UDC 549.313.6 (437.6)

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NEW DATA ON TYPOMORPHISM OF TETRADYMITE Bi_2Te_2S FROM TYPOLOCALITY ŽUPKOV, SLOVAK REPUBLIC

Complex investigations of tetradymite Bi_2Te_2S from Župkov area (Slovak Republic) found as museum sample in Lviv National University is carried out by methods of electronic microscopy, local microprobe analysis and *X*-ray diffraction. It is established, that tetradymite occur as almost perfectly shaped crystals of rhombohedral and pinacoidal habits or as crystals with habit transitive between them. The main simple forms of crystals established are {0001}, {1011} and {0112}. Tetradymite crystals are commonly look like cutted trigonal pseudo-pyramids, lamellar crystals as well twinned formation of tetrade-crystals. Chemical composition of the mineral has established based on data of statistical distribution of atoms into crystallochemical positions and tetradymite formula is established to be similar to $Bi_{1.86}Sb_{0.14}Te_2S_{0.94}Se_{0.06}$. Crystalline structure of the mineral is specified by using Rietveld method. The historical importance of the studied samples is also considered. Some data on tellurides of tetradymite group obtained earlier at their studying in the frame of joint international project "Comparative mineralogo-geochemical analysis Au-Ag-Bi-Te-Se of mineralization in neovolcanites of Ukraine and Slovakia (region Carpathians)" carried out 2008—2010 years are also used.

Keywords: tetradymite, bismuth telluride, crystal morphology, crystal structure, Župkov area, Slovakia.

Introduction. Many minerals according to their rare occurrence, peculiar morphology and large size might be related to so-called natural mineralogical memories. As a rule, these minerals remain available only in mineralogical collections. Probably, to such natural memories should be also related the sample of tetradymite collected in Župkov area. Samples of tetradymite have got wide popularity and can make pride of leading mineralogical museums of many European countries. The mineral itself is unique mineralogical species which is characterized by unique set of rare elements in its composition as wells as perfection and extravagance of its crystal shape. Crystal aggregates of this mineral samples stored in collection of mineralogical museum of Lviv University have been studied on caring out investigations according to joint Ukrainian-Slovak project titled as "Comparative mineralogical-geochemical analysis of Au-Ag-Bi-Te-Se neovolcanic mineralization of Ukraine and Slovakia

a

b

Fig. 1. Museum label of tetradymite sample collected from Župkov area at least 100 years ago (*a*) and historical site of first finding of tetradymite sample from Župkov area (*b*)

(Carpathian region)". According to the museum label (Fig. 1, *a*), the sample of tetradymite was collected from Župkov area at least 100 years ago. It is interesting, that the sizes and quality of crystals of sulfotelluride favourably differ from samples described in earlier papers published here in Ukraine and Slovakia. It is this fact that predetermined necessity of studying this mineral sample with using modern level of equipments, with giving special attention to typomorphic features of the mineral.

Unfortunately, because of intensive anthropogenous activity, the findings of such unique minerals became rare events. Some attempts to add new samples to mineralogical collections by possible new finding of tethradimite in Župkov area have not reached much success. Therefore it is necessary to give due respect to inhabitants of village Župkov, and their head Mr. Ján Tomáš (Michazhu), for their careful attitude for storing historical place of the first finding of tetradymite mineral (Fig. 1, *b*, 2). As a result of such an attitude, the tetradymite becomes original "brand" of Župkov area, drawing additional attention of tourists to this region.

