ORLOVITE, $KLi_2TiSi_4O_{10}(OF)$, A NEW MINERAL OF THE MICA GROUP[1]

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Orlovite is a new mineral of the mica group, the titanium analogue of polylithionite. It was discovered in highly quartz rocks in association with pectolite, baratovite, faizievite, aegirine, polylithionite, leucosphenite, fluorite and other minerals in a moraine of the Darai-Pioz glacier (Tajikistan). The mineral is colourless with a glassy to pearly luster. It occurs in flaky aggregates up to 2 cm in size. Cleavage is perfect along (001). Mohs hardness is 2−3. Density (measured) D_m = 2.91(2) g/cm^3, density (calculated) D_c = 2.914 g/cm^3. The mineral is optically negative, biaxial, n_p = 1.600, n_m = 1.620, n_g = 1.625, all ± 0.002, $2V_m$ = -52(2)°, $2V_c$ = -52.6°. Orlovite is monoclinic, *C*2, a = 5.199(3)Å; b = 9.068(7)Å; c = 10.070(4)Å; α = 90°, β = 99.35 (2)°, γ = 90°, V = 468.4(4)Å^3, Z = 2. The strongest X-ray lines [(*d*, Å), (*I*, %), (*hkl*)]: 9.96 (40) (001), 4.48 (67) (002), 3.87 (40) (111), 3.33 (100) (-121), 2.860 (35) (-113), 2.600 (28) (130), 2.570 (30) (-131), 2.400 (31) (014), 1.507 (20) (-206). IR − spectra (the strongest absorption bands) are as follows: 3600, 1130, 1087, 985, 961, 878, 776, 721, 669, 613, 567, 530, 512, 458, 405 cm^{-1}. Chemical composition (microprobe, Li_2O, Rb_2O − ICP OES, H_2O − SIMS, wt.%): SiO_2 − 58.31, TiO_2 − 18.05, Nb_2O_5 − 0.50, Al_2O_3 − 0.22, FeO − 0.40, MnO − 0.03, K_2O − 11.13, Cs_2O − 0.24, Li_2O − 7.25, Rb_2O − 0.69, H_2O − 0.21, F − 4.35, -O=F_2 − -1.83, total − 99.55.
The empirical formula of orlovite is $(K_{0.97}Rb_{0.03}Cs_{0.01})_{1.01}Li_{2.00}(Ti_{0.93}Nb_{0.02}Fe_{0.02}Al_{0.02})_{0.99}Si_4O_{11.04}(F_{0.94}OH_{0.10})_{1.04}$. Simplified formula $KLi_2TiSi_4O_{10}(OF)$. The mineral is named to honor the well-known Russian mineralogist, doctor of mineralogy Yury Leonidivich Orlov (1926−1980), Director (1976−1980) of the A.E. Fersman Mineralogical museum, RAS, specialist in the mineralogy of diamonds and gem stones, and author of more than 50 works including the classical monographs "Mineralogy of Diamond" and "Morphology of Diamond".
4 tables, 3 figures, 25 references.
Keywords: orlovite, titanian mica, new mineral, Darai-Pioz, Tajikistan, alkaline rocks.

Site of occurrence and association

Orlovite was discovered in samples of the Upper Darai-Pioz alkaline massif, collected on a moraine of the Darai-Pioz glacier (Garmsky region, Central Tadjikistan). The first data on the geological structure of the region, and the petrography and mineralogy of the massif were obtained by Moskvin (1937). The most comprehensive works on the Darai-Pioz massif, including a geological map on the scale 1:25000, and details of the mineralogy, geochemistry and geochronology is that of Vyacheslav D. Dusmatov (1968; 1969; 1970; 1971). The Darai-Pioz alkaline massif is remote, and its central part is cut by a glacier, that moves from north to south. Due to this fact, bedrock outcrops are inaccessible. Moreover, the massif itself is exposed as steep cliffs of the glacial valley. For this reason, the major work on the mineralogy and petrography of the massif has been done on blocks of rocks in the moraine of the Darai-Pioz glacier.

