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LASER "RAMAN" SPECTROSCOPY OF ANGLESITE AND CUBANITE FROM DEPOSIT "CHELOPECH"

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ABSTRACT. Using a laser "Raman" spectroscopy are found not listed at this moment minerals in the deposit "Chelopech", namely Anglesite ($PbSO_4$) and Cubanite ($CuFe_2S_3$). The main advantages of spectroscopic methods are successful chemical and structural characteristics of the samples in sizes less than 1 µm in diameter, as well as rapid and specific identification of minerals and ores. The values of the acquired spectral peaks in the analysis of minerals from the studied rock samples, differed by about 1-2 cm^{-1} with those of a database RRUFF and in literature, which is perfectly acceptable, as the difference could be due to the inclusions of another minerals or elements within the researched mineral, or interference in medium during the process of analysis. Anglesite is a typical Pb-containing secondary mineral. Spatial and structural relationships of mineral are the basis to be assigned to galena-sphalerite mineral association in the deposit. In the studied samples are found together with the ore minerals cerusite, pyrite, galena, sphalerite and tennantite, and the gangue minerals quartz, barite, anhydrite and kaolinite. The newly determined cubanite is found in association with pyrite, chalcopyrite, tennantite, sphalerite, quartz and anatase. This Cu-Fe-sulfide is more typical for a high-temperature type of hydrothermal deposits, where occurs together with pyrrhotite. Cubanite from the deposit "Chelopech" is a rare ore mineral deposited in the main stage of hydrothermal mineral formation and belongs to the pyrite-chalcopyrite mineral association.

ЛАЗЕРНА „РАМАН" СПЕКТРОСКОПИЯ НА АНГЛЕЗИТ И КУБАНИТ ОТ НАХОДИЩЕ „ЧЕЛОПЕЧ"

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РЕЗЮМЕ. С помощта на лазерна „Раман" спектроскопия са установени неописвани към този момент минерали в находище „Челопеч", а именно англезит ($PbSO_4$) и кубанит ($CuFe_2S_3$). Основни предимства на спектроскопския метод са успешната химическа и структурна характеристика на проби с размер по-малък от 1 µм в диаметър, както и бързата и специфична индентификация на минерали и руди. Стойностите на получените спектрални пикове при анализиране на минерали от изследваните скални препарати се различават с около 1-2 cm^{-1}, с тези от база данни RRUFF и по литературни данни, което е напълно допустимо, като разликата би могла да се дължи на включения от друг минерал в рамките на изследвания образец, включения от химични елементи или смущения в средата при процеса на анализиране. Англезитът е типичен Pb-съдържащ вторичен минерал. Пространствените и структурни отношения на минерала са основание той да бъде причислен към галенит-сфалеритовата минерална асоциация в находището. В изследваните образци се среща съвместно с рудните минерали церусит, пирит, галенит, сфалерит и тенантит, както и с нерудните кварц, барит, анхидрит и каолинит. Новоустановеният кубанит е в асоциация с пирит, халкопирит, тенантит, сфалерит, кварц и анатаз. Този Cu-Fe-сулфид е по-характерен за високотемпературен тип хидротермални находища, в които се среща съвместно и с пиротин. Кубанитът от находище „Челопеч" е рядък руден минерал, отложен най-вероятно в началото на основния хидротермален стадий на минералообразуване и принадлежи към пирит-халкопиритовата минерална асоциация.

Introduction

The laser "Raman" spectroscopy has been applied to minerals since its discovery in 1928th (Raman and Krishnan, 1928). It should be noted that "Raman" spectra of minerals is not strictly defined in comparison with those of gases and liquids. This means that the positions and relative intensities of the waves may differ slightly in one spectrum to other, depending on the orientation of the crystal lattice and/or the presence of impurities or defects in the crystal structure (White, 2009). "Raman" spectroscopy is a suitable method for qualitative determination of mineral species. The intensity (the height of the wave spectra) can not be used for carrying out a quantitative analyzes and determining the concentration of a chemical element in a studied sample. The positions (shift) of the wave's peaks, but not the intensity are reported usually in the literature.