Tetradymite in ore process (General information). The tetradymite among all tellurides is considered to be the most abundant mineral, but this mineral does not form large concentrations in earth crust. Tetradymite is a characteristic mineral of gold, rare-metal, metasomatic (skarn) deposits. From the analysis of paragenetic associations it might be seen, that tetradymite occurs in various hydrothermal deposits, from deep hydrothermal till epithermal ones. In small amounts it might be found in skarn, greisen and hydrothermal (mainly, middle temperature) deposits of bismuth, tungsten, molybdenum, lead-zinc and copper mineralization [15, 19]. The presence of bismuth in many deposits is caused by occurrence of telluride-native bismuth and telluride-selenide-sulphide associations [2, 3]. Many deposits show presence of characteristic gold-bismuth-tetradymite associations, with tetradymite being commonle associated with native gold and bismuth tellurides. The tetradymite itself is commonly used for possible discovery and outlining of various types of gold ores, evaluation of mineralisation prospects of ore at flanks and deep levels of deposits as well as for solving some decision on other problems arised at the stages of searches and prospection. Besides Slovakia, findings of tetradymite have been also reported in following areas — Romania in Bai¸ta (Rezb'anya), Ciclova, Moravi¸ta (Moravicza), Oravi,ta (Oravicza); Russia (Ural); Usbekistan (Kurama Mauntais); Norway (Narverud and Seljord), Sweden (Boliden); USA (Trail Creek, Blaine, Idaho; in New Mexico, Sylvanite district; Virginia, at the Whitehall mines, Spotsylvania); Canada (near Liddle Creek, West Kootenay and at the White Elephant mine, near Vernon, British Columbia; Red Lake at Bigstone Bay, Lake of the Woods, Ontario; in Quebec, at the McWatters mine, RouynTownship, and in the Eureka mine, Abitibi); China (the Dashuigou tellurium deposit). Some places of тetradymite findings have been also reported for Slovakia. But at the same time in Ukraine, despite wide abundance of Bi-Te mineralization occurrences within the Vyghorlat-Ghuta ridge of Transcarpathian region the tetradymite has not been found yet.

General information on tetradymite features. Natural bismuth compounds from tetradymite group (Bi_xX_y; X = Te, Se, S) is complex group of minerals which have layered structure and form a number homologues for which Bi : X ratio is de-

