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CHUKHROVITE-(Nd), $\text{Ca}_3(\text{Nd,Y})\text{Al}_2(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$, A NEW MINERAL

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In specimens from the oxidized zone of the Kara-Oba deposit (Central Kazakhstan), a new neodymium-dominant analogue of chukhrovite-(Y) and chukhrovite-(Ce) has been found; it has been named chukhrovite-(Nd). The new mineral occurs in the form of isometric grains and small crystals represented by a combination of {100} and {111} faces, with sizes ranging from 0.05 to 0.4 mm; it forms zones within the larger crystals of chukhrovite-(Y) also. Chukhrovite-(Nd) is associated with quartz, fluorite, halloysite, chukhrovite-(Y), anglesite, gearksutite, creedite, and the jarosite group minerals. The mineral is colourless, rarely white. Streak is white. Hardness is 3.5-4 on Mohs' scale. Density (meas.) is 2.42(3) g/cm³, density (calc.) is 2.42 g/cm³. The mineral is transparent, and in thin sections it has anomalous grey interference colours, $n = 1.443(2)$ (589 nm). Chemical composition (electron microprobe instrument, wt %) is following: CaO – 20.03; Y₂O₃ – 1.94; La₂O₃ – 2.32; Ce₂O₃ – 1.37; Pr₂O₃ – 1.37; Nd₂O₃ – 6.26; Sm₂O₃ – 1.90; Gd₂O₃ – 1.12; Dy₂O₃ – 0.44; Ho₂O₃ – 0.10; Al₂O₃ – 12.09; SO₃ – 9.38; F – 28.93; H₂O (by difference) – 24.93, less O = F 12.18, total 100.00 wt%. Empirical formula is $\text{Ca}_{3.06}(\text{Nd}_{0.32}\text{Y}_{0.13}\text{La}_{0.12}\text{Sm}_{0.09}\text{Ce}_{0.07}\text{Pr}_{0.07}\text{Gd}_{0.05}\text{Dy}_{0.02}\text{Ho}_{0.01})_{0.90}\text{Al}_{2.03}\text{Si}_{1.01}\text{O}_{3.96}\text{F}_{13.06}\cdot 11.87\text{H}_2\text{O}$. Ideal formula is $\text{Ca}_3(\text{Nd,Y})\text{Al}_2(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$. Cubic, space group Fd3, $a = 16.759(3)$ Å, $V = 4707.0(1)$ Å³, $Z = 8$. Strong lines of X-ray powder pattern are following (d-I(hkl)): 9.7-10(111); 5.92-7(220); 3.22-8(511); 2.555-7(533); 2.240-5(642); 2.180-6(731); 1.827-5(842). The IR spectrum is as follows: 3548, 3423, 1630, 1090, 586, 465 cm⁻¹. The type specimen of the new mineral is at the Fersman Mineralogical Museum, RAS (Moscow). 3 tables, 3 figures, and 11 references.

During the study of samples from the oxidized zone of ore deposits in Kazakhstan, a new neodymium-dominant analogue of chukhrovite-(Y) and chukhrovite-(Ce) has been found; it was named chukhrovite-(Nd)* according to the protocol in force for names of rare-earth minerals (Levinson, 1996).

Occurrence and mineral assemblages

Chukhrovite-(Nd) has been found in specimens from the oxidized zone of a molybdenum-tungsten deposit in Kara-Oba (Central Kazakhstan). The Kara-Oba ore field is located on the northeastern flank of the Chu-Iliisk ore belt in the central part of a volcano-tectonic structure. The deposit is connected with the multiphase Late Permian (260 ± 5 Ma) intrusive massif of leucocratic granites breaking the effusive-fragmental series of Lower-Middle Devonian. There are four types of ore veins of different age at the deposit: molybdenite-quartz, wolframite-quartz, huebnerite-sulphide-quartz, and quartz-fluorite. Except for the latter type, the veins are accompanied by the zones of circum-vein greisens. The geology and mineralogy of the deposit have

been considered in a number of publications (Shcherba, 1960; Ermilova *et al.*, 1960; Ermilova, 1964; Shcherba *et al.*, 1988; *etc.*). Chukhrovite-(Y) from the oxidized zone of this deposit was described as chukhrovite by L.P. Ermilova with co-authors (1960).

