NATURAL $Pb_9Sb_8S_{21}$ FROM KUTNÁ HORA, CZECH REPUBLIC, FIRST OCCURRENCE, CHEMISTRY AND X-RAY POWDER DIFFRACTION DATA

RICHARD PAŽOUT

Department of Chemistry of Solid State, Institute of Chemical Technology Prague, Technická 6, 166 28 Prague

E-mail: richard.pazout@vscht.cz

Submitted July 25, 2007; accepted October 8, 2007

Keywords: Chalcogenides, Pb-Sb sulphosalts, Natural $Pb_9Sb_8S_{21}$, Semseyite

Natural $Pb_9Sb_8S_{21}$, known as the mineral semseyite, was newly identified in the Kutná Hora ore district, Central Bohemia, Czech Republic. Chemical compositional data and X-ray powder diffraction data are presented in the paper. Chemical composition was determined by electron microprobe analysis which revealed increased content of Bi and Se. Unit cell parameters have been calculated. Semseyite has a monoclinic unit cell with a = 13.626(18), b = 11.960(12), c = 24.325 (45), β = 105.83 (11), V = 3813.96 Å³, space group C2/c. Lenghtening of a and b parameters compared to the published structure is accompanied by shortening of the c parameter reflecting the actual chemical composition.

INTRODUCTION

Chalcogenides (sulphosalts) is a class of inorganic compounds of metals and semi-metals with sulphur. The general formula commonly accepted for these phases is $A_mB_nX_p$, where A is metallic element, usually Pb, Ag, Cu, Sn, In, Fe, Hg, Tl, B is semi-metallic (formally trivalent) element As, Sb or Bi and X is S, Se and Te [1].

Chalcogenide systems have come to the focus of attention for their specific electrical (semi-conductive) properties as perspective materials for long-term data storage or materials for solar batteries. Both synthetic and natural chalcogenides are studied. It has been observed that some synthetized phases have no counterpart in natural chalcogenide systems and vice versa. The impossibility to synthetize phases found in natural chalcogenide systems is ascribed - among other things - to the presence of stabilizing minority elements. On the other hand chalcogenide phases have been synthetized that have not been identified in nature [2].

Presented in this article are chemical and structural data of natural chalcogenide phase $Pb_9Sb_8S_{21}$, known as the mineral semseyite. The study is a part of a research of phases in natural chalcogenide systems of Pb–Sb, Ag–Pb–Sb, Ag–Pb–Bi, Ag–Pb–Bi–Sb a Ag–Cu–Pb–Bi–Sb. Within this research, two occurrences of semseyite, $Pb_9Sb_8S_{21}$, have been found in the Kutná Hora vein Ag–Pb–Zn polymetallic deposit, Central Bohemia, Czech Republic. This phase is new among chalcogenides found in the Kutná Hora ore district and its elevated content of bismuth is unusual on a world scale.

EXPERIMENTAL

Localization, mineralogical setting and description

Kutná Hora Ag–Pb–Zn polymetallic deposit (60 km east of Prague, Central Bohemia, Czech Republic) is a hydrothermal vein type deposit of the Variscan age. It was one of the main European producers of silver in the 14th to 16th century with hundreds of mines on some twelve major lodes (veins). This silver-rich ore deposit is a representative of polymetallic ores with prevailing sulfides and sulphosalts of Ag, Pb, Zn, Cu, Fe, Sb, and As (and in the northern part also of Sn and Bi). Geologically and mineralogically, two mineral assemblages are present in the deposit, one "silver-rich" in the southern part of the deposit and one "pyrite-rich" in the northern part. The silver-rich assemblage consists mainly of freibergite - $Ag_{7.2}Cu_{3.6}Fe^{2+}_{1.2}Sb_3AsS_{13}$, miargyrite - $AgSbS_2$, pyrargyrite - Ag_3SbS_3, native silver, allargentum - Ag_6Sb, galena - PbS, tetrahedrite - $Cu_9Fe^{2+}_3Sb_4S_{13}$, pyrite - FeS_2, sphalerite - ZnS, berthierite - $Fe^{2+}Sb_2S_4$ and Pb–Sb(–Ag) sulphosalts (boulangerite - $Pb_5Sb_4S_{11}$, jamesonite - $Pb_4Fe^{2+}Sb_6S_{14}$ and owyheeite - $Ag_{1.5}Pb_{4.5}Sb_{5.5}S_{14}$) in quartz-kutnohorite gangue. The pyrite-rich assemblage consists mainly of Ag-bearing galena, pyrite, chalcopyrite - $CuFe^{2+}S_2$, arsenopyrite - $Fe^{3+}AsS$, sphalerite, pyrrhotite - FeS, marcasite - FeS_2, freibergite/tetrahedrite, stannite - $Cu_2Fe^{2+}SnS_4$ and Pb–Sb(–Ag) sulphosalts in quartz gangue and no kutnohorite. [3]. Typical of this assemblage is the presence of Bi and Sn, completely absent in the "silver-rich" assemblage in the southern part of the deposit, making space for a whole suite of Pb–Bi–Sb–Ag chalcogenides not known from elsewhere in the Czech Republic.