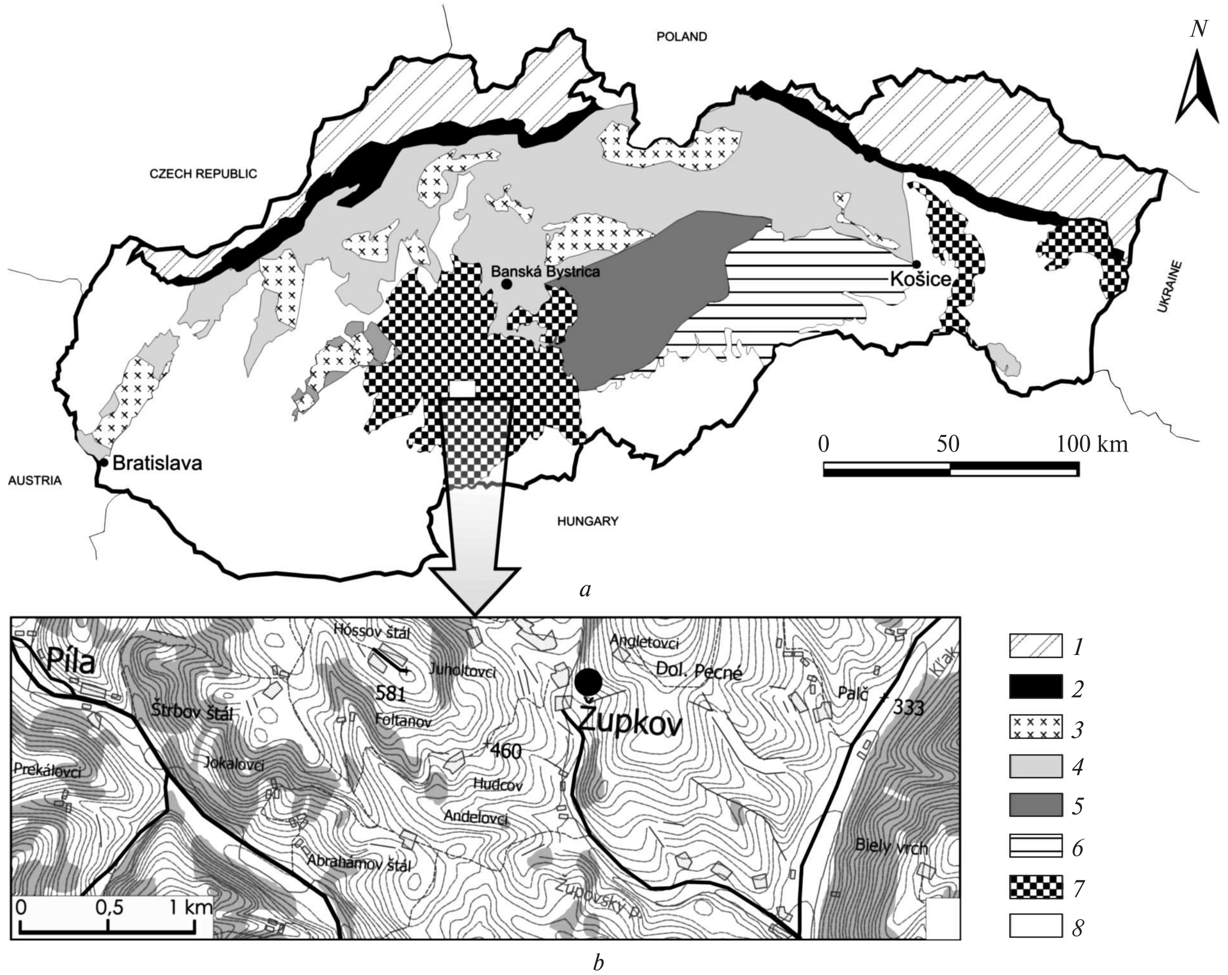

Fig. 2. Župkov area, historical place of the first finding of tetradymite mineral: *1* — Flysh zone; *2* — Klippen belt; *3* — Tatric Unit (core mountains); *4* — Upper Paleozoic to Paleogene sequences; *5* — Veporic Unit; *6* — Gemeric Unit; *7* — Tertiary to Quarternary volcanites (mostly Neogene); *8* — Neogene to Quarternary basins

fined by various sequences of packing of two types of layers. The description of unknown varieties is often complicated by their small sizes and presence of intergrowing aggregates. The results of investigations obtained have shown that bismuth tellurides are commonly not chemical compounds of strictly stoichiometric composition and they represent solid solutions of variable composition [4, 5]. Many papers published indicate presence of different varieties, the stoichiometry and composition of which do not relate to widely known minerals. It is the fact that many bismuth tellurides are considered to be inexactly distinguished minerals. Among minerals with such characteristics found in territory of Ukraine and Slovakia are vehrlite and vyghorlatite [13, 14, 21].

Based on the results of studying ore manifestations in Carpathian regions of both Ukraine and Slovakia it is established, that despite some rare occurrence of tetradymite, it is surely a very product of the chemical reactions occurring in earth crust. Tetradymite paragenesises are defined by the processes of acid-basic differentiation, pH factor values in solutions, sulphur and tellurium-activity potentials. Sulfotellurides of two homologic groups, tetradymite and joseite, are established in Carpathian region [22]. Steady association of joseite *B* and native bismuth is characteristic of argillizites of Smerekiv Kamin region. At the same time antagonism between bismutite and tetradymite is also observed [11].

