

Tashelgite, $\text{CaMgFe}^{2+}\text{Al}_9\text{O}_{16}(\text{OH})$, a New Mineral Species from Calc-Skarnoid in Gorny Shoria¹

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Abstract—A new mineral species has been discovered at the calc-skarnoid occurrence near the mouth of the Tashelga River, Kuznetsky Alatau, Gorny Shoria, Russia, and named after the locality of its discovery. Associated minerals are calcite, hibonite, grossular, vesuvianite, hercynite, magnetite, corundum, perovskite, scapolite, diopside, and apatite. The new mineral occurs as prismatic or finely fibrous crystals up to 1.5–2.0 mm in length, their parallel intergrowths, and felty aggregates as large as 10 mm across. Tashelgite is bluish green, translucent to transparent, with vitreous luster; $D_{\text{calc}} = 3.67 \text{ g/cm}^3$. The IR spectrum does not contain bands of OH groups. Tashelgite is biaxial (–), with $\alpha = 1.736(2)$, $\beta = 1.746(2)$, $\gamma = 1.750(2)$; $2V_{\text{meas}} = -20(2)^\circ$. Dispersion is strong, $r < v$. Pleochroism is distinct: X (blue-green) $> Y$ (yellowish green) $> Z$ (almost colorless). Chemical composition (electron microprobe, average of five-point analyses, Fe_2O_3 is estimated from the ratio of intensities $I(\text{Fe}_{K\beta_5})/I(\text{Fe}_{K\beta_1})$ in the X-ray spectrum, H_2O was determined as a weight loss on heating in vacuum up to 1000°C), wt %: 7.98 CaO, 6.75 MgO, 0.45 MnO, 11.32 FeO, 1.40 Fe_2O_3 , 70.70 Al_2O_3 , 1.8(2) H_2O , 100.40 in total. The empirical formula calculated on the basis of 17 oxygen atoms is $\text{H}_{1.27}\text{Ca}_{0.90}\text{Mg}_{1.06}\text{Mn}_{0.04}\text{Fe}_{1.00}^{2+}\text{Fe}_{0.11}^{3+}\text{Al}_{8.80}\text{O}_{17.00}$. The idealized formula is $\text{CaMgFe}^{2+}\text{Al}_9\text{O}_{16}(\text{OH})$. According to single-crystal X-ray structural data, tashelgite is monoclinic, pseudoorthorhombic, space group Pc ; unit cell parameters are: $a = 5.6973(1)$, $b = 17.1823(4)$, $c = 23.5718(5) \text{ \AA}$; $\beta = 90.046(3)^\circ$; $V = 2307.5(1) \text{ \AA}^3$, $Z = 8$. The crystal structure of tashelgite is unique and characterized by ordering of all cations; Al occupies sites with octahedral and tetrahedral coordination. The cation ordering has also been confirmed by IR spectroscopy. The strongest lines of the X-ray powder diffraction pattern (d , $\text{\AA}$)]- $I[hkl]$ are: 11.79–48 [002], 2.845–43 [061], 2.616–100 [108], 2.584–81 [146], 2.437–44 [163], 2.406–61 [057], 2.202–72 [244]. The type specimen of tashelgite has been deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia.

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The mineral described below has been studied for more than half a century. Mokievsky (1953) mentioned it for the first time in the section “Chronicle” of *Zapiski of All-Union Mineralogical Society* journal, where a report by E.I. Nefedov at the Joint Scientific Session of the Fedorov Institute and the All-Union Mineralogical Society on the discovery of nine new minerals was reviewed. Among other things, the optical and physical parameters and associated minerals of a “new complex Al, Mg, Ca, and Fe oxide” called lodochnikovite were present. Later on, these preliminary data were republished in several articles (Nefedov,

1955; Kuz'min, 1961; *Mineraly ...*, 1967), however, the quantitative chemical composition, crystal structure, thermal and spectroscopic parameters had not been determined at that time. Because of poor characterization, lodochnikovite was not approved as a new mineral species.

This study presents the results of a detailed examination of this mineral as a prerequisite to its approval as an independent mineral species. A new mineral, *tashelgite*, was named after its type locality (the Tashelga occurrence in the Tashelga River valley).