The samples with natural chalcogenides described in this article were found by the author during the investigation of ore samples from medieval mine dumps of the Old Bohemian Lode and the Guntecko-hlousecke Lode in the northern part of the deposit. Both lodes belong to the "pyrite-rich" lodes. The first occurrence of semseyite was discovered at the Old Bohemian Lode (sample ST 170). Semseyite forms grey black grain aggregates (maximum size 4 mm) intergrowing with galena and associated with boulangerite, jamesonite, freibergite and chalcopyrite (Figure 1). Two different mineral associations were observed in the bulk quartz gangue material of the sample ST 170: in the majority of its volume the gangue material contains only a "poor" paragenesis: interspersed grains of arsenopyrite, sphalerite and pyrite. In the other part of the gangue material a noticeable enrichment occurs: chalcopyrite lens up to several centimetres appear, accompanied by coarse-grained aggregates of galena intergrowing with semseyite, massive fibrous aggregates of grey boulangerite (with a slight greenish tint), steel grey jamesonite and grey black grains of freibergite. Neither Ag–Pb–Sb nor Ag–Pb–Bi sulphosalts of the homologous series gustavite–lillianite were detected.

The second occurrence of semseyite (sample HL 11 B) comes from the Gruntecko-hlousecke Lode. A sample of quartz gangue contains grain aggregates of pyrite and galena. In the bulk of white quartz, lens of dark grey "dürrerz" type quartz appear averaging 10 mm. This type of quartz contains grain aggregates of galena accompanied by silvery light, grey to grey black grain aggregates up to the size of 3 mm with metallic lustre. Two, by appearance identical lens with ore aggregates were used for the preparation of polished sections. In the polished section HL 11 B, only semseyite and galena were detected and an increased content of Bi and Ag was not detected in either phase. The second polished section HL 11 A was on the other hand rich in Ag and Bi phases and yielded gustavite - $AgPbBi_3S_6$, schirmerite and galena with an increased content of Bi and Ag.

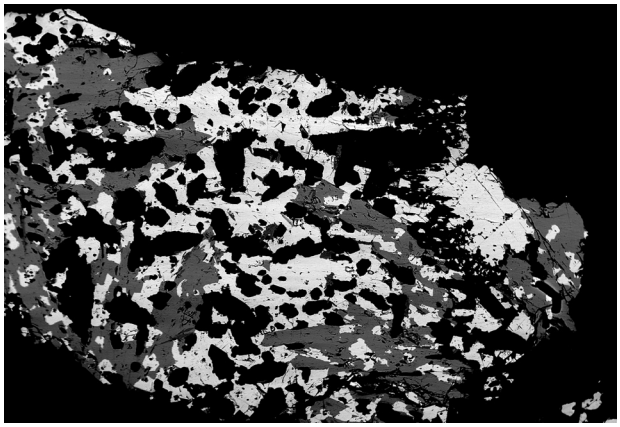

Figure 1. Aggregates of $Pb_9Sb_8S_{21}$ (semseyite - grey) and PbS (galena) with elevated content of Bi and Ag (white) from Kutna Hora polymetallic deposit (sample ST 170). BSE micrograph. Width of the micrograph is 1200 μm.