One of the characteristic features of the Darai-Piez alkaline massif is the wide variety of minerals of micas present: muscovite, annite, taeniolite, polylithionite (Ganzeev *et al.*, 1976; Vladykin *et al.*, 1995; Vladykin, Dusmatov, 1996), sokolovaite (Pautov *et al.*, 2006) and orlovite. In addition, in the Darai-Pioz alkaline pegmatites, the authors have discovered three more tetrasilica lithium-caesium micas − potentially new minerals that are now under study. These minerals are as follows: caesium analogue of orlovite: $CsLi_2TiSi_4O_{10}(OF)$, caesium analogue of taeniolite: $CsLiMg_2Si_4O_{10}F_2$ and the Fe^{+2} analogue of sokolovaite: $CsLiFe_2Si_4O_{10}F_2$. Orlovite is a titanium analogue of polylithionite, and it is the first completely titanian mica from the mica group. High-titanium micas (3−14 wt.% TiO_2) belonging to the phlogopite-annite series from alkaline

[1] − The mineral was considered and recommended for publication by the Commission on New minerals and mineral names of the Russian mineralogical society and approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA on 2th of April 2009.

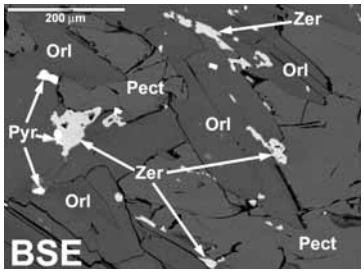
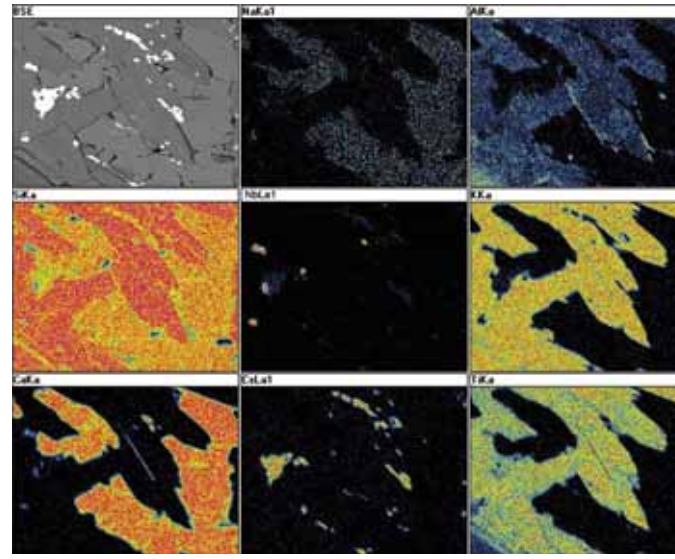


Fig. 1. Intergrowth of orlovite (Orl) with zeravshanite (Zer), pyrochlore (Pyr) and pectolite (Pect.) Image in the BSE mode and in the characteristic X-rays of the elements indicated. Scale bar is 200 µm.



basalts and some types of metamorphic rocks have been described by numerous researchers (Rosenbusch, 1910; Freudenberg, 1920; Prider, 1939; Ushakova, 1971; Mansker *et al.*, 1979; Dymek, 1983; Ryabchikov *et al.*, 1981: Koval` *et al.*, 1988; Cruciani and Zanazzi, 1994; Shaw, Penczak, 1996; Greenwood, 1998; Ibhi *et al.*, 2005; Chukanov *et al.*, 2008; 2010). Unlike orlovite, all of them are titanium-bearing micas, but not completely titanian.