We have found chukhrovite-(Nd) in the specimens formed by columnar milky-white quartz. Within the quartz there are small (up to 5 mm in length) lamellar grains of huebnerite. In numerous small cavities and interstices of columnar quartz crystals, are powdery and microcrystalline crusts of jarosite, poorly shaped crystals of anglesite (up to 4 mm in size), druses of small crystals of creedite, massive snowy-white fine-grained aggregations of gearksutite or halloysite are often observed. In these specimens chukhrovite-(Nd) is presented by aggregations of isometric colourless grains and small, often poorly shaped crystals formed seemingly by a combination of cubic and octahedral faces (Fig. 1), with sizes ranging from 0.05 to 0.4 mm. Examining thin sections of chukhrovite-(Nd) grains and crystals from this association in COMPO and AEI modes, it was not possible to reveal any zoning or sectoring of mineral individuals.

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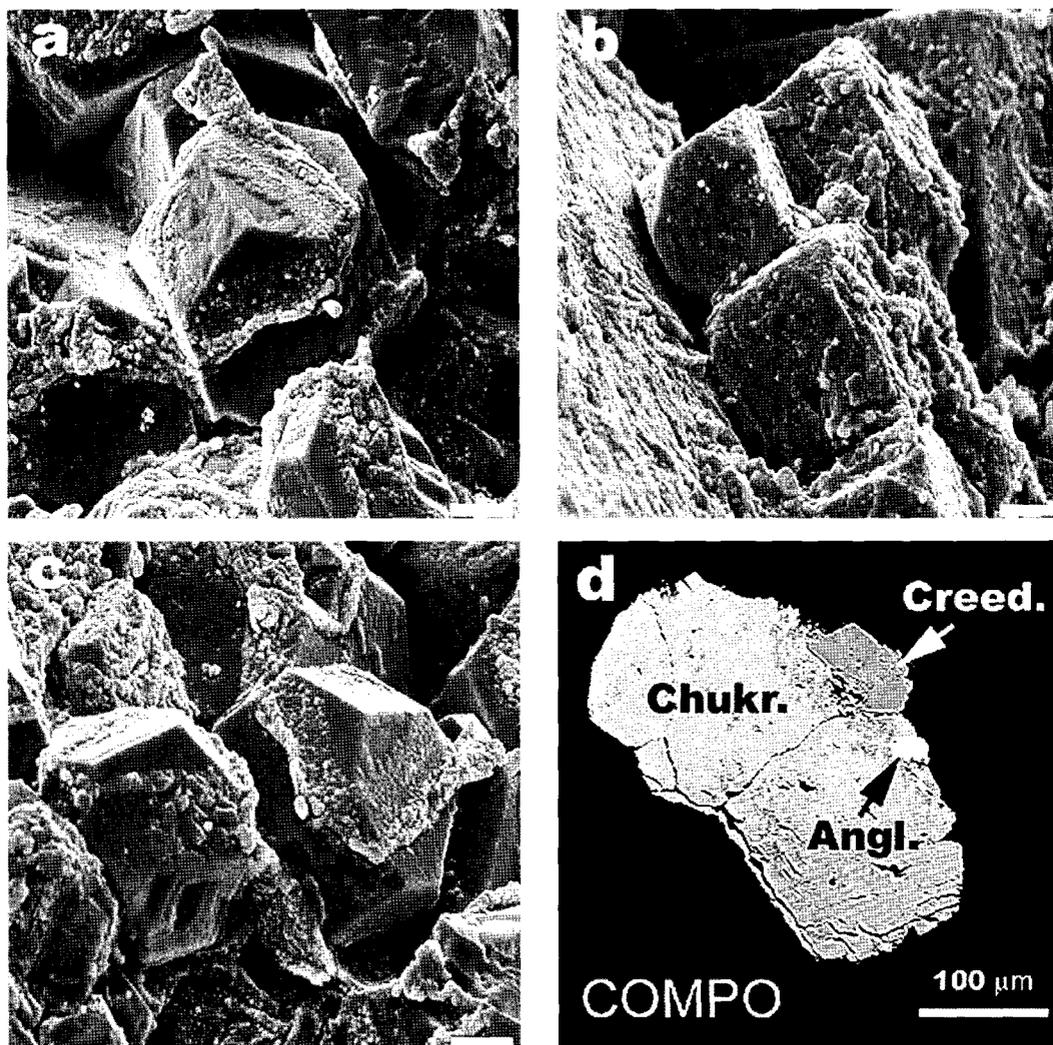


