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PŮVODNÍ PRÁCE/ORIGINAL PAPER

# Stibioclaudeite from the Zlatá Idka Ag-Au-Sb deposit, Spišsko-gemerské rudohorie Mts., Slovakia

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## Abstract

A rare mineral, stibioclaudeite, ideally  $\text{AsSbO}_3$  was discovered at the dump of the Najvyšší Štefan adit at the Zlatá Idka Ag-Au-Sb deposit near Zlatá Idka, Spišsko-gemerské rudohorie Mts., Košice-okolie Co., Košice Region, Slovakia. It occurs as colourless prismatic crystals up to 5 mm with perfect cleavage, developed on fractures of quartz gangue with abundant stibnite, arsenopyrite and minor pyrite. The unit-cell parameters of stibioclaudeite from the Zlatá Idka (for the monoclinic space group  $P2_1/n$ ) refined from the PXRD data are:  $a$  4.5715(17) Å,  $b$  13.112(2) Å,  $c$  5.4182(15) Å,  $\beta$  94.97(3) and  $V$  323.55(14) Å<sup>3</sup>. Its chemical composition corresponds to the average empirical formula  $\text{As}_{1.09}\text{Sb}_{0.91}\text{O}_{3.00}$ . Raman spectrum of stibioclaudeite is also given. Stibioclaudeite was formed by the *in-situ* weathering of primary ore minerals at the base of the supergene zone under the relatively reducing conditions.

**Key words:** stibioclaudeite, chemical composition, Raman spectroscopy, Zlatá Idka, Gemeric Unit, Spišsko-gemerské rudohorie Mts., Slovak Republic

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## Introduction

Stibioclaudeite,  $\text{AsSbO}_3$  is a rare supergene mineral, which was first described from the famous Tsumeb mine in Namibia by Origlieri et al. (2009). Later it was also discovered at the Borgofranco Ag-Sb-Pb-As mine in Piedmont (Campostrini et al. 2012) and Fenugu Sibiri Pb mine in Sardinia (Caboni et al. 2018), both in Italy. Another occurrence of stibioclaudeite was reported from the Wet Swine Gill in the Caldbeck Fells, Cumbria, UK (Green et al. 2014), originally described by Leppington, Green (1998) as antimonian claudeite. Finally, stibioclaudeite was identified as daughter phase in polyphase fluid inclusions in spodumene from Greenbushes pegmatite in Western Australia (Anderson, McCarron 2011).

The sixth occurrence of stibioclaudeite in the world was recently discovered at the Zlatá Idka Ag-Au-Sb deposit in Slovakia and its description is presented in this short paper.

## Geological setting

The Zlatá Idka Ag-Au-Sb deposit is situated around 3 km NW of the Zlatá Idka village, 19 km NW of the Košice town in the Spišsko-gemerské rudohorie Mts., Košice-okolie Co., Košice Region, Slovakia. Samples with stibioclaudeite were collected at the dump of the Najvyšší Štefan adit, which exploited the subsurface parts of the Štefan vein. GPS coordinates (WGS84) of this dump are: 48.769129° N and 20.973672° E, 942 m a.s.l.

The Zlatá Idka Ag-Au-Sb deposit is consisting of system of hydrothermal quartz±carbonate veins with Ag-Au-Sb ore mineralization hosted predominantly in Early Paleozoic metarhyolites and metasediments of the Bystrý

potok Formation, belonging to the Gelnica Group and Gemeric tectonic unit (Bajaník et al. 1984; Grecula et al. 1995). The hydrothermal veins are dominantly NE - SW trending and are parallel arranged, forming around 6 km long and 1 km wide ore belt. The most important ore veins (from west to east) are Matej, Štefan, František, Bertalan (Bartolomej), Trojičná, Jozef, František-Jozef, Všechnvátých and Katalin (Katarína) (Rozložník 1912; Grecula et al. 1995).

Hydrothermal ore mineralization at the Zlatá Idka deposit is representing a specific type of unusual Ag-Sb-Au-Pb-Zn ore assemblage, which is different from the typical siderite-sulfide or quartz-stibnite type veins widespread in the Gemeric unit and has no equivalent in the Western Carpathians (Pršek, Lauko 2009; Mikuš, Števkó unpublished data). The dominant gangue mineral is quartz accompanied by minor amounts of minerals of the dolomite-ankerite series and at some veins siderite is also abundant (e.g. Jozef or Anton vein). Jamesonite, berthierite, stibnite, arsenopyrite, sphalerite, pyrite and Ag-rich members of the tetrahedrite group are the most common ore minerals accompanied by wide spectrum of other minerals including acanthite, antimony, aurostibite, boulangerite, bournonite, chalcopyrite, galena, gold, nisbite, pyrrhotite (?), pyrrhotite, senandorite, stephanite (?) and ullmannite (Varček 1979; Grecula et al. 1995; Pršek, Lauko 2009). Only a little attention has been paid to the supergene minerals at this locality so far. Anglesite, cerussite, cervantite, goethite, oxyplumboroméite and valentinite were briefly described (Zepharovich 1873; Pršek, Lauko 2009).

