06	6.08	2.66	0.84	3.95
Nb_2O_5	0.15	0.12	0.19	0.17	0.00	0.08	0.08	0.19
Na_2O	0.12	0.15	0.18	0.19	0.15	0.26	0.13	0.18
K_2O	2.87	2.95	2.96	2.91	3.03	2.89	3.00	2.92
Li_2O	3.06	3.00*	3.01*	3.04*	3.10*	3.05*	3.02*	3.03*
F	2.27	2.00	1.15	2.00	1.02	1.07	2.65	1.46
H_2O^{**}	0.13	0.26	0.66	0.26	0.76	0.71	0.00	0.53
	99.75	99.94	99.97	100.78	99.01	99.56	100.76	100.02
-O = F	0.95	0.84	0.48	0.84	0.43	0.45	1.11	0.61
Total	98.80	99.10	99.49	99.94	98.58	99.11	99.65	99.41
Apfu (Si + Al = 12)								
K	0.91	0.93	0.94	0.91	0.93	0.90	0.95	0.92
Na	0.06	0.07	0.09	0.09	0.07	0.13	0.06	0.09
A	0.97	1.00	1.03	1.00	1.00	1.03	1.01	1.01
Ca	7.02	6.99	6.99	6.89	6.90	6.93	7.06	7.05
Mn	0.03	0.05	0.03	0.04	0.03	0.02	0.03	0.03
M1	7.05	7.04	7.02	6.93	6.93	6.95	7.09	7.08
Sn	1.14	1.23	1.28	1.12	0.20	0.88	1.15	0.74
Ti	0.64	0.55	0.54	0.42	1.09	0.73	0.65	0.78
Zr	0.13	0.12	0.09	0.37	0.72	0.32	0.10	0.47
Nb	0.02	0.01	0.02	0.02	0.00	0.01	0.01	0.02
Fe	0.04	0.06	0.05	0.08	0.05	0.05	0.06	0.06
M2	1.97	1.97	1.98	2.01	2.06	1.99	1.97	2.07
Li	3.05	3.00						
Si	12.00	11.94	11.94	11.94	11.98	11.96	11.95	11.97
Al	0.00	0.06	0.06	0.06	0.02	0.04	0.05	0.03
T	12							
F	1.78	1.57	0.90	1.56	0.77	0.83	2.06	1.14
OH	0.22	0.43	1.10	0.44	1.23	1.17	0.00	0.86

Note: an. 1, 2, 4, 7 – aleksandrovite, 3, 6 – possibly hydroxyl-analogue of aleksandrovite, 8 – baratovite, 5 – katayamalite, analyses obtained using Camebax-microbeam, 15 kV, 30 nA (WDS). Li_2O^* – calculated content. Analyst L.A. Pautov.

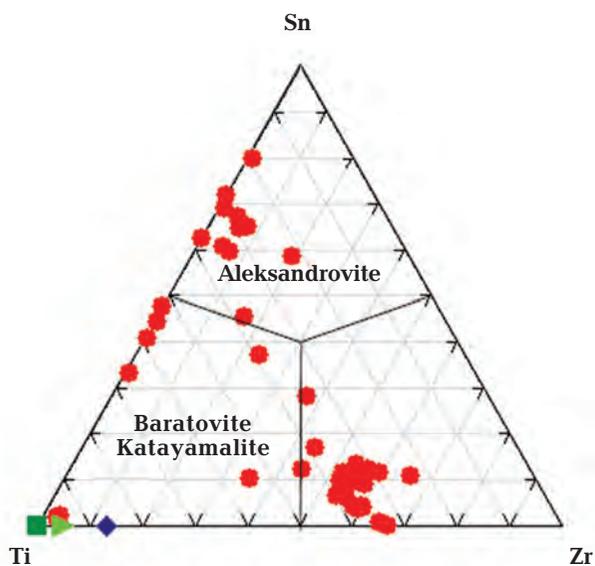


Fig. 5. Variations of octahedral cations content (atomic numbers) in the minerals of baratovite group. Blue rhombus – baratovite (Dusmatov et al., 1975), pale-green triangle – baratovite (Requir et al., 1999), dark-green square – katayamalite (Murakami et al., 1983), red rounds – minerals of baratovite group (the author's data).