Orlovite occurs in a rock consisting mainly of quartz (up to 80%) with several rare accessory minerals. We have discovered more than 30 boulders, fragments of this rock, from 0.2 up to 2 m in diameter, with different degrees of roundness. All examples of this rock have been found in the moraine sediments of the glacier; it is not found in the bedrock. Unfortunately, this rock had no contacts with any other rock-type in the boulders. This rock is composed of middle to coarse-grained aggregates of quartz of icy appearance. Appearance of these Si-rich rocks is very characteristic because of the presence of idiomorphic black crystals of aegirine with brilliant facets, large violet-pink plates sogdianite, red-brown translucent lenticular crystals of stillwellite-(Ce), poorly-bounded crystals of pale yellow-pink reedmergnerite, green elongated prismatic crystals of turkestanite and large crystals of polylithionite. In addition, galenite, calcite, neptunite, sugilite, pyrochlore, minerals of the eudialyte group, tadjikite, baratovite, native bismuth, sphalerite, fluorite, fluorapatite, fluoapophyllite, sokolovaite, kapitsaite-(Y), pekovite, zeravshanite, and faizievite occurs in this rock. A characteristic feature of this essentially quartz rock is the presence of brown polymineral aggregates (up to 25 cm in size) consists of pectolite, quartz, fluorite, aegirine, polylithionite and other minerals. Segregations of orlovite occur mainly in intergrowth with pectolite, quartz, baratovite, neptunite, leucosphenite, zeravshanite, faizievite and pyrochlore (Fig. 1). Orlovite forms lamellar, colorless grains up to 2 mm in size.

Physical properties

Orlovite is colorless, in aggregates it appears white. In hand specimens it can not be distinguished from polylithionite. In the short-wave ultra-violet light, it luminesces with a bright yellow light, in long-wave ultra-violet light it does not luminesce. Streak is white. It is characterized by glassy up to pearly luster. Cleavage is perfect on (001). In thin sheets the mineral is flexible. Mohs hardness is estimated to be 2−3. Hardness of microindentation equals to 94 kg/mm^2 (an average value out of 15 measurements ranged from 87 up to 106 kg/mm^2). Microhardness is measured using a PMT-3 device loaded with a 10 g weight, graduated on NaCl. The density was determined using the flotation method in Clerici solution. The measured density of the mineral is 2.91 (2) g/cm^3. Calculated density is 2.014 g/cm^3. Orlovite is optically negative, biaxial, $2V_{meas}$ = -52.5(2)°, $2V_{calc}$ = -52.6°. The indices of refraction measured at 589 nm by the immersion method are: n_p = 1.600(2), n_m = 1.620(2), n_g = 1.625(2), all ± 0.002. Dispersion is weak, $r < v$. The IR-spectrum of orlovite was obtained with an Avatar IR-FT spectrometer (Thermo Nicolet); the major absorption bands are: 3600,

1130, 1087, 985, 961, 878, 776, 721, 669, 613, 567, 530, 512, 458, 405 cm^{-1}. The IR-spectrum is close to that of polylithionite (Fig. 2).

Chemical composition

Orlovite was analysed with an JEOL JCXA-50A electronic microprobe analyzer and with using of ICP-OES and SIMS methods (Tab. 1). JCXA-50A was operated at 20 κV and 2 nA for energy-dispersive work (EDS) and at 15 κV and 25 nA for wave length spectrometers (WDS). Si, Ti, Nb, Al, Fe, Mn, Cs, and K were analyzed by EDS and F was measured by WDS. Standards were as follows: microcline USNM143966 (Si, Al, K), ilmenite USNM 96189 (Ti, Fe), synthetic $LiNbO_3$ (Nb), metal manganese (Mn), synthetic $CsTbP_4O_{12}$ (Cs), MgF_2 (F). Grains of the new mineral are homogenous and free of ingrowths of other minerals. The data were processed using a ZAF-correction program. Concentrations of Li and Rb in the mineral were obtained by ICP-OES. The mineral was digested in concentrated $HF + HNO_3$ and evaporated to damp salts. Further HNO_3 was added and the solution was evaporated to the dry residue for complete removal of all fluorides. The resulting residue was diluted in 2% HNO_3 and the solution was analyzed using an ICP-OES Vista Pro instrument (Varian). The H_2O content of orlovite was determined using SIMS (secondary-ionic mass-spectrometry). The analysis was done on a Cameca IMS-4F in the Institute of Microelectronics and Computer Science of the Russian Academy of Sciences; the method is that of Smirnov *et al* (1995). The beam of primary ions O^{2-} was used and absolute concentrations of each element were calculated from the ions intensities relative to Si ($E/ {}^{30}Si^+$ ratio), using calibrating constants. The mineral was normalized to Si = 4, giving the empirical formula $(K_{0.97}Rb_{0.03}Cs_{0.01})_{1.01}Li_{2.00}(Ti_{0.93}Nb_{0.02}Fe_{0.02}Al_{0.02})_{0.99}Si_4O_{11.04}(F_{0.94}OH_{0.10})_{1.04}$. The simplified formula of orlovite is $KLi_2TiSi_4O_{11}F$. The compatibility index $(1\text{-}K_p/K_c) = 0.121$, corresponding to the poor category. It is probable that the refraction indices are strongly influenced

