

UDC 549.657.42

## ZERAVSHANITE, $\text{Cs}_4\text{Na}_2\text{Zr}_3(\text{Si}_{18}\text{O}_{45})(\text{H}_2\text{O})_2$ , NEW CESIUM MINERAL FROM DARA-I-PIOZ MASSIF (TAJIKISTAN)

Leonid A. Pautov

Fersman Mineralogical Museum RAS, Moscow, pla@fmm.ru

Atali A. Agakhanov

Fersman Mineralogical Museum RAS, Moscow, atali@fmm.ru

Yulia A. Uvarova

Geological Department, Manitoba University, Winnipeg, Canada

Elena V. Sokolova

Geological Department, Manitoba University, Winnipeg, Canada

Frank C. Hawthorne

Geological Department, Manitoba University, Winnipeg, Canada

New cesium mineral zeravshanite with formula  $\text{Cs}_4\text{Na}_2\text{Zr}_3(\text{Si}_{18}\text{O}_{45})(\text{H}_2\text{O})_2$  (monoclinic system, sp. group  $C2/c$ ,  $a = 26,3511(8)\text{Å}$ ,  $b = 7,5464(3)\text{Å}$ ,  $c = 22,9769(8)\text{Å}$ ,  $\beta = 107,237(1)^\circ$ ,  $V = 4363,9(4)\text{Å}^3$ ,  $Z = 4$ ) was found in the moraine of Dara-i-Pioz glacier located at the joint of Zeravshan, Turkestan and Alay Ranges (Tajikistan). The mineral was named after *type locality*. Zeravshanite forms of grains (from 0.02 up to 0.2 mm in size) in the quartz rock with aegirine, polyolithionite, pectolite, reedmergnerite, sogdianite, leucosphenite, stillwellite-(Ce), microcline, baratovite, fluorite, galena, turkestanite, minerals of tazhikite and eudialyte groups, neptunite, pekovite, cesium analogue of polyolithionite etc. Zeravshanite is colorless, transparent. Hardness is 6 on Mohs' scale. Micro-indentation,  $\text{VHN} = 838\text{ kgs/mm}^2$ . Density is 3.09(5) (exp.), 3.17 (calc.)  $\text{g/cm}^3$ . Zeravshanite is biaxial, optical negative.  $2V$  (calc.) =  $-63^\circ$ . Optic angle dispersion is medium,  $v > r$ .  $n_p = 1,582(2)$ ,  $n_m = 1,598(2)$ ,  $n_g = 1,603(2)$ . The IR-spectrum (strong absorption bands) is following: 1089, 1045, 978, 709, 662, 585, 538  $\text{cm}^{-1}$ . The chemical composition (wt %, average on 6 electron microprobe analyses) is:  $\text{SiO}_2$  — 52.20,  $\text{TiO}_2$  — 0.43,  $\text{ZrO}_2$  — 16.41,  $\text{SnO}_2$  — 0.46,  $\text{Fe}_2\text{O}_3$  — 0.21,  $\text{Na}_2\text{O}$  — 3.06,  $\text{K}_2\text{O}$  — 0.09,  $\text{Cs}_2\text{O}$  — 26.58,  $\text{H}_2\text{O}$  (calc.) — 1.74, total — 101.18. The strong lines of X-ray powder diagram are following (d, I): 6.32(5); 3.65(5); 3.35(10); 3.25(4); 2.82(5); 2.62(7); 1.946(4); 1.891(4); 1.865(4). Crystal structure is determined with  $R = 2.8\%$ . The sample with new mineral is kept in the Fersman Mineralogical Museum RAS (Moscow, Russia). 2 tables, 4 figures, 4 references

New cesium mineral with formula  $\text{Cs}_4\text{Na}_2\text{Zr}_3(\text{Si}_{18}\text{O}_{45})(\text{H}_2\text{O})_2$  (monoclinic system, sp. group  $C2/c$ ,  $a = 26,3511(8)\text{Å}$ ,  $b = 7,5464(3)\text{Å}$ ,  $c = 22,9769(8)\text{Å}$ ,  $\beta = 107,237(1)^\circ$ ,  $V = 4363,9(4)\text{Å}^3$ ,  $Z = 4$ ) was found in the moraine of Dara-i-Pioz glacier located at the joint of Zeravshan, Turkestan and Alay Ranges (Tajikistan) in essentially quartz rock with polyolithionite, pectolite, reedmergnerite, aegirine, leucosphenite etc. The mineral was named zeravshanite\* after *type locality*.