Table 4. Calculation of the powder X-ray data of aleksandrovite

$d_{exp.}$	$I_{exp.}$	$d_{calc.}$	hkl	$d_{exp.}$	$I_{exp.}$	$d_{calc.}$	hkl
9.74	8	9.704	0 0 2	2.395	3	2.403	5 1 3
7.78	4	7.858	2 0 0	2.347	4	2.374	3 3 3
		7.715	2 0 -2	2.313	3	2.316	6 0 2
7.16	5	7.121	1 1 1	2.190	6	2.190	3 3 -7
5.76	6	5.755	1 1 2			2.188	7 1 0
4.86	21	4.874	3 1 -1	2.090	5	2.092	6 2 2
		4.852	0 0 4			2.089	7 1 1
		4.848	3 1 -2	2.066	3	2.065	8 0 -6
4.62	9	4.615	3 1 0			2.064	0 4 5
		4.611	1 1 -4	2.049	4	2.048	5 3 -7
4.25	15	4.250	4 0 -2	2.015	6	2.015	1 3 7
4.19	4	4.184	3 1 1	1.991	7	1.991	1 1 9
4.11	16	4.122	2 2 -2	1.973	4	1.974	6 2 3
		4.104	3 1 -4			1.972	0 2 9
3.90	13	3.895	2 2 1	1.950	25	1.952	4 2 6
3.864	9	3.862	1 1 4			1.948	8 2 -4
3.712	33	3.712	3 1 2	1.940	18	1.940	5 3 -8
3.635	6	3.633	3 1 -5	1.912	4	1.912	2 2 -10
3.567	8	3.565	2 0 4	1.895	4	1.896	7 3 -1
3.534	3	3.520	2 2 -4			1.895	3 3 -9
3.495	5	3.498	2 0 -6	1.847	16	1.847	7 3 0
3.444	14	3.439	0 2 4			1.847	4 4 -7
3.267	10	3.271	1 1 5	1.814	4	1.814	9 1 -2
3.234	100	3.235	0 0 6	1.802	4	1.803	0 2 10
3.206	34	3.208	2 2 3	1.785	4	1.785	3 3 7
		3.206	5 1 -2			1.785	6 4 0
		3.204	4 2 -2	1.772	5	1.772	2 2 9
3.102	12	3.103	1 3 1			1.772	9 1 -1
3.061	10	3.059	4 2 0	1.744	5	1.746	9 1 -8
3.039	28	3.037	0 2 5			1.746	3 5 -5
2.988	3	2.992	5 1 0			1.743	6 2 5
2.963	14	2.958	1 3 2	1.719	9	1.720	0 4 8
2.944	14	2.942	5 1 -5			1.719	2 0 -12
2.894	42	2.893	3 1 4			1.719	9 1 0
		2.893	4 2 1			1.718	7 3 2
2.826	6	2.827	1 1 6			1.718	6 4 -7
2.777	9	2.772	1 3 3	1.705	5	1.705	6 2 -11
2.752	9	2.750	5 1 -6			1.705	5 1 -12
		2.748	3 3 -3	1.695	5	1.696	1 5 -6
2.698	11	2.697	4 2 2			1.696	6 0 -12
2.664	3	2.661	3 3 1	1.671	2	1.671	4 4 -9
2.601	3	2.605	4 0 4	1.645	6	1.645	7 3 3
		2.605	5 1 2	1.634	3	1.634	10 0 -8
2.570	6	2.572	1 3 4			1.633	9 3 -4
		2.572	6 0 -6	1.616	8	1.616	9 3 -6
2.547	3	2.547	5 1 -7			1.616	6 4 3
		2.544	4 0 -8			1.615	7 3 -10
2.525	4	2.526	3 3 2			1.615	0 4 9
		2.526	3 1 -8	1.602	5	1.602	8 4 -4
2.450	5	2.450	6 2 -3			1.602	6 2 -12
2.425	42	2.426	0 0 8				
		2.424	6 2 -4				

Note: obtained using diffractometer DRON-2, $FeK\alpha$ – radiation, $0.5^\circ/\text{min}$. Internal standard – quartz. Analyst – L.A. Pautov.

served. To prevent this we used a strip of black paper as a shield X-Ray film. Aleksandrovite by the set of reflections and their intensities on the powder X-ray diffraction data is similar to baratovite. Mineral is monoclinic, space group $C2/c$ (on the analogy of baratovite), the cell parameters are $a = 17.01(2)$, $b = 9.751(6)$, $c = 21.00(2)$ Å, $\beta = 112.45(8)^\circ$, $V = 3219(7)$ Å³, $Z = 4$.