Table 1. **Chemical composition of orlovite (wt.%)**

Components	1	2	3	4	5	6	7	8	9	10	Average
Al_2O_3	0.09	0.28	0.18	0.44	0.08	0.30	0.15	0.46	0.07	0.13	0.22
SiO_2	57.98	58.40	59.34	57.56	57.66	58.88	58.32	57.95	58.56	58.42	58.31
K_2O	10.87	11.24	10.99	11.45	11.35	11.01	10.97	10.99	11.13	11.26	11.13
TiO_2	18.03	17.70	18.01	17.56	18.54	18.15	18.11	17.78	18.27	18.09	18.05
Nb_2O_5	0.30	0.38	0.58	0.69	0.41	0.61	0.55	0.35	0.53	0.63	0.50
FeO	0.28	0.34	0.48	0.25	0.55	0.46	0.39	0.50	0.26	0.44	0.40
MnO	0.04	0.00	0.06	0.03	0.01	0.04	0.07	0.01	0.05	0.03	0.03
Cs_2O	0.22	0.34	0.39	0.11	0.19	0.09	0.29	0.40	0.31	0.02	0.24
Rb_2O^*	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69
Li_2O^*	7.25	7.25	7.25	7.25	7.25	7.25	7.25	7.25	7.25	7.25	7.25
F	4.35	4.35	4.35	4.35	4.35	4.35	4.35	4.35	4.35	4.35	4.35
H_2O	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Total	100.58	101.18	102.53	100.59	101.29	102.04	101.35	100.94	101.68	101.52	101.38
-O=F	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83
Total	98.75	99.35	100.70	98.76	99.46	100.21	99.52	99.11	99.85	99.69	99.55
Calculation at Si = 4 *apfu*											
Al	0.01	0.02	0.01	0.04	0.01	0.02	0.01	0.04	0.01	0.01	0.02
Si	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
K	0.96	0.98	0.95	1.02	1.00	0.95	0.96	0.97	0.97	0.98	0.97
Ti	0.95	0.91	0.91	0.92	0.97	0.93	0.93	0.92	0.94	0.93	0.93
Nb	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02
Fe^{+2}	0.02	0.02	0.03	0.01	0.03	0.03	0.02	0.03	0.01	0.03	0.02
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.01
Rb	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Li	2.01	2.00	1.97	2.03	2.02	1.98	2.00	2.01	1.99	2.00	2.00
F	0.95	0.94	0.93	0.96	0.95	0.93	0.94	0.95	0.94	0.94	0.94
H	0.10	0.10	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10

Note. * — *the data are received by the ICP-OES method. Analysts A.A. Agakhanov and L.A. Pautov. .*

