

UDC 549.6

KYRGYZSTANITE*, $\text{ZnAl}_4(\text{SO}_4)(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$, A NEW MINERAL FROM THE KARA-TANGI DEPOSIT, KIRGIZIA

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Kyrgyzstanite is a new hydrous sulphate of aluminium and zinc with the formula $\text{ZnAl}_4(\text{SO}_4)(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$ (monoclinic, sp. group $\text{P2}_1/\text{n}$, $a = 10.246(9) \text{ \AA}$, $b = 8.873(4) \text{ \AA}$, $c = 17.22(1) \text{ \AA}$, $\beta = 96.41(7)^\circ$, $V = 1556(3) \text{ \AA}^3$, $Z = 4$), which has been found in vanadium-bearing slates of the Kara-Tangi deposit (Batken region, Kirgizia) in assemblage with quartz, calcite, alumohydrocalcite, nickelalumite, and allophane. The mineral forms crusts of radiating fibrous aggregates of split crystals. The dominant forms are as follows: {001}, {110}, {010}, and {310}. Colour is light blue to greenish. The mineral is transparent; lustre is vitreous. The Mohs' hardness is 2–2.5; $\text{VHN} = 70 \text{ kg/mm}^2$. Cleavage is perfect on {001}. Density is 2.25(1) (meas), 2.242 g/cm^3 (calc). Kyrgyzstanite is optically negative, biaxial; $n_p = 1.517(1)$, $n_m = 1.525(1)$, $n_g = 1.527(1)$, $2V_{\text{calc}} = 53^\circ$. Dispersion is strong, $r < v$. Orientation is $c \wedge Np = 6^\circ$. Strong lines on X-ray powder diagram are as follows (d, I): 8.60(100), 7.93(70), 4.83(80), 4.27(100), 2.516(70), 2.292(80), 1.998(95), 1.896(65), 1.720(65). Chemical composition (electron microprobe analysis, wt %, average on 6 measurements) is as follows: ZnO 10.02, NiO 4.13, CuO 0.58, FeO 0.32, V_2O_5 0.08, Al_2O_3 38.45, SiO_2 0.33, SO_3 15.00, H_2O 31.10 (wet chemistry), total 99.01. The empirical formula is $(\text{Zn}_{0.65}\text{Ni}_{0.29}\text{Cu}_{0.04}\text{Fe}_{0.02}\text{Al}_{4.00}\text{Si}_{0.03}\text{SO}_4)_{0.99}(\text{OH})_{12.12} \cdot 2.81\text{H}_2\text{O}$.

Kyrgyzstanite is a structural analogue of nickelalumite. Crystal structure of the latter was solved on a single crystal of zinc-rich variety from the same geological formation; it represents brucite-like octahedral layers along {001} (octahedra Al and M). In the interlayer space the single $(\text{SO}_4)^{2-}$ tetrahedra and H_2O molecules are localized. The IR spectrum is given. Mineral genesis is hydrothermal. Kyrgyzstanite was named in honour of Kirgizia (the Republic of Kyrgyzstan), where it was first discovered. Type material has been deposited in the collection of the Fersman Mineralogical Museum, Moscow.

4 tables, 4 figures, 9 references

While carrying out of field works in the summers of 2002–2003, at the area of distribution of vanadium-bearing carbon-flinty slates in Batken region (Kirgizia) at the Kara-Tangi deposit, a zinc analogue of nickelalumite*, kyrgyzstanite, $(\text{Ni,Zn})\text{Al}_4(\text{SO}_4)(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$, was found; it was named in honour of the Republic of Kyrgyzstan, where this mineral was discovered, and where carbon-flinty slates are distributed. We did not name the mineral «zincalumite» in order to avoid confusion with the already existing mineral «zincaluminate».

Occurrence and assemblage

The uranium deposit Kara-Tangi worked in the 1960's is located in a folded zone of the Turkestan range foothills at the northern slope of the Katran-Tau mountains. It is connected to

a zone of strongly folded chlorite-sericite slates of Upper-Silurian age. Within the limits of the deposit, the horizons of boudinated carbon-flinty slates are widespread; uranium-vanadium mineralization is connected to them. The size of the lenses ranges from single meters to several tens of meters. The mineral has been found in the dump and the adit mouth at the right side of Kara-Tangi.