The Tashelga occurrence is situated in Gorny Shoria, Kemerovo oblast, close to the mouth of the Tashelga River at the interfluvium of the Mras-Su and Tom rivers. The coordinates of the occurrence are $53^\circ22'60.3\text{N}$, $88^\circ17'07.1\text{E}$. In geological terms, the occurrence is localized in the Tomsk inlier, the north-

¹ The new mineral tashelgite and its name were approved by the Commission on New Minerals, Nomenclature, and Mineral Classification, International Mineralogical Association July 5, 2010 (IMA No. 2010-017).

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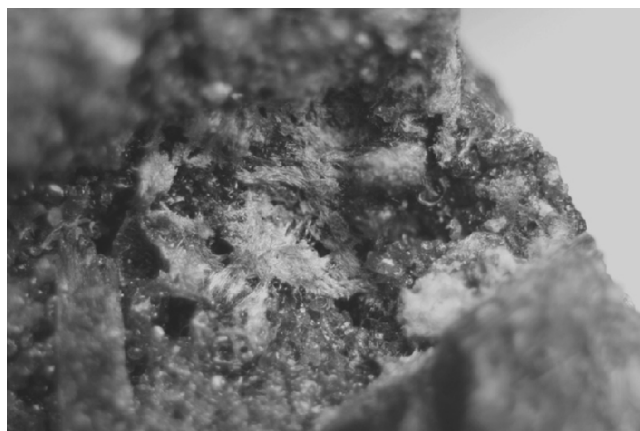


Fig. 1. Felty segregation of tashelgite associated with hibo-nite (gray lamellar crystal on the left), vesuvianite, and corundum (white) in skarnoid. Width of image is 3 cm.



Fig. 2. SEM image of long-prismatic crystals of tashelgite. Width of image is 40 μm .

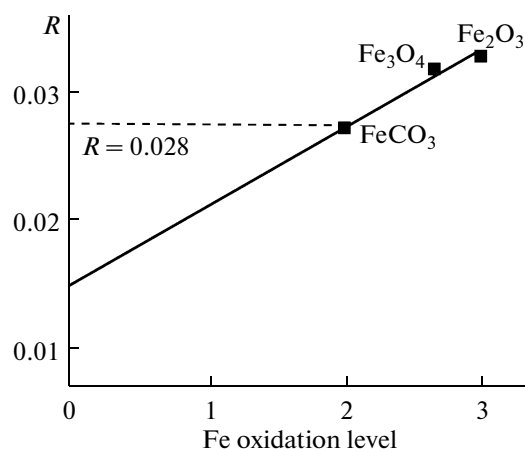


Fig. 3. $R = I(\text{Fe}_{K\beta_5})/I(\text{Fe}_{K\beta_1})$ versus oxidation level of iron. Horizontal line at $R = 0.028$ corresponds to tashelgite.

ern spurs of Kuzhetsk Alatau, where the Proterozoic–Paleozoic fold basement crops out.

The Tashelga occurrence comprises calc-skarnoid zones tens of centimeters in thickness striped by trenches. In addition to predominant calcite, skarnoid consists of an unusual assemblage that includes rare mineral hibo-nite, pinkish brown garnet close to grossular in composition, honey-colored vesuvianite, magnetite, black spinel (hercynite), corundum (leucosapphire), apatite, and perovskite. At the margins of the mineralized zones, diopside and scapolite appear (Ananyev and Konovalenko, 2008). The content of calcite in skarnoid exceeds 50%. Calcite is grayish white with a light blue tint. Other minerals are dispersed or make up nodular intergrowths up to 15 cm in size. Hibonite is predominant in products of acid leaching of skarnoid. It comes first as a euhedral mineral forming perfect tabular crystals up to 20–30 mm across. Tashelgite and vesuvianite rank below hibonite in the degree of idiomorphism. Other minerals are anhedral; their individuals are small, ranging from fractions of to a few millimeters. Vesuvianite, grossular, hercynite, and leucosapphire are “fused,” and corundum crystals resemble snowflakes in shape. Tashelgite crystals are characterized by rounded edges and apices. In the fraction insoluble in HCl, the hibonite and vesuvianite contents are 50 and 40%, respectively; about 3% fall on grossular, and 2%, on hercynite and leucosapphire; the concentration of the remainder measures at fractions of a percent.

