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Klebelsbergite, $Sb_4O_4(OH)_2SO_4$: redefinition and synthesis

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Abstract

Klebelsbergite is verified as a valid mineral species, in museum specimens from the type locality, Baia Sprie (Felsöbánya), Rumania.

Klebelsbergite occurs as pale yellow to orange-yellow crystals radially grown on stibnite. Wet-chemical analysis of synthetic klebelsbergite, supported by electron microprobe analyses of natural material, gives Sb 71.78, S 4.65, H_2O 2.69, O 20.88% (by difference). The empirical cell contents are $Sb_{4.07}O_{5.00}(SO_4) \cdot 1.03H_2O$ with an ideal formula $Sb_4O_4(OH)_2SO_4$. The crystals are tabular or acicular elongated [001], flattened {010}. The mineral is orthorhombic, *Pcmb* or $Pc2_1b$, $a = 11.279(2)$, $b = 14.909(3)$, $c = 5.7648(6)$A; $Z = 4$. D(meas) = 4.62(6), D(calc) = 4.69g/cm^3. The strongest lines of the X-ray powder pattern are 6.22(s)(120), 3.892(s)(211), 3.545(s)(221), 3.150(s)(301), 3.131(vs)(231), 2.830(s)(012), 2.435(s)(132), 1.805(s)(213). Klebelsbergite has vitreous luster, yellow streak, and no distinct cleavage. The mineral is optically biaxial with large $2V_x$ about 70°, $\beta \cong 1.95$, and is not pleochroic. VHN = 200 (10g load).

Single crystals of klebelsbergite were synthesized by boiling 2 g of Sb_2O_3 with 600 ml of 1 N H_2SO_4 for four days. Synthetic crystals are tabular, elongated [001], flattened {010}. The space group, cell parameters, and powder-diffraction data are essentially identical to those of natural klebelsbergite. The crystals decompose by dehydration at 273°C.

Introduction

Klebelsbergite was first described by Zsivny in 1929 from Felsöbánya, Hungary (now Baia Sprie, Rumania). He reported that the mineral was essentially a basic antimony sulfate, containing a little H_2O, Fe, Mg, Na, K and traces of Bi and P_2O_5 by microchemical tests. He also showed that it was monoclinic with a β angle of 91.8°, biaxial negative, $X = b$, $Y{:}c = 1.8°$, $n > 1.74$. In the following 50 years, several reports concerning this mineral have appeared (Manilici *et al.*, 1965; Radulescu and Dimitrescu, 1966; Antonovici and Vanghelie, 1972); however, none of them gave a complete description of this rare mineral. Antonovici and Vanghelie (1972), in the only detailed study of this mineral since Zsivny, examined museum specimens of klebelsbergite. They reported that the mineral contained 61.86 percent antimony by X-ray fluorescence analysis and more than one percent sulfur by spectrographic analysis. They also presented an X-ray powder diffraction chart with the three strongest lines given as 6.19(100), 3.43(80), and 2.47A(90).

Our work gives for the first time the chemical formula, crystal data, and physical and chemical properties of klebelsbergite. This study has been done using museum specimens from the Smithsonian Institution labelled as klebelsbergite from the type locality, Baia Sprie, Rumania; NMNH #137949, R6535, B12631, B12640, B12647, and B16076.

A short version of this manuscript was submitted to the IMA Commission on New Minerals and Mineral Names. It was determined that a vote of the commission was not necessary (Max H. Hey, written communication).

Physical properties

Klebelsbergite occurs as aggregates of very small platy or acicular crystals (Fig. 1), maximum size about 0.8 × 0.08 × 0.02 mm, with a pale yellow to orange-yellow color. The streak is white to yellow and the luster is vitreous. The mineral is brittle and has no distinct cleavage. The density determined by Ber-