### Locality and mineral assemblage

Zeravshanite was found during studying of rock samples from Verkhniy Dara-i-Pioz massif collected by L.A. Pautov and A.A. Agakhanov together with V.Yu. Karpenko and P.V. Khvorov at the moraine of Dara-i-Pioz glacier (Harm Region, Tajikistan). Dara-i-Pioz massif is located at the upper coarse of the same name river (left tributary of Yarkhych River), and glaciers cover significant area of the massif. The uncovered parts of massif are difficult of access, because of that the most part of mineralogical and petrographical observations were made on

rock blocks in moraine material of Dara-i-Pioz glacier. Geology and mineralogy of the massif were considered in a number of publications (Dusmatov, 1968, 1971, Belakovskiy, 1991, etc.). The bright mineralogical peculiarity of Dara-i-Pioz alkaline massif is the presence of proper minerals of cesium in it. These are cesium kupletskite, telyushenkoite discovered at Dara-i-Pioz, and now zeravshanite. Apparently, the list of cesium minerals from Dara-i-Pioz isn't finished on that: recently cesium micas and a number of undetermined cesium silicates were found, and now they are studied.

Zeravshanite was found in the samples of rock composed mainly by quartz with subordinate amount of aegirine, polyolithionite, reedmergnerite, pectolite, and a whole number of other accessory minerals. This rock occurs rarely in the moraine of Dara-i-Pioz glacier. All its findings are represented by blocks with different degree of roundness and with sizes up to half-meter, very rarely larger. Unfortunately, the authors never found the contacts of this quartz rock with any other rock that doesn't allow judging with some validity about form of

\* It was considered by the RMS KNMMN and approved by the IMA KNMMN on September 21, 2003

bodies composed by this rock and about its genesis. Some researchers consider it as quartz cores of pegmatites, others are inclined to see in it the fragments of proper silicite veined bodies. The appearance and mineral composition of this rock is very exotic, and it is difficult to give the simple interpretation and name in the limits of existed rock classification. As it was mentioned, quartz is the main mineral of the rock. Quartz has ice-like appearance, more often absolutely transparent, but it looks white because of inter-grain borders and cracks. The structure is inequigranular, from medium-grained to coarse-grained, and rarely up to gigantic-grained. Very often the equimedium-grained parts without strong borders are observed, which are composed by isometric polyhedra, quartz granules. The well-shaped black tabular crystals of aegirine (up to 5 cm in size), large lamellae of polyolithionite (up to 20 cm in size), semitransparent grass-green crystals of leucosphenite, lentil-shaped crystals of stillwellite-(Ce), the nests of coarse-grained reedmergnerite, single crystals and intergrowths of white microcline, pink to violet tabular segregations of sodianite-sugilite series mineral (up to 20 cm in size), columnar to needle-shaped crystals of dark-green hydrated high-uranium turkestanite are sporadically impregnated in quartz. Rarely pyrochlore, neptunite, galena, calcite, kapitsaite-(Y), berezanskite, tienshanite, darapiosite, dusmatovite, tazhikite group minerals, baratovite, native bismuth, sphalerite, fluorite, fluorapatite, and fluorapophyllite are noted in this rock. The distribution of mentioned minerals in the rock is extremely uneven, without some orientation of individuals of accessory minerals. The typical peculiarity of described rock is the brown polymineral aggregates (up to 25 cm in size) with strong borders, which occur only in this rock and are composed predominantly by pectolite with subordinated amount of aegirine, fluorite, quartz, polyolithionite, neptunite, very rare by pekovite and cesium analogue of polyolithionite. For the first time zeravshanite was found in the edge zone of pectolite aggregate at the border with quartz in the form of unshaped grains (0.02–0.1 mm in size) and intergrowths or tabular individuals up to 0.2 mm in the largest dimension (Fig. 3) in intergrowth with pectolite and undetermined silicate of cesium and calcium. Zeravshanite occurs very rare, it was found only in single samples from many tens of micro-sections of pectolite aggregates. Other findings of zeravshanite were made also in described quartz rock, but without apparent connection with pectolite aggregates. In the

