

Balkanite, $\text{Cu}_9\text{Ag}_5\text{HgS}_8$, A New Mineral from the Sedmochislenitsi Mine, Bulgaria

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Abstract

Balkanite is a new copper-silver-mercury sulfide from the high-grade copper ores of the Sedmochislenitsi lead-zinc-copper stratiform deposit, Bulgaria. The associated minerals are bornite, chalcocite, djurleite, digenite, tennantite, stromeyerite, mercurian silver, and cinnabarite. Microprobe analysis gave: Cu 37.4, Ag 33.1, Hg 14.0, S 17.2, for a total of 101.7 wt percent. Balkanite is orthorhombic with space group $P222$, $Pmm2$, or $Pmmm$, and a 10.62 ± 0.02 , b 9.42 ± 0.02 , c $3.92 \pm 0.04\text{\AA}$, and $Z = 1$. Its density, as measured on synthetic material, is 6.32 g/cm. The mineral is steel-gray, with metallic luster, and strongly anisotropic; white-gray in polished sections. Figures are given for the reflectivity. Vickers microhardness range from 79.4–91.6 kg/mm² (about 3½ on Mohs' scale).

Introduction

Balkanite was found in 1961–1962 in six samples ranging in size from 1 to 4 cm, originating from the Sedmochislenitsi mine, Vratsa district, in the western part of the Stara Planina, Bulgaria. Most of these samples are, in fact, polished sections. As an unknown silver mineral it was reported by Stoinov, Atanassov and Lilov (1964), while some of the more recent papers by Atanassov (1970, 1971) contain data on its chemical composition. To date, balkanite is the only known sulfide of copper, silver and mercury, either as a mineral or as a synthetic product. It was approved as a new mineral and mineral name by the Commission of New Minerals and Mineral Names, IMA, in April 1971. The suggested name balkanite stems from the medieval and popular name of the Stara Planina, the main mountain range giving its name to the Balkan Peninsula.

Description of the Type Locality

The Sedmochislenitsi stratiform deposit results from the hydrothermal metasomatism developed around a system of tectonic faults cutting limestones and dolomites of Middle Triassic age. Two types of industrial ores are mined in the deposit, lead-zinc ores in the upper levels and copper ores at greater depths. Considerable differences in mineral composition exist among the copper mineralizations from the middle and lower levels. Two clear-cut mineral associations are observed:

a) *A tennantite-chalcopyrite association*, which is characteristic of the middle levels of the deposit. Tennantite and chalcopyrite are the main ore minerals, whereas galena, sphalerite, tetrahedrite and high-silver freibergite (up to 22.2 wt percent Ag) are present in smaller amounts along with pyrite and marcasite. A sequence of silver minerals, mainly sulfosalts, is paragenetically connected with this association; these are pyragyrite, pyrostilpnite, stephanite, polybasite, pearseite, acanthite, jalpaite and minor amounts of native silver.

b) *A tennantite-bornite association*, wherein the main ore minerals are tennantite, bornite, chalcopyrite and primary chalcocite, is characteristic of the lowest levels. It is accompanied by another well-defined silver mineral association: stromeyerite, mackinstryite and comparatively large amounts of native silver which is usually mercury-bearing. The mercury content in mercurian silver varies over a wide range even within a single mineral grain (Atanassov, 1969). The silver from samples containing cinnabarite and balkanite shows a higher and more constant mercury content. It should be noted that no silver sulfosalts are found in the tennantite-bornite association.

Balkanite is a rare mineral in the mineral paragenesis of the deposit and occurs only in the tennantite-bornite association in samples taken from ore body 2 at the 890 meter level. The associated minerals are: tennantite, bornite, chalcocite, mer-

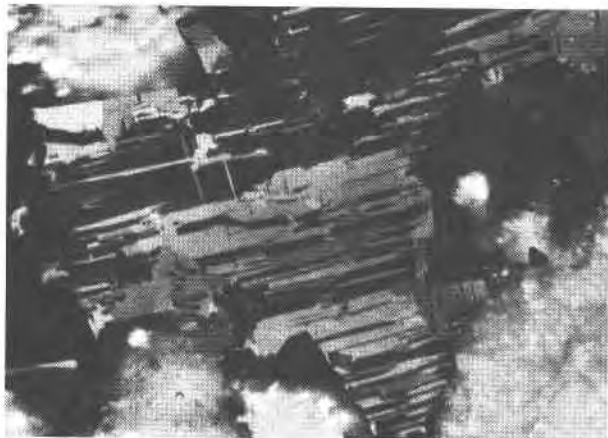


FIG. 1. Lamellar balkanite crystals. The elongation of the lamellae is parallel to the *c*-axis. Crossed nicols. Magnification 340 \times .