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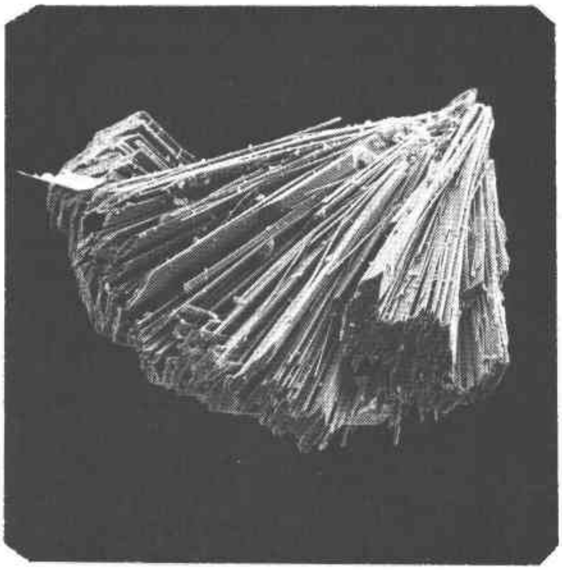

Fig. 1. SEM photograph of natural klebelsbergite from Baia Sprie, Rumania (225×).

man balance is 4.62(6) g/cm^3 (average of 6 measurements using more than 10mg of sample each time). The Vickers hardness number (VHN) is 200 with a 10g load.

Klebelsbergite is optically biaxial, negative, with $2V$ about 70°. Because of its high reactivity with index-of-refraction liquids of high index, the refractive indices could not be measured; however, quick observation before the crystals dissolved showed that β is near 1.95. Birefringence $\beta - \gamma$ is about 0.035 (by retardation). The mean index of refraction, 1.95, was calculated from the Gladstone–Dale relationship using the ideal chemical formula, $Sb_4O_6H_2SO_4$, calculated density of 4.64 g/cm^3, and the constants given by Mandarino (1976), and this supports the above observation that β is about 1.95. The optical orientation is $X = b$, $Y = c$ and $Z = a$. The mineral is not pleochroic.

Klebelsbergite is weakly magnetic when it contains iron as an impurity. This feature enabled us to separate klebelsbergite from other minerals with the Franz isodynamic separator. The mineral is not luminescent in either long- or short-wave ultraviolet radiation.

Crystallography

In the original description by Zsivny (1929), klebelsbergite was described as monoclinic; however, the true symmetry has been revealed to be orthorhombic by our X-ray diffraction studies of single crystals. Weissenberg and precession photographs show that the space group is either $Pcmb$ or $Pc2_1b$. The lattice constants are $a = 11.279(2)$, $b = 14.909(3)$, and $c = 5.7648(6)$A, calculated from the powder-diffraction data using the least-squares refinement program of Appleman and Evans (1973). The powder-diffraction pattern of klebelsbergite was obtained with a Guinier-Hägg camera using Cu$K\alpha_1$ radiation and BaF_2 internal standard; the data are given in Table 1. Indexing of ambiguous reflections was aided by intensity measurements from single-crystal photographs.

Crystals of klebelsbergite are generally flattened to tabular on {010} and elongated in the [001] direction. Well-developed crystals were occasionally observed; however, the small crystal size and especially the thickness of less than 20 μm prevented us from carrying out detailed measurements of the interfacial angles. Under the optical microscope, the apical angle, indicated by an arrow in Figure 2, was measured to be about 124°. This value is found to be close to the supplemental angle of $(101)\wedge(\bar{1}01) = 54.14°$ calculated from the lattice constants. A section normal to the c axis shows a flattened hexagon; therefore the platy crystal can be described as having a major {010} pinacoid and a minor probably {120} prism.

As is seen in Figure 2, klebelsbergite crystals tend to grow as parallel blades elongated along the c axis, stacked in the b-axis direction in lamellar fashion. Precession photographs parallel to the (010) plane revealed very slight distortion among the stacked crystals; *i.e.* the (010) plane rotates slightly around the b axis. As a result, the crystals show a monoclinic appearance, and this is considered to be the reason klebelsbergite was described as monoclinic in the original description (Zsivny, 1929). Zsivny reported a beta angle of 91.8° with optical orientation Y:c = 1.8°, and this is well explained as the distortion around the b axis.

Synthesis

Single crystals of klebelsbergite (maximum size about 1 × 0.1 × 0.03mm) have been synthesized by boiling 2 g of Sb_2O_3 with 600 ml of 1 N H_2SO_4 solution for four days.

