

NEW DATA ON KALUSHITE (SYNGENITE)

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ABSTRACT

A lot of kalushite (syngenite) crystals from Kalush area (the Precarpathians, Ukraine) are studied using goniometry, scanning electron microscopy, infrared absorption and reflection spectroscopy and microthermometry of fluid inclusions. Most of the crystals have {100} pinacoidal habit. Main simple forms of the crystals are {100}, {010}, {001}, {101}, { $\bar{1}01$ }, {110} and {011}. Infrared spectra of the crystals obtained are typical for syngenite and confirm its structure peculiarities. Kalushite begins to crystallize at 60 – 67°C. At the end of this process temperature falls to 40 – 47°C.

Key words: kalushite (syngenite), crystallomorphology, simple forms, infrared spectroscopy, fluid inclusions, genesis.

INTRODUCTION

Most than 50 mineral species were discovered in the Carpathian region (Szakáll and Papp 1996). Only two of them were found in the Ukrainian part of the Carpathians: syngenite from Kalush area (the Precarpathians) and karpatite from Oleneve area (the Transcarpathians). Syngenite was described almost simultaneously by J.Rumph and V.Zepharowicz in 1872 (Korobtsova 1955). The former author had discovered this mineral on half year earlier and named it as kalushite, the later one named his find as syngenite. Later syngenite was found in other occurrences of the Precarpathians (Morshyn, Stebnyk). These crystals were described by R.Zuber in 1904, J.Tokarski in 1910 and 1913 and Cz.Kuzniar in 1934. In 1955 (Korobtsova 1955) considerable progress has been made in the systematic research of kalushite. Our main goal in this study is to present results of complex investigations of kalushite from new occurrence and to compare them with already published data. Statistically representative set of kalushite crystals (about 500 samples) from gypsum – clay cap (sole mark 265 – 270 m) of Dombrove quarry of Kalush-Golyn' group deposits was examined. Kalushite crystals were extracted from gray clay. of The crystal size is 0.5-30 mm along [001]. Crystals are transparent or semitransparent. Their faces are often covered by microcrystals of mirabilite.

GEOLOGICAL SETTING

All finds of kalushite were made in potassium-magnesium salts deposits and occurrences of the Precarpathian marginal trough: Kalush, Morshyn and Stebnyk. The deposits are situated in Miocene

molasse sedimentary rocks: in clays with seams of argillithes, aleurolites and sandstones. Kalush potassium-bearing strata is spread within the limits of two synclines: Kalush and Golyn'. New find of kalushite crystals was made in sediments of Golyn' syncline. Here potassium-bearing strata has thickness of 300-600 m. It contains layer and breccial clays with lens of halite and potassium salts which are represented by langbeinite-kainite rock and sylvinite. In the Precarpathian deposits kalushite associates with halite, sylvite, gypsum, mirabilite and glaserite. The kalushite crystals were also found in the places of contemporary crystallization from high-salinity mines solutions.

MINERALOGICAL RESULTS

Crystallomorphology. Kalushite crystallography has been sufficiently studied by J. Rumpf in 1872, V.Zepharowicz in 1872, 1873, K.Ubra in 1873, A.Laskiewicz in 1927, 1934, 1936 (Korobtsova 1955) and L.Gorogotskaya in 1966. Our investigations of many kalushite crystals from Dombrove occurrence give evidence that their habit is often determined by {100} pinacoid (Fig.1,3).

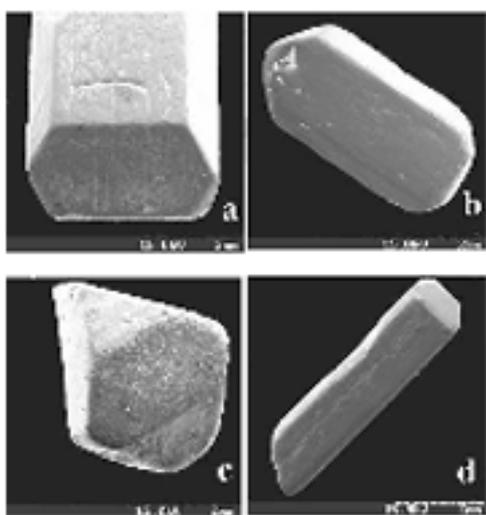


Fig.1



Fig.2

Fig.1. Some morphological types of kalushite crystals from Dombrove quarry (SEM): a – thick tabular {100} pinacoidal crystal, b – thin tabular {100} pinacoidal crystal with well-developed {011} faces, d – {110} prismatic crystal (top view), d - {100} pinacoidal crystal with [001] prolongation