Physical properties

Aleksandrovite – is a colourless and transparent mineral with vitreous lustre and pearl lustre on the cleaved surface. Streak is white. Cleavage is perfect along (001), fracture is even. A density was found using the flotation method in thallium malonate formate (Clerici solution) is 3.05(2) g/cm³. Calculated density is 3.07(2) g/cm³. Microhardness of the mineral (an average value out of 15 measurements using PMT-3, loaded with a 50 g weight) VHN = 300 kg/mm² (value dispersion is 276–319). Mohs hardness is estimated to be 4–4.5. It fluoresces light-blue under short-wave UV light (254 nm).

Aleksandrovite is optically biaxial negative. The indices of refraction measured at 589 nm on the spindle needle in immersion liquids are: $n_p = 1.629(2)$, $n_m = 1.635(4)$, $n_g = 1.638(2)$; $2V$ (calculated) = -70.3° . Dispersion of optical axis is strong, $r > v$. In thin sections (0.03 mm thick) aleksandrovite differs from baratovite by the higher interference colour (aleksandrovite has white and baratovite has up to grey colour the highest), notable lower refractive indices and optical sign. In the zoned crystals between baratovite and aleksandrovite zones the Becke bright line is easily visible. The anomalous interference colours are observed in the close-to-extinction positions. Elongation is positive. The angle of extinction on the sections with distinct cleavage fractures (parallel to the elongation of the grains) varies from nearly straight extinction to 22° .

Unfortunately, the small size of homogeneous aleksandrovite crystals, its relatively low birefringence and anomalous extinction of many grains made the Fedorov universal stage method of optical orientation investigation inapplicable.

IR spectrum of aleksandrovite was detected in microtablet with KBr using spectrometer Specord 75IR. Aleksandrovite IR-spectrum is similar to that of baratovite (Fig. 6), the major

absorption strips are: 1083, 1024, 974, 950, 673, 607, 568, 520, 470, 440 cm^{-1} .

Compatibility index according to Gladstone-Dale relation is $1 - (K_p/K_c) = -0.005$ (superior) for D_{calc} (density calculated) = 3.07 and -0.005 for D_{meas} (density measured) = 3.05 g/cm^3 .

The comparative characteristics of aleksandrovite and baratovite are given in the Table 5.

The type specimen with aleksandrovite is stored in the Fersman Mineralogical Museum RAS in Moscow (registration number 3825/1).

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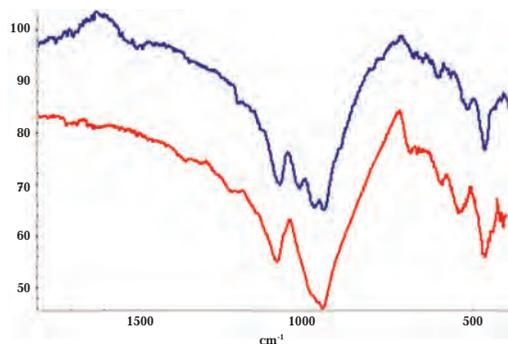


Fig. 6. IR-spectra of aleksandrovite (the upper spectrum) and baratovite, (Darai-Pioz massif) № 80873 from the Fersman Mineralogical Museum RAS collection (the lower spectrum).

Table 5. Comparative characteristics of aleksandrovite and baratovite

	Aleksandrovite	Baratovite*
Formula	$\text{KLi}_3\text{Ca}_7\text{Sn}_2\text{Si}_{12}\text{O}_{36}\text{F}_2$	$\text{KLi}_3\text{Ca}_7(\text{Ti,Zr})_2\text{Si}_{12}\text{O}_{36}\text{F}_2$
Singony	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a , Å	17.01	16.94
b , Å	9.751	9.746
c , Å	21.00	20.907
β	112.45	112.50
Z	4	4
Intensive	4.86	4.8288
lines of	3.712	3.6966
powder	3.234	3.2192
X-ray	3.206	3.1913
data, d/n	3.039	3.0510
	2.894	2.8839
	2.425	2.4144
	1.950	1.9437
Density (calculated), g/cm^3	3.05(2)	2.92
Optical	(–)	(+)
sign		
n_p	1.629	1.672
n_m	1.635	1.672
n_g	1.638	1.673

Note: * – X-ray data are from JCPDS 33-0811

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