The crystals obtained are colorless and transparent, having the same luster as natural crystals. The crystal habit is also similar to that of natural crystals: tabular on {010}, elongated along [001], with the dominant form {010} (Fig. 3). The crystals often developed radially with a parallel growth along [001] as in natural crystals. The VHN is 130 with 10 g

Table 1. X-ray powder-diffraction data for klebelsbergite

Natural klebelsbergite				Synthetic klebelsbergite			
hkl	d calc	d obs	I*	hkl	d calc	d obs	I
020	7.45	7.47	w	020	7.44	7.45	w
120	6.22	6.22	s	120	6.21	6.21	s
101	5.13	5.14	ms	101	5.137	5.136	ms
111	4.85	4.85	m	111	4.856	4.854	ms
121	4.228	4.231	mw	121	4.228	4.228	m
211	3.892	3.892	s	211	3.893	3.892	vs
040	3.727	3.731	vw	040	3.722	3.720	w
				131	3.569	3.568	w
221	3.546	3.545	s	221	3.546	3.545	s
320	3.357	3.350	vvw	140	3.535	3.534	m
301	3.149	3.150	s	301	3.150	3.148	s
231	3.131	3.131	vs	231	3.130	3.129	vs
240	3.110	3.110	vw	240	3.106	3.105	w
311	3.081	3.083	ms	311	3.081	3.081	s
321	2.901	2.902	mw	321	2.901	2.901	m
002	2.882	2.882	w	002	2.885	2.886	w
012	2.830	2.830	s	012	2.833	2.833	s
400	2.820	2.821	m	400	2.819	2.819	ms
241	2.737	2.736	m	241	2.735	2.735	m
022	2.688	2.688	ms	022	2.690	2.691	ms
420	2.637	2.639	w	420	2.636	2.637	mw
122	2.615	2.618	vw	122	2.617	2.617	vw
				151	2.576	2.577	vvw
212	2.529	2.531	vw	212	2.531	2.531	w
411	2.497	2.497	m	411	2.497	2.496	ms
060	2.485	2.485	w	060	2.482	2.481	m
132	2.435	2.435	s	132	2.436	2.436	s
				222	2.428	2.428	vw
				421	2.398	2.396	m
251	2.397	2.398	mw	251	2.396		
042	2.280	2.280	mw	042	2.280	2.281	m
440	2.249	22.248	w	440	2.247	2.247	mw
161	2.237	2.239	vw	161	2.235	2.235	w
				322	2.188	2.188	w
				351	2.164	2.164	vw
520	2.159	2.159	vw	520	2.158	2.158	w
				242	2.114	2.115	vw
441	2.095	2.094	mw	441	2.094	2.094	ms
332	2.078	2.078	w	332	2.078	2.079	m
				052	2.072	2.072	vvw
152	2.038	2.038	vvw	152	2.038	2.038	vw
402	2.016	2.015	m	402	2.016	2.017	ms
412	1.997	1.998	m	412	1.998	1.998	ms
171	1.967	1.967	w	171	1.965	1.965	w
361	1.951	1.950	mw	361	1.949	1.950	ms
				422	1.946	1.946	s
252	1.945	1.945	ms	252	1.945		
451	1.930	1.931	m	451	1.929	1.928	s
				540	1.929		
103	1.894	1.894	mw	103	1.896	1.896	ms
271	1.883	1.883	mw	271	1.881	1.88111	s
062	1.882			600	1.879		
600	1.880	1.880	w				
113	1.879						
460	1.864	1.861	m	460	1.863	1.863	s
				162	1.856	1.857	vvw
				123	1.838	1.837	vw
				541	1.829	1.830	vw
620	1.823	1.823	mw	620	1.822	1.822	ms
				352	1.815	1.815	vw
213	1.806	1.805	s	213	1.807	1.807	s
611	1.775	1.774	m	611	1.7743	1.7735	ms
442	1.773			442	1.7730		
223	1.767	1.768	vw	223	1.7684	1.7688	w
				280	1.7674	1.7646	w
512	1.764	1.764	w	512	1.7644		
				371	1.7627	1.7627	w
				551	1.7165	1.7170	vw
072	1.713	1.711	mw	072	1.7121	1.7124	m
313	1.700	1.700	mw	313	1.7011	1.7012	m
143	1.689	1.690	vvw	143	1.6896	1.6895	w
631	1.682	1.682	m	631	1.6813	1.6813	m
				640	1.6777	1.6774	vw
532	1.673	1.673	m	532	1.6729	1.6727	m
				452	1.6697	1.6696	vw
272	1.639	1.640	vvw	272	1.6383	1.6384	vw
243	1.635	1.635	vw	243	1.6354	1.6349	w
				471	1.6289	1.6291	w
				333	1.6187	1.6193	vvw
				542	1.6035	1.6032	vw
153	1.599	1.598	vvw	153	1.5995	1.5994	w
				413	1.5799	1.5797	vw
720	1.575	1.575	w	602	1.5748	1.5746	mw
602	1.575			720	1.5745		