The main advantages of spectroscopic methods are successful chemical and structural characteristics of a sample in sizes less than 1 µm in diameter, as well as easily and proper identification of minerals and ores. To ascertain the relative presence and qualitative determination of minerals in a studied rock samples, it is used a method of obtaining spectra in a system of spots, located over the entire surface of the sample (Haskin et al., 1997). Serious advantage of the method in the qualitative diagnostics of minerals is the speed of obtaining the result (within 1-2 minutes) and lack of preliminary preparation of the sample for analysis. It is recommended that the analysis to be conducted on fresh mineral surface. This method provides a means of obtaining spectra of very small mineral grains with different orientations, which in turn opens the possibility for new future geochemical identification of ore minerals.

Despite considerable advantages of the "Raman" spectroscopy as a method for diagnosis of ore minerals, it is relatively rarely used and the database RRUFF for comparison of the spectra is still not entirely completed. Micro-Raman spectral analyses of minerals from the gold-copper deposit "Chelopech" are not published till now and this study is the first attempt.

Materials and methods

30 polished rock sections for conducting the mineralogical studies of ore bodies of block № 149 form sector "West" in the gold-copper deposit "Chelopech" are prepared. Small-sized mineral grains are found after microscopic observation of the samples. Determination of these mineral grains by standard microscopy was difficult. 10 polished sections are selected on which is carried out a laser "Raman" spectroscopy by which are found not listed at this moment minerals in gold-copper deposit "Chelopech", namely anglesite ($PbSO_4$) and cubanite ($CuFe_2S_3$). Analyzes are carried out at room temperature in the Laboratory of fluid inclusions of the University of Leoben (Austria). Laser "Raman" micro-spectrometer Horiba Jobin-Yvon, laser with a nominal power of 100 mW and a wavelength of 514 and 532 nm are used (Fig. 1). The “Raman” device includes a microscope Olympus BX60, camera CCD CV-252, connected to a monitor for direct observation, computer system and specialized software LabSpec.

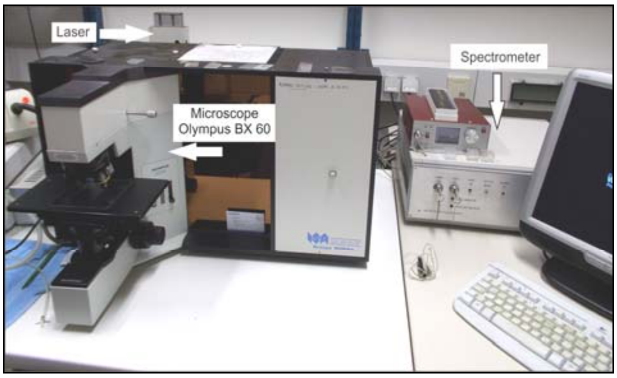

Fig. 1. Lasers "Raman" micro-spectrometer HORIBA in the Laboratory of fluid inclusions of the University of Leoben, Austria

The data acquisition was performed by 5x5 seconds exposure and added various filters (from D0,6 to D2), depending on the stability of the mineral, as spectra were recorded with a spectral resolution within 1 - 2 cm^{-1}. The method is essentially a non-destructive one, but the majority of the ore minerals burn at a long and high-intensity laser radiation. Spectra manipulation consists in a basic data treatment, such as base line adjustment and peak fitting within the figures.

One hundred ninety-four spectra of ore and gangue minerals which include pyrite, marcasite, pyrrhotite, tennantite, tetrahedrite, chalcopyrite, enargite, famatinite, sphalerite, hematite, cerusite, anglesite, cubanite, anatase, quartz, dolomite, apatite, zircon and others are obtained within the framework of the studies. The subsequent interpretation and analysis of spectral data is accomplished with the software product CrystalSleuth, which provides an opportunity to compare the obtained spectra with the database RRUFF. The database RRUFF was created in order to maintain a full range of high quality spectral data from well characterized minerals (Downs, 2006). This database is internet based and freely accessible, which facilitates its use, sharing and adding. It is a growing demand for this type of mineral database due to the increased popularity and use of the "Raman" methodology in modern geological and mineralogical practice.