Kyrgyzstanite was encountered in cracks and small cavities in carbon-flinty slates in the form of thin crystal crusts and spherulites composed by radiating-fibrous aggregates, and rarely, separate lamellar split crystals and their intergrowths (Fig. 1) with the size of individuals ranging from 0.2 to 1 mm in assemblage with quartz, calcite, alumohydrocalcite and Zn-rich nickelalumite. One of less split mineral crystals with a well-shaped vertical face band was measured on a two-circle goniometer; however, the

* The mineral was considered and recommended for publication by the RMS (Russian Mineralogical Society) and approved by the IMA Commission on New Minerals and Mineral Names on September 1, 2004.

** At present, the status of nickelalumite is in an indeterminate situation. Description of this mineral was initially published (Martini, 1980) together with two new minerals, its nitrate analogues: mbobomkulite and hydrombobomkulite. In spite of sufficient complete description of nickelalumite, only the two latter minerals were approved by the IMA CNMMN. Nevertheless, nickelalumite was entered in such recognized handbooks as Fleisher's Glossary of Mineral Species 2004 (The Mineralogical Record Inc., 2004) and Hey's Mineral Index (3rd edition, Chapman and Hall, 1993). Recent studies of nickelalumite from Kirgizia (Karpenko *et al.*, 2004a) and also the refinement of the crystal structure of this mineral (Uvarova *et al.*, 2005) confirmed nickelalumite as a valid mineral species. In this connection, the authors have received some recommendations from E. Burke, chairman of the IMA CNMMN. While using the term «nickelumite» in this article, the authors realize the mineral did not pass a formal voting and in parallel carry on work on the rehabilitation of nickelalumite as a recognized mineral species.

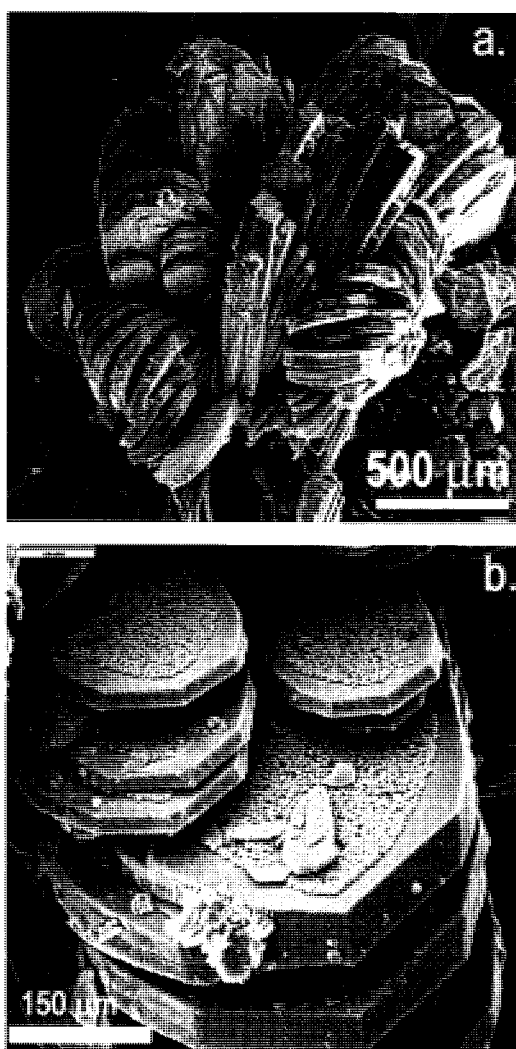


Fig. 1. REM-photo of kyrgyzstanite crystals: a) intergrowth of split crystals; b) fragment of Figure 1a. Kyrgyzstanite crystals are covered by allopheane crust.

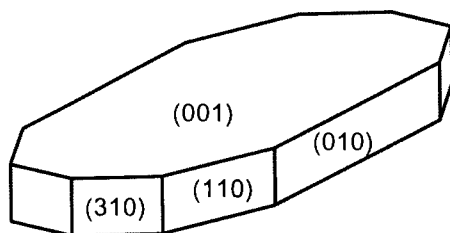


Fig. 2. Drawing of ideal kyrgyzstanite crystal.