Table 1. (continued)

Natural klebelsbergite				Synthetic klebelsbergite			
hkl	d calc	d obs	I*	hkl	d calc	d obs	I
462	1.565	1.5655	m	462	1.5649	1.5644	ms
082	1.565			082	1.5640		
423	1.553	1.5529	m	423	1.5539	1.5534	ms
253	1.553			253	1.5533		
182	1.550	1.549	w	711	1.5432	1.5431	vw
711	1.5435	1.5435	vvw	622	1.5407	1.5403	vw
622	1.5406	1.5401	vvw	651	1.5323	1.5321	mw
291	1.5322	1.5318	m	291	1.5306	1.5306	m
433	1.5126	1.5132	w	433	1.5133	1.5132	m
163	1.5065	1.5067	vw	163	1.5067	1.5067	w
				481	1.4998	1.4997	vw
				353	1.4844	1.4841	w
1.10.0	1.4781	1.4777	vvw	1.10.0	1.4762	1.4764	w
472	1.4640	1.4630	vw	472	1.4634	1.4633	w
				642	1.4503	1.4502	w
523	1.4354	1.4355	w	523	1.4360	1.4358	m
				014	1.4359		
				741	1.4321	1.4318	vw
192	1.4248	1.4238	mw	114	1.4244	1.4242	ms
114	1.4238			192	1.4237		
024	1.4150	1.4149	w	024	1.4163	1.4163	m
800	1.4099	1.4095	vw	800	1.4095	1.4091	mw
363	1.4093			363	1.4094		
124	1.4040	1.4040	vw	124	1.4053	1.4053	mw
712	1.4002	1.4005	vw	712	1.4003	1.4003	m
3.10.0	1.3859	1.3859	mw	2.10.1	1.3968	1.3969	w
				652	1.3921	1.3919	mw
034	1.3842	1.3839	w	034	1.3853	1.3850	m
				820	1.3849		
				273	1.3831	1.3833	mw
				751	1.3760	1.3755	vw
671	1.3691	1.3686	vvw	671	1.3682	1.3681	w
482	1.3684			482	1.3676		
811	1.3638	1.3636	mw	811	1.3635	1.3631	ms
				234	1.3453	1.3456	mwb
				044	1.3452		
314	1.3403	1.3401	vw	392	1.3408	1.3409	w
				613	1.3388	1.3387	vw
0.10.2	1.3243	1.3240	vw	0.10.2	1.3232	1.3225	w
680	1.3235			680	1.3225		
				840	1.3182	1.3180	vw
761	1.3162	1.3158	vvw	761	1.3156	1.3155	w
334	1.2989	1.2988	vw	334	1.2999	1.2998	mw
				591	1.2997		
841	1.2855	1.2856	vvw	841	1.2851	1.2851	vw
473	1.2731	1.2733	vvw	752	1.2718	1.2713	w
424	1.2647	1.2646	m	802	1.2665	1.2656	m
254	1.2645			672	1.2657		
				900	1.2529	1.2531	w
822	1.2486	1.2483	vw	822	1.2486	1.2481	w
851	1.2445	1.2446	w	851	1.2441	1.2438	mw
				5.10.0	1.2426	1.2425	w
0.12.0	1.2424	1.2421	vw	0.12.0	1.2408	1.2405	w
				713	1.2308	1.2306	vw
				354	1.2272	1.2274	vw
				832	1.2272		
				0.11.2	1.2255	1.2251	mw
				653	1.2252		
				901	1.2244		
				911	1.2203	1.2205	vw
				264	1.2178	1.2179	w
				444	1.2140	1.2139	mw
				691	1.2140		
				592	1.2108	1.2110	w
				921	1.2082	1.2080	vw
				573	1.2057	1.2057	vvw
4.10.2	1.1987	1.1985	w	842	1.1990	1.1991	mw
				772	1.1732	1.1733	vw
				3.12.1	1.1545	1.1547	w
				2.10.3	1.1526	1.1526	vvw
				583	1.1505	1.1508	vw
				493	1.1460	1.1460	vvw
				604	1.1444	1.1442	w
				464	1.1406	1.1406	w
				374	1.1379	1.1381	vw
				5.11.1	1.1378		
				673	1.1364	1.1363	vw
				184	1.1345	1.1345	w
				951	1.1324	1.1325	vw
				10.0.0	1.1276	1.1277	w
				554	1.1252	1.1253	vw
				4.11.2	1.1239	1.1239	w
				1.13.1	1.1179	1.1181	w
				634	1.1151	1.1152	mw
				833	1.1083	1.1086	mw
				235	1.1024	1.1027	vvw
				145	1.0971	1.0974	w
				564	1.0914	1.0918	w
				843	1.0874	1.0874	w