The minerals of the Tashelga skarnoid were formed in the following sequence: hibonite, grossular, first-generation vesuvianite, magnetite, hercynite, and second-generation vesuvianite. Leucosapphire and tashelgite are the latest minerals. They not only overgrow, but partially ingrow into vesuvianite II and occur as isolated megacrysts with polysynthetic twins in massive calcite. Felty segregations of tashelgite frequently fill interstices in hibonite–vesuvianite–garnet–spinel clusters (Fig. 1). Microinclusions of late magnetite and one inclusion of perovskite were detected in tashelgite with electron microprobe. In addition to these minerals, rare apatite disseminations are observed in calcite. The time of their formation remains ambiguous.

Tashelgite occurs as long prismatic acicular (a is direction of elongation) slightly flattened crystals (major unit forms $\{001\}$ and $\{010\}$) and their parallel intergrowths up to $0.2 \times 0.3 \times 2$ mm in size (Fig. 2). The polysynthetic twins parallel to $\{001\}$ have rough linear striation. Frequently, tashelgite occurs as felty interwoven-fibrous to radial segregations (up to 10 mm across).

Individuals of the new mineral are blue-green translucent and less frequently transparent, with vitreous luster. Fibrous segregations of tashelgite are occasionally white. Cleavage and parting are absent. The mineral is brittle. The Mohs hardness is 7.5. The cal-

culated density is 3.67 g/cm^3 . Tashelgite does not dissolve in hydrochloric and sulfuric acids.

T.N. Ivanova from the Department of Mineralogy, Moscow State University, has determined crystallographic properties. The refractive indices and birefringence determined by focal screening are consistent with previous data reported by Nefedov (Mokievsky, 1953). The refractive indices are $\alpha = 1.736(2)$, $\beta = 1.746(2)$, $\gamma = 1.750(2)$, $2V_{\text{calc}} = -20(2)^\circ$. The $2V$ value cannot be calculated from the refractive indices, because β and γ are close to each other. Pleochroism is as follows: X (blue-green) $> Y$ (light yellowish green) $> Z$ (almost colorless). Dispersion is strong $r < v$. The orientation is $X = a$, $Y \approx b$, $Z = c$.

The chemical composition of tashelgite (Table 1) was determined on a scanning electron microscope equipped with EDS operating at an acceleration voltage of 15.7 kV and a current of 0.5 nA. The size of the measured surface is $16 \times 16 \mu\text{m}^2$. Five-point analyses were carried out. F, Cl, Na, Si, P, S, K, Ti, V, Cr, Ni, Zn, Sr, Nb, Ba, REE, and Pb contents are below the detection limit. The content of water was determined as the weight loss after ignition of the mineral in vacuum at 1000°C .

The integral intensity of line $\text{Fe}_{K\beta_5}$ in the X-ray spectrum was applied to determine Fe valence. This value depends on both the oxidation level of Fe and the total content of Fe in the mineral. The intensity of line $\text{Fe}_{K\beta_1}$ is determined only by total Fe. Therefore, the $R = I(\text{Fe}_{K\beta_5})/I(\text{Fe}_{K\beta_1})$ value can be used to estimate the Fe oxidation level. The X-ray spectrum of tashelgite in the region of lines $\text{Fe}_{K\beta_5}$ and $\text{Fe}_{K\beta_1}$ was recorded

Table 1. Chemical composition of tashelgite

Component	Content, wt %	Range, wt %	Standard
CaO	7.98	7.75–8.33	Wollastonite
MgO	6.75	6.51–7.09	Diopside
MnO	0.45	0.26–0.59	Mn
FeO	11.32		Fe_2O_3
Fe_2O_3	1.40	12.09–12.84	
Al_2O_3	70.70	70.10–71.61	Al_2O_3
H_2O	1.8(2)		
Total	100.40		