Table 1. Chemical composition of chukhrovite-(Nd) and chukhrovite-(Y)

Constituent	1		2	3
	Chukhrovite-(Nd) wt %	range	Chukhrovite-(Nd) wt %	Chukhrovite-(Y) wt %
CaO	20.03	19.19–20.73	19.89	21.41
Y ₂ O ₃	1.94	1.52–2.71	2.37	5.44
La ₂ O ₃	2.32	1.91–2.86	2.50	1.04
Ce ₂ O ₃	1.37	1.06–1.67	3.36	2.12
Pr ₂ O ₃	1.37	1.22–1.59	1.01	0.17
Nd ₂ O ₃	6.26	5.45–6.58	5.28	2.31
Sm ₂ O ₃	1.90	1.75–2.21	1.35	1.07
Gd ₂ O ₃	1.12	0.67–1.47	0.69	0.83
Dy ₂ O ₃	0.44	0.20–0.68	0.25	0.89
Ho ₂ O ₃	0.10	0.03–0.26	0.07	n.d.
Al ₂ O ₃	12.09	11.74–12.42		
SO ₃	9.38	9.03–9.87		
F	28.93	28.48–29.37		
H ₂ O (by difference)	24.93			
-F=O	-12.18			
Total	100.00			

Fig 1. a, b, c – general view of chukhrovite-(Nd) crystals. SEM photo. Scale bar length is 10 μm; d – intergrowths of chukhrovite-(Nd) (Chukr.) with creedite (Creed) and anglesite (Angl)

Note:

1 – average value calculated by 8 analyses and fluctuation of values for non-zonal grains of mineral from the first specimen; 2, 3 – incomplete electron microprobe analyses of zoned-sectioned grain of chukhrovite from the second specimen (sample # 1208, V.I. Stepanov's collection, FMM). Analyses numbers correspond to points marked on the Figure 2. Analyses by L.A. Pautov.