* Relative intensities estimated visually (s, strong; m, medium; w, weak; v, very; b, broad.)

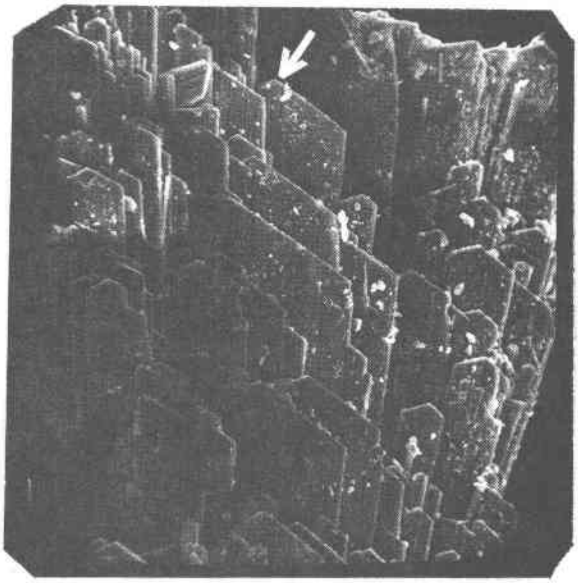

Fig. 2. SEM photograph of natural klebelsbergite from Baia Sprie, Rumania (400×).

load, as compared to 200 measured on natural crystals. The powder-diffraction data obtained with a Guinier–Hägg camera using Cu$K\alpha_1$ radiation and CaF_2 standard are given in Table 1. The data agree very well with those for natural klebelsbergite. The crystal symmetry and the space group are the same as the natural mineral, *i.e.* orthorhombic *Pcmb* or *Pc*2$_1$*b*. Cell dimensions refined from the powder data are a = 11.2763(7), b = 14.890(1) and c = 5.7707(4)A, in excellent agreement with natural klebelsbergite; the difference is almost within one standard deviation. The measured density of the synthetic material is 4.61(4) g/cm^3 which agrees well with the calculated density 4.69 g/cm^3 and that measured on natural crystals, 4.62(6) g/cm^3. Thus the synthetic crystals have been identified as klebelsbergite.

Chemistry

Wave-length scans using an ARL-SEMQ electron microprobe disclosed that klebelsbergite contains major Sb and S and minor Fe. No other elements ($Z \geqq 9$) were detected. The presence of sulfate ion was confirmed by a spot test with $BaCl_2$ solution.

As very little material was available, wet-chemical analyses were carried out only on synthetic klebelsbergite. Sb was determined by $KBrO_3$ titration, and SO_4^{2-} gravimetrically with $BaCl_2$ solution (Hillebrand and Lundell, 1953). Water was determined by the Penfield method and the sample was heated to 300°C. The result is given in Table 2, which yields the empirical formula $Sb_{4.07}O_{5.00}SO_4 \cdot 1.03H_2O$ (on the basis of $SO_4 = 1$), and ideally $Sb_4O_6H_2SO_4$, which can be expressed as either $Sb_4O_4(OH)_2SO_4$ or $Sb_4O_5SO_4H_2O$. On the basis of IR spectroscopy, $Sb_4O_4(OH)_2SO_4$ is favored (see below); however, $Sb_4O_5SO_4 \cdot H_2O$ cannot be ruled out completely.[2]