Electron microprobe analysis

The chemical composition was determined by point quantitative chemical analysis carried out by the electron microprobe analyzer JEOL JXA-8600 (University of Salzburg, analyst Dan Topa) with LINKeXL system in wave-length dispersive mode (WDS) and the following conditions: 25 kV, 35 nA, counting time 20 s for peaks, 7 s for background, beam diameter 5 μm. The following standards and X-ray lines were used: PbS (Pb$L\alpha$), Ag metal (Ag$L\alpha$), Sb2S3 (Sb$L\alpha$), $CuFeS_2$ (Fe$K\alpha$, Cu$K\alpha$).Bi_2S_3 (Bi$L\alpha$, S$K\alpha$), CdTe (Cd$L\alpha$) and Bi_2Se_3 (Se$K\alpha$). Measured data were corrected by the ZAF-4 method.

X-ray powder diffraction

X-ray powder diffraction data of semseyite were collected on the diffractometer X´Pert PRO Panalytical, step-scanning 0.02°/34 s, radiation Cu$K\alpha$, 40 kV, 30 mA,. angular range 3.3-55° 2θ, point detector with secondary graphite monochromator (Institute of Chemical Technology Prague). A very small amount of the sample ST 170 was placed on the surface of a silicon sample holder. Quartz contained in the analyzed sample was used as an internal standard to check the possible displacement. The positions of quartz reflections in the measured sample were identical to those published in the literature. The obtained powder pattern was processed using X-ray powder diffraction software HighScore Plus [4] which found angular positions and intensities of reflections. Theoretical values of angular positions and their *hkl* indices calculated by the program HKLGEN [5] were used for indexing the experimental powder pattern, intensities of reflections were checked against those calculated by the program Lazy Pulverix [6]. The calculation of unit cell parameters was carried out by least-squares method implemented in the program Firestar-2. [7], extrapolation function used: $\cos\theta \times \cot\theta + \cot 2\theta$.

RESULTS AND DISCUSSION

Average chemical composition of semseyite from Old Bohemian Lode (Table 1, sample ST 170, 8 point analyses) can be expressed on the basis of 38 atoms per formula unit (*apfu*) by empirical formula $(Pb_{9.10}Fe_{0,03})_{\Sigma=9.13}(Sb_{7.70}Bi_{0,14})_{\Sigma=7.84}(S_{20.96}Se_{0,07})_{\Sigma=21,02}$.

This phase shows an increased content of Bi (mean 0.83 wt.% or 0.14 *apfu*), minute surplus of Pb (0.1 *apfu*) and a small deficit of Sb+Bi (0.16 *apfu*). An interesting feature is a presence of selenium in the average amount of 0.15 wt. % or 0.65 *apfu*. 0.14 *apfu* of Bi means that for Z = 4 there are approximately 10 atoms of antimony replaced by bismuth in every 18 cells. The same calculation for selenium gives one sulphur atom replaced by selenium in every four cells. Putting it on the same scale, 40 atoms of antimony are replaced by bismuth and 18 atoms of sulphur are replaced by selenium in every 72 cells.

Table 1. Chemical composition of semseyite from Old Bohemian Lode in wt.%.

ST 170	Pb	Cu	Fe	Ag	Cd	Sb	Bi	Se	S	Total
1	54.64	0.02	0.00	0.00	0.00	26.19	0.89	0.15	19.60	101.49
2	54.09	0.00	0.03	0.00	0.00	26.99	0.92	0.16	19.82	102.00
3	54.32	0.00	0.01	0.00	0.00	26.38	0.84	0.14	18.98	100.66
4	54.08	0.00	0.12	0.00	0.00	25.90	1.12	0.12	18.77	100.10
5	54.55	0.00	0.02	0.00	0.00	27.22	0.67	0.16	19.73	102.36
6	52.26	0.00	0.16	0.02	0.00	27.65	0.90	0.22	18.02	99.22
7	53.95	0.03	0.01	0.00	0.00	27.28	0.65	0.11	19.57	101.60
8	53.90	0.00	0.02	0.00	0.00	27.18	0.70	0.12	19.50	101.43
mean	53.97	0.01	0.05	0.00	0.00	26.85	0.83	0.15	19.25	101.11
	Formula on the basis of 38 atoms, Z = 4									
	Pb	Cu	Fe	Ag	Cd	Sb	Bi	Se	S	Total
1	9.139	0.010	0.002	0.000	0.000	7.454	0.148	0.066	21.181	38.000
2	8.955	0.000	0.019	0.000	0.000	7.606	0.150	0.068	21.201	38.000
3	9.253	0.000	0.009	0.000	0.000	7.646	0.141	0.062	20.889	38.000
4	9.286	0.000	0.074	0.000	0.000	7.568	0.190	0.056	20.825	38.000
5	9.031	0.000	0.013	0.000	0.000	7.668	0.111	0.068	21.109	38.000
6	9.117	0.000	0.106	0.007	0.000	8.207	0.155	0.100	20.308	38.000
7	8.997	0.014	0.006	0.000	0.000	7.743	0.108	0.049	21.082	38.000
8	9.013	0.001	0.010	0.000	0.000	7.734	0.115	0.054	21.073	38.000
mean	9.099	0.003	0.030	0.001	0.000	7.703	0.140	0.065	20.959	38.000