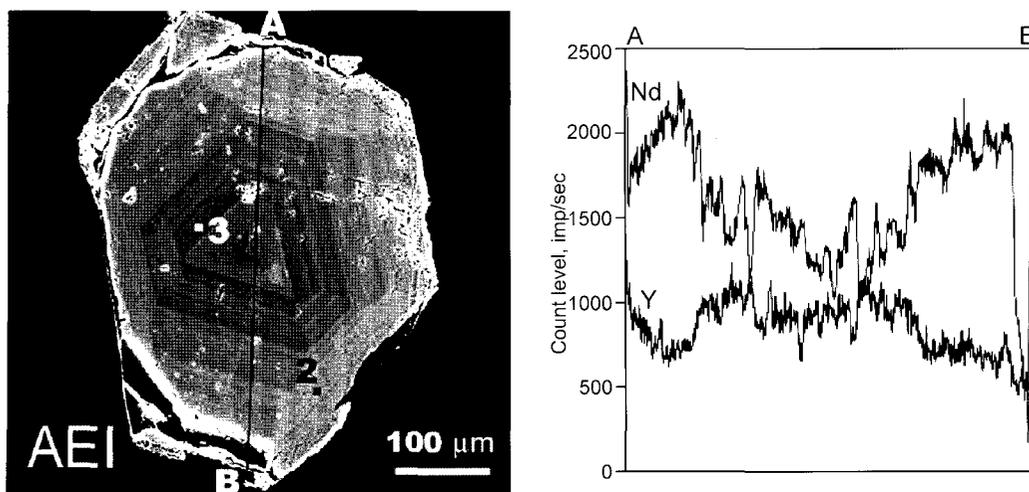


Fig 2. Zoned-sectored crystal of chukhrovite and concentration profile of Nd and Y. Absorbed electron current image (inversed). Contrast is caused by average atomic number: the lighter parts correspond to heavier matrix. AB – profile line. 2, 3 – points of a local analysis, numbers correspond to analyses numbers in the Table 1

The second finding of the new mineral was made in the sample # 1208 from V.I. Stepanov's collection kept in the Fersman Mineralogical Museum. On the label belonging to this specimen the following is mentioned: «*Chukhrovite. Intergrowths of pinkish cube-octahedrons with white gearsutite. Kara-oba, vein # 8, Djambul quarry, NE Akdala, Central Kazakhstan. Collected in 1950, V.I. Stepanov*». The specimen is represented by a piece of milky-white quartz of columnar constitution (8x6x2 cm in size) with powdery coatings and crusts of ochreous colour and white, chalk-like concretions of gearsutite and halloysite. Rarely in the quartz there are small laths of ferberite and pseudomorphs of goethite after pyrite. The ochreous colour of the powdery coatings on the surface of the quartz is caused by fine-grained aggregates of jarosite, plumbojarosite, beudantite, and as yet undetermined iron hydroxides. In cavities among broken quartz crystals and along cracks there are segregations and individual crystals of the chukhrovite group mineral, up to 1 mm in diameter. Some crystals are water-clear, others are opaque and have a weak pink tint. Separate zones of growth that could be observed in zoned and sectored crystals in COMPO and AEI (Fig. 2) correspond to chukhrovite-(Nd) by chemical composition.

If not mentioned specifically, in all cases below the data on chukhrovite-(Nd) is from the first specimen.

Physical properties

Chukhrovite-(Nd) is a transparent mineral, most often colourless, and rarely, when translucent, white. The lustre is vitreous, slightly greasy. Streak is white. The mineral is brittle.

Cleavage on {111} is not easily visible. Hardness is 3.5-4 on Mohs' scale. Micro-indentation hardness measurements with VHN load of 30 gram gave a mean value 193 kg/mm² (from 177 to 213 kg/mm²). Density determined by suspending of mineral grains in Clerici solution was 2.42(3) g/cm³; calculated density was 2.421 g/cm³.

In immersion the sample is colourless, it has anomalous interference colours from dark-grey to grey and undulating running extinction. Refractive index measured in a mixture of glycerine with water at 589 nm is $n = 1.443(2)$.

Infrared spectrum of chukhrovite-(Nd) obtained with Specord-75IR spectrometer (tablet of mineral with KBr) is characterized by following strong absorption bands: 3548, 3423, 1630, 1090, 586, 465 cm⁻¹ (Fig. 3). The presence of crystallization water in mineral is confirmed by bands in the ranges 3600-3200 cm⁻¹ and 1630 cm⁻¹ and sulphate tetrahedra indicated by the strong band at 1090 cm⁻¹.

The compatibility Index of properties and chemical composition, which was calculated by Gladstone and Dale equation, is $1 - (\text{Kp}/\text{KC}) = 0.012$ (excellent).