Tellurium minerals are rather rarely found in general and large segregations is an extremely rare finding. Therefore studying of so large samples of tetradymite collected from Župkov area would make it possible to solve some problems about composition and structure of bismuth tellurides, the problems for which a lot of confusions and uncertainties are observed. Minerals of tetradymite group are extremely stable in narrow range and at extreme

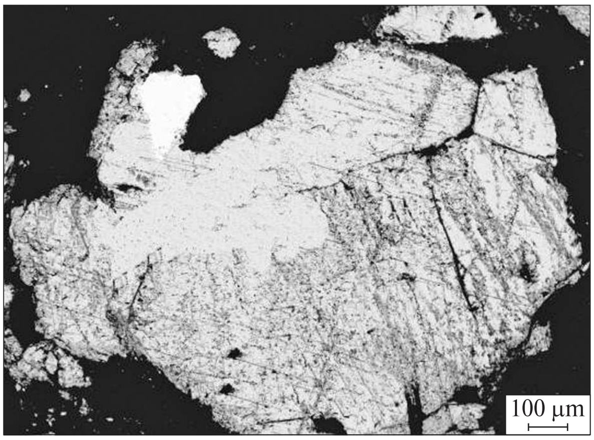

Fig. 3. Tetradymite grain completely replaced with secondary oxides (non-uniform grey mass). At the left top only fragment (white) of not altered telluride analysed might be found. SEM — Scanning Electron Microscope, BEI — Back-scattered Electron Image

values of physical and chemical conditions (*PT*-parameters, concentration and activity of components Te and Bi, acid-base balance). Some early reports on tetradymite arappeared to be related with its first finding in Župkov area [8].

Sample description and geological position of tetradymite finding. Hydrothermal mineralization with tetradymite from Župkov metalogenetically belongs to Novobansko-Kľakovský ore district, for which are characteristic several other ore occurrences in Vtáčnik Mts. Besides Bi-Te mineralization in vicinity of Župkov is known hydrothermal base-metal mineralization near Horné Hámre, Píla and Veľké Pole [12, 23].

Sarmathian pyroxenic andezites of Vtačnik Fm are host rocks for tetradymite mineralization. Their

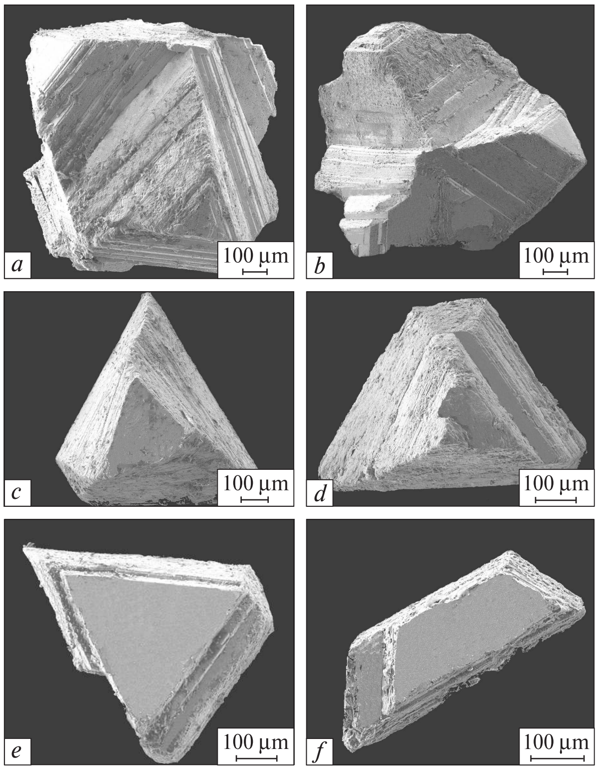

Fig. 4. a, *b* — twinned crystals of tetradymite — tetrades; *c*, *d* — rhombohedral crystals of tetradymite in the form of cutted trigonal pseudo-pyramids; *e*, *h* — pinacoidal lamellar crystals of tetradymite

matrix is microlithic and hyalopilithic with characteristic hypersthene, augite, Ca-Na feldspars and magnetite. Extrusive domes of pyroxene-hornblenditic andesite of Plešinská Fm and lava flows of pyroxenic or hornblend-pyroxenic andesites with epiclastic volcanic breccias are composed of feldspar, augite, hypersthene ± amphiboles. In this