Note: Total Fe recalculated to FeO is 12.58 wt %; FeO and Fe_2O_3 are separated by applying the ratio of line intensity $I(\text{Fe}_{K\beta_5})/I(\text{Fe}_{K\beta_1})$ in the X-ray spectrum of Fe (Fig. 3). The content of Fe_2O_3 is recalculated from total FeO. Content of H_2O is determined on the basis of thermal analysis as weight loss after ignition in vacuum up to 1000°C .

with a Tescan Vega IIXMU SEM equipped with an INCA 700 WDS operating at an acceleration voltage of 20 kV, a current of absorbing electrons on the Faraday cup of 200 nA, and a crystal analyzer LiF. The following standards were used: siderite, magnetite, and hematite (the oxidation level of Fe is 2.0, 2.67, and 3.0, respectively) (Fig. 3).

The empirical formula calculated on the basis of 17 O atoms is $\text{H}_{1.27}\text{Ca}_{0.90}\text{Mg}_{1.06}\text{Mn}_{0.04}\text{Fe}_{1.00}^{2+}\text{Fe}_{0.11}^{3+}\text{Al}_{8.80}\text{O}_{17.00}$. The following chemical composition corresponds to the idealized formula of tashelgite

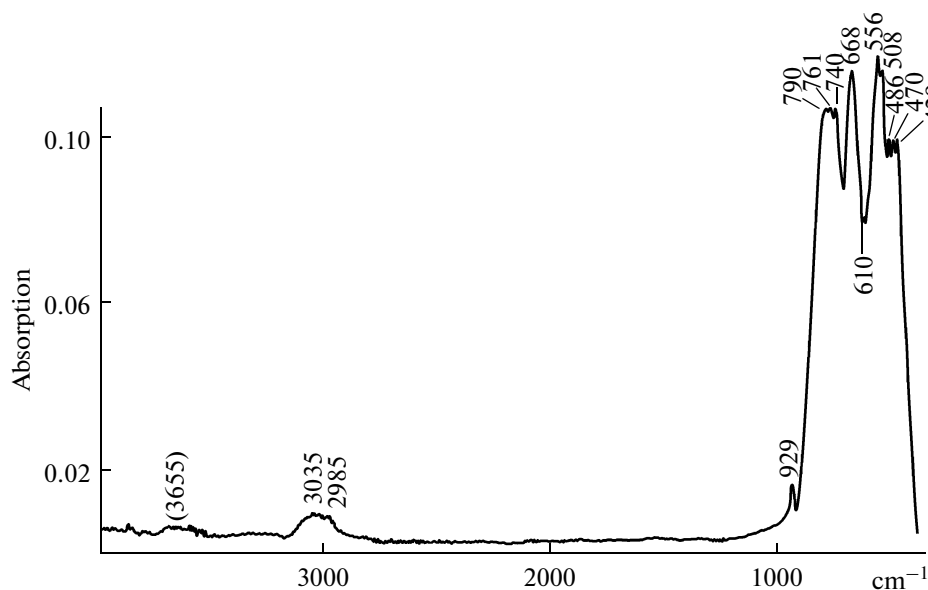


Fig. 4. IR spectrum of tashelgite.

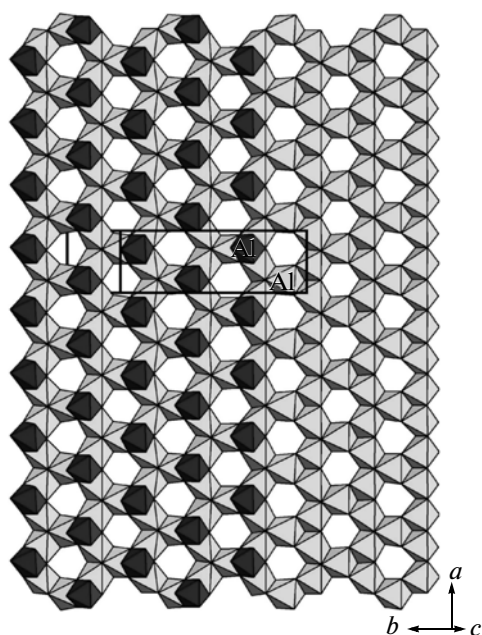


Fig. 5. Tashelgite ribbon of the edge-shared Al octahedra with attached discrete Al octahedra.