Results and discussion

The anglesite ($PbSO_4$) is a typical Pb-containing secondary mineral. In the studied samples it occurs together with cerusite, pyrite, galena, sphalerite and tennantite, rarely with enargite, chalcopyrite, cubanite, covellite and famatinite, and gangue minerals quartz, barite, anhydrite and kaolinite (Fig. 2 a and b). The sulphate minerals such as barite, anhydrite and anglesite are formed after the main ore forming processes in the deposit and belong to the fourth stage of mineralization: quartz - carbonate – barite stage. These minerals probably are formed as a result of the interaction of cool and with nearly neutral pH magmatic fluids with the host rocks. The spatial and structural relationships of anglesite give grounds to be assigned to the galena-sphalerite mineral association in the ore deposit.

The anglesite is more frequently found in the upper levels of epithermal systems where the zone of oxidation is favourable for the forming of sulphate minerals. Under certain conditions due to the depth supergene weathering, minerals such anglesite and cerusite could be discovered within the deeper parts of the deposits containing Pb-Zn mineralization.

Pyrite forming the matrix, in which anglesite and cubanite have been detected, is observed and analyzed in detail in earlier studies (Terziev, 1968a and 1968b; Petrov et al., 2013, and etc.) in the form of two generations that differ in their structures and relationships with other minerals. The first generation often forms colloform aggregates with concentric-zonal, typical "bird's eye" or "atoll"-like structures, among which is registered a cubanite (Fig. 2 c and d). The colloform aggregates are accompanied by fine semi-euhedral to xenomorphic fine grains pyrite located nearby the larger pyrite-marcasite aggregates, which are representatives of pyrite-marcasite association formed probably at hydrothermal-sedimentary conditions before deposition of the main economic associations in the deposit. The second generation pyrite formed relatively massive aggregates, indicating areas of growth, marked by alternation of light and dark stripes. Fine size of the stripes do not allow precise determination of trace elements by microprobe analyses, but using a laser “Raman” spectrometer would prove that the differences in optical properties in stripes are due to different chemical composition. Anglesite is observed and con firmed by "Raman" spectroscopy exactly amidst a zonal pyrite of the second generation in the analysed samples from the "Chelopech" deposit.