Table 1. **Chemical composition of tetradymite from Župkov area**

Number of analysis	Bi	Te	S	Se	Sb	Total	References
1	59.84	35.24	4.92	Traces		100	Dena, 1899
2	58.30	36.05	4.32	0.75		99.42	" "
3	59.20	35.80	4.60	Traces		99.60	" "
4	60.36	35.25	4.20	"		99.81	Dena et al., 1951
5	58.10	36.00	4.33	0.68		99.11	Sejkora et al., 2004
6	58.89	35.90	4.18	0.87	0.11	99.95	Lviv (Ukraine)
7	58.54	35.76	4.27	0.25	0.28	99.10	" "
8	58.41	34.97	4.36	1.08		98.82	" "

Crystallochemical formulas of tetradymites:

6. $Bi_{2.000}Te_{1.996}(S_{0.925}Se_{0.078})_{1.003}$

7. $Bi_{2.010}Te_{2.011}(S_{0.956}Se_{0.023})_{0.979}$

8. $Bi_{1.987}Te_{1.949}(S_{0.967}Se_{0.097})_{1.003}$

N o t e. Analysis: 1—4 — after Dena, 5 — after Sejkora, 6—8 — are carried out in Technical Center of NAS of Ukraine, *JXA*-8200, an analyst V.B. Sobolev.

part are often represented conglomerates of lower Štiavnica stratovolcano structure (Badenian) which occurs at the base of volcanic complex, mainly in the vicinity of Župkov. Their thickness is up to 100 m. Paleoalpine units (Hronicum) are rarely represented by shales, sandstones and conglomerates of Permian Malužiná Fm. Vtáčnik Mts. is divided into 2 different parts by fault zone of NE direction. Fault zone is located between Píla and Nová Lehota. NW direction from fault zone is block that base forms Veporic unit, SE direction from fault (also tetradymite locality) forms volcanites of Štiavnica stratovolcano and filling of Kremnica graben with intensive fault tectonic of Štiavnica caldera rim and Žiar basin [23].

Tetradymite locality represent short prospecting adit nowadays inaccessible with a rest of small dump near Župkov village, 8 km NW direction from Žarnovica. Small adit was excavated on the south slope of Hlaváč hill NW from Župkov in the gray andesites with the marked spherical jointing. Dump is situated on the right side of the adit. Grey andesite is partly penetrated with small veinlets of white chabazite. Bi-Te mineralization is related to strongly hydrothermal altered grayish yellow silicified andesite as well as to propylitized andesite. Most of the tetradymite samples come from white clayish layer (5—30 cm thick) from the base of the dump [20].

The mineralogical material investigated by us has been represented by separate lump of ore in metasomatically altered andesite of quartz-kaolinitic composition with pocket-like concentrations of macrocrystalline tetradymite. Separate crystal aggregates with sizes of up to 5 mm along elongation were studied. Segregations of dark grey crusts of Bi_2O_3 composition are observed in the mineral. Montanite forms shells (0.1—0.2 mm thick) on tetradymite which is also intensively replaced. It is grey, greyish brown, greenish, light yellow, pinkish brown mineral which has greasy lustre, in small fragments is transparent.

Typical chemical composition of tetradymite. Microprobe uinvestigations of tetradymite established in argillizites has been complicated by presence of the products of secondary alterations represented by montanite, described by Sejkora [20]. Montanite forms submicroscopic network of crusts penetrating into mineral grains along cleavage. Reliable results (Table 1, an. 6—8). were obtained only in separate sites of grains which have not undergone to secondary alterations (Fig. 3).

Crystal morphology of tetradymite. Findings of well faceted twinned crystals of tetradymite were reported from Župkov region, near Banská Štiavnica. Some crystals of tetradymite from Transylvania had sizes of 2.5 × 1.4 × 1.3 cm. And tetrade structures that are characteristic for the mineral have found direct reflexion in the mineral name (tetradymos), after original Greek word [8].