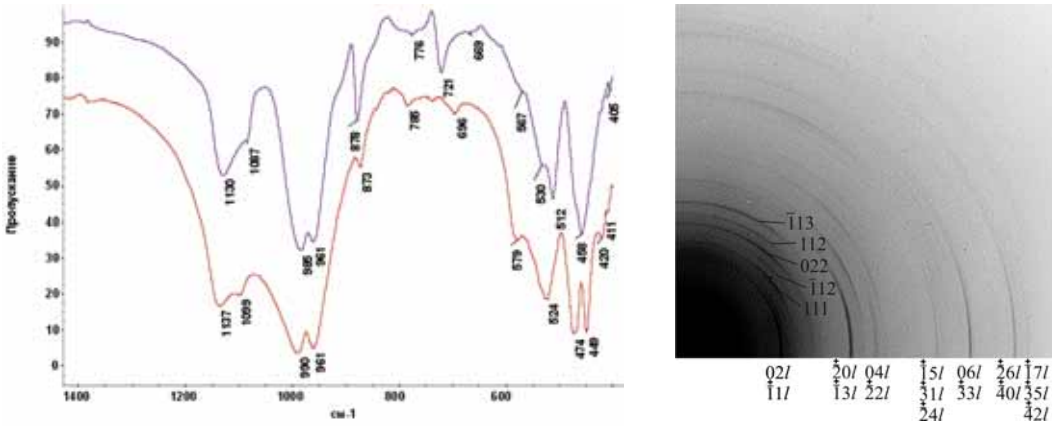


Fig. 2. IR-spectra of orlovite (upper) and polylithionite (bottom) from Darai-Pioz. Preparation – tablets of mineral with KBr. FT-IR spectrometer Avatar (Thermo Nicolet). Analyst A.A. Agakhanov.
Fig. 3. Oblique texture electron diffraction pattern of orlovite (substrate tilted 60° from normal).

by the degree of distortion of Ti-O polyhedra in different minerals. For example, such problems are also encountered in calculating the compatibility index for layered titanosilicates from the lamprophyllite group for which $(1-K_p/K_c)$ also classifies as poor.

X–ray and electron diffraction data

It was not possible to study the new mineral by single-crystal X-ray diffraction as all crystals are strongly deformed. The X-ray powder diffraction pattern of orlovite (Tab. 2) were measured using DRON-2 diffractometer with Cu*K*α-radiation. To eliminate the effect of possible preferred orientation, a Debye powder pattern was obtained on a RKU-114M camera using Fe*K*α-radiation. We used quartz as an internal standard. The cell dimensions were refined from the powder diffraction pattern with a monoclinic cell (space group *C*2), $a = 5.199(3)$; $b = 9.068(7)$; $c = 10.070(4)$Å, $\beta = 99.35(4)°$, $V = 468.4(4)$, $Z = 2$. The unit cell parameters of orlovite and polylithionite are close.

Electron diffraction studies of orlovite were performed with EMR-100M electronograph

operated at 100 kV. Oblique texture electron diffraction patterns (substrate tilted 60–63° from normal) (Fig. 3) revealed high degree of crystal structure crystallinity, monoclinic symmetry, polytype modification 1M(3T), space group *C*2 and unit cell parameters: $a = 5.21(1)$; $b = 9.026(3)$; $c = 10.05(1)$ (Å); $\beta = 99.6(1)°$; $V = 466(2)$ Å^3. Comparison of orlovite with similar minerals is shown in Table 4.

The holotype specimen of orlovite is stored in the Fersman Mineralogical Museum, RAS, Moscow (registration number 3824/1).

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Table 2. **X-ray powder-diffraction data of orlovite**

Powder pattern		Diffraction pattern		Calculated	
I	d_{meas}, Å	*I*	d_{meas}, Å	d_{calc}	*hkl*
2	9.92	40	9.96	9.936	001
2	4.95	12	4.98	4.968	002
7	4.48	67	4.48	4.465	110
		8	4.32	4.307	-111
4	3.87	40	3.87	3.873	111
10	3.33	100	3.33	3.326	-121
2	3.12	12	3.12	3.114	112
				3.111	013
4	2.86	35	2.860	2.861	-113
1	2.67	2	2.669	2.674	023
3	2.60	28	2.600	2.604	130
3	2.57	30	2.570	2.572	-131
				2.565	200
2	2.50	16	2.489	2.484	004
				2.497	113
3	2.40	31	2.400	2.396	014
				2.391	201
				2.389	-132
2	2.136	16	2.137	2.135	-133
				2.142	202
1	2.070	4	2,083	2.084	212
				2.062	042
2	1.993	16	1.990	1.987	005
		3	1.732	1.733	-301
				1.728	134
				1.727	115
2	1.654	17	1.654	1.655	204
				1.656	006
				1.647	-135
1	1.557	8	1.557	1.557	242
				1.556	026
				1.555	224
2	1.507	20	1.507	1.507	-206
				1.503	-331
1	1.348	9	1.348	1.349	-236
				1.551	-136
				1.551	-325
2	1.300	15	1.300	1.301	117
				1.298	206

Note: Debye-Sherrer method — RKD-114, Fe-anode, Mn-filter, URS-50IM. Diffractometer DRON-2, Fe-anode, graphite monochromator, 1°/min. Internal standard — quartz. Analyst A.A.Agakhanov.