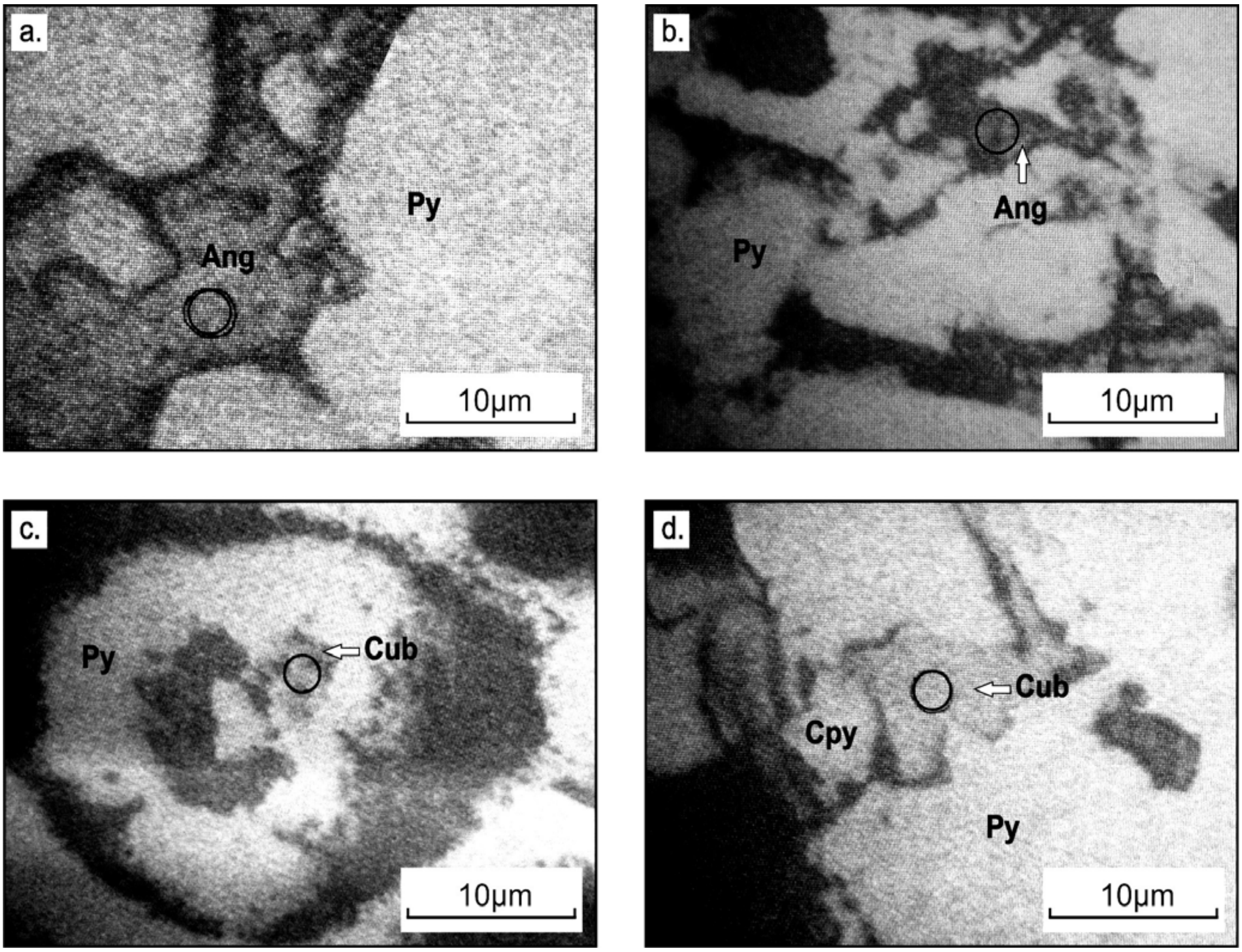

Fig. 2. Microphotos of ore minerals in polished sections from the Western sector of the gold-copper deposit "Chelopech" shot on the microscope with reflected light which is a part of the Raman device.

- **a. – anglesite among pyrite matrix;**
- **b. – mineral grain of anglesite among pyrite and gangue minerals (black);**
- **c. – grain of cubanite among the "atoll"-like pyrite;**
- ***d.* – mineral aggregate of cubanite in contact with chalcopyrite in matrix of pyrite and gangue minerals.**

Legend: Ang - anglesite; Cpy - chalcopyrite; Cub - cubanite; Py - pyrite. With a circle is marked the location of laser radiation.

It should be noted that the volume of the studied polished samples and the number of registered mineral grains anglesite and cubanite is too small to be able credibly attach these minerals to the typical spatial distribution of mineral associations within the ore bodies of the deposit.

It is presented on Figure 3 the obtained spectrum of anglesite from the "Chelopech" deposit compared with those of database RRUFF (№ R050408, natural anglesite from the "Tsumeb" deposit, Namibia) and after Griffith (1970). The positions of the main waves in the spectrum of the mineral are marked by numbers. Typical peaks in the "Raman" spectral waves of anglesite from the "Chelopech" deposit and published data are presented in Table 1, as in Figure 3 are included only the spectra obtained at 514nm wavelength.

On the presented figures, it is clear that the characteristic peaks are marked at 78, 93, 138, 153, 184, 438, 449, 605, 643, 975, 1056 and 1157cm^{-1}. Some values of these peaks vary by about 1–2 cm^{-1} in the spectra of anglesite according to the published data, which is perfectly acceptable and they are within the sensitivity of the spectroscope. It follows that the micro-spectral analysis is trustworthy, but it is advisable that the presence of the mineral to be confirmed by other types of analyzes. A confirmation with other types of analysis (e.g. microprobe analysis) should be obtained for the cubanite as well.