The tetradymite from Župkov area forms almost perfect crystals of sharp rhombohedral and pinacoidal habits or crystals with habits that are transitive between them (Fig. 4). The main simple forms of crystals are represented by {0001}, {1011} and {0112}. Almost all crystals show half development along the basic crystallographic axis, and they look like the cutted trigonal pseudo-pyramids (Fig. 4, *c*, *d*). Various lamellar crystals with predominant pinacoidal shape (Fig. 4, *e*, *f*) as well as twinned species of tetrade crystals (Fig. 4, *a*, *b*) are commonly found. Zones of rhombohedrons show distinct horizontal striation which promotes their perfect cleavage on (0001). Earlier such crystal habits of tetradymite from Župkov area have been described by Haidinger [8] and Muthmann [16].

Results of X-rays investigations. The tetradymite is crystallised in trigonal syngony (hexagonal-scalenohedral class). For the first time its structure has

Table 2. **Symmetry and parameters of elementary cell of tetradymite from Mineralogical museum of Lviv National University**

Formula	$Bi_{1.86}Sb_{0.14}Te_2S_{0.94}Se_{0.06}$
Symmetry	Trigonal — Hexagonal Scalenohedral Class
Spatial group	*Rm*
Symbol Figure	*hR*36
a (Å)	4.2581 (5)
c (Å)	29.638 (7)
V (Å³)	465.3(0.1)
R-factor, R_f	7.16
Bragg *R*-factor, R_{wp}	9.48

N o t e. The theoretical, experimental and differential profile of diffraction patterns of samples are shown on Fig. 5. Parameters of atoms are shown in Table 3.

Table 3. **Parameters of atoms in structure of tetradymite**

Atom	ПСТ	*x/a*	*y/b*	*z/c*	B_i	Occupancy, %
Bi1	6*c*	0.00000	0.00000	0.39226	2.901	92.9(2)
Sb1	6*c*	0.00000	0.00000	0.39226	2.901	7.1(2)
Te1	6*c*	0.00000	0.00000	0.78519	4.403	100
S1	3*a*	0.00000	0.00000	0.00000	1.202	93.9(2)
Se1	3*a*	0.00000	0.00000	0.00000	1.202	6.1(2)

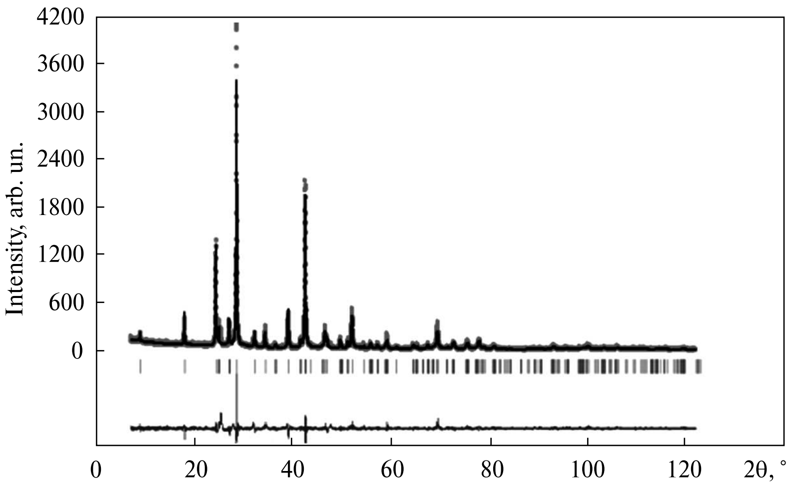

Fig. 5. Observed and calculated diffraction patterns (dots signs and line, respectively) for tetradymite. Tick marks indicate positions of allowed reflections of tetradymite. The lower curve shows the difference between the observed and calculated patterns