Table 1. Chemical composition of kyrgyzstanite (wt %)

Constituent	1	2	3	4	5	6	Average composition
ZnO	8.34	9.13	9.45	9.50	10.73	13.02	10.02
NiO	5.51	4.16	4.34	5.37	3.05	2.36	4.13
CuO	1.17	0.97	0.95	0.15	0.19	0.06	0.58
FeO	0.53	0.41	0.41	0.00	0.38	0.20	0.32
V ₂ O ₅	0.03	0.23	0.00	0.00	0.13	0.06	0.08
Al ₂ O ₃	38.01	38.72	37.85	37.72	38.99	39.42	38.45
SO ₃	14.84	15.21	14.54	14.80	15.95	14.63	15.00
SiO ₂	0.26	0.30	0.42	0.40	0.09	0.52	0.33
H ₂ O	30.10	30.10	30.10	30.10	30.10	30.10	30.10
Total	98.79	99.23	98.06	98.04	99.61	100.37	99.01
Formula coefficients, calculation on 4 Al atoms							
Zn ⁺²	0.55	0.59	0.63	0.63	0.69	0.83	0.65
Ni ⁺²	0.40	0.29	0.31	0.39	0.21	0.16	0.29
Cu ⁺²	0.08	0.06	0.06	0.01	0.01	0.00	0.04
Fe ⁺²	0.04	0.03	0.03	0.00	0.03	0.01	0.02
V ⁺⁵	0.00	0.01	0.00	0.00	0.01	0.00	0.00
[8]Me	1.07	0.98	1.03	1.03	0.95	1.00	1.01
Al ⁺³	4.00	4.00	4.00	4.00	4.00	4.00	4.00
S ⁻⁶	0.99	1.00	0.98	1.00	1.04	0.95	0.99
Si ⁺⁴	0.02	0.03	0.04	0.04	0.01	0.04	0.03
(OH) ⁻	12.24	12.07	12.25	12.22	11.85	12.26	12.12
H ₂ O	2.85	2.74	2.88	2.93	2.80	2.51	2.81

Note. Analysts are A.A. Agakhanov and V.Yu. Karpenko. Coefficients for (OH)⁻ and H₂O are calculated by charge balance

fluctuation of readings was from one to two degrees. When the mean values of signal were compared with theoretical values of spherical coordinates with simplest indexes, they corresponded to the {110}, {010}, and {310} forms (Fig. 2). Often spherulites and crusts of kyrgyzstanite are replaced by white allopheane and as well as bohmite.

Physical properties

Colour of kyrgyzstanite is light blue, greenish. The mineral is transparent; lustre is vitreous. The Mohs' hardness is 2-2.5. Micro-indentation hardness (VHN) of 70 kg/mm² (mean value of 20 measurements between 47 to 87 kg/mm²). Micro-hardness was obtained with PMT-3 instrument at a load of 20 g, calibrated by NaCl. Cleavage is perfect on (001). The mineral is easily split on to plates. Mineral density was deter-

Table 2. Coincidence indexes of some sulphates of aluminium

Mineral	Formula	$k \text{ Al}_2\text{O}_3$		Coincidence index	
		for sulphates	for other minerals	for sulphates	for other minerals
Basaluminite	$\text{Al}_4(\text{SO}_4)(\text{OH})_{10}(\text{H}_2\text{O})_{4.5}$	0.233	0.217	0.078	0.023
Cyanotrichite	$\text{Cu}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}(\text{H}_2\text{O})_2$	0.269	0.253	0.032	0.007
Chalcoalumite	$\text{CuAl}_4(\text{SO}_4)(\text{OH})_{12}(\text{H}_2\text{O})_3$	0.255	0.238	0.088	0.035
Kyrgyzstanite*	$(\text{Zn}, \text{Ni})\text{Al}_4(\text{SO}_4)(\text{OH})_{12}(\text{H}_2\text{O})_3$	0.250	0.237	0.067	0.018

Note. Data for calculation were taken from Handbook of mineralogy (Anthony *et al.*, 2003)

* – our data were used for calculation.

mined by grain balancing in a water solution of Clerici liquid. Experimental density is $2.25(2) \text{ g/cm}^3$, calculated density is 2.242 g/cm^3 . Kyrgyzstanite is optically negative, biaxial. Refraction indexes measured by immersion method (at 589 nm) are as follows: $n_p = 1.517(2)$, $n_m = 1.525(2)$, $n_g = 1.527(2)$. Calculated angle $2V = -53^\circ$. Dispersion is strong, $r < v$. Orientation is $c \wedge N_p = 6^\circ$. The mineral is insoluble in water; it dissolves during heating in HCl (1:1). The IR spectra of kyrgyzstanite were obtained with the IR Fourier spectrometer Nicolet; mineral sample was pressed into KBr tablet with a weight of 20 mg (Fig. 3). Bands at 600, 935, and 1100 cm^{-1} correspond to stretching vibrations of SO_4 -tetrahedra; an intensive band at 1632 cm^{-1} is connected with bending vibrations $\delta_{\text{H}_2\text{O}}$; range $3300\text{--}3500 \text{ cm}^{-1}$ conforms to stretching asymmetrical vibrations of (OH) groups.