Table 2. Chemical composition of semseyite from Gruntecko-hloušecké Lode in wt.%.

HL 11 B	Pb	Cu	Fe	Ag	Cd	Sb	Bi	Se	S	Total
1	53.93	0.00	0.03	0.00	0.00	28.46	0.01	0.00	20.15	102.6
2	53.75	0.00	0.03	0.00	0.00	28.52	0.01	0.04	20.40	102.7
mean	53.84	0.00	0.03	0.00	0.00	28.49	0.01	0.02	20.28	102.66
	Formula on the basis of 38 atoms, Z = 4									
	Pb	Cu	Fe	Ag	Cd	Sb	Bi	Se	S	Total
1	8.807	0.000	0.017	0.000	0.000	7.911	0.002	0.000	21.264	38.000
2	8.716	0.000	0.017	0.000	0.000	7.871	0.001	0.016	21.379	38.000
mean	8.762	0.000	0.017	0.000	0.000	7.891	0.001	0.008	21.321	38.000

Table 3. Chemical composition of galena from Old Bohemian Lode in wt.%.

ST 170	Pb	Cu	Fe	Ag	Cd	Sb	Bi	Se	S	Total
1	85.52	0.00	0.04	0.48	0.15	0.31	1.33	0.23	13.35	101.42
2	85.96	0.04	0.03	0.20	0.16	0.13	0.56	0.02	13.62	100.73
3	85.81	0.05	0.06	0.26	0.08	0.00	0.82	0.01	13.52	100.60
4	85.87	0.00	0.03	0.26	0.11	0.07	0.82	0.04	13.56	100.75
mean	85.79	0.02	0.04	0.30	0.12	0.13	0.88	0.08	13.51	100.88
	Formula on the basis of 2 atoms, Z = 4									
	Pb	Cu	Fe	Ag	Cd	Sb	Bi	Se	S	Total
1	0.974	0.000	0.002	0.010	0.003	0.006	0.015	0.007	0.983	2.000
2	0.978	0.001	0.001	0.004	0.003	0.003	0.006	0.001	1.002	2.000
3	0.981	0.002	0.002	0.006	0.002	0.000	0.009	0.000	0.998	2.000
4	0.980	0.000	0.001	0.006	0.002	0.001	0.009	0.001	0.999	2.000
mean	0.978	0.001	0.002	0.007	0.003	0.002	0.010	0.002	0.995	2.000

It is not known to the author of this article that semseyite with this amount of bismuth was published from any locality throughout the world.

The chemical composition of PbS (galena) associated with this Bi-bearing phase (Table 3) exhibits an increased content of Bi (mean 0.88 wt. % or max. 0.01 *apfu*) and Ag (mean 0.3 wt. % or. 0.007 *apfu*) compared to galenas from other parageneses and lodes of the Kutná Hora ore district. Ag–Bi substitution in PbS is a different case from the Bi^{3+}–Sb^{3+} substitution in chalcogenides because PbS forms solid solution with $AgBiS_2$ [8]. The highest levels of Bi and Ag in PbS from the Kutná Hora deposit were found in those galenas which were associated with Ag–Pb–Bi–Sb sulphosalts of the lillianite homologous series ($AgPbBi_3S_6$ - gustavite and $AgPb(Sb,Bi)_3S_6$ - Bi-rich andorite). In these galenas the maximum mean content of Bi amounts to as much 6.34 wt.% or 0.071 *apfu* and the content of Ag to as much as 2.98 wt % or 0.065 *apfu*.