In case if there are vast differences in the shift of the spectrum, or the presence of additional, well-defined peaks, it could be due to inclusions of other minerals within the studied sample, inclusions of trace elements and/or interference in the environment during the process of analyzing. In certain cases and in a more precise analysis, except the type of mineral it could be inferred and the nature of the inclusions of other chemical elements in the structure of the studied sample.

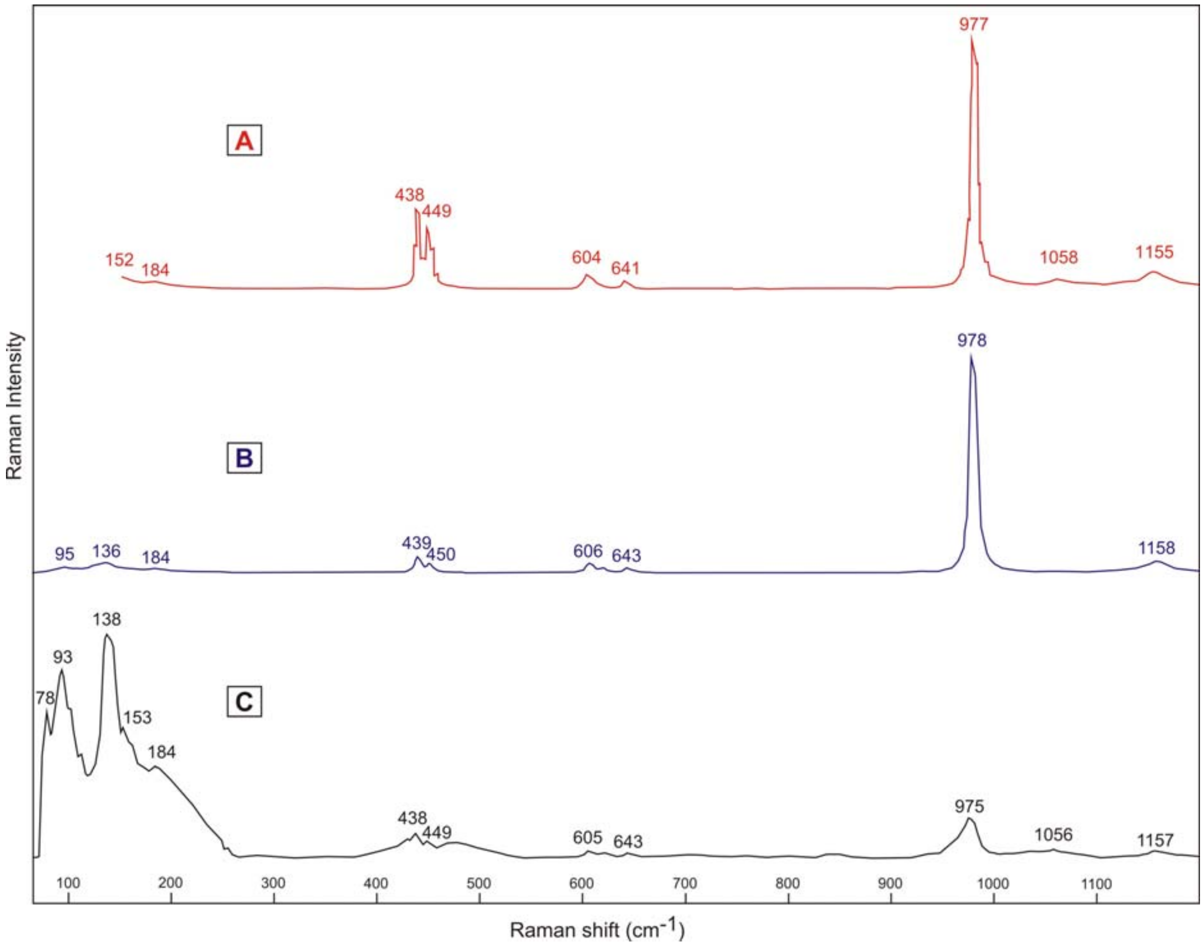

Fig. 3. "Raman" spectra of anglesite ($PbSO_4$) at 514 nm wavelength (A: anglesite after Griffit, 1970; B: anglesite by database RRUFF № R050408, "Tsumeb" deposit, Namibia; C: anglesite - analysis № 15-6-10, "Chelopech" deposit, Bulgaria)