Chemical composition

The chemical composition of kyrgyzstanite was studied with electron microprobe instrument JXA-50A equipped with energy-dispersive spectrometer Link (Table 1). Analyses were made on EDS with accelerating voltage to 20 kV, electron microprobe current was $3 \times 10^{-9} \text{ A}$. The following standards were used: microcline USNM 143966 (Si, Al), ilmenite USNM 96189 (Fe), gahnite USNM 145883 (Zn), metallic V and Cu (V, Cu), NiO (Ni), barite (S). Grains of the new mineral are homogenous and free from intergrowths of other minerals. Calculation of concentrations was made with using ZAF correction.

Water was detected by weight loss during combustion of a 5 mg sample. Ignition was made in a platinum boat in a muffled furnace at $500\text{--}550^\circ\text{C}$.

The empirical formula of the mineral is as follows: $(\text{Zn}_{0.65}\text{Ni}_{0.28}\text{Cu}_{0.04}\text{Fe}_{0.02})_{0.99} \text{Al}_{4.00}\text{Si}_{0.03}(\text{SO}_4)_{0.99}(\text{OH})_{12.12} \cdot 2.81\text{H}_2\text{O}$, the ideal formula is $\text{ZnAl}_4(\text{SO}_4)(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$ (calculation on 4 Al atoms).

Since kyrgyzstanite is a hydroxyl-bearing sulphate of aluminium and zinc, the compatibility index $(1 - k_p/k_c)$ can be calculated in two ways, using different values of k for Al_2O_3 . Depending on the mineral belonging to either mineral class, there are different k values for sulphates and selenates (0.242), for nesosilicates and inosilicates (0.176), and for other mineral classes (0.207) (Mandarino, 1981). If k is used for other mineral classes, the compatibility index is 0.018, which corresponds to «superior» degree; if it uses k for sulphates and selenates, the index is 0.067, which is classed as «fair». We have calculated the compatibility indexes for a number of hydroxyl-bearing sulphates of aluminium with similar chemical compositions (Table 2), using different k for Al_2O_3 , and found that the best results can be obtained with a calculation of $k_{\text{Al}_2\text{O}_3}$ for other classes (0.207).

X-ray data

X-ray powder diagram of kyrgyzstanite was obtained by photomethod using the RKU 114 mm camera, $\text{FeK}\alpha$ radiation, Mn filter (Table 3). Quartz was used as internal standard.

Similarity of physical properties, chemical composition, and X-ray powder diffraction data shows that kyrgyzstanite and nickelalumite are, in all probability, the members of an isomorphous series. Recently Yu. Uvarova with co-authors solved the crystal structure of zinc-roch nickelalumite from the same deposit (Uvarova *et al.*, 2005). By virtue of aforesaid, we shall note brief data of this study. Nickelalumite, $(\text{Ni}, \text{Zn})\text{Al}_4(\text{SO}_4)(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$, belongs to the monoclinic system and has the following unit cell parameters: $a = 10.2567(5) \text{ \AA}$, $b = 8.8815(4) \text{ \AA}$, $c = 17.0989(8) \text{ \AA}$, $\beta = 95.548(1)^\circ$, $V = 1550.3(2) \text{ \AA}^3$; space group $P2_1/n$, $Z = 4$. Its crystal structure was solved by direct method and refined with factor $R_1 = 5.7\%$ for 1554 unique reflexes ($F_o > 4\sigma F$)

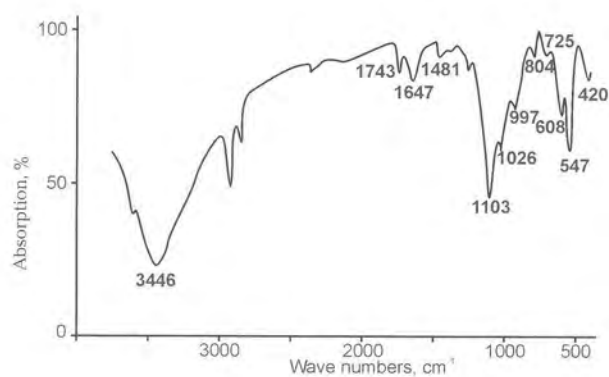


Fig. 3. The IR spectrum of kyrgyzstanite.