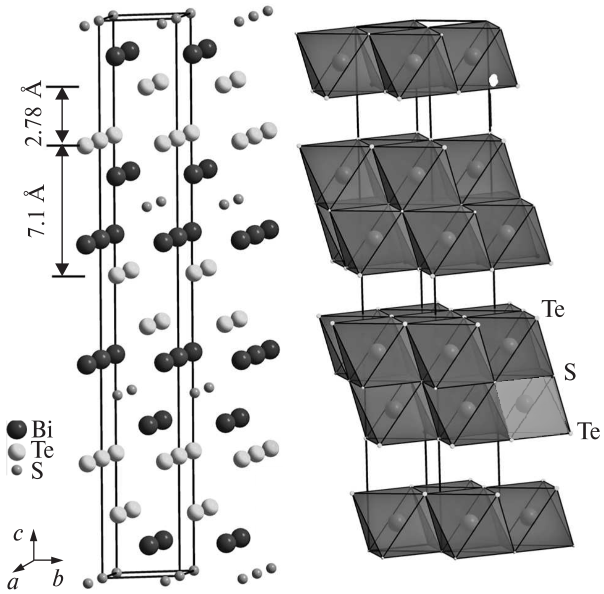

Fig. 6. Structural model of the investigated tetradymite

been estimated by Harker [9] and most likely for the sample collected in Župkov area. The references to Hungary made in article most likely indicate to the record in the set of samples collected till 1918. This fact is additionally proved by indication on the old administrative location of area of selection of the sample mentioned in the museum catalogue. Crystallo-structural investigations of completely ordered tetradymite with stoichiometry of Bi_2Te_2S appropriate to it were not carried out. Pauling [17] and Bayliss [1] provide data on minerals isostructural to tetradymite, but with different stoichiometry and chemical composition. The data presented in free databases [6, 7] as well as in ICDD PDF-4 [10] are not precise.

Specification of crystal structure of the tetradymite (sampled from Župkov area) were carried out by powder method in *X*-ray laboratory of Lviv National University. Experimental data on intensities and reflexion angles has been received on diffractometer STOE STADI P with the linear position-sensible detector (PSD) accordingly to the scheme of the modified Gin'e geometry, in the Bregg-Brentano mode ($CuK\alpha_1$-radiation; Iogan type Ge-bended monochromator [111]; $2\ \theta/\omega$ — scanning; interval of angles — $4.000 \leq \leq 2\theta \leq 110.065°$, scanning step is 0.015°; temperature at registering $T = 24.0 \pm 2$ °C, $U = 40$ кB, $J = 40$ mA).

The *X*-ray profile and phase analysis have been carried out with using software package STOE WinXPOW (version 2.21) [24]. Determination of parameters of elementary cell has been carried out with using LATCON program. All calculations connected with interpretation and specification of crystal structure of tetradymite were made by wholeprofile Rietveld method with using the program of FullProf [18]. Starting structure models of tetradymite were taken from Structural data cited in MINCRYST [25].

Results of calculations are summarized in Table 2. Chemical composition of the mineral has been specified with taking into account the statistical data on distribution of atoms on crystallochemical positions.

The theoretical, experimental and differential profile of diffraction patterns of samples are shown on Fig. 5. Parametres of atoms are shown in Table 3.

Results of specification of structure indicate for the affinity of the calculated parameters of structure to the modell ones. Structure (Fig. 6) is characterized by total ordering of positions of Te, Bi and S which layers alternate along an *c* axis in sequence of Te-Bi-S-Bi-Te as it was early mentioned in paper [17]. Interatomic distances of Bi-Te and Bi-S are almost equal (3.00 and 2.99 Å, accordingly). Bismuth is located in coordination similar to octahedral one [$BiTe_3S_3$] as a part of two-layer packages with atoms Te from above and from below. Packages are displaced relatively to each other. The distance between packages reaches 2.78 Å at package thickness of 7.1 Å. Interatomic distance Te-Te of the adjacent packages is 3.72 Å. Statistical data on distribution of atoms of different grade into positions indicates that Sb enters into position Bi, and Se does into position S.

Conclusions. Detailed investigations of unique samples of tetradymite from Župkov area by using scanning electronic microscopy and microprobe analysis made it possible to establish crystallographic features of the mineral and to specify chemical composition as well as structure of tetradymite by Rietveld method.