$\text{CaMgFe}^{2+}\text{Al}_9\text{O}_{16}(\text{OH})$ ($Z = 8$), wt %: 8.82 CaO, 6.34 MgO, 11.29 FeO, 72.13 Al_2O_3 , 1.42 H_2O ; the total is 100.00. The FTIR spectrum of tashelgite (Fig. 4)

recorded with an ALPHA (BRUKER) spectrometer contains the following absorption bands (cm^{-1} , s is strong band, w is weak band): 3655w (very weak band corresponding to the stretching vibrations of major OH groups), 3035w, 2985w (stretching vibrations of amphoteric OH groups in the apices of Al-centered tetrahedra), 929w (presumable bending vibrations assigned to $\text{M}\cdots\text{O}-\text{H}$), 790, 761, 740, 668s (stretching vibrations of tetrahedra), 610, 556s, 508s, 486, 470, 429 (stretching vibrations of octahedra). The characteristic bands of CO_3 , BO_3 , BO_4 , and H_2O are absent in the IR spectrum of tashelgite. Numerous narrow well-resolved absorption bands indicate a high degree of cation ordering in the mineral. The IR spectrum of tashelgite is unique and can be used as a diagnostic feature of the mineral.

From the outset of the examination of tashelgite, we ran into the problem of determining its crystal structure. Repeated attempts over the last three decades to perform X-ray single crystal studies failed. Even minute individuals of this mineral turned out to be polycrystalline segregations as the finest clusters of acicular crystals.

The X-ray single crystal study of tashelgite (Rastvetaeva et al., 2010) showed that the mineral is monoclinic (pseudoorthorhombic). The space group of tashelgite is Pc ; the unit cell parameters are $a = 5.6973(1)$, $b = 17.1823(4)$, $c = 23.5718(5)$ Å; $\beta =$

Table 2. Atomic coordinates and equivalent displacement parameters of cations in the structure of tashelgite