Fig.2. Cavities of dissolution on (100) face of kalushite crystal from Dombrove quarry, x 110

Kalushite crystals of {100}+{110} pinacoidal-prismatic habit and {110} prismatic habit are very rare. Owing to peculiarities of kalushite structure (Gorogotskaya 1966) crystals are often prolonged along [001]. Well-developed and widespread forms on investigated crystals are represented by {100}, {010}, {001}, {101}, { $\bar{1}01$ }, {110} and {011}. The facets of most kalushite crystals, which have been exposed to natural etching, contain a multitude of cavities (Fig.2).

List of all known simple forms of syngenite crystals, their distribution and development according to their interplanar distances is given in the table. This list is based on the crystallographic data published by V.Goldschmidt (1922), J.Dana et al. (1953), Eu.Lazarenko et al. (1962) and L.Gorogotskaya (1966). Theoretical coordinates φ , ρ and d_{hkl} have been calculated by us according

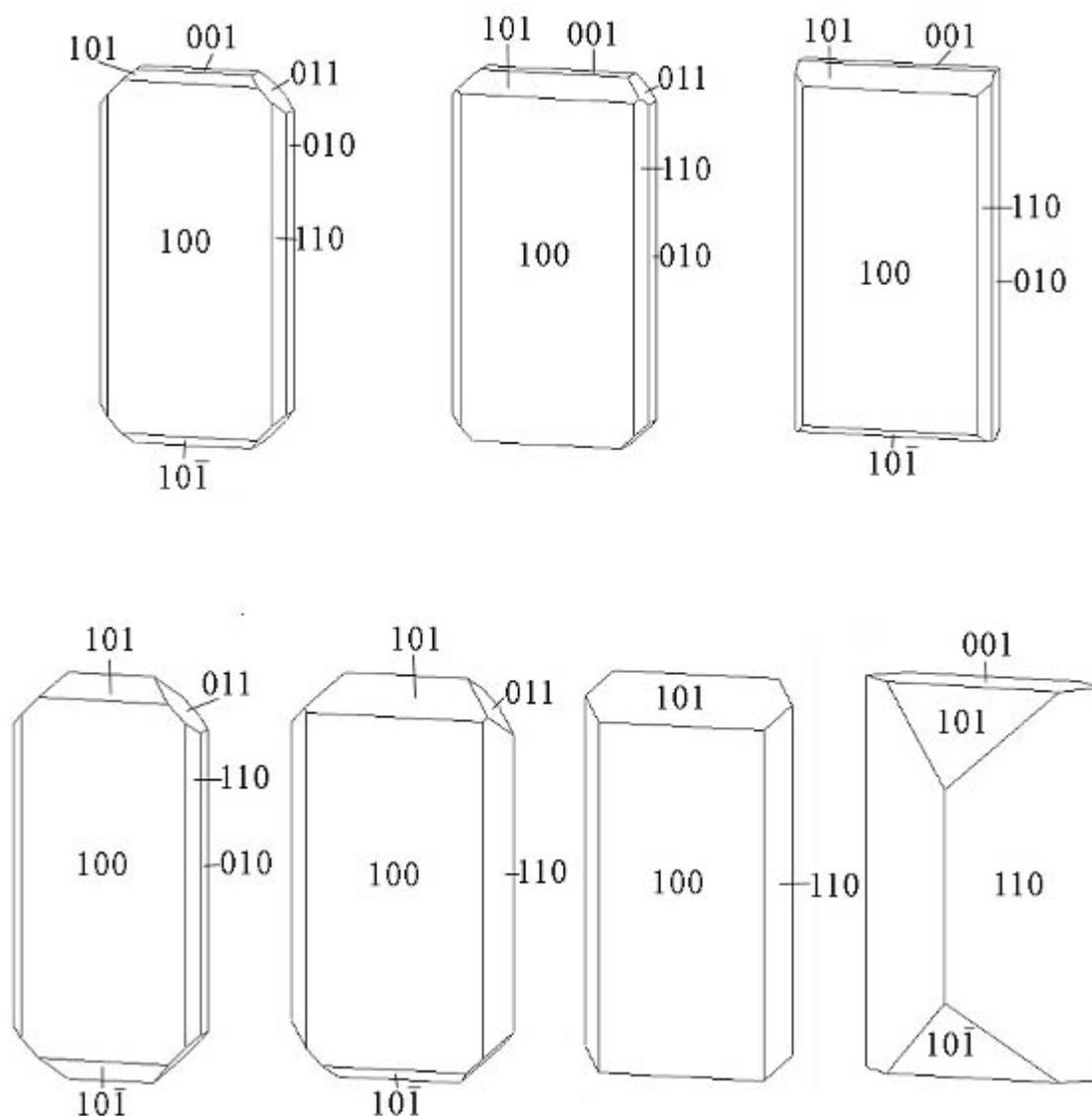


Fig.3. Main morphological types of kalushite crystals from Dombrove quarry

to x-ray data (JCPDS 1978 #28-739 ($a_0=9.777(2)$, $b_0=7.147(2)$, $c_0=6.250(2)$, $\beta=104^\circ 01' (2)$). It is clear that the forms with big values of d_{hkl} are most frequently occurring and well-developed faces on syngenite crystals.

Infrared spectroscopy. In IR-spectrum of kalushite, obtained with using of standard method of pellets with KBr (spectrophotometer UR-20, Carl Zeiss, Jena), corresponds to IR-spectrum of syngenite from Kalush (Adler and Kerr 1965) and Inowroclaw (Fijat and Starczyk 1970; Moenke 1962). The following absorption bands of S–O bonds of SO_4 tetrahedra are observed: ν_3 (asymmetric stretchings) - 1190,