Table 1. The results of calculation of zeravshanite debayegram

<i>I</i>	<i>d<sub>exp.</sub></i>	<i>d<sub>calc.</sub></i>	<i>hkl</i>
2	7.31	7.271	202
5	6.32	6.327	-402
		6.292	400
1	5.43	5.453	-312
1	4.57	4.561	-114
2	4.24	4.279	-512
		4.201	114
1	4.18	4.195	600
5	3.65	3.658	006
		3.636	404
10	3.35	3.367	-712
		3.356	-223
		3.349	222
4	3.25	3.263	206
		3.246	710
		3.241	-422
9	3.14	3.144	-224
1	2.89	2.907	224
5	2.82	2.833	-716
		2.820	406
7	2.62	2.626	026
		2.622	910
		2.608	-518
3	2.517	2.517	10 0 0
		2.514	714
1	2.478	2.483	-916
		2.481	-822
		2.468	226
2	2.276	2.279	-2.0.10
		2.279	-334
		2.264	-532
1	2.227	2.230	-918
2	2.185	2.187	-12.0.4
3	2.146	2.149	532
2	2.095	2.097	12.0.0
		2.094	10.2.0
1	2.071	2.072	518
4	1.946	1.951	-2.2.10
		1.942	-736
4	1.891	1.892	-12.2.4
4	1.865	1.865	-538
		1.864	-14.0.2
3	1.829	1.830	734
		1.829	0.0.12
3	1.816	1.818	-936
		1.814	-7.1.12
1	1.786	1.784	044
1	1.764	1.762	-14.0.8
1	1.736	1.737	12.22
2	1.674	1.677	046
		1.672	-14.2.2
1	1.649	1.650	10.2.6
		1.646	0.2.12
1	1.632	1.633	246
		1.631	-16.0.6
1	1.546	1.547	14.2.2
1	1.534	1.534	13.3.0
3	1.500	1.500	-7.3.12
2	1.454	1.454	14.2.4
		1.453	-2.4.10

Note:

RKD 114, Fe anod, Mn filter, URS-50IM.  
Analyst L.A. Pautov

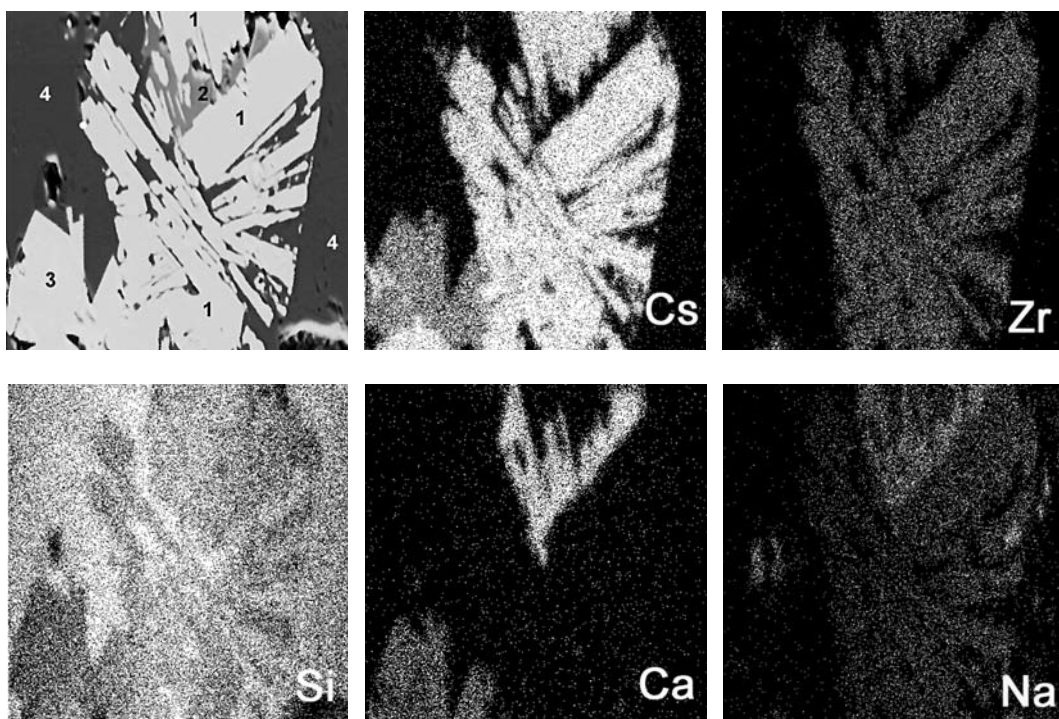


FIG. 3. The intergrowth of lamella grains of zeravshanite (1) with pectolite (2) and undetermined Cs-Ca silicate (3) in quartz (4). The image in COMPO regime and characteristic X-ray radiation of mentioned elements. Field of vision width is 200 mkm