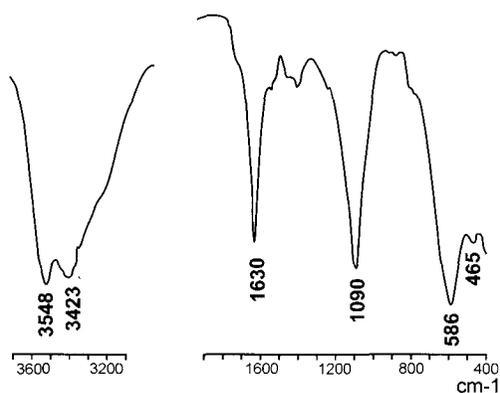


Fig. 3. Infrared spectrum of chukhrovite-(Nd)

Chemical composition

Chemical composition of the new mineral was determined with by JXA-50A (JEOL) electron microprobe instrument equipped with three wave spectrometers and an energy-dispersive spectrometer. The energy-dispersive spectrometer analyses were obtained at accelerating voltage $U = 20$ kV and electron microprobe current $I = 2$ nA, beam diameter was $2 \mu\text{m}$. The etalons were as follows: anorthite USNM 137041 (Ca, Al, Si); Y_2O_3 (Y); LaF_3 (La); CeF_3 (Ce); NdPO_4 (Nd); SmPO_4 (Sm); PrPO_4 (Pr); GdPO_4 (Gd); Dy_2O_3 (Dy); Ho_2O_3 (Ho); BaSO_4 (S). Fluorine was determined with a wave spectrometer at accelerating voltage $U = 15$ kV, electron microprobe current $I = 25$ nA, and beam diameter $5 \mu\text{m}$. Calculation of concentrations was made by CARAT program. The homogeneity of the grains was checked by scanning their profiles with wave spectrometers.

Zonal distribution of yttrium and rare-earth elements in the grains of chukhrovite-(Nd) from the first specimen was not revealed. Average chemical composition and fluctuation of component contents by analyses of 8 grains are given in Table 1. Because of the lack of material the water was not determined by the direct method; its content was calculated by difference. Empirical formula (based on the sum of cations, $\text{Ca} + \text{REE} + \text{Al} = 6$) from these analyses is as follows: $\text{Ca}_{3.06}(\text{Nd}_{0.32}\text{Y}_{0.15}\text{La}_{0.12}\text{Sm}_{0.09}\text{Ce}_{0.07}\text{Pr}_{0.07}\text{Gd}_{0.05}\text{Dy}_{0.02}\text{Ho}_{0.01})_{0.90}\text{Al}_{2.03}\text{S}_{1.01}\text{O}_{3.96}\text{F}_{13.06} \cdot 11.87\text{H}_2\text{O}$. The ideal formula is $\text{Ca}_3(\text{Nd,Y})\text{Al}_2(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$.

In comparison, the crystals of the mineral from the second specimen have pronounced zoning and sectoring (fig. 2). In the photo the light growth zones and sectors are enriched by neodymium and accordingly depleted by yttrium. In such crystals the separate zones correspond by chemical composition to chukhro-

Table 2. Results of calculation of X-ray powder pattern of chukhrovite-(Nd)

l	$d_{\text{meas}}, \text{\AA}$	$d_{\text{calc}}, \text{\AA}$	hkl
10	9.7	9.676	1 1 1
7	5.92	5.925	2 2 0
3	5.04	5.053	3 1 1
1	4.87	4.838	2 2 2
4	4.20	4.190	4 0 0
3	3.85	3.845	3 3 1
8	3.22	3.225	5 1 1
1	2.957	2.963	4 4 0
3	2.836	2.833	5 3 1
4	2.646	2.650	6 2 0
7	2.555	2.556	5 3 3
3	2.343	2.347	7 1 1
5	2.240	2.239	6 4 2
6	2.180	2.182	7 3 1
1	2.096	2.095	8 0 0
3	1.975	1.975	8 2 2
2	1.936	1.935	7 5 1
5	1.827	1.829	8 4 2
1	1.756	1.757	9 3 1
4	1.681	1.684	7 7 1
1	1.641	1.643	10 2 0
0.5	1.611	1.613	10 2 2
0.5	1.562	1.563	9 5 3
1	1.511	1.511	11 1 1
1	1.461	1.464	9 7 1
0.5	1.418	1.416	10 6 2
0.5	1.358	1.359	10 6 4
1	1.282	1.282	11 7 1
0.5	1.201	1.200	13 5 1
0.5	1.141	1.140	14 4 2
0.5	1.077	1.075	11 11 1
0.5	1.063	1.064	12 10 2
0.5	1.039	1.041	13 9 3
0.5	1.009	1.009	16 4 2