1138, 1126, 1110 cm^{-1} , ν_1 (symmetric stretchings) - 1005 и 985 cm^{-1} ; ν_2 - 470 и 442 cm^{-1} and ν_4 - 675, 645, 605 and shoulder 620 cm^{-1} (bendings). The broad band with main maximum at 3315 cm^{-1}

Simple forms of syngenite crystals

Table

Simple forms	Well-developed forms	Wide spread forms	Theoretical coordinates		d_{hkl} , theoretical data	d_{hkl} , x-ray data (JCPDS 1978, #28-739)
			φ	ρ		
100	++++*	++++*	90° 00'	90° 00'	9.486	9.490
010	+++	+++	0° 00'	90° 00'	7.147	
001	+++	++	90° 00'	14° 01'	6.064	
$\bar{1}01$	+++	++	-90° 00'	22° 06'	5.784	
110	+++	+++	36° 51'	90° 00'	5.708	5.710
101	+++	+++	90° 00'	42° 09'	4.626	
011	++++	+++	15° 55'	42° 17'	4.624	4.624
$\bar{1}11$	++	++	-24° 53'	43° 57'	4.496	4.496
$\bar{2}01$	+	+	-90° 00'	46° 42'	4.271	
210	++	++	56° 17'	90° 00'	3.952	3.954
111	+	+	45° 59'	51° 32'	3.883	3.887
$\bar{2}11$	+	+	-50° 31'	53° 59'	3.667	
120	+	+	20° 32'	90° 00'	3.344	3.347
211			60° 44'	60° 48'	3.042	
310	+++	+++	66° 01'	90° 00'	2.892	2.891
$\bar{1}12$			-10° 08'	23° 57'	2.856	2.855
$\bar{2}21$	++	++	-31° 15'	63° 57'	2.741	2.741
221			41° 44'	66° 54'	2.448	2.447
410			71° 33'	90° 00'	2.251	2.250
411			73° 03'	71° 33'	1.968	
510			75° 03'	90° 00'	1.834	
203			90° 00'	34° 28'	1.716	
430			44° 59'	90° 00'		
520			61° 54'	90° 00'		
610			77° 28'	90° 00'	1.544	
$\bar{3}04$			-90° 00'	13° 36'	1.518	
124			43° 24'	31° 02'	1.338	
710			79° 13'	90° 00'	1.331	
720			69° 08'	90° 00'	1.267	
304			90° 00'	36° 33'	1.254	
810			80° 32'	90° 00'	1.170	
$\bar{7}04$			-90° 00'	41° 54'	1.159	
504			90° 00'	46° 55'	1.065	
650			41° 58'	90° 00'	1.060	
10.3.0			68° 10'	90° 00'	0.881	