Quantitative analyses of natural klebelsbergite were carried out with the electron microprobe using an operating voltage of 15kV and a sample current of 0.15 microamps. Valentinite, barite, and olivine were used as standards for Sb, S, and Fe, respectively. The results are given in Table 2. Concentration of iron varies from 0.0 to 0.5 percent and is thought to be present substituting for antimony as explained below. The rather large discrepancy of sulfur content between the two analyses, wet-chemical and microprobe, is considered to be due to inadequate data correction of the microprobe data. The ideal chemical formula $Sb_4O_6H_2SO_4$ with $Z = 4$ is suitable for the space groups *Pcmb* or *Pc*2$_1$*b*. The theoretical density for the ideal formula is 4.69 g/cm^3, which agrees well with the measured density 4.62(6) g/cm^3. Klebelsbergite is readily soluble in HCl(1 : 1), and NaOH(10 percent), slowly soluble in tartaric acid (20

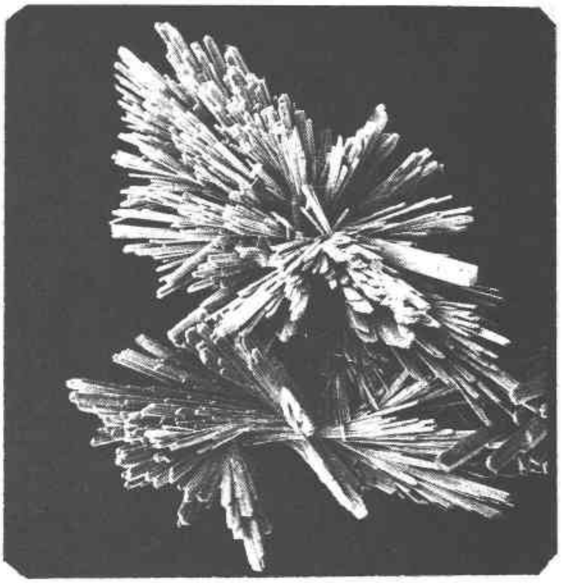

Fig. 3. SEM photograph of synthetic klebelsbergite (60×).

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[2] After this paper was accepted for publication, we received a preprint from Drs. S. Menchetti and C. Sabelli of the Università di Firenze describing their recent determination of the klebelsbergite structure (Menchetti and Sabelli, in preparation). They found that the correct formula is indeed $Sb_4O_4(OH)_2SO_4$, and that the space group is *Pc*2$_1$*b*.

percent), and very slowly soluble in HNO_3(1:1) and H_2SO_4(1:1).

The color of klebelsbergite is more or less yellow; however, the depth of the yellow color varies from specimen to specimen. To elucidate the origin of the color, microprobe analyses were made on various specimens with different depths of color. The result indicates that there is a clear positive correlation between the iron concentration and the depth of the color. Iron-free synthetic klebelsbergite is colorless. Therefore, the origin of the yellow color is ascribed to the iron impurity. To establish the valence of iron, spot tests were made using 0.1 N potassium ferri- and ferro-cyanide solutions. HCl(1:3), HNO_3(1:1) and tartaric acid (20 percent) were used to dissolve the crystals. The tests clearly indicate the presence of both trivalent and divalent iron; however, trivalent iron is much more abundant.

Table 2. Chemical analysis of klebelsbergite

	1	2	3	4	5	6
Sb	71.78	0.5896	4.066	4	71.51	70.8
S	4.65	0.1450	1	1	4.71	3.2
Fe	----					0.5
H_2O	2.69	0.1493	1.030	1	2.64	
O*	20.88	1.305	9.000	9	21.14	
Total	100.00				100.00	

1. Synthetic klebelsbergite by wet-chemical analysis (wt.%)
2. Molecular quotient
3. Mole number basis S=1 (or SO_4=1)
4. Ideal mole number
5. Theoretical $Sb_4O_6H_2SO_4$
6. Natural klebelsbergite by microprobe analysis

* by difference

Thermal treatments

DTA/TGA

DTA/TGA spectra were taken under He atmosphere on a 100 mg sample of synthetic klebelsbergite. Heating rate was 4°C/min, and the temperature ranged from room temperature to 940°C. The spectra are characterized by an endothermic peak at 273°C with a weight loss of 2.4 percent, which is attributed to a dehydration reaction. The value corresponds well with the result of quantitative analyses of water (see Table 2). After the thermal analysis, the specimen was X-rayed and was found to be Sb_2O_4.