curian silver, chalcopyrite, cinnabarite, stromeyerite, mackinstryite, wittichenite, native bismuth, rammelsbergite, djurleite, digenite, pyrite, calcite, barite and aragonite.

Type Material

The samples in which balkanite was found are kept in the Mineralogical Museum of the Higher Institute of Mining and Geology, Sofia (Specimen No. 619) and in the Museum of the University 'KI, Ohridski', Sofia (Specimen No. 1351).

Synthesis

The very small amount of available natural material was insufficient for a detailed study. Therefore

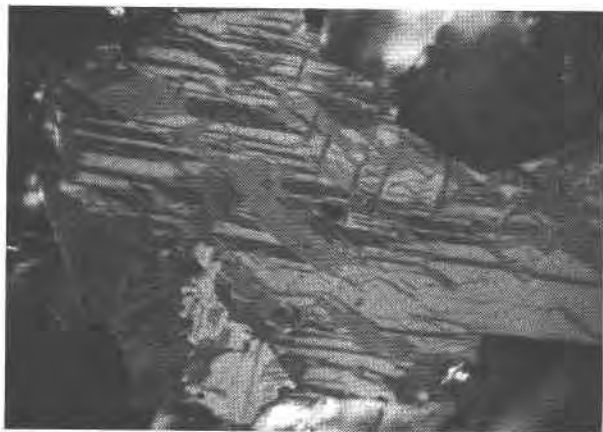


FIG. 2. Balkanite lamellae along several directions. The larger lamellae are internally laminated. Crossed nicols. Magnification 330 \times .



FIG. 3. Grained balkanite with polysynthetic twins. Crossed nicols. Magnification 330 \times .

synthesis was attempted on the basis of the chemical analysis of the natural material. The synthesis was achieved in evacuated quartz tubes from a stoichiometric mix of Cu_2S , HgS , Ag and S, heated for 48 hours at 550°C and furnace cooled. A comparatively coarse crystalline material was obtained while very small crystals were formed at the top of the tube. The physical properties and X-ray powder patterns of the natural material and the synthetic product are identical. Under the microscope minor amounts of chalcocite, djurleite and covellite are observed in the synthetic material.

Morphology and Physical Properties

Balkanite occurs as grains up to 2–3 mm, in or around small fissures and rock cavities. Rod-like prismatic balkanite crystals from 0.01 to 0.2 mm were found in druse-like cavities overlying barite, chalcocite, bornite and mercurian silver, and covered by calcite and aragonite.

The balkanite crystals are elongated along the *c*-axis and have an almost isometric cross-section. They are bounded by prismatic faces striated parallel to the elongation and by a flat bipyramid with bright faces. Goniometer measurements were impossible, owing to the small size of the crystals and the striation of the prismatic faces.

In polished sections the balkanite crystals are euhedral to subhedral and are almost always twinned (Figs. 1, 2), consisting of two or three lamella systems which are visible both with and without analyzer, owing to the strong anisotropy of the mineral. The larger lamellae are sometimes made up of smaller ones (Fig. 2). Balkanite aggregates