Table 1.
"Raman" spectral waves peaks of anglesite (cm^{-1})

An. №15-6-10 "Chelopech" deposit	RRUFF database №R050408 "Tsumeb" deposit	after Buzgar, 2009 "Monte Poni" deposit	after Griffith, 1970	after Beny, 1991
78				
93	95			96
138	136			133
153			152	
184	184		184	181
438	439		438	438
449	450	450	449	449
605	606	553	604	605
		611	617	617
643	643	646	641	643
975	978	978	977	977
1056		1058	1058	1052
				1140
1157	1158	1157	1155	1156

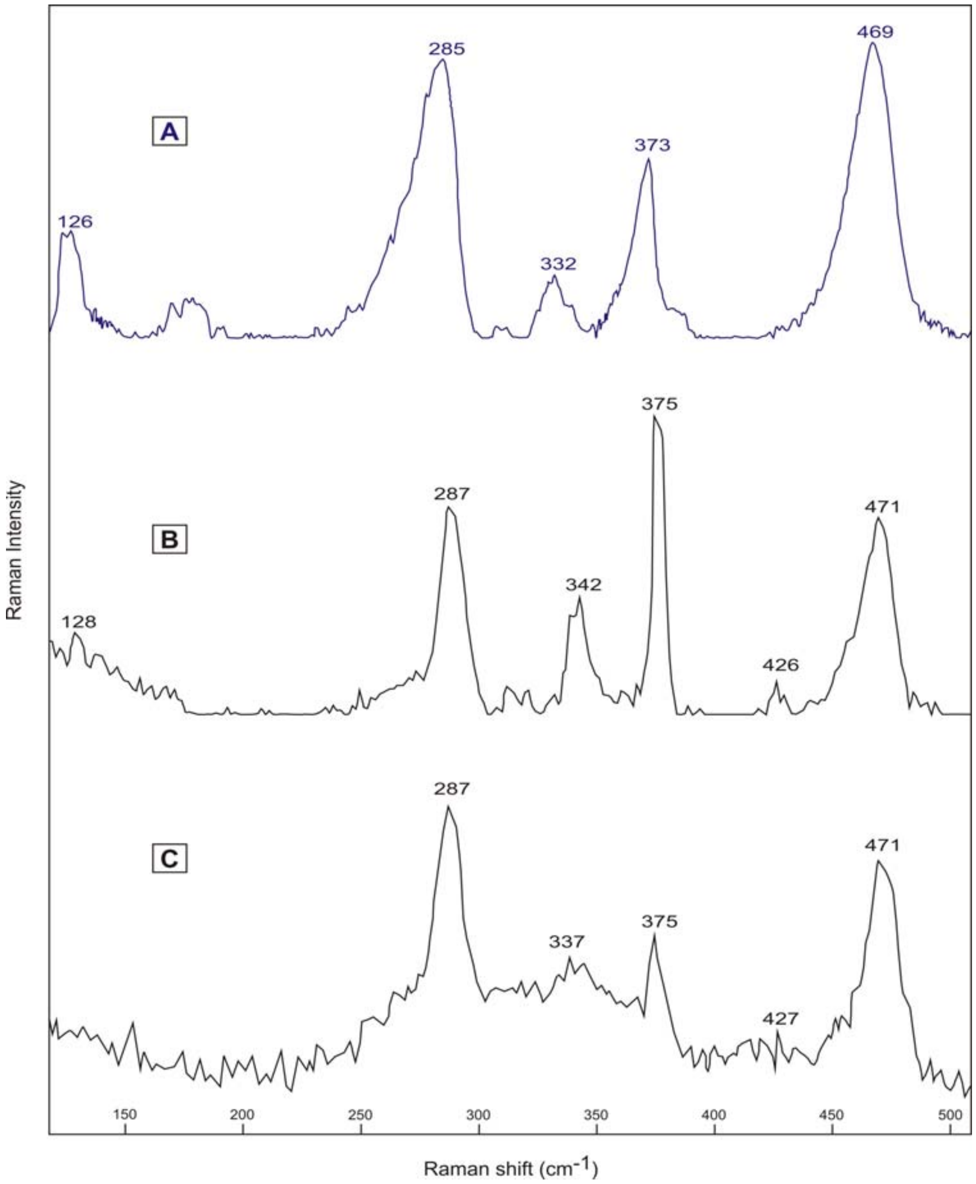

Fig. 4. "Raman" spectra of cubanite ($CuFe_2S_3$) at 532 nm wavelength (A: cubanite by database RRUFF № R061068, "Hendersen-2" deposit, Canada; B: cubanite - analysis № 15-6-11, "Chelopech" deposit, Bulgaria; C: cubanite - analysis № 26-4-02, "Chelopech" deposit, Bulgaria)

Table 2.
"Raman" spectral waves peaks of cubanite (cm^{-1})

An. №15-6-11 “Chelopech” deposit	An. №26-4-02 “Chelopech” deposit	RRUFF database №R061068 “Henderson-2” deposit	Synthetic cubanite (after Chandra et. al., 2001)
128		126	
287	287	285	286
		332	328
342	337		
375	375	373	374
426	427		
471	471	469	469

The newly identified in the deposit "Chelopech" cubanite ($CuFe_2S_3$) is in an association with pyrite, chalcopyrite, tennantite, sphalerite, quartz and anatase. This Cu-Fe-sulfide is typical for high-temperature type of hydrothermal deposits, where occurs together with pyrrhotite, pentlandite, pyrite and sphalerite. The most often it is found as intergrowths with chalcopyrite and pyrite.

The cubanite from the "Chelopech" deposit is a rare ore mineral, deposited probably at the beginning of the main hydrothermal ore-forming stage and it belongs to the pyrite-chalcopyrite mineral association. According to the published data cubanite from the "Hendersen-2" deposit, Canada (database RRUFF № R061068), the positions of