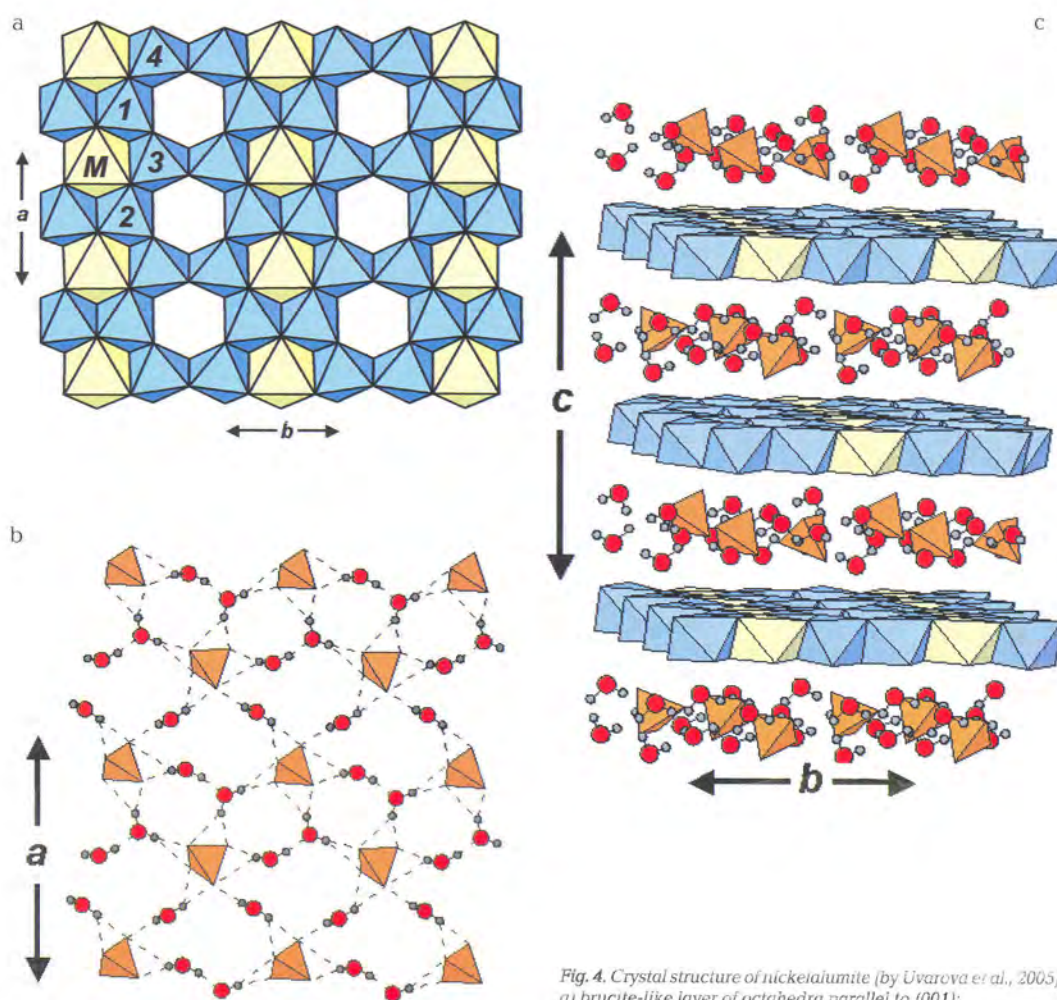


Fig. 4. Crystal structure of nickelaumite [by Uvarova et al., 2005]:
 a) brucite-like layer of octahedra parallel to (001);
 b) hydrogenous bonds of (SO_4) tetrahedra and (H_2O) groups;
 c) perspective view of crystal structure along (001).
 M octahedra are light yellow, Al octahedra are pale blue,
 S tetrahedra are orange; atoms of oxygen are marked by red circles;
 atoms of hydrogen are marked by small grey circles