TABLE 1. REFLECTIVITIES OF BALKANITE AND ASSOCIATED MINERALS

Mineral		Wavelengths (nm)												
		435	440	460	480	500	520	540	560	580	600	620	640	660
Natural Balkanite	Rg [†]	35.2	35.4	35.6	35.4	35.0	34.0	34.0	33.4	32.8	32.4	32.1	31.8	31.5
	Rp [†]	30.4	30.6	31.0	31.0	30.2	38.9	28.0	27.2	26.5	16.0	25.6	25.1	24.9
Synthetic Balkanite	Rg [†]	34.0	34.2	34.7	34.9	34.4	33.6	33.0	32.4	31.8	31.4	31.0	30.7	30.5
	Rp [†]	27.5	27.7	28.4	28.0	27.4	26.7	25.9	25.4	25.0	24.7	24.5	24.4	24.3
Mackin- stryite	Rg [†]	39.2	38.9	37.7	36.7	35.4	34.2	33.3	32.6	31.9	31.4	30.7	30.2	29.8
	Rp [†]	31.1	31.2	31.1	30.5	29.6	28.8	28.0	27.4	27.0	26.5	26.2	26.0	25.7
Stromey- erite	Rg [†]	39.5	39.3	37.6	35.2	33.1	31.4	30.3	29.5	29.0	28.6	28.4	28.2	28.0
	Rp [†]	30.3	30.0	29.3	28.7	28.2	27.7	27.2	26.8	26.5	26.4	26.2	26.2	26.1
Chalco- cite	Rg [†]	36.8	36.7	36.3	35.8	35.1	34.1	33.1	32.2	31.3	30.8	30.2	29.9	29.6
	Rp [†]	36.4	36.2	36.0	35.3	34.8	33.8	32.5	31.7	31.0	30.2	29.4	28.8	28.4
Wittiche- nite	Rg [†]	35.5	35.5	35.9	36.4	36.5	36.5	36.4	36.0	35.8	35.5	35.1	34.7	34.4
	Rp [†]	32.4	32.3	31.5	31.7	32.0	32.4	32.7	32.7	32.6	32.4	32.1	31.8	31.4
Tennantite	R	30.4	30.5	30.8	30.9	31.0	30.5	30.2	30.0	29.7	29.2	28.8	28.5	28.2
Metallic Si (Standard)	R	43.5	43.0	41.2	39.9	38.9	38.9	37.1	36.4	35.8	35.4	35.0	34.7	34.4

consisting of graphically and subgraphically twinned grains are also observed (Fig. 3). Isolated lamellae and systems of lenticular balkanite exsolutions were occasionally observed in chalcocite grains (Figs. 4, 5).

Balkanite is steel-gray with metallic luster. In color, luster, striation and crystal habit it is almost indistinguishable from chalcocite and stromeyerite. No cleavage was observed. Density (6.318 g/cm³) was measured only on synthetic balkanite because of the small amount of natural mineral available. The Vickers microhardness, determined from 20 measurements on natural material and from 10 on synthetic material was 79.4–91.6 kg/mm² and 82.4–93.4 kg/mm² respectively (about 3.5 on Mohs' scale). The measurements were carried out with a PMT-3 equipment using a load of 10 g. Under the same conditions a value of 20.5 kg/mm² was found for NaCl.

Under the microscope balkanite is white-gray. It differs from chalcocite and djurleite by its strong anisotropy, but its polishing hardness is about the same. From stromeyerite it differs by its higher relief and the lack of a violet hue; from tennantite by its lower relief and anisotropy; and from wittichenite by its bluish hue and stronger anisotropy. Balkanite can be distinguished from mackinstryite only after instrumental measurement of the dispersion of reflectivity over a sufficiently large interval of the visible light spectrum.

In Table 1, the reflectivities of natural and synthetic balkanite are compared with optically-similar minerals from the same deposit.

Diagnostic etch reactions are also useful in differentiating balkanite from the associated minerals. Balkanite reacts with 20 percent KCN, 5 percent HgCl₂ and 20 percent FeCl₂ and does not react with 1:1 HNO₃ 1:1 HCl and 40 percent KOH.

X-Ray and Thermal Data

The X-ray powder patterns of the synthetic and natural material (Table 2) differ substantially from those of other known mineral species and cannot be interpreted as a mixture of copper, silver and mercury minerals.