Detailed sampling at the dump of the Najvyšší Štefan adit is indicating that ore exploitation locally reached the

base of the supergene zone of the Štefan vein. Large blocks of quartz gangue with abundant slightly to strongly altered stibnite, berthierite, arsenopyrite and pyrite were discovered here. Thin fractures in such ore blocks are occasionally filled by crystals and aggregates of supergene minerals, especially valentinite, oxyplumboroméite, scorodite, anglesite, sulphur and rarely also stibioclaudeite.

### Analytical methods

Powder X-ray diffraction data of stibioclaudeite were collected on a Bruker D8 Advance diffractometer (National Museum, Prague) with a solid-state 1D LynxEye detector using CuK $\alpha$  radiation and operating at 40 kV and 40 mA. The powder pattern was obtained using a Bragg-Brentano geometry in the range 23 - 75° 2 $\theta$ , in 0.01° steps with a counting time of 20 s per step. Positions and intensities of reflections were found and refined using the PearsonVII profile-shape function with the ZDS program package (Ondruš 1993) and the unit-cell parameters were refined by the least-squares algorithm implemented by Burnham (1962). The experimental powder pattern was indexed in line with the calculated intensities values obtained from the crystal structures of stibioclaudeite (Origlieri et al. 2006) based on the Lazy Pulverix program (Yvon et al. 1977).

The quantitative (WDS) chemical analyses of stibioclaudeite were performed using a Cameca SX100 electron microprobe (Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic). The following conditions, standards and X-ray lines were used: 15 kV, 5 nA, 10  $\mu$ m wide beam, albite (NaK $\alpha$ ), apatite (CaK $\alpha$ , PK $\alpha$ ), baryte (BaL $\alpha$ ), Bi (BiM $\alpha$ ), celestine (SrL $\beta$ , SK $\alpha$ ), clinoclase (AsL $\alpha$ ), Co (CoK $\alpha$ ), CuFeS $_2$  (CuK $\alpha$ ), diopside (MgK $\alpha$ ), halite (ClK $\alpha$ ), hematite (FeK $\alpha$ ), LiF (FK $\alpha$ ), Ni (NiK $\alpha$ ), rhodonite (MnK $\alpha$ ), sanidine (AlK $\alpha$ , KK $\alpha$ , SiK $\alpha$ ), Sb $_2$ S $_3$  (SbL $\alpha$ ), vanadinite (PbM $\alpha$ , VK $\alpha$ ) and ZnO (ZnK $\alpha$ ). Contents of the above-listed elements, which are not included in the table, were analysed quantitatively, but their contents were consistently below the detection limit (ca. 0.03 - 0.05 wt. % for individual elements). Raw intensities were converted to the concentrations of elements using automatic "PAP" matrix-correction algorithm (Pouchou, Pichoir 1985).

The Raman spectra of stibioclaudeite were collected in the range 4000 - 40 cm $^{-1}$  using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope (National Museum, Praha). The Raman signal

was excited by an unpolarised red 633 nm He-Ne gas laser and detected by a CCD detector. The experimental parameters were: 100x objective, 10 s exposure time, 300 exposures, 25  $\mu$ m pinhole spectrograph aperture and 8 mW laser power level. The spectra were repeatedly acquired from different grains in order to obtain a representative spectrum with the best signal-to-noise ratio. The eventual thermal damage of the measured point was excluded by visual inspection of the excited surface after measurement, by observation of possible decay of spectral features at the start of excitation and by checking for thermal downshift of Raman lines. The instrument was set up by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser-frequency calibration) and standardized white-light sources (intensity calibration). Spectral manipulations were performed using the Omnic 9 software (Thermo Scientific).



Fig. 1 Prismatic crystals of stibioclaudeite from the Zlatá Idka Ag-Au-Sb deposit. Field of view is 4 mm. Photo by L. Hrdlovič.

Table 1 X-ray powder diffraction data of stibioclaudeite from the Zlatá Idka Ag-Au-Sb deposit.