on diffractometer Bruker P4 (MoK α radiation, Smart 4K CCD detector). In the crystal structure there are five octahedral sites. Among them, the M site is occupied predominantly by Ni and Zn with a small amount of V and Fe: $(\text{Ni}_{0.55}\text{Zn}_{0.39}\text{V}_{0.02}\text{Fe}_{0.01})_{\Sigma 0.97}(<\text{M-OH}> = 2.079 \text{ \AA})$. Four other sites are occupied predominantly by Al ($<\text{Al-OH}> = 1.900 \text{ \AA}$). There is one S site with tetrahedral coordination ($<\text{S-O}> = 1.468 \text{ \AA}$) and also three sites occupied by H_2O molecules, and twelve sites occupied by (OH) groups. Main elements of nickelalumite structure are the octahedral layers along (001) consisting of Al and M octahedra (Fig. 4a, c). Al octahedra are connected by common edges and form six-fold rings with another octahedron in the centre. A half of these octahedra are occupied by Ni and Zn (M site); the remaining half of these octahedra are vacant. This framework is analogous to brucite, in which a sixth part of the octahedral sites is vacant. (SO_4) tetrahedra and H_2O molecules are localized in the inter-layer space and connected with each other by hydrogenous bonds (Fig. 4b, c).

Nickelalumite is stoichiometrically close to mbobomkulite, $(\text{Ni,Cu}^{2+})\text{Al}_4[(\text{NO}_3)_1(\text{SO}_4)_2(\text{OH})_{12}(\text{H}_2\text{O})_3]$, hydrombobomkulite, $(\text{Ni,Cu}^{2+})\text{Al}_4[(\text{NO}_3)_1(\text{SO}_4)_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}]$ (Martini, 1980), and chalcoalumite, $\text{CuAl}_4(\text{SO}_4)(\text{OH})_{12} \cdot (\text{H}_2\text{O})_3$ (Larsen, 1925; Williams, BaSaw Khin, 1971). The crystal structures of these minerals are unstudied, but the unit cell parameters are close to the ones of nickelalumite. Octahedral layers in the crystal structure of nickelalumite are topologically close to the same layers of alvanite, $(\text{Zn,Ni})\text{Al}_4(\text{VO}_3)_2(\text{OH})_{12}(\text{H}_2\text{O})_2$ (Pertlik, Dunn, 1990) and ankinovichite, $\text{NiAl}_4(\text{VO}_3)_2(\text{OH})_{12}(\text{H}_2\text{O})_2$ (Karpenko *et al.*, 2004b). The presence of chains composed of doubled tetrahedra $[\text{VO}_3]_2^{1-}$ distinguishes the crystal structure of nickelalumite. Comparative characteristics of X-ray data, physical, and crystal structural properties of kyrgyzstanite, chalcoalumite, and nickelalumite are given in Table 4.

Acknowledgements

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Table 3. X-ray powder diagram of kyrgyzstanite

l_0	$d_{\text{meas.}}$	$d_{\text{calc.}}$	hkl
100	8.60	8.557	0 0 2
70	7.93	7.877	0 1 1
80	4.83	4.798	0 1 3
30	4.71	4.755	1 0 3
20	4.61	4.607	2 0 -2
100	4.27	4.278	0 0 4
30	3.85	3.854	0 1 4
20	3.50	3.502	0 2 3
30	3.355	3.360	1 0 -5
50	3.193	3.193	0 1 5
50	3.056	3.060	3 1 1
10	2.796	2.797	2 2 3
		2.795	0 3 2
50	2.723	2.721	1 3 -2
70	2.516	2.518	4 0 -2
30	2.489	2.489	2 3 -2
20	2.442	2.440	1 0 -7
80	2.292	2.288	4 1 2
30w	2.230	2.230	4 1 -4
		2.230	3 3 0
30w	2.210	2.208	4 2 0
20w	2.099	2.100	4 1 -5
		2.098	3 0 -7
95	1.998	1.999	2 4 -2
65w	1.896	1.897	3 2 -7
		1.897	4 1 5
30	1.849	1.849	4 3 2
40	1.807	1.806	2 4 4
65	1.720	1.720	2 3 7
20	1.697	1.697	3 3 6
50w	1.558	1.558	1 3 9
40w	1.480	1.480	2 2 10
30	1.469	1.469	2 5 -6
30	1.457	1.457	5 4 2
		1.457	0 6 2
20	1.144	1.444	3 1 10
		1.444	7 1 -1
		1.444	0 4 9
30w	1.395	1.396	7 0 -5
		1.394	2 6 2
20	1.372	1.372	5 1 -10
		1.372	4 5 -5
40	1.355	1.355	3 5 -7
		1.355	0 4 10
30	1.311	1.311	7 3 -1
		1.311	1 6 -6
30	1.296	1.296	2 5 8
10	1.274	1.274	0 4 11

