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Studies on Lanthanoids-Antimony-Chalcogenides. I. Synthesis and Crystal Data of Three New Lanthanum Antimony Chalcogenides

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Three new La-Sb chalcogenides were synthesized by hydrothermal or evacuated silica tube methods. (1) $LaSbO_2S_2$: a bright-red needle crystal; crystal system, hexagonal; space group, $P6_3/m$; lattice constants, $a=14.954(3)$, $c=3.898(2)$ Å, and $Z=6$. (2) $La_6Sb_8S_{21}$: a blackish-red columnar crystal with metallic luster, orthorhombic, $P222$, $a=14.317(2)$, $b=15.239(4)$, $c=8.685(1)$ Å, and $Z=2$. (3) $La_3Sb_3S_{10}$: a bright-red plate-like crystal, monoclinic, $a=13.209(6)$, $b=14.229(6)$, $c=5.583(1)$ Å, $\beta=94.54(3)°$, and $Z=2$.

There has been much attention in rare earth chalcogenides because of their interesting electric, magnetic, and optical properties. However, so far very few investigations have been made concerning the preparation of single crystals of rare earth antimony chalcogenides. Lemoine *et al.*,[1] reported the synthesis and the structure analysis of $Eu_3Sb_4S_9$, yet it has been mentioned that the oxidation number of europium is +2, not the general oxidation number for rare-earth elements. The only well characterized rare-earth antimony sulfide containing Ln^{3+} is $Pr_8Sb_2S_{15}$[2].

This work has been done as a part of our study on the crystal chemistry of sulfosalt compounds having a general chemical formula $A_mB_nX_p$, where A=metal, B=As,Sb, and X=O,S,Se.[3,4] These compounds have been characterized by the chemical nature of the element A.[5] The purpose of this study is to elucidate the crystal chemical behavior of rare-earth elements in sulfosalt compounds. This paper reports the methods of preparation of single crystals and the crystal data of three new lanthanum antimony chalcogenides.

Experimental

Two methods of syntheses were employed for the preparation of the three compounds. One is an evacuated silica tube method. A double silica tube method was adopted to protect against explosion, because a silica tube was easily attacked at high temperature. The other is a hydrothermal method, which was applied to the single crystal growth of $LaSbO_2S_2$. The reagents used were lanthanum metal chips (99.9%), sulfur powder (99.99%), and antimony trisulfide (99.99%).

Syntheses of La-Sb-S ternary compounds by the silica tube method were carried out as follows. Weighed quantities of La, Sb, S, and Sb_2S_3 were mixed and placed in a double silica tube, and then sealed under vacuum (less than 10^{-3} Torr, 1 Torr≈133.322 Pa). The reaction tube was placed in an electric furnace. The synthesis was usually continued over a week, in which the tube was first maintained at the reaction temperature of 1200 °C or 1000 °C, then kept at 1000 °C or 900 °C for three days at least, and finally the temperature was slowly lowered to room temperature.

The hydrothermal synthesis was made using a stellite bomb of the test-tube type. A starting material was a polycrystalline material obtained by the silica tube method. About 70 mg of the starting material and 0.07 ml of solvent (H_2O, 3%NaOH or 5%Na_2S) were sealed in a gold tube (length: 35 mm, inner diameter: 2.8 mm). Conditions employed were: the temperature range 350—500 °C; the pressure 800—1000 kg/cm^2 for 5—10 d.

The products were examined by the X-ray powder diffraction method, Weissenberg and precession cameras, SEM-XMA, and an automatic four-circle diffractometer. Chemical analyses were made by an electron microprobe analyzer using an operating voltage of 20 kV and a probe current of 0.015 μA. Synthetic Sb_2S_3 and La_2TiO_5 were used as the standards.

Results and Discussion

Three new compounds have been obtained from our synthesis. Their chemical compositions are given in Table 1.

Characterization of Crystals. $LaSbO_2S_2$ is a needle crystal and bright-red in color. The maximum size of the single crystal is 0.3×0.03×0.03 mm^3. The presence of oxygen in $LaSbO_2S_2$ was determined by the appearance of Sb–O absorption in the IR spectra (see *Infrared Spectroscopy*). The starting material did not contain any oxygen. The source of oxygen is considered to be the silica tube used as a container, since it was easily attacked at high temperature. The melting point of $LaSbO