vite-(Nd), and the others correspond to chukhrovite-(Y). Incomplete analyses (obtained with energy-dispersive spectrometer at $U = 20$ kV, $I = 2$ nA) are given in Table 1. The Y and Nd concentration profiles across the crystal, were obtained with wave spectrometers. They are shown on Figure 2.

X-ray data

X-ray study of the mineral was made by powder method. X-ray powder pattern was obtained using RKU-114 mm camera, Mn filtered FeK radiation. Corrections were inserted by separate

Table 3. Comparison of data on chukhrovite-(Nd), chukhrovite-(Y), chukhrovite-(Ce), and menyailovite

	Chukhrovite-(Nd) Ca ₃ (Nd,Y)Al ₂ (SO ₄)F ₁₃ ·12H ₂ O	Chukhrovite-(Y) Ca ₃ (Y,Ce)Al ₂ (SO ₄)F ₁₃ ·12H ₂ O	Chukhrovite-(Ce) Ca ₃ (Ce,Nd)Al ₂ (SO ₄)F ₁₃ ·12H ₂ O	Menyailovite Ca ₄ AlSi(SO ₄)F ₁₃ ·12H ₂ O
Space group	<i>Fd3</i>	<i>Fd3</i>	<i>Fd3</i>	<i>Fd3</i>
<i>a</i> , Å	16.759	16.80	16.80	16.722(2)
Z	8	8	8	8
Strong lines on X-ray powder pattern, d (l)	9.7(10)		9.75(10)	9.63(10)
	5.92(7)		5.93(8)	5.91(7)
	4.20(4)	3.261(9)	4.20(5)	4.173(4)
	3.22(8)	2.843(8)	3.22(7)	3.219(7)
	2.555(7)	2.572(9)	2.56(6)	2.551(7)
	2.240(5)	2.193(10)	2.24(5)	2.235(5)
	2.180(6)	1.834(10)	2.17(6)	2.178(8)
	1.827(5)	1.684(8)	1.824(5)	1.824(5)
	1.512(8)			
Density (measured), g/cm ³	2.42	2.274 – 2.398		2.25
<i>n</i>	1.443	1.42 – 1.44	1.443	1.430
Reference	Our data	Ermilova <i>et al.</i> , 1960	Walenta, 1978	Vergasova <i>et al.</i> , 2004

film with NaCl. Indexing was made by analogy with chukhrovite-(Y). Calculation of X-ray powder pattern is given in Table 2. The mineral has cubic symmetry, space group *Fd3*, *a* = 16.759(3) Å, *V* = 4707.0(1) Å³, *Z* = 8.

Discussion

At present it is possible to distinguish the chukhrovite group, including three rare-earth silicon-free minerals with general formula Ca₃REEAl₂(SO₄)F₁₃·12H₂O, i.e. chukhrovite-(Y), chukhrovite-(Ce), chukhrovite-(Nd), and the silicon-bearing REE-free mineral, menyailovite, with the formula Ca₄AlSi(SO₄)F₁₃·12H₂O. The scheme of isomorphism among REE-minerals of this group and menyailovite can be represented as: Al_{VII}³⁺ + REE_{VII}³⁺ = > Si_{VII}⁴⁺ + Ca_{VII}²⁺. It is very difficult to judge the scale and borders of such isomorphism in natural specimens of the chukhrovite group minerals, because there are only a limited number of published chemical analyses available. By these few analyses of natural rare-earth chukhrovites the ratio Ca:REE is close to 3:1, in artificial analogues of chukhrovite the significant deviation from this ratio was obtained (Sokolova, Konovalova, 1981). However, there is no strict evidence that the synthetic analogue of chukhrovite chemical analyses obtained by wet chemistry methods reflects the composition of a homogenous phase.