Conditions: URS-50IM, FeK α radiation, Mn filter, sample – rubber post ($d=0.15 \text{ mm}$), camera RKD-114; w – widening of line; data used for calculation of unit cell parameters are marked by semi-bold. Analyst V. Yu. Karpenko

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100	8.60	8.557	002
70	7.93	7.877	011
80	4.83	4.798	013
30	4.71	4.755	103
20	4.61	4.607	202
100	4.27	4.278	004
30	3.85	3.854	014
20	3.50	3.502	023
30	3.355	3.360	105
50	3.193	3.193	015
50	3.056	3.060	311
10	2.796	2.797	223
		2.795	032
50	2.723	2.721	132
70	2.516	2.518	402
30	2.489	2.489	232
20	2.442	2.440	107
80	2.292	2.288	412
30w	2.230	2.230	414
		2.230	330
30w	2.210	2.208	420
20w	2.099	2.100	415
		2.098	307
95	1.998	1.999	242
65w	1.896	1.897	327
		1.897	415
30	1.849	1.849	432
40	1.807	1.806	244
65	1.720	1.720	237
20	1.697	1.697	336
50w	1.558	1.558	139
40w	1.480	1.480	2210
30	1.469	1.469	256
30	1.457	1.457	542
		1.457	062
20	1.144	1.444	3110
		1.444	711
		1.444	049
30w	1.395	1.396	705
		1.394	262
20	1.372	1.372	5110
		1.372	455
40	1.355	1.355	357
		1.355	0410
30	1.311	1.311	731
		1.311	166
30	1.296	1.296	258
10	1.274	1.274	0411

Conditions: URS-501M, FeK α radiation, Mn filter, sample – rubber post ($d=0.15 \text{ mm}$), camera RKD-114; w – widening of line; data used for calculation of unit cell parameters are marked by semi-bold. Analyst V.Yu. Karpenko

Table 4. Comparative characteristic of kyrgyzstanite, chalcoalumite, and nickelalumite

	Kyrgyzstanite	Chalcoalumite, Bisbee, Arizona (Williams and Khin, 1971)	Nickelalumite, Mbobomkulu (Martini, 1980)
Formula	$\text{ZnAl}_4(\text{SO}_4)(\text{OH})_{12}\cdot 3\text{H}_2\text{O}$	$\text{Cu}^{+2}\text{Al}_4(\text{SO}_4)(\text{OH})_{12}\cdot 3\text{H}_2\text{O}$	$(\text{Ni}, \text{Cu}^{+2})\text{Al}_4[\text{SO}_4, (\text{NO}_3)_2](\text{OH})_{12}\cdot 3\text{H}_2\text{O}$
Space group, system.	P21/n	P21	Mon. s.
a , Å	10.246	17.090	10.175
b , Å	8.873	8.915	8.860
c , Å	17.220	10.221	17.174
β , °	96.41°	95.88°	95.95°
Z	4	4	4
Strong lines on	8.60(100)	8.502(100)	8.543(100)
X-ray powder diagram	7.93(70)	7.898(22)	7.877(20)
$d_{\text{meas.}}(\text{Å})$	4.83(80)	4.786(22)	
	4.27(100)	4.250(91)	4.267(10)
		4.178(23)	
		3.287(45)	
	2.516(70)	2.520(11)	2.507(15)
	2.292(80)		2.289(15)
	1.998(95)		1.997(20)
	1.896(65)		
	1.720(65)		
Colour	Bluish, turquoise	Turquoise-green, pale grey	Pale blue
D, g/cm ³			
(meas./calc.)	2.25/2.227	2.29/2.25	2.24/2.28
	Biaxial (-)	Biaxial (+)	Biaxial (+)
n_p	1.517	1.523	1.532
n_m	1.525	1.525	—
n_y	1.527	1.532	1.543

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