Decomposition

Decomposition experiments were carried out in an evacuated Pyrex glass tube (15 cm in length; 5 mm ID). A 100 mg sample of synthetic klebelsbergite was placed at the end of a sealed glass tube, then the other end was closed. The tube was placed in a horizontal furnace; the end of the tube containing the sample was located inside the furnace along with a thermocouple, while the other end (about 4 cm) was kept outside of the furnace. On heating to 300°C, a condensation of vapor was observed at the cool end. The specimen was heated for 1 hour, after which the dehydration product and the condensed liquid were tested.

The product kept the original shape; however, it became translucent with a slightly brownish color. The precession photograph of a "single crystal" which had been heated in the same way as above gave diffuse spots which approach a powder pattern, and this indicates that a single crystal changes into the polycrystalline state by dehydration. The X-ray powder diffraction pattern of the dehydration product has the following 8 strongest lines: 4.55(4), 3.35(1), 3.12(10), 2.80(1), 2.665(6), 1.926(3), 1.886(3), 1.615(3)A; the pattern as a whole shows a similarity to that of senarmontite, Sb_2O_3. The product dissolved in HCl solution (1:1) and gave a brown colloidal residue. Successive addition of $BaCl_2$ solution (10 percent) into the HCl solution caused an abundant white precipitate to form. This observation indicates that the sulfate ion remains in the structure after heating to 300°C. However, there is evidence of a partial decomposition of sulfate ion; the condensed liquid was strongly acidic, indicating that a small part of the sulfate ion decomposed on heating and the resultant SO_2 gas dissolved in the liquid.

Infrared spectroscopy

IR spectra were measured by the conventional KBr method for the region from 4000 to 645 cm^{-1}. Figure 4 shows the spectra of synthetic klebelsbergite (a), of synthetic klebelsbergite heated at 300°C for 1 hour (b), and of natural klebelsbergite (c). Since spectra of both natural and synthetic klebelsbergite have essentially the same features, we treat them together in the following discussion; the values in the parentheses are those for synthetic klebelsbergite. A sharp absorption of 3435 (3435) cm^{-1} is attributed to the O–H stretching vibration, and it disappeared on heating to 300°C for 1 hour: spectrum (b). Judging from the absence of any sizable peak in the 1650 cm^{-1} region, this absorption is more likely to be due to the stretching vibration of hydroxyl ion than to that of water of hydration; the O–H bending frequency usually occurs near 1650 cm^{-1} in the cases of water of hydration and absorbed water, but not in the case of hydroxyl ion (Gadsden, 1975). Although there is a very weak broad absorption in the 1650