The fact of occurrence of tetradymite and its typomorphic features have great value as a search sign. It is empirically established that both absence or presence of tetradymite, is connected with gold ore concentration. The decision of this problem can be one of the most important research problems within the limits of the joint Slovakian-Ukrainian project.

Besides, we managed to restore some historical aspects of this sample. Similar works are probably needed for studying rare samples of minerals and both have purely scientific importance and are necessary in the mineralogical-historical plan of professional continuity of similar researches.

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Received 08.12.2014

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НОВІ ДАНІ ПО ТИПОМОРФІЗМУ ТЕТРАДИМІТУ Bi_2Te_2S З РЕГІОНУ ЖУПКОВ, СЛОВАЦЬКА РЕСПУБЛІКА

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За допомогою методів електронної мікроскопії, локального мікрозондового аналізу та рентгенівської дифракції проведено комплексне дослідження музейних зразків тетрадиміту Bi_2Te_2S Львівського національного університету з району Жупков (*Župkov*) (Словацька Республіка). Встановлено, що мінерал утворює майже досконалі кристали гострoромбоедричного і пінакоїдального або перехідного між ними габітусів. Головні прості форми кристалів: {0001}, {1011} і {0112}. Часто кристали мають вид зрізаних тригональних псевдопірамід, пластинчастих кристалів, а також двійникові утворення кристалів-четверників. Хімічний склад мінералу уточнено з врахуванням статистики розподілу атомів за кристалохімічними позиціями і він відповідає формулі $Bi_{1,86}Sb_{0,14}Te_2S_{0,94}Se_{0,06}$. За допомогою повнопрофільного методу Рітвельда проведено усі обчислення, що пов'язані з розшифруванням і уточненням кристалічної структури тетрадиміту. Розглянуто історичний аспект цінності вивчених зразків. Враховано дані, отримані раніше під час вивчення телуридів групи тетрадиміту за проектом "Порівняльний мінералого-геохімічний аналіз Au-Ag-Bi-Te-Se мінералізації в неовулканітах України і Словаччини (регіон Карпати)" протягом 2008—2010 рр.

Ключові слова: тетрадиміт, телурид вісмуту, кристалічна морфологія, кристалічна структура, область Жупков, Словаччина.

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НОВЫЕ ДАННЫЕ ПО ТИПОМОРФИЗМУ ТЕТРАДИМИТА Bi_2Te_2S ИЗ РЕГИОНА ЖУПКОВ, СЛОВАЦКАЯ РЕСПУБЛИКА

С помощью методов электронной микроскопии, локального микрозондового анализа и рентгеновской дифракции проведено комплексное исследование музейных образцов тетрадимита Bi_2Te_2S Львовского национального университета из района Жупков (*Župkov*) (Словацкая Республика). Установлено, что минерал образует почти совершенные кристаллы остроромбоэдрического и пинакоидального или переходного между ними габитусов. Основные простые формы кристаллов: {0001}, {1011} и {0112}. Часто кристаллы имеют вид срезанных тригональных псевдопирамид, пластинчатых кристаллов, а также двойниковые образования кристаллов-четверников. Химический состав минерала уточнен с учетом статистики распределения атомов по кристаллохимическим позициям и он отвечает формуле $Bi_{1,86}Sb_{0,14}Te_2S_{0,94}Se_{0,06}$. С помощью полнопрофильного метода Ритвельда проведены все вычисления, связанные с расшифровкой и уточнением кристаллической структуры тетрадимита. Рассмотрен исторический аспект ценности изученных образцов. Использованы также данные, полученные раньше при изучении теллуридов группы тетрадимита по проекту "Сравнительный минералого-геохимический анализ Au-Ag-Bi-Te-Se минерализации в неовулканитах Украины и Словакии (регион Карпаты)" в течение 2008—2010 гг.

Ключевые слова: тетрадимит, теллурид висмута, кристаллическая морфология, кристаллическая структура, область Жупков, Словакия.