the "Raman" spectra's peaks are indicated at 126, 285, 332, 373 and 469 cm^{-1} (Fig. 4). The micro-Raman spectroscopy studies on synthetic cubanite showed strong wave modes at 286, 374 and 469 cm^{-1} and weak at 328 cm^{-1} (Table 2). It is assumed that the peaks at 286, 332 374 cm^{-1} mark the group of Fe-S, and that at 469 cm^{-1} of the Cu-S in the wavelength range of natural cubanite at room temperature (Chandra et. al., 2001). The studied mineral grains of cubanite are within the range of 2-3 µm, often sprout with chalcopyrite in pyrite matrix. Namely microscopic inclusions of chalcopyrite and pyrite in the analysis of cubanite from the "Chelopech" deposit are due to relatively well expressed wave's peaks at 342 and 426 cm^{-1} in analysis № 15-6-11, and at 337 and 427 cm^{-1} in analysis № 26-4-02. On the presented Figure 4 and Table 2 it is shown a strong similarity between the two wave regimes in the spectrum of studied cubanite, although both analyses were performed on samples from different ore bodies within one and the same ore block.

Conclusions

The laser "Raman" spectroscopy as quick and generally non-destructive method which provides an easy opportunity for a qualitative characteristic not only of liquids, gases and homogeneous solid materials, but also to the zonal, heterogeneous and impure ore and gangue minerals.

In addition to those listed so far advantages of this method we can add the ability to compare and clarify the ore-forming and geochemical relation of the same mineral in different ore environment.

Together with the microscopy, X-ray and geochemical assays the laser "Raman" spectroscopy it is a modern powerful diagnostic tool for mineral identification in ore deposits studied.

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