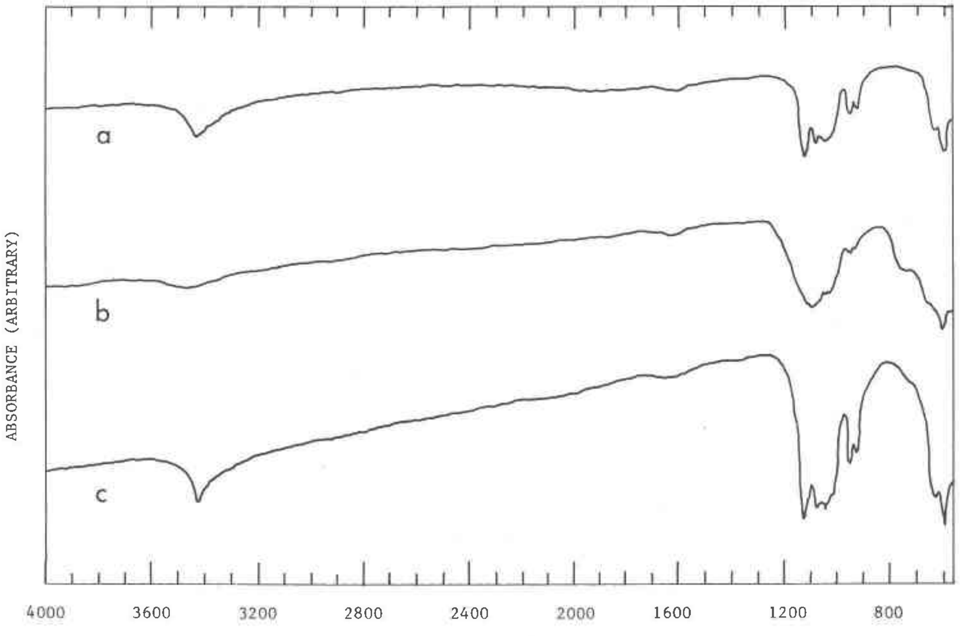

Fig. 4. Infrared spectra: (a) synthetic klebelsbergite; (b) synthetic klebelsbergite heated at 300°C for 1 hr.; (c) natural klebelsbergite from Baia Sprie, Rumania.

cm^{-1} region, it can be attributed to the absorbed water in the KBr, since spectrum (b) has a similar peak. The broad absorption in the 3450 cm^{-1} region in spectrum (b) can be assigned to the same origin.

Absorptions at 1130 (1130), 1080 (1085), 1050 (1045) cm^{-1} are here attributed to the ν_3 vibration of SO_4^{2-} ion, 955 (955) and 935 (930) cm^{-1} are to ν_1, 635 (635) and 600 (600) cm^{-1} are to ν_4 (Gadsden, 1975; Miller and Wilkins, 1952; Miller *et al.*, 1960). In the free tetrahedral SO_4^{2-} ion, ν_1 is the non-degenerate stretching vibration and is infrared inactive, and ν_3 and ν_4 are triply degenerate vibrations and are infrared active. Distortion of the tetrahedron causes ν_1 to be active, and removes the degeneracy of ν_3 and ν_4, therefore the clear multiplet character of the above peaks in the ν_3 and ν_4 regions is explained by the presence of significant distortion of the SO_4^{2-} tetrahedron in the klebelsbergite structure. The doublet character of ν_1 may possibly be explained by the presence of several kinds of S–O bonds. On heating, as seen in spectrum (b), the above splittings in the ν_3 and ν_4 regions become degenerate, and ν_1 absorption almost extinguished. This implies that the symmetry of SO_4^{2-} increases and becomes close to T_d symmetry. There is also evidence of a partial decomposition of SO_4^{2-} ion on heating (see "Thermal treatment"). This may be related to the apparent increase in SO_4^{2-} symmetry shown in the IR spectra.

In addition, spectrum (b) shows the appearance of a rather strong peak at 745 cm^{-1}. This value reminds us that senarmontite (the low-temperature form of Sb_2O_3) has very strong absorption at 740 cm^{-1} (Miller and Wilkins, 1952). X-ray powder-diffraction patterns of the heated sample show a possible structural similarity to senarmontite (see "Thermal treatment"). Combined with the above change in the absorption peaks of SO_4^{2-} ion, this observation may indicate that the structure of klebelsbergite changes to an antimony oxide-type structure on heating.

Association and paragenesis

Klebelsbergite is found as fan-shaped aggregates composed of many small crystals (Fig. 1) from Baia Sprie, Rumania. Associated minerals are stibnite, barite, and valentinite. We observed that klebelsbergite crystals almost always grew on stibnite crystals. Large euhedral crystals of barite (more than 1 cm) with stibnite inclusions are commonly observed. Surfaces of the stibnite crystals often show evidence of corrosion. It seems clear that the source of the antimony in klebelsbergite is stibnite. The mineral relationships suggest that stibnite crystallized first, followed by barite, and finally klebelsbergite.

A characteristic feature of the mineral assemblage is the intimate association of valentinite with klebelsbergite. Valentinite is found as small massive spherical crystals on the surface of stibnite crystals. The color is pale yellow to dark yellow, and the appearance resembles that of klebelsbergite except for the habit. Microprobe analyses of the valentinite crystals showed the presence of iron in unusually high concentrations. The concentration of iron was generally higher at the rim than at the core of the spherical crystals; in some cases iron concentrations of up to 5 weight percent were observed. The yellow color is likely due to the iron. Valentinite is very probably an alteration product of stibnite.

The above investigation clearly shows that klebelsbergite is a valid mineral species. It is the only naturally-occurring sulfate of antimony. Hereby the NMNH specimens are all designated as neotypes.

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