Atom	x/a	y/b	z/c	$B_{\text{eq/iso}}, \text{\AA}^2$	Atom	x/a	y/b	z/c	$B_{\text{eq/iso}}, \text{\AA}^2$
Al1	0.951(1)	0.1671(2)	0.0342(2)	0.8(1)	Al25	0.701(2)	0.1982(2)	0.5651(2)	0.7(1)
Al2	0.460(1)	0.1678(2)	0.0341(2)	0.7(1)	Al26	0.713(2)	0.2528(5)	0.9489(4)	1.0(1)
Al3	0.952(1)	0.2859(3)	0.6478(2)	1.1(5)	Al27	0.707(2)	0.3031(3)	0.3289(1)	1.6(1)
Al4	0.457(1)	0.2862(2)	0.6494(1)	0.4(1)	Al28	0.196(2)	0.0278(3)	0.3952(1)	1.6(1)
Al5	0.698(2)	0.2470(4)	0.4475(3)	0.4(2)	Al29	0.703(2)	0.4504(2)	0.6819(1)	1.1(1)
Al6	0.447(1)	0.1088(2)	0.4790(2)	0.7(1)	Al30	0.701(2)	0.5087(2)	0.3176(1)	0.4(1)
Al7	0.951(1)	0.1116(3)	0.4801(2)	0.7(2)	Al31	0.701(2)	0.0041(2)	0.0751(1)	0.9(1)
Al8	0.450(1)	0.4428(2)	0.0864(1)	0.5(1)	Al32	0.713(1)	0.0521(3)	0.2156(2)	1.3(1)
Al9	0.955(1)	0.4427(3)	0.0855(2)	0.9(1)	Al33	0.188(1)	0.2153(3)	0.7664(2)	0.6(1)
Al10	0.217(2)	0.4717(2)	0.8825(1)	0.6(1)	Al34	0.206(2)	0.2789(2)	0.1272(1)	0.4(1)
Al11	0.704(3)	0.1940(3)	0.8320(2)	1.6(1)	Al35	0.192(2)	0.1233(3)	0.6050(1)	0.7(2)
Al12	0.207(2)	0.4242(2)	0.6154(1)	0.9(1)	Al36	0.203(3)	0.3744(2)	0.2862(2)	0.8(1)
Al13	0.953(1)	0.3868(3)	0.4129(2)	1.0(2)	Fe1	0.200(1)	0.2812(1)	0.5172(1)	1.17(4)
Al14	0.455(1)	0.3898(4)	0.4144(2)	1.0(2)	Fe2	0.702(1)	0.0547(1)	0.9351(1)	1.55(5)
Al15	0.702(2)	0.3055(2)	0.0634(1)	0.5(1)	Fe3	0.705(1)	0.1103(1)	0.3513(1)	1.32(5)
Al16	0.202(2)	0.0791(2)	0.2796(2)	1.3(1)	Fe4	0.209(1)	0.3315(1)	0.9867(1)	1.8(1)
Al17	0.199(1)	0.0303(3)	0.0070(1)	1.1(1)	Mg1	0.211(2)	0.1683(3)	0.9078(2)	1.0(2)
Al18	0.965(1)	0.2145(3)	0.2464(2)	1.0(2)	Mg2	0.698(2)	0.3884(2)	0.5456(1)	0.3(1)
Al19	0.446(1)	0.2146(4)	0.2451(3)	1.7(2)	Mg3	0.200(1)	0.2190(2)	0.3744(1)	0.4(1)*
Al20	0.954(1)	0.0599(3)	0.8084(2)	1.2(2)	Mg4	0.705(1)	0.4434(1)	0.9588(1)	0.3(1)*
Al21	0.946(1)	0.3274(3)	0.8576(2)	1.4(2)	Ca1	0.197(2)	0.4165(2)	0.7514(1)	2.4(1)
Al22	0.451(1)	0.0545(4)	0.8081(3)	1.8(2)	Ca2	0.209(1)	0.0841(1)	0.1430(1)	0.6(2)
Al23	0.446(1)	0.3330(3)	0.8592(2)	1.3(2)	Ca3	0.702(2)	0.3742(1)	0.2009(1)	1.3(1)
Al24	0.204(2)	0.4729(1)	0.4995(1)	0.7(1)	Ca4	0.705(2)	0.1281(1)	0.6947(1)	1.4(1)

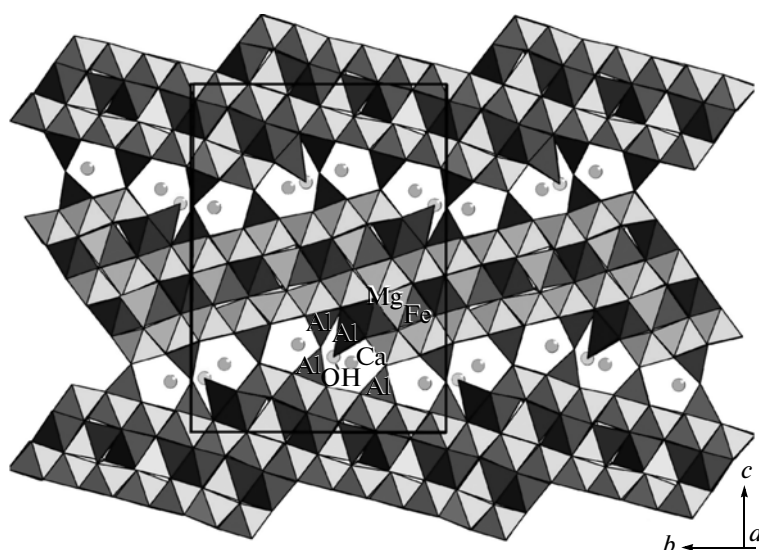


Fig. 6. General view of the crystal structure of tashelgite projected onto bc .