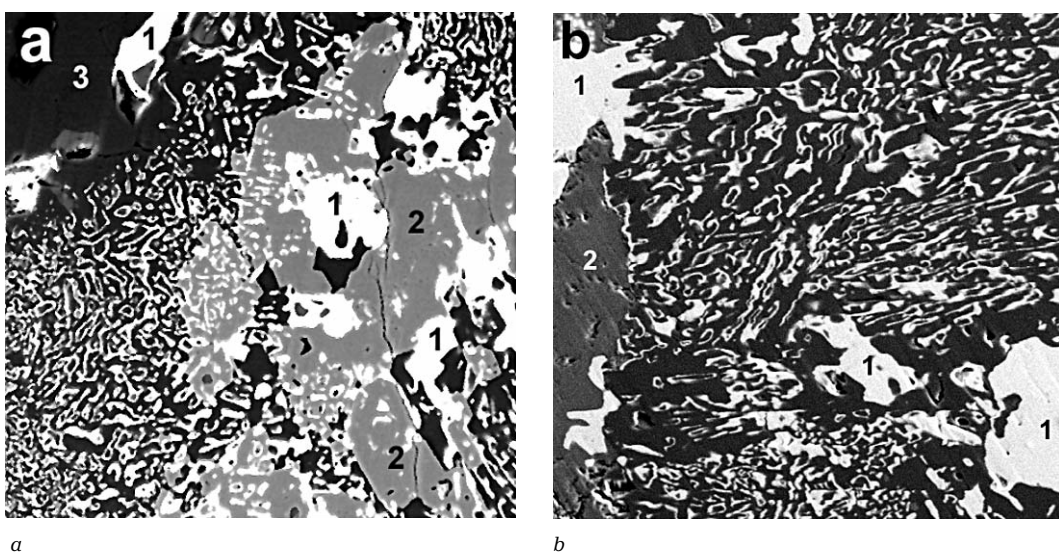


FIG. 4. a) Graphic intergrowths of zeravshanite (1) with quartz (black) and aegirine (2). Field of vision width is 100 mkm.  
b) Graphic intergrowths of zeravshanite (1) with quartz (black). The dark-gray is pectolite (2). Field of vision width is 60 mkm

latter case zeravshanite is represented by grains with indented outlines and graphic intergrowths with quartz, aegirine, arfvedsonite, and rarely with pectolite (Fig. 4).

### Physical properties

Zeravshanite is absolutely colorless, water-transparent mineral. It is practically indistinct from quartz by its appearance. The luster is vitreous, slightly stronger than the luster of quartz. The mineral hasn't luminescence in the short-wave and long-wave ultraviolet light. The hardness is 6 on Mohs' scale. Micro-indentation, VHN = 838 kgs/mm<sup>2</sup> (the average value by 12 measures with fluctuation of single measures from 805 up to 880 kgs/mm<sup>2</sup>) at the load 50 g. The micro-indentation was obtained by PMT-3 instrument, calibrated by NaCl. The density of the mineral was determined by balancing of mineral grains in Clerichi solution, it is equal 3.09(5) g/cm<sup>3</sup>. The observation was made at vertical position of microscope table in the glass with hole, in which mineral grains and solution were placed. The single gas-liquid inclusions were observed in all grains that, undoubtedly, resulted in some understatement of measured density in comparison with calculated density, 3.17 g/cm<sup>3</sup>. Zeravshanite is optical negative, biaxial mineral. 2V (calc.) = -63°. Optic angle dispersion is medium,  $v > r$ . Refractive indexes were measured on rotated needle,  $n_p = 1.585(2)$ ;  $n_m = 1.598(2)$ ;  $n_g = 1.603(2)$  (for light with wave length 589 nm). Very insignificant amount of new mineral wasn't allowed obtaining the exhaustive optic constants. It wasn't succeeding study of its optic orientation and measure the value of angle 2V. The cleavage in one direction was observed on single grains in immersion preparations. The grains lain in preparation on cleavage plane gave in conoscope the section close to that perpendicular to obtuse bisector. The elongation of elongated fragments is negative. The IR-spectrum of the mineral obtained by Specord-75IR (the sample was micro-tablet of the mineral in KBr) has the following most strong absorption bands: 1089, 1045, 978, 709, 662, 585, 538 cm<sup>-1</sup>.