Minerals of the chukhrovite group are studied up to different level. By contemporary

nomenclature known as chukhrovite-(Y) with strong predominance of yttrium over lanthanides was the first mineral of this group discovered at the Kara-Oba deposit (Ermilova *et al.*, 1960). In the first description two chemical analyses were given, the rare-earth elements were determined by X-ray spectral method from the sediment precipitated from the mineral. Yttrium was not determined, but calculated by difference. The predominance of yttrium over lanthanides in many samples of chukhrovite from Kara-Oba is also confirmed by our microprobe electron analyses.

Another specimen of Y-dominant chukhrovite was found by M.I. Novikova (1973) in Siberia. Although unsuccessful in obtaining the complete chemical analysis of this mineral, the sum of rare-earth elements was determined, measuring 14.11%; the spectrum of these elements was detected by X-ray method. We shall note that in this work there are the contents of rare-earth oxides expressed in weight percents and relative weight percents of rare-earth elements from the sum of rare-earth oxides, but not atomic or molecular percents. That results in confusion: in reference literature the references on the work of M.I. Novikova (1973) have appeared as descriptions of chukhrovite-(Ce) although the simple re-calculation of weight percents in atomic ones shows the prevalence of yttrium over any other element from the lanthanides group.

S.V. Ryabenko with co-authors (1985) found the chukhrovite group mineral in a totally different occurrence at the Katugin deposit

(Transbaikalie). It occurred in nest segregations of cryolite with other fluorides. Unfortunately, in the aforementioned work there are no quantitative data about individual rare-earth elements and yttrium; moreover, it is not clear whether yttrium was detected. In this publication there is only a figure, spectrum of rare-earth elements, with not quite clear units on ordinates axis.

For the first time chukhrovite-(Ce) was described at Clara deposit (Oberwolfach, FRG) in barite and fluorite veins (Walenta, 1978). There is no quantitative data on the yttrium content in the mineral in that paper. Apparently, this is the single finding of Ce-dominant chukhrovite up till now. It would be interesting to study Clara deposit chukhrovite-(Ce) again a material of this finding to determine rare-earth elements and yttrium. As it was mentioned before, the mineralogical reference books give wrong information about chukhrovite-(Ce) from Siberia by M.I. Novikova (1973) since that mineral is evidently a chukhrovite-(Y).

The ratio of calcium to the sum of rare-earth elements and yttrium (in atoms per formula unit) is close to 3:1 for all enumerated natural rare-earth minerals from the chukhrovite group that gives the possibility to suppose the ordered distribution of calcium and rare-earth elements in the crystal structure of the mineral. However, at present there is only one work devoted to the study of the crystal structure of rare-earth chukhrovite, which was made by photomethod ($R = 13\%$) and which did not confirm this assumption (Bokii, Gorogotskaya, 1965). The crystal structure of menyailovite (Vergasova *et al.*, 2004) was not studied, but the crystal structure of its synthetic analogue ($R = 2.5\%$) has been determined (Mathew *et al.*, 1981). Thus, refinement of crystal structure of rare-earth representatives of the chukhrovite group and re-study of chukhrovite-(Ce) are the most important tasks in the study of this group of minerals.

Comparative characteristics of the chukhrovite group minerals are given in Table 3.

The sample with the grain of chukhrovite-(Nd) is kept in the Fersman Mineralogical Museum RAS (Moscow).

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