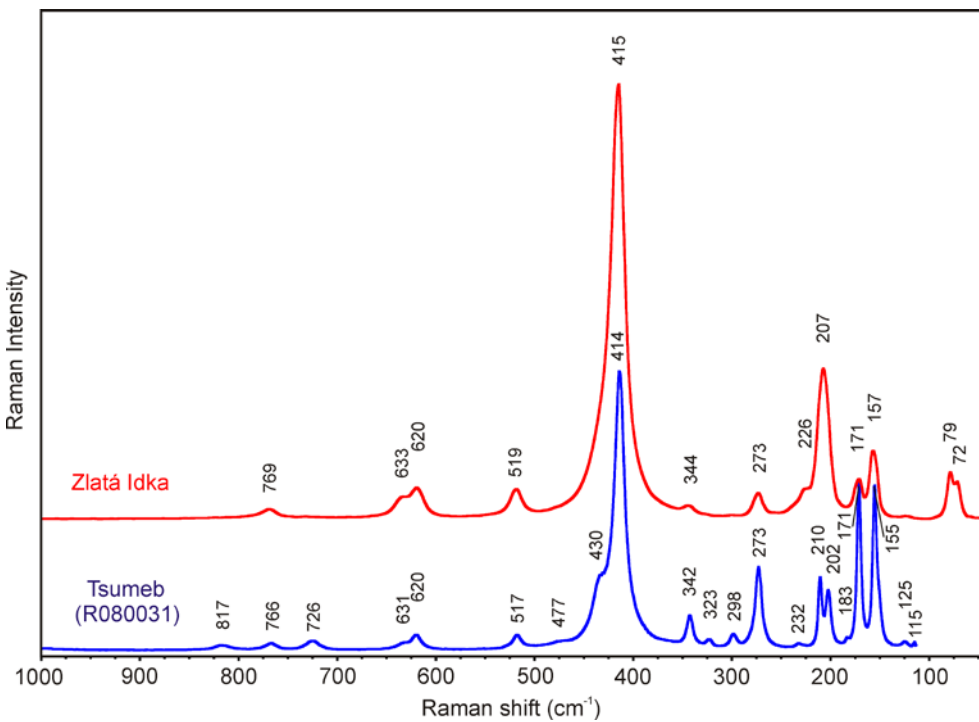
$l_{obs.}$	$d_{obs.}$	$d_{calc.}$	$h$	$k$	$l$	$l_{obs.}$	$d_{obs.}$	$d_{calc.}$	$h$	$k$	$l$
4.2	6.564	6.556	0	2	0	0.3	2.1144	2.1141	-1	3	2
0.9	4.996	4.991	0	1	1	0.5	2.0834	2.0836	0	4	2
1.6	3.629	3.640	-1	0	1	0.7	2.0624	2.0629	1	5	1
2.1	3.508	3.507	-1	1	1	0.4	2.0251	2.0256	0	6	1
1.8	3.398	3.397	0	3	1	0.5	1.8794	1.8808	0	5	2
3.7	3.346	3.341	1	0	1	0.5	1.8706	1.8702	2	4	0
100.0	3.279	3.278	0	4	0	0.5	1.8187	1.8198	-2	0	2
2.7	3.237	3.238	1	1	1	1.0	1.7693	1.7696	0	7	1
1.3	3.155	3.153	1	3	0	2.8	1.7321	1.7324	1	7	0
6.1	2.802	2.802	0	4	1	0.3	1.6640	1.6638	0	3	3
		2.797	-1	3	1	1.1	1.6387	1.6390	0	8	0
0.3	2.699	2.699	0	0	2	4.0	1.5680	1.5683	0	8	1
0.7	2.654	2.654	1	3	1	0.1	1.4811	1.4802	-1	7	2
0.7	2.642	2.643	0	1	2	0.5	1.3871	1.3876	1	9	0
1.0	2.2765	2.2772	2	0	0	0.3	1.3547	1.3541	-1	6	3
0.8	2.1281	2.1277	-1	5	1	0.3	1.3076	1.3071	-2	8	1
0.2	2.1181	2.1183	1	2	2						

**Table 2** Unit-cell parameters of stibioclaudeite from the Zlatá Idka Ag-Au-Sb deposit (for monoclinic space group  $P2_1/n$ ) compared with published data for stibioclaudeite and claudeite.

stibioclaudeite		a [Å]	b [Å]	c [Å]	$\beta$ [°]	V [Å <sup>3</sup> ]
Zlatá Idka	this paper	4.5715(17)	13.112(2)	5.4182(15)	94.97(3)	323.55(14)
Tsumeb	Origlieri et al. (2006)	4.5757(4)	13.1288(13)	5.4216(5)	95.039(4)	324.44
synth.	Bodenstein et al. (1983)	4.58(1)	13.16(2)	5.44(1)	95.0(1)	326.6
claudeite		a [Å]	b [Å]	c [Å]	$\beta$ [°]	V [Å <sup>3</sup> ]
Jáchymov	Origlieri et al. (2009)	4.5460(4)	13.0012(14)	5.3420(5)	94.329(2)	314.83(2)