### X-ray data

X-ray powder diagram of the mineral (Table 1) was obtained by photomethod in RKU 114 mm camera on Fe radiation with Mn filter. Silicon was used as inner standard. The debye-gram is individual and doesn't coincide with

any known mineral or synthetic compound. Crystal structure of zeravshanite (Uvarova *et al.*, 2004) with ideal formula Cs<sub>4</sub>Na<sub>2</sub>Zr<sub>3</sub>(Si<sub>18</sub>O<sub>45</sub>)(H<sub>2</sub>O)<sub>2</sub> (monoclinic system, unit cell parameters are following:  $a = 26.3511(8)$ ,  $b = 7.5464(3)$ ,  $c = 22.9769(8)$  Å,  $\beta = 107.237(1)^\circ$ ,  $V = 4363.9(4)$  Å<sup>3</sup>, sp. group  $C2/c$ ,  $Z = 4$ ), was solved by direct method and refined with  $R_1 = 2.8\%$  on 4508 independent reflexes [ $F_o > 4\sigma|FI|$ ] with diffractometer Bruker P4 (MoK $\alpha$  radiation, CCD detector). In the crystal structure of the mineral there are 9 tetrahedral Si-sites ( $\langle Si-O \rangle = 1.614$  Å); two [6]-coordinated M-sites occupied by Zr with small amounts of Ti, Fe<sup>3+</sup>, and Sn ( $\langle M-O \rangle = 2.067$  Å); one [5]-coordinated Na-site ( $\langle Na-O, H_2O \rangle = 2.406$  Å); two A-sites occupied predominantly by Cs (with small amounts of Na and K), from which A(1)-site is [12]-coordinated and A(2)-site is [11]-coordinated ( $\langle A(1)-O, H_2O \rangle = 3.371$  Å and  $\langle A(2)-O \rangle = 3.396$  Å). In the crystal structure of zeravshanite Si-tetrahedra form the layers {Si<sub>18</sub>O<sub>45</sub>}<sup>18-</sup> consisting of 5- and 8-membered Si-O rings (Fig. 1). The topology of the layers can be described as connected wollastonite-like chains {Si<sub>3</sub>O<sub>6</sub>}<sup>6-</sup>. The tetrahedra of (10 - 1) Si-O layers and M- and Na-polyhedra equally divide the mutual vertices forming mixed construction {Na<sub>2</sub>Zr<sub>3</sub>(Si<sub>18</sub>O<sub>45</sub>)(H<sub>2</sub>O)<sub>2</sub>} with holes containing A atoms (Fig. 2). The square Na-pyramids jointed by mutual vertices form zigzag chains along [010]. Each Na-pyramid has mutual edge with M(2)-octahedron at that the *cys*-decoration of chain of Na-pyramids by M(2)-octahedra is realized. Also there is the entirely occupied (H<sub>2</sub>O)-site. Atoms of H are determined. (H<sub>2</sub>O) groups form ligands with Na and A(1) with weak O-H bonds (~2.9 Å) in the limits of mixed construction.

### Chemical composition

The chemical composition of zeravshanite was studied by electron microprobe instrument JCXA-50A (JEOL) equipped by modernized energy-dispersive spectrometer LINK and by three wave spectrometers. The analyses on all elements were made on EDS under accelerating voltage 20 kV and electron microprobe current 3 nA. The standards were following: anorthite USNM 137041 (Si), ilmenite USNM 96189 (Ti, Fe), synthetic jadeite (Na), microcline USNM 143966 (K), synthetic ZrO<sub>2</sub> (Zr), synthetic SnO<sub>2</sub> (Sn), synthetic CsTb(PO<sub>3</sub>)<sub>4</sub> (Cs). Six mineral grains were analyzed. The distribution of main components of zeravshanite was studied by wave spectrometers; any heterogeneity or zoning wasn't discovered. The concentra-

Table 2. Chemical composition of zeravshanite (wt %)