Chemical composition of semseyite from Gruntecko-hloušecke Lode (Table 2, sample HL 11 B, 2 point analyses) yielded the empirical formula $(Pb_{8.76}Fe_{0,02})_{\Sigma=8.78}Sb_{7.89}(S_{21.32}Se_{0.01})_{\Sigma=21,33}$. This sample exhibits a small deficit of Pb (0.24 *apfu*) and Sb (0.11 apfu) and a surplus of sulphur (0.32 *apfu*). Galena associated with this phase does not show increased amounts of any minority element (Table 4).

Bi-bearing natural $Pb_9Sb_8S_{21}$ from Kutná Hora (sample ST 170) has been found to have unit cell parameters: a = 13.626(18), b = 11.960(12), c = 24.325(45), β = 105.83(11), V = 3813.96 Å^3, space group $C2/c$. While the cell volume is nearly identical to that of the published structure [9], a noticeable difference is seen at the c parameter - which in the case of chalcogenides is the so called "sulphosalt" parameter. This is the parameter in the direction of the elongation of the needle-like habit of sulphosalt crystals and it is a multiple of 4 Å. The calculated c parameter of 24.325(45) Å is by 0.128 Å shorter than that of the determined structure which is 2.84 of the standard deviation. The chemistry, especially the Bi content, is responsible for the lenghtening of the a and b parameters which is accommodated

Table 6. X-ray powder diffraction data of semseyite from Kutná Hora (ST 170).

d_{obs}	I_{rel}	h	k	l	d_{calc}
11.861	8	0	0	2	11.701
6.540	11	2	0	-2	6.528
6.514	14	1	1	2	6.500
5.394	12	1	1	3	5.378
5.331	8	0	2	2	5.325
4.531	20	1	1	4	4.511
3.878	53	2	2	-4	3.886
3.822	65	1	3	0	3.814
3.822	65	1	3	-1	3.813
3.726	34	1	3	-2	3.714
3.585	20	3	1	-5	3.573
3.317	45	1	3	-4	3.318
3.303	41	3	1	3	3.301
3.280	78	3	1	-6	3.278
3.258	100	4	0	0	3.277
3.027	48	1	1	6	3.348
2.859	65	4	2	-4	2.865
2.859	65	3	3	1	2.858
2.769	33	4	2	-5	2.761
2.741	35	3	1	-8	2.736
2.724	35	2	4	0	2.720
2.697	73	2	2	6	2.689
2.365	13	4	2	4	2.365
2.252	33	5	3	-2	2.248
2.252	33	5	3	-3	2.247
2.228	29	0	4	7	2.229
2.153	50	4	4	-5	2.157
2.153	34	1	5	-5	2.145
2.055	37	1	5	-6	2.060

Table 4. Chemical composition of galena from Gruntecko-hloušecké Lode in wt.%.

HL 11B	Pb	Cu	Fe	Ag	Cd	Sb	Bi	Se	S	Total
1	87.62	0.00	0.06	0.00	0.16	0.09	0.08	0.02	13.42	101.45
2	88.00	0.00	0.07	0.01	0.13	0.07	0.00	0.07	13.40	101.76
mean	87.81	0.00	0.07	0.01	0.14	0.08	0.04	0.05	13.41	101.61
	Formula on the basis of 2 atoms, Z = 4									
	Pb	Cu	Fe	Ag	Cd	Sb	Bi	Se	S	Total
1	1.001	0.000	0.002	0.000	0.003	0.002	0.001	0.001	0.990	2.000
2	1.003	0.000	0.003	0.000	0.003	0.001	0.000	0.002	0.987	2.000
mean	1.002	0.000	0.003	0.000	0.003	0.002	0.000	0.001	0.989	2.000

Table 5. Unit cell parameters of natural $Pb_9Sb_8S_{21}$, semseyite from Kutná Hora (sample ST 170) in comparison with published structure [9] (monoclinic space group $C2/c$).

		a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
Semseyite	structure [9]	13.603(3)	11.936(8)	24.453(7)	106.047	3815.62
Semseyite	Kutná Hora (this work)	13.626(18)	11.960(12)	24.325(45)	105.83(11)	3813.96

by the contraction of the "sulphosalt" *c* parameter to preserve the cell volume corresponding to the monoclinic $Pb_9Sb_8S_{21}$ without changing the symmetry. Refined unit cell parameters of semseyite (sample ST 170) are listed in Table 5. X-ray powder diffraction data are in Table 6.