Table 3. **Electron diffraction data of orlovite**

№	*I*	d_{meas}, Å	*hkl*	d_{meas}, Å
		1 ellipse		
1	8	4.461*	110	4.465
2	2	4.302*	$\bar{1}11$	4.311
3	7	3.863*	111	3.866
4	4	3.593*	$\bar{1}12$	3.585
5	8	3.343*	022	3.336
6	5	3.096*	112	3.101
7	8	2.860*	$\bar{1}13$	2.861
8	2	2.663*	023	2.665
9	3	2.492*	113	2.489
10	1	2.304	$\bar{1}14$	2.313
		2 ellipse		
11	10	2.592	130	2.596
			$\bar{2}01$	2.594
12	9	2.569	200	2.569
			$\bar{1}31$	2.565
13	8	2.382	201	2.391
			$\bar{1}32$	2.384
14	6	2.140	202	2.139
			$\bar{1}33$	2.130
15	2	1.966	133	1.962
			$\bar{2}04$	1.953
16	1	1.732	134	1.721
			$\bar{2}05$	1.713
17	6	1.647	204	1.651
			$\bar{1}35$	1.644
18	4	1.513	135	1.515
			$\bar{2}06$	1.508
19	6	1.343	136	1.343
			$\bar{2}07$	1.338
20	3	1.295	206	1.294
			$\bar{1}37$	1.289
		3 ellipse		
21	6	2.256	040	2.257
22	5	2.237	220	2.232
23	5	2.140	$\bar{2}22$	2.156
24	1	2.049	042	2.054
		4 ellipse		
26	5	1.705	$\bar{3}11$	1.705
			150	1.703
			$\bar{2}41$	1.702
		5 ellipse		
26	8	1.504*	060	1.504
		6 ellipse		
27	7	1.286	$\bar{4}00$	1.284
			$\bar{2}62$	1.282
		7 ellipse		
28	1	1.251	170	1.251
			$\bar{4}21$	1.251
			$\bar{3}51$	1.252

Note: EMR-100M electronograph, oblique texture electron diffraction pattern of orlovite (substrate tilted 68° from normal), standard — TlCl. Analyst G.K. Bekenova

** — Reflections for calculation of unit cell parameters. Intensity of reflections is estimated visually. * — Reflections according to which parameters of unit cell are calculated. Intensity of reflections are estimated visually.*

Table 4. **Comparison data for orlovite, polylithionite and tainiolite**

Featuresof mineral	Orlovite	Polylithionite	Tainiolite
Source	This work	JCPDS 21-952; Anthony *et al.*, 1995	JCPDS 31-1045; Anthony *et al.*, 1995
Formula	$CsLi_2TiSi_4O_{10}(OF)$	$KLi_2AlSi_4O_{10}F_2$	$CsLiMg_2Si_4O_{10}F_2$
Space group	*C*2	*C*2/*m*	*C*2/*m*
a, Å	5.199	5.186	5.227
b, Å	9.068	8.968	9.057
c, Å	10.070	10.029	10.133
β, °	99.35	100.4	99.86
Z	2	2	2
Strong lines of X-ray	9.96 (40)	9.87 (20)	9.95 (85)
d_{meas}, Å (*I*)	4.48 (67)	4.93 (90)	4.98 (35)
	3.87 (40)	4.47 (50)	4.51 (25)
	3.33 (100)	3.59 (100)	3.611 (20)
	2.860 (35)	3.31 (100)	3.325 (100)
	2.600 (28)	3.29 (90)	3.106 (30)
	2.570 (30)	3.07 (100)	2.883 (25)
	2.400 (31)	2.867 (70)	2.602 (20)
	1.990 (16)	2.580 (70)	2.575 (25)
	1.507 (20)	1.974 (90)	2.396 (35)
		1.641 (40)	1.995 (30)
Density, g/cm^3 (meas/calc)	2.91/2.914	2.58–2.82/2.84	2.83–2.90/2.80
Optical properties (optical sign)	Biaxial (-)	Biaxial (-)	Biaxial (-)
n_p	1.600	1.53	1.522–1.540
n_m	1.620	1.551–1.556	1.553–1.570
n_g	1.625	1.555–1.559	1.553–1.570

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