**Table 3** Quantitative WDS analyses of stibioclaudeite from the Zlatá Idka Ag-Au-Sb deposit (wt.%).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
As <sub>2</sub> O <sub>3</sub>	44.20	45.98	45.46	45.40	46.74	44.04	46.27	45.77	46.67	44.23	45.32	44.07	44.58	43.97	44.22
Sb <sub>2</sub> O <sub>3</sub>	55.85	55.16	56.25	56.07	55.07	55.71	55.43	55.35	54.21	56.70	56.04	56.88	57.05	56.70	57.30
total	100.05	101.13	101.71	101.47	101.81	99.76	101.70	101.12	100.88	100.93	101.37	100.95	101.63	100.67	101.52
As <sup>3+</sup>	1.077	1.102	1.087	1.088	1.111	1.076	1.103	1.098	1.118	1.069	1.087	1.066	1.070	1.067	1.064
Sb <sup>3+</sup>	0.923	0.898	0.913	0.912	0.889	0.924	0.897	0.902	0.882	0.931	0.913	0.934	0.930	0.933	0.936
O <sup>2-</sup>	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000

**Fig. 2** Raman spectrum of stibioclaudeite from Zlatá Idka in comparison of spectrum of sample from Tsumeb (RRUFF R080031; Lafuente et al. 2015.)

## Results

Stibioclaudeite is rare mineral at the studied locality. It forms colourless, translucent to transparent prismatic crystals up 5 mm long with perfect cleavage and resinous lustre (Fig. 1), resembling gypsum. Crystals of stibioclaudeite are developed on fractures of quartz gangue with abundant altered aggregates of stibnite, arsenopyrite and minor pyrite, typically in proximity or on the contact of slightly altered stibnite and arsenopyrite and rim of brownish porous supergene mass of cervanite and amorphous Fe-Sb-As gels. No other supergene minerals were observed in direct association with stibioclaudeite.

The peak positions in X-ray powder pattern of stibioclaudeite from the Zlatá Idka (Table 1) agree well with data calculated from the crystal structure of this mineral (Origlieri et al. 2006), experimental PXRD data of stibioclaudeite

have not been published yet. Significant differences observed in intensities of individual diffraction maxima are due to the preferred orientation effects, especially perfect cleavage on {010}. The refined unit-cell parameters of studied stibioclaudeite, compared with published data for stibioclaudeite and claudeite from other localities, are given in Table 2.

Quantitative WDS chemical analyses of stibioclaudeite from the Zlatá Idka deposit and the corresponding empirical formulae are shown in Table 3. Studied stibioclaudeite is chemically homogenous and compositionally close to the ideal end member composition with average ( $n = 15$ ) empirical formula (based on O = 3 apfu) expressed as  $\text{As}_{1.09}\text{Sb}_{0.91}\text{O}_{3.00}$ .

The experimental Raman spectrum of stibioclaudeite from the Zlatá Idka deposit (Fig. 2) corresponds very well



with spectrum of stibioclaudeite from the Tsumeb mine published by Origlieri et al. (2009) (identical spectrum is given in RRUFF database (Lafuente et al. 2015) under number R080031). The region 4000 - 1000  $\text{cm}^{-1}$  of spectrum shows no active Raman modes of greater significance than background, demonstrating that stibioclaudeite is nominally anhydrous. Mercier, Sourisseau (1978) and Bahfenne (2011) studied closely related claudeite and observed antisymmetric stretching modes of  $\text{AsO}_3$  in the area 600 - 900  $\text{cm}^{-1}$ , symmetric stretching modes in 500 - 600  $\text{cm}^{-1}$  and symmetric deformation modes in 300 - 500  $\text{cm}^{-1}$ . Due to the presence of antimony in the crystal structure of stibioclaudeite, a shift of the band wavenumbers to lower values can be predicted according to Hooke's Law (Nakamoto 2009).

## Conclusions

A new occurrence of rare supergene mineral, stibioclaudeite was discovered at the Štefan vein, Zlatá Idka Ag-Au-Sb deposit, Spišsko-gemerské rudohorie Mts., Slovakia. Studied stibioclaudeite was formed by the *in-situ* weathering of primary ore minerals such as arsenopyrite and stibnite at the base of the supergene zone under the relatively reducing conditions, probably very similar to those observed by Green et al. (2014) at the Wet Swine Gill in UK.

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