CONCLUSIONS

Two occurrences of natural chalcogenide phase $Pb_9Sb_8S_{21}$, known as the mineral semseyite, were detected at two different lodes of the Kutná Hora ore district, Czech republic. After $Pb_5Sb_4S_{11}$ and $Pb_4FeSb_6S_{14}$, this is only the third confirmed Pb–Sb chalcogenide phase from the deposit. Semseyite from the Old Bohemian Lode contains increased levels of Bi which substitutes for Sb, and also of Se. X-ray powder diffraction analysis yielded unit cell parameters showing a slight lengthening of the *a* and *b* parameters accompanied by a contraction of *c* parameter reflecting the chemistry and resulting configurational ordering to preserve the symmetry.

Acknowledgement

This work was supported by the project 203/07/0040 of the Grant Agency of the Czech Republic. The author would also like to thank to Dan Topa (University of Salzburg) for microprobe analysis, Jiří Sejkora (National Museum Prague) for many helpful hints on X-ray diffraction part of the article and to Jaroslav Maixner (Institute of Chemical Technology Prague) for careful reading of the manuscript.

References

1. Makovicky, E.: *European Mineralogical Union Notes in Mineralogy 1*, 237 (1997).
2. Light M. E.: *Structural Studies of Mineral Silicates and Synthetic Sulfosalts Characterised by Mixed Occupancies*, Cardiff (1997).
3. Holub M., Hoffman V., Mikuš M., Trdlička Z.: Sbor. geol. věd, Lož. Geol. Mineral. *23*, 60 (1982).
4. HighScore Plus, *Full Powder Pattern Analysis Software*, V2.0a, Almelo (2004).
5. LeBail A.: HKLGEN: A program for generating hkl, multiplicity, d(hkl), 2-theta from a wavelength, a space group, cell parameters, 1998.
6. Yvon K., Jeitschko W. and Parthé E.: J. Appl. Cryst. *10*, 73 (1977).
7. Fergusson I. F., Rogerson A. H., Wolstenholme J. F. R., Hughes T. E., Huyton A.: Firestar -2. *A computer program for the evalutuation of X-ray powder measurements and the derivation of crystal lattice parameters*, 1987.
8. Foord E. E., Shawe D. R.: Can. Mineral. *27*, 363 (1989).
9. Kohatsu J. J. and Wuensch, B. J.: Am. Mineral. *59*, 1127 (1974).

$Pb_9Sb_8S_{21}$ Z RUDNÍHO REVÍRU KUTNÁ HORA, PRVNÍ VÝSKYT, CHEMICKÉ SLOŽENÍ A RENTGENOVÁ PRÁŠKOVÁ DIFRAKČNÍ DATA

RICHARD PAŽOUT

Ústav chemie pevných látek,
Vysoká škola chemicko-technologická,
Technická 6, 166 28 Praha 6

Přírodní fáze o složení $Pb_9Sb_8S_{21}$, známá jako minerál semseyit, byla nově identifikována v rudním revíru Kutná Hora. Cílem práce bylo stanovení chemického složení fáze včetně obsahu minoritních prvků a rentgenová prášková difrakční analýza s cílem zjištění mřížkových parametrů a jejich korelaci s chemickým složením.Chemické složení bylo stanoveno metodou elektronové mikroanalýzy ve vlnově disperzním modu a odhalilo zvýšené obsahy bismutu a selenu. Byly vypočteny mřížkové parametry. Semseyit má monoklinickou buňku s parametry a = 13.626(18), b = 11.960(12), c = 24.325 (45), β = 105.83 (11), V = 3813.96 A^3, prostorová grupa $C2/c$. Prodloužení mřížkových parametrů a a b v porovnání s publikovanou strukturou je doprovázeno zkrácením "sulfosolového" mřížkového parametru c, které odrážejí chemické složení přírodní fáze se zvýšeným obsahem bismutu při zachování objemu základní buňky a symetrie.