Laue, rotation and oscillation photographs of a 0.15 mm long crystal showed that the mineral is

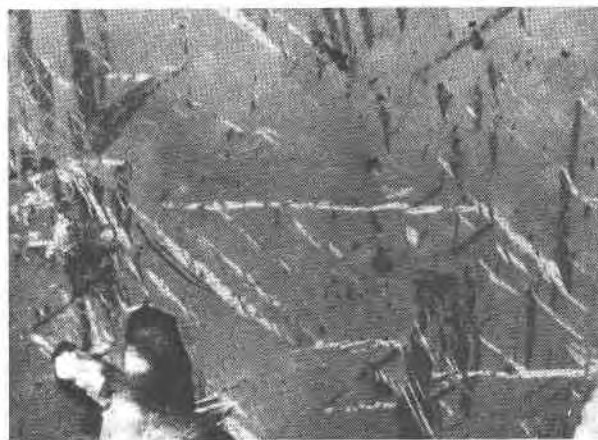


FIG. 4. Balkanite lamellae (light gray and dark gray) in chalcocite (gray). Crossed nicols. Magnification 300 ×.

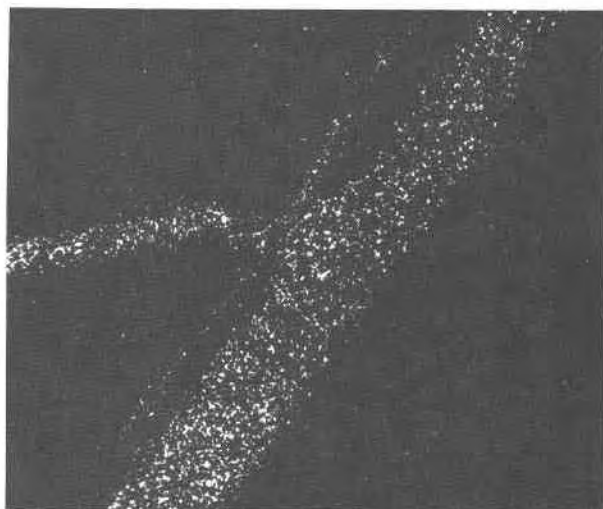


FIG. 5. Micrograph in backscattered $HgLa$ radiation. Balkanite lamellae in chalcocite.

orthorhombic with cell dimensions $a = 10.62 \pm 0.02 \text{ \AA}$, $b = 9.42 \pm 0.02 \text{ \AA}$, $c = 3.92 \pm 0.04 \text{ \AA}$. The space group is $P222$, $Pmm2$, or $Pmmm$. Density, as calculated from the two chemical analyses and a cell volume of 392.1 \AA^3 , is 6.421 and 6.497 g/cm^3 . The density (6.32 g/cm^3) of synthetic balkanite is slightly lower, perhaps because of chalcocite, djurleite, covellite and, possibly, of air bubbles.

The DTA curve of synthetic balkanite displays endothermic peaks at 90 , 140 , 450 and 690°C , the first and the third being relatively weaker. All effects are reversible on the cooling curve. The peak at 690°C should be attributed to the melting of the sample, while the remaining ones are most probably due to polymorphic transitions.

The DTA curve recorded in air also shows the endothermic peaks at 90 and 140°C , but after 350°C a very strong and broad exothermic effect appears, connected with the oxidation of the sample.

Chemical Composition and Formula

The chemical composition of balkanite was determined with a Cameca MS 46 electron microprobe in the Laboratory for Experimental Mineralogy of the Siberian Department of the Academy of Sciences of the USSR, Novosibirsk. The results of two full analyses are summarized in Table 3.

Table 3 includes also the results of the calculation of the analyses on the basis of eight S atoms, which corresponds almost exactly to $Z = 1$. The suggested

idealized formula is $Cu_9Ag_5HgS_8$. As compared with the atomic ratios in Table 3, such a formula exaggerates both the copper and silver content. The calculated density for this formula would be 6.68 , which is considerably larger than the observed value. On the other hand, a composition $Cu_9Ag_5HgS_8$ has a calculated density of 6.41 , which is closer to the experimental value, but it would hardly be realistic to assume such atomic ratios in view of the analytical results.