* most developed and most spread forms

and shoulders 3520 and 3385 cm^{-1} is usually attributed to stretching vibrations of the water molecule ν_{OH} , the band 1675 cm^{-1} to its bending vibrations δ_{OH} . Interpretation of the band 750 cm^{-1} is not obvious as of the previous ones. Its shift to 550 cm^{-1} in the spectrum of the deuterated sample (deuteration in autoclave at $125 - 150^\circ\text{C}$ during 24 hours) allows to attribute it undoubtedly to librating vibration of water molecule ($\nu_{\text{OH}}/\nu_{\text{OD}}=1,36$), which is involved into hydrogen bonds with sulphate oxygen atoms belonging to one of the two different SO_4 -groups. Other SO_4 -group in syngenite structure has no water molecules in its nearest surrounding (Corraza and Sabelli 1967).

For two non-equivalent sulphate groups the factor-group calculation (group $\text{P}2_1/\text{m} - \text{C}_{2\text{h}}^2$, $Z=2$ (Corazza and Sabelli 1967)) gives two independent IR-active sets of vibrations: $2 \times [\nu_1(\text{B}_u) + \nu_2(\text{A}_u + \text{B}_u) + \nu_3(\text{A}_u + 2\text{B}_u) + \nu_4(\text{A}_u + 2\text{B}_u)]$. Five from the six possible bends in ν_3 vibrations region were registered in IR- reflection spectra measured on (100), (010) and (101) faces of kalushite single crystal. In the deuterated sample spectrum on the complicated absorption band ν_3 six maxima are unambiguously fixed whereas in the region of ν_4 vibrations only four intense well resolved bands are seen. Heating at 250°C leads to the total loss of the water and to forming of some anhydrous sulphate. Mineral, moistened by water in air, is slowly transforming to gyps. This transformation is confirmed by its IR-spectrum.

Fluid inclusions. Some groups of fluid inclusions (primary and secondary, Fig.4) have been determined in the kaluszite crystals.

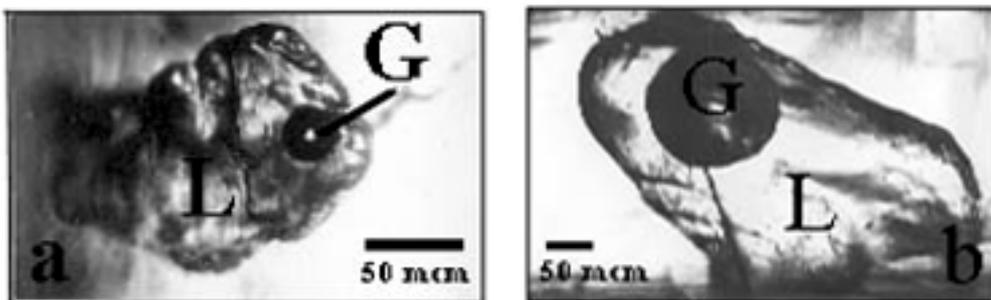


Fig.4. Gas-liquid inclusions in kalushite crystals from Dombrove quarry: a – primary inclusion, $T_{\text{homogenization}}$ of 64°C ; b – secondary overfilled inclusion

Primary inclusions of the first group have either isometric form of negative crystals ($50-70\text{ }\mu\text{m}$ in size) or complex one with a size up to $1-3\text{ mm}$. Most of big inclusions have high degree of filling. All inclusions take place in the central part of the crystals. Inclusions composition is: aqueous solution ($90-95\%$) + gas ($1-2\%$) + solid phases ($3-9\%$, isotropic mineral is prevailed). Disappearance temperature of gaseous phase is equal or less then $60 - 67^\circ\text{C}$ ($\pm 1^\circ\text{C}$). Eutectic temperature is in the range from $-8,3$ to $-9,0^\circ\text{C}$ ($\pm 0,2^\circ\text{C}$).

