Synthesis of Oxide-Chalcogenides. I. Hydrothermal Synthesis of Sarabauite $CaSb_{10}O_{10}S_6$ and Related Compounds*

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Single crystals of a recently described metal oxide sulfide mineral sarabauite and three related oxide-sulfides of alkaline earths and antimony were hydrothermally synthesized. (1) $CaSb_{10}O_{10}S_6$: color, carmine red; crystal system, monoclinic; space group, C2/c. (2) Compound in Sr–Sb–O–S system (O<S), blackish silver, monoclinic, $P2_1/a$. (3) Compound in Ba–Sb–O–S system (O>S), reddish orange, triclinic P1 or P$\bar{1}$. (4) Compound in Ba–Sb–S–O system (O<S), blackish brown, monoclinic, $P2_1/a$.

A new oxide-sulfide of calcium and antimony with the formula $CaSb_{10}O_{10}S_6$ was first found as a beautiful scarlet colored mineral from the Sarabau mine, Malaysia, and reported as a mineral sarabauite.[1] The mineral and three compositionally related compounds in the M^{II}–Sb–O–S system (where M^{II} represents an alkaline earth metal), have been hydrothermally synthesized. This paper reports the preparation and chemical and physical properties of sarabauite and the three related oxide sulfide compounds. The three compounds have not been found in nature. Their preparation has not been reported.

Experimental

The following CP-grade reagents were used for the syntheses: CaO, $SrCO_3$, $BaCO_3$, Sb_2S_3, and Sb_2O_3. They were taken in the required ratios and mixed in an agate motor. Seventy milligrams of the mixture and 0.07 ml of water were sealed in either a gold or platinum tube: length 35 mm, inner diam. 2.7 mm. The conventional hydrothermal method, using stellite bombs of the test-tube type, was employed throughout the investigation. Syntheses were conducted under hydrothermal conditions in the temperature range 100—650 °C under 500—2000 kg/cm^2 pressure for 1—360 h.

The products were examined by means of the Weissenberg and precession methods, X-ray powder diffraction method, DTA, TGA, and microscope. Some were subjected to electron microprobe analysis.

Results and Discussion

Sarabauite. Single crystals up to 3 mm long have been synthesized by subjecting a mixture of the composition CaO: Sb_2S_3: Sb_2O_3 in the ratio 1: 2: 3 for three days at 400 °C and 1000 kg/cm^2 pressure. The crystals are transparent with a carmine red color similar to that of natural sarabauite. The twelve strongest X-ray powder reflections obtained by the diffractometer method are given in Table 1, together with the reflections for natural sarabauite for the sake of comparison. They are in good agreement. The unit cell dimensions for the synthesized $CaSb_{10}O_{10}S_6$ calculated from the powder data are a=25.39(4), b=5.655(5), c=16.92(3) Å and β=117.5(2)°. The values are very close to those for natural sarabauite: a=25.37(2), b=5.654(1), c=16.87(1) Å and β=117.58(4). The Weissenberg and precession photographs of the product reveal that it belongs to the same space group as sarabauite *i.e.* C2/c.[2] Thermal analyses (DTA and TGA) were performed at a heating rate of 2.5 °C/min. The DTA curve (Fig. 1) shows two exothermic peaks starting at 410 and 490 °C. The former is accompanied by weight loss. The corresponding peaks for natural sarabauite are found to start at 420 and 490 °C. The decomposition products at 490 °C

TABLE 1. X-RAY POWDER REFLECTIONS OF SYNTHESIZED $CaSb_{10}O_{10}S_6$ AND NATURAL SARABAUITE (Cu/Ni, diffractometer method)

$CaSb_{10}O_{10}S_6$		Sarabauite		
d/Å	I/I_0	d/Å	I/I_0	hkl
11.25	20	11.33	20	200
4.469	20	4.462	36	$\bar{3}12$
4.227	40	4.227	42	$\bar{6}02$
3.931	20	3.924	30	$\bar{1}13$
3.470	50	3.466	78	312
3.218	100	3.215	100	$\bar{5}14$
3.184	40	3.182	60	511
3.162	50	3.164	50	$\bar{8}02$
2.820	70	2.817	88	020
2.720	40	2.718	28	$\bar{2}06$
2.587	20	2.583	40	$\bar{4}21$
2.058	20	2.058	29	025