Constituent	1	2	3	4	5	6	Average
SiO <sub>2</sub>	52.50	52.47	52.35	52.39	51.32	52.18	52.20
TiO <sub>2</sub>	0.23	0.51	0.95	0.88	0.02	0.00	0.43
ZrO <sub>2</sub>	17.16	16.98	15.53	14.82	16.72	17.23	16.41
SnO <sub>2</sub>	0.02	0.04	0.74	1.93	0.00	0.00	0.46
Fe <sub>2</sub> O <sub>3</sub>	0.22	0.26	0.26	0.00	0.022	0.33	0.21
Na <sub>2</sub> O	3.08	3.35	3.03	3.01	2.97	2.94	3.06
K <sub>2</sub> O	0.01	0.07	0.01	0.38	0.00	0.07	0.09
Cs <sub>2</sub> O	26.50	25.65	27.25	25.61	27.02	27.47	26.58
H <sub>2</sub> O calc.	1.74	1.74	1.74	1.74	1.74	1.74	1.74
Total	101.46	101.07	101.86	100.76	100.01	101.96	101.18
Formula calculated on 18 atoms of Si							
Si	18.00	18.00	18.00	18.00	18.00	18.00	18.00
Ti	0.06	0.13	0.25	0.23	0.01	0.00	0.11
Zr	2.87	2.84	2.60	2.48	2.86	2.90	2.76
Sn	0.00	0.01	0.10	0.26	0.00	0.00	0.06
Fe	0.06	0.07	0.07	0.00	0.06	0.09	0.06
Na	2.05	2.23	2.02	2.01	2.02	1.97	2.05
K	0.00	0.03	0.00	0.017	0.00	0.03	0.04
Cs	3.87	3.75	4.00	3.75	4.04	4.04	3.91
H <sub>2</sub> O calc.	2	2	2	2	2	2	2
O	44.91	45.06	45.01	44.91	44.85	44.95	44.95

Note: analysts L.A. Pautov, A.A. Agakhanov

tions were calculated with use of ZAF-correction. The results of analyses are given in the Table 2. Unfortunately, it was impossible to determine the amount of water by direct method because of extremely small amount of new mineral; and so in the Table 2 the amount of water is given by data of crystal structure study. Chemical formula of zeravshanite calculated on 18 atoms of Si by results of electron microprobe analyses is following: (Cs<sub>3.91</sub>Na<sub>0.05</sub>K<sub>0.04</sub>)<sub>4.00</sub>Na<sub>2.00</sub>(Zr<sub>2.76</sub>Ti<sub>0.11</sub>Fe<sup>3+</sup><sub>0.06</sub>Sn<sub>0.06</sub>)<sub>2.99</sub>(Si<sub>18</sub>O<sub>44.92</sub>)(H<sub>2</sub>O)<sub>2</sub>. The chemical formula of the mineral by results of crystal structure study is quite close to the formula calculated by chemical analysis: (Cs<sub>3.80</sub>Na<sub>0.18</sub>K<sub>0.02</sub>)<sub>4.00</sub>Na<sub>2.00</sub>(Zr<sub>2.73</sub>Ti<sub>0.19</sub>Fe<sup>3+</sup><sub>0.04</sub>Sn<sub>0.04</sub>)<sub>3.00</sub>(Si<sub>18</sub>O<sub>45</sub>)(H<sub>2</sub>O)<sub>2</sub>. The ideal formula of zeravshanite is Cs<sub>4</sub>Na<sub>2</sub>Zr<sub>3</sub>(Si<sub>18</sub>O<sub>45</sub>)(H<sub>2</sub>O)<sub>2</sub>. The coincidence index is (1-K<sub>p</sub>/K<sub>c</sub>) = 0.004 (superior).

Zeravshanite doesn't have analogues among minerals of inorganic synthetic compounds.

The sample with zeravshanite was given to the Fersman Mineralogical Museum RAS (Moscow).

## Acknowledgments

The authors thank Vladimir Yu. Karpenko, Pavel V. Khvorov for help in carrying out of field works at the moraine of Dara-i-Pioz glacier and in laboratory studies, and Vyacheslav D. Dusmatov, Igor V. Pekov, and Dmitrii I. Belakovskiy for valuable advices.

The work was supported by the grant of Russian Foundation for Basic Research (04-05-64118).

## References

- Belakovskiy D.I.* Die seltenen Mineralien von Dara-i-Pioz im Hochgebirge Tadshikistans. *Lapis*. **1991**. 16. № 12. p. 42–48.
- Dusmatov V.D.* To mineralogy of one of the alkaline rocks massifs. // In book: Alkaline Rocks of Kirgizia and Kazakhstan. (Shchelochnye Porody Kirgizii i Kazakhstana). Frunze. **1968**. P. 134–135. (Rus.).
- Dusmatov V.D.* Mineralogy of Dara-i-Pioz Alkaline Massive (South Tyan-Shan). (Mineralogiya Shchelochnogo Massiva Dara-i-Pioz (Yuzhnyi Tyan'-Shan')). PhD Thesis. M. **1971**. 18 p. (Rus.).