TABLE 2. X-RAY POWDER PATTERNS OF SYNTHETIC AND NATURAL BALKANITE

hkl	$d_{\text{calc.}} \text{ \AA}$	Synthetic balkanite		Natural balkanite	
		$d_{\text{meas.}} \text{ \AA}$	I	$d_{\text{meas.}} \text{ \AA}$	I
120	4.30	4.291	2	4.30	1
001	3.91	3.900	3	3.88	2
101	3.675	3.654	5	3.66	4
220	3.522	3.512	6	3.50	5
111	3.423	3.440	5	3.44	4
310	3.310	3.302	4	3.32	2
201	3.152	3.160	6		
030	3.140	3.143	7	3.15	6
021	3.012	3.008	8	3.09	7
130	3.010	2.984	10	2.98	10
211	2.989				
320	2.829	2.826	7	2.81	5
230	2.704	2.702	8	2.89	7
301	2.627	2.625	5	2.61	8
221	2.620	2.614	9		
410	2.555	2.550	10	2.55	10
311	2.530	2.529	5	2.53	4
031	2.452	2.464	8	2.45	8
330	2.349	2.350	5	2.35	3
420	2.312	2.309	4m	2.31	2b
240	2.153	2.155	1	2.15	1
411	2.140	2.140	1	2.14	1
510	2.072	2.069	7	2.06	5
430	2.027	2.027	3	2.02	1
421	1.992	1.991	8	1.985	8
340	1.961	1.962	9	1.955	9
002	1.960				
511	1.832	1.831	3	1.825	2
431	1.801	1.802	3	1.799	2
600	1.770	1.765	5	1.764	5
440	1.762				
241	1.620	1.621	0.5	1.621	1
232	1.589	1.586	1	1.581	1
630	1.542	1.542	2	1.537	3
242	1.449	1.449	1	1.450	1
161	1.444	1.444	0.5	1.440	0.5
640	1.415	1.415	1	1.420	1

Operating conditions - Synthetic balkanite: Diffractometer trace, filtered copper radiation. Natural balkanite: powder photograph, 57.3 mm Debye Scherrer camera. Filtered copper radiation. Exposure 5 hours.

TABLE 3. CHEMICAL COMPOSITION OF BALKANITE FROM SEDMOCHISLENITSI

Elements	Wt. %	I Atomic ratio	Wt. %	II Atomic ratio
Cu	37.4	8.78	37.1	8.76
Ag	33.1	4.58	33.3	4.69
Hg	14.0	1.04	13.8	1.04
S	17.2	8.00	16.9	8.00
Total	101.7	-	101.1	-
Operating conditions and standards				
CuKa,	30 kV,	10 mA	- natural chalcocopyrite	
AgLa,	15 kV,	30 mA	- synthetic miargyrite and elementary silver	
HgKa,	30 kV,	10 mA	- synthetic cinnabarite	
SKa,	15 kV,	30 mA	- synthetic stibnite	
Absorption corrections according to Springer (1966)				

Origin

Balkanite is a result of low-temperature hydrothermal activity. Together with chalcocite, djurleite, digenite, stromeyerite, wittichenite, silver and mercurian silver, it is one of the last-formed minerals of the deposit. Balkanite and chalcocite very frequently replace tennantite and bornite, thus forming zonal aggregates with an inner zone consisting of intimately mixed balkanite and chalcocite grains up to 2–3 nm in size and an outer zone which is relatively coarser grained. The replacement of bornite by balkanite and chalcocite is connected also with the formation of chalcopyrite. Flame-like exsolutions of chalcopyrite are observed around balkanite veinlets cutting bornite grains. Such exsolutions of chalcopyrite in bornite also occur around chalcocite and stromeyerite veinlets (Stoinov, Atanassov, and Lilov, 1964).

The balkanite lamellae in chalcocite are also of interest (Figs. 4 and 5). Evidently, they constitute exsolutions of balkanite formed upon temperature decrease from a high-temperature polymorph of chalcocite in which mercury and silver may be present in larger amounts. Very possibly this is the high-temperature hexagonal phase of chalcocite (Skinner, 1966) which, at temperatures above 103.5°C, is stable for all compositions along the chalcocite–stromeyerite join. The Cu/Ag ratio in balkanite favors such an explanation. No data are available

as yet concerning the participation of mercury and its influence on the phase relationships in the Ag_2S — Cu_2S systems.

The lamellar structure of most balkanite grains indicates transformation twinning. Furthermore, the internal lamellae within the larger lamellae may well mark a second phase transition upon temperature decrease. The DTA curves upon heating and cooling as well as the paragenetic relationships in the deposits show that these phase transitions occur at relatively low temperatures between 90 and 150°C.

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