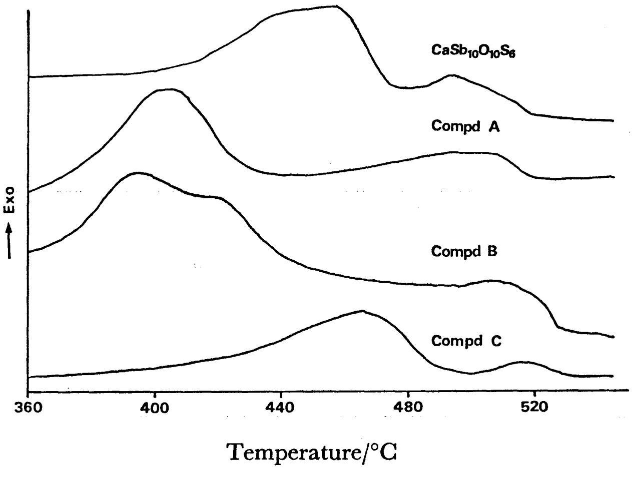

Fig. 1. DTA curves of $CaSb_{10}O_{10}S_6$, Compd A, Compd B, and Compd C.

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were found by X-ray analysis to be Sb_2O_3, Sb_2O_4, and $CaSb_2O_6$.

The density 4.9 g/cm³ determined by a Berman balance agrees with the calculated density 4.96 g/cm³ for $CaSb_{10}O_{10}S_6$ if we adopt the measured unit cell data and $Z=4$. The synthesized crystals have been identified as sarabauite $CaSb_{10}O_{10}S_6$.

Crystal habits of the synthesized sarabauite are tabular or columnar parallel to the b-axis. The former is characterized by the well developed {100} face.

The sarabauite phase was found to be formed in the temperature range 230—560 °C at a 1000 kg/cm² pressure. The product often included recrystallized acicular Sb_2S_3 and polygonal Sb_2O_3. The rate of sarabauite formation is scarcely influenced by variations in pressure up to 2000 kg/cm². One experiment carried out in a silica tube at 500 °C resulted in sarabauite formation at a 20 kg/cm² pressure. Formation of sarabauite proceeded so rapidly that the sarabauite phase appeared within 1 h at 500 °C and 1000 kg/cm². The presence of water is essential for the formation of sarabauite. Attempts at synthesis in a dry atmosphere at temperatures below 500 °C were unsuccessful.

Three compounds related to the above were prepared as follows: compound A, Sr–Sb–O–S system; compound B and compound C, Ba–Sb–O–S system. Their chemical compositions are given in Table 2. The analysis was carried out with an electron microprobe analyzer, measurements being made at 15 kV using Sb_2S_3, Sb_2S_2O, Sb_2O_3, $BaSO_4$, and $SrCO_3$ as standards. Since the correction procedures for the oxide–sulfide system are not well established in electron microprobe analysis, the values given should be considered approximate. The crystallographic data are summarized in Table 3. The crystal system and possible space group were determined by means of Weissenberg and precession photographs. The unit cell dimensions were obtained on an automated four-circle diffractometer using Mo $K_{\alpha 1}$ radiation for A and B and Cu $K_{\alpha 1}$ radiation for C. The 12 strongest X-ray powder lines are given in Table 4. Indexing is in line with the space groups, unit cell constants and X-ray intensity data of the single crystals.

Table 2. Electron microprobe chemical analysis of compounds A, B, and C

	Compd A		Compd B		Compd C	
	wt%	r[a]	wt%	r[a]	wt%	r[a]
Sr	4.7	0.9				
Ba			10.9	1.4	7.6	1.0
Sb	72.1	10	68.9	10	69.4	10
O	6.5	6.9	9.3	10	6.2	6.8
S	18.6	9.8	11.6	6.4	16.1	8.8
Total	101.9		100.7		99.3	

a) Atomic ratio, basis Sb=10.

Sr–Sb–O–S System: *Compound A*. A mixture of $SrCO_3$: Sb_2S_3: Sb_2O_3 in the ratio 1: 2: 3 was maintained for 214 h at 450 °C and 1030 kg/cm². The color of the crystal is blackish silver and by transmitted light red, giving a metallic luster and columnar shape elongated along the b-axis, and often showing parallel growth. The determined density is 4.6 g/cm³ which is slightly less than the 4.9 g/cm³ for sarabauite. The DTA and TGA curves are characterized by an exothermic peak starting at 380 °C, accompanied by weight loss, and one starting at 460 °C (Fig. 1). An X-ray powder study for the product at 460 °C showed that it consists of a mixture of Sb_2O_4 and $SrSb_2O_6$. Compound A is formed in the temperature range 460—540 °C under 1000 kg/cm².

Ba–Sb–O–S System: *1) Compound B*. A mixture of $BaCO_3$: Sb_2S_3: Sb_2O_3 in the ratio 1: 2: 3 was maintained at 520 °C and 500 kg/cm² for 219 h. The crystals obtained are reddish orange and transparent, possessing resinous luster similar to that of sarabauite.