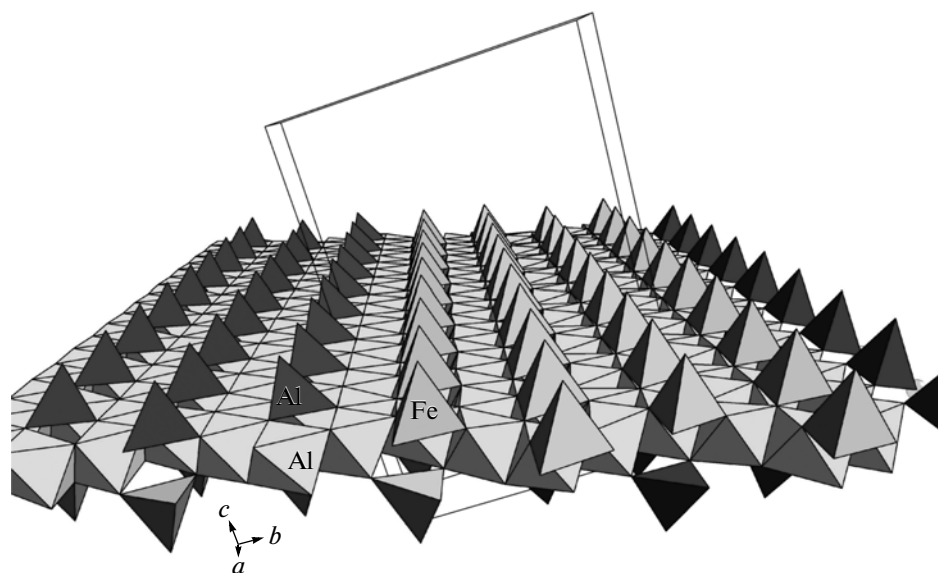


Fig. 7. Tashelgite ribbon composed of edge-shared Al octahedra with attached Al-, Mg- and Fe tetrahedra (perspective image).

$90.046(3)^\circ$; $V = 2307.5(1) \text{ \AA}^3$, $Z = 8$; $a : b : c = 0.3316 : 1 : 1.3719$. The crystal structure of the mineral was solved by applying the X-ray diffraction data of a single crystal $0.03 \times 0.02 \times 0.35 \text{ mm}$ in size collected with an Xcalibur Oxford Diffraction diffractometer, CCD detector, and MoK_α radiation. The structure of tashelgite was modeled by direct methods; the sites of 116 unique atoms were refined by the least squares method using 4773 unique reflections taking into account twinning and an absorption correction to the R factor of 5.16%. The coordinates of cations and their displacement parameters are given in Table 2. Due to the inconvenience of the table, anions were omitted; their

coordinates were published earlier (Rastsvetaeva et al., 2010).

Most Al atoms Al(1–23) are in octahedra (Al–O distances are in the range of 1.68–2.14 $\text{\AA}$). Edge-shared octahedra make up the ribbons extending along short direction x angularly axes y and z , which are a cut from the spinel-type layer. Atoms Al(24–28) also form octahedra with an Al–O distance of 1.76–2.06 $\text{\AA}$, which are arranged between neighboring ribbons and serve as “dividers” between them (Fig. 5). The neighboring ribbons are superimposed on each other with a shift along the y axis. As a result, a stepped layer in which the thickness of two ribbons alternates with that

Table 3. X-ray powder-diffraction data on tashelgite

$I_{\text{obs}} \%$	$d_{\text{obs}} \text{ \AA}$	$d_{\text{calc}} \text{ \AA}$	hkl	$I_{\text{obs}} \%$	$d_{\text{obs}} \text{ \AA}$	$d_{\text{calc}} \text{ \AA}$	hkl
48	11.79	11.79	002	21	2.345	2.347	164
15	9.63	9.72	012			2.345	225
13	7.13	7.15	013			2.343	073
16	5.85	5.89	004	24	2.275	2.276	216
19	5.61	5.57	014	72	2.202	2.202	244
13	5.28	5.27	111	19	2.108	2.108	227
17	4.64	4.65	121	27	2.071	2.072	083
		4.63	033	21	2.017	2.018	084
20	4.56	4.55	015	33	1.991		
20	3.341	3.345	125	11	1.951		
20	3.322	3.332	134	10	1.911		
11	3.232	3.234	106	10	1.8554		
21	3.134	3.135	027	11	1.6734		
10	3.068	3.067	135	12	1.6292		
16	2.961	2.964	144	20	1.6042		
43	2.845	2.843	061	16	1.5535		
19	2.788	2.787	028	20	1.5166		
19	2.778	2.777	055	29	1.4754		
100	2.616	2.617	108	11	1.4443		
81	2.584	2.587	118, 056, 137	12	1.4285		
		1.584	146	13	1.4060		
39	2.501	2.500	162	13	1.3930		
44	2.437	2.433	163	10	1.0012		
61	2.406	2.405	057	10	0.9941		
		2.403	072, 147				