The second group of primary inclusions ($0.2 - 0.3\text{ mm}$ in size) consists of tubular and tabular negative crystals, which coincide with $[001]$. Gaseous bubble appears at cooling and disappears at the

temperature $40 \div 47^\circ\text{C}$. T_{eutectic} is between -22.4 and $-22.6 \pm 0.2^\circ\text{C}$. $T_{\text{ice melting}}$ is from -8.3 to 12.8°C . Liquid inclusions in kalushite with T_{eutectic} is similar to the system $\text{NaCl} - \text{H}_2\text{O}$ ($T_{\text{eutectic}} = -21.1^\circ\text{C}$) and $\text{NaCl} - \text{KCl} - \text{H}_2\text{O}$ ($T_{\text{eutectic}} = -22.9^\circ\text{C}$). Its concentration is from 12.1 to 16.7 wt. % NaCl equiv.

Kalushite formation is a result of the anhydrite and halite rocks interaction with solution enriched with KCl and K_2SO_4 . For growth of kalushite high concentration of KCl in solutions is necessary (more 8% of KCl after Lepeshkov I. M.) (Korobtsova 1955); it is in good agreement with our data on fluid inclusions.

CONCLUDING REMARCS

The kalushite crystals from Dombrove quarry often show a combination of simple forms with big values of d_{hkl} . Therefore the crystallization conditions of kalushite were optimal. At the beginning the kalushite crystals grow from KCl-enriched solutions at the temperature equal or less then $60 - 67^\circ\text{C}$ (KCl - H_2O system has the $T_{\text{eutectic}} = -10.8^\circ\text{C}$). At the end of kalushite crystallization it was held from NaCl-enriched solutions at the temperature equal or less then $40 - 47^\circ\text{C}$. Concentration of solutions was 12,1-19.7 wt. % NaCl equiv.

Results of detailed investigation of absorption IR-spectra of powdered sample and IR-reflection spectra, measured on three different single crystal faces, allowed to confirm non-equivalency of two sulphate groups in the syngenite structure. IR-spectra of deuterated sample gave a possibility to attribute the band at 750 cm^{-1} to librating vibration of water molecule, involved into hydrogen bonds with oxygens of two different sulphate tetrahedra of the same type.

REFERENCES

- Adler H.H. and Kerr P.F. (1965) Vibrations in the infrared spectra, molecular symmetry and site symmetry of sulphate minerals. – Amer. Mineral., vol. 50, N 1-2, p. 132 – 147
- Corrazza E. and Sabelli C. (1967) The crystal structure of syngenite, $\text{K}_2\text{Ca}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$. -Zeit. Kristal. Bd. 124, H. 6, s.398 – 408
- Dana D.J., Dana S. E., Palache Ch., Berman H. and Frondel C. (1953) The system of mineralogy, vol.2/1 Publ. House of Foreign Literature, Moscow. –774p. (in Russian)
- Fijat J., Stanezyk I. (1970) Syngenite z Inowroclawa. – Pr. mineral., PAN Krakowie. N 24, p. 22 – 28
- Goldschmidt V. (1922) Atlas der Krystallformen. Band 8, tafel 69,70, text p. 111, 112
- Gorogotskaya L.I. (1966) Syngenite (kalushite) – $\text{K}_2\text{Ca}[\text{SO}_4] \cdot \text{H}_2\text{O}$, the crystal structure and some properties of mineral connected with it.- Mineral. Collection of L'vov University, N 20/ 4, p. 481 – 489 (in Russian)
- Korobtsova M.S. (1955) Mineralogy Potassium salts deposits of Eastern Precarpathians. In: Problem of Mineralogy of Sedimentary Formations. Vol.2. L'vov National University Publ., L'vov, Ukraine, p.3 – 137 (in Russian)
- Lazarenko Eu. K., Gabinet M.P. and Slyvko E.P. (1962) Mineralogy of Sedimentary Formations of the Precarpathians. L'viv National University Publ., L'viv, Ukraine. – 482 p. (in Ukrainian)
- Moenke H. (1962) Mineralspektren, tafel 4.39, 4.41
- Szakáll Sándor and Papp Gábor (1966) Mineral species discovered in the Carpathian area. Herman Otto Museum Publ. House, Miskolc. – 24 p. (in English and Hungarian)