The habit is tabular or columnar parallel to the b-axis. The measured density is 5.4 g/cm³. Figure 1 shows the result of DTA. The curve consists of two exothermic peaks starting at 370 and 500 °C, the former being accompanied by weight loss resulting from thermal decomposition. The temperature range for the formation of compound B is similar to that for sarabauite: 290—550 °C under 1000 kg/cm².

2) Compound C. Crystals up to 1 mm in length have been prepared by heating the mixture for B at 500 °C and 1000 kg/cm² for 110 h. The color is blackish brown and by transmitted light, red, respectively. C is a sulfur rich oxide–sulfide as compared to B (Table 2). It is characterized by its extremely large unit cell (Table 3). It appears columnar in shape, showing parallel growth along the b-axis in many cases. The product usually contains some of compound B. The result of DTA, given in Fig. 1, shows two exothermic peaks, one starting at 420 °C with weight loss and the other at 500 °C. The optimum temperature range

Table 3. Crystallographic data

		$CaSb_{10}O_{10}S_6$	Compd A	Compd B	Compd C
Crystal system		monoclinic	monoclinic	triclinic	monoclinic
Space group		C2/c	$P2_1/a$	P1 or $P\bar{1}$	$P2_1/a$[a]
Cell parameters	a/Å	25.39(4)	27.217(4)	13.949(3)[b]	38.286(3)
	b/Å	5.655(5)	5.7759(5)	5.5511(9)	5.7156(4)
	c/Å	16.92(3)	16.657(2)	11.083(3)	22.343(2)
	α/°			100.15(2)	
	β/°	117.5(2)	91.09(1)	67.53(2)	
	γ/°			97.07(2)	99.266(8)

a) 1st setting. b) The corresponding reduced cell[3] (a', b', c', α', β', and γ') is given as follows: $a'=c$, $b'=a$, $c'=b$, $\alpha'=\gamma$, $\beta'=\alpha$, and $\gamma'=\beta$.

TABLE 4. TWELVE STRONGEST X-RAY POWDER REFLECTIONS OF COMPOUNDS A, B, AND C (Cu/Ni, diffractometer method)

Compd A			Compd B			Compd C		
d/Å	I/I_0	*hkl*	*d*/Å	I/I_0	*hkl*	*d*/Å	I/I_0	*hkl*
4.298	40	$\bar{4}11$	10.10	40	101	3.936	30	$\bar{3}14$
		403	4.124	60	302			610
3.583	80	610	3.470	50	401	3.678	60	314
3.393	100	014			012	3.393	50	$\bar{7}14$
3.108	60	$\bar{6}04$			$11\bar{2}$	3.294	60	11.0.2
3.054	80	604	3.388	50	212	3.127	40	$\bar{2}16$
2.899	70	020	3.289	40	$\bar{1}1\bar{3}$			11.0.3
2.839	30	$\bar{1}21$	3.111	50	$\bar{3}1\bar{3}$			$\bar{1}16$
		121	2.945	100	$31\bar{1}$	2.935	50	10.1.0
2.758	30	320			$\bar{3}11$	2.906	40	12.0.3
		812			403			10.1.1
2.677	30	$\bar{4}15$	2.788	80	411	2.834	50	$\bar{4}20$
2.467	20	10.1.0			$\bar{4}01$	2.797	100	008
		$\overline{10}.0.3$	2.690	60	104	2.767	50	$\bar{5}21$
2.092	50	624	2.661	80	304			$\bar{3}17$
		008	2.558	40	503	2.712	60	$\bar{5}22$
1.888	30	14.0.2	1.994	40	$\bar{4}03$	2.526	50	11.0.6
					505			
					023			

for the synthesis of compound C is 450—500 °C under a pressure of 1000 kg/cm^2.

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Note added in proof

A new oxide-selenide of barium and antimony, Compound D, has been synthesized by heating a mixture of BaO:Sb_2Se_3:Sb_2O_3 in the ratio 1:2:3 with 5% NaOH solution for 110 h under hydrothermal conditions.

The crystals are red, and transparent having resinous luster and columnar shape. X-Ray data show them to be hexagonal, space group $P6_3$ or $P6_3/m$, with $a=14.41(1)$, and $c=5.552(3)$ Å. The strongest X-ray powder lines are: 12.62(30)(100), 4.168(40)(300), 3.601(30)(220), 3.333(50)(301), 3.124(40)(040), 3.027(90)(221), 2.943(60)(311), 2.727(100)(140). The DTA curve shows an exothermic peak starting at 495 °C, accompanied by weight loss. Compound D is formed in the temperature range 300—650 °C under 1000 kg/cm^2.