Note: The d_{calc} values are calculated applying the unit cell parameters obtained from the X-ray powder diffraction pattern.

of three ribbons. The next group of atoms Al(29–32) is in tetrahedra (Al–O = 1.65–1.85 Å) forming diorthogroups participating in integration of the stepped layers into three-dimensional structure (Fig. 6). Two other tetrahedral, Al(33–34) with Al–O = 1.62–1.89 Å, are arranged on the outer side of the layers and participate in integration via their apices. Tetrahedra Al(35–36) (Al–O = 1.69–1.89 Å) are also combined into the layers but by H-bonding of OH groups arranged at a free apex of each tetrahedron.

Atoms of Mg(1–4) make up tetrahedra with Mg–O = 1.81–2.04 Å, which occur within the layer and combine the ribbons. All ferrous atoms are tetrahedrally coordinated with Fe–O distances ranging from 1.79 to 2.07 Å. Iron and magnesium tetrahedra, alternating, butt ribbons into the layers (Fig. 7).

Thus, the structure of the mineral is unique and contains functionally different Al atoms with three types of coordination: octahedra, tetrahedra, and diorthogroups. The crystallochemical formula of

tashelgite is ($Z = 4$) $\text{Ca}_2\text{Mg}_2^{\text{IV}}\text{Fe}_2^{(2+)\text{IV}}$.

$[\text{Al}_{14}^{\text{VI}}\text{O}_{31}(\text{OH})][\text{Al}_2^{\text{IV}}\text{O}][\text{Al}^{\text{IV}}][\text{Al}^{\text{IV}}(\text{OH})]$, where Roman numerals denote atom coordination and ribbons of Al octahedra, interlayer Al diorthogroups, and two kinds of interlayer Al tetrahedra—OH-free and hydrated—are in brackets. OH groups were determined on the basis of local valence balance.

Tashelgite has no close analogues and is a new structural type. In stoichiometry of cations Ca/(Mg, Fe, Al) = 1/11, the mineral is the closest to hexagonal diaoyudaoite (Zhu, 1992) with Na/Al = 1/11. These minerals are, however, distinct in composition and structure.

The X-ray powder diffraction pattern of tashelgite (Table 3) was recorded with a DRON-3 diffractometer (Cu anode, Ni filter, $V = 20$ kV, $I = 15$ mA, 1 degree/min). The strong reflections of the X-ray powder diffraction pattern are (d , Å— $I[hkl]$): 11.79–48 [002], 2.845–43 [061], 2.616–100 [108], 2.584–81 [146], 2.437–44 [163], 2.406–61 [057], 2.202–72

[244]. The unit cell dimensions calculated from the X-ray powder diffraction pattern [$a = 5.697(1)$, $b = 17.183(3)$, $c = 23.571(3)$ Å; $\beta = 90^\circ$; $V = 2307.7(2)$ Å³, $Z = 8$] are close to those calculated from the X-ray single crystal data.

The compatibility of chemical compositions, refractive indices, and calculated densities estimated from the Gladstone–Dale criterion is excellent ($1 - K_p/K_C = 0.026$).

In conclusion, note that the Tashelga skarnoid is composed of a unique assemblage, whose analogues are unknown. The distinguishing feature of this rock is the extremely high Al content, which predetermined the formation of rare calcium aluminate hibonite, $\text{Ca}(\text{Al}, \text{Fe}, \text{Ti})_{12}\text{O}_{19}$, and the new mineral tashelgite together with common Al-rich minerals (hercynite and corundum).

The type material of tashelgite has been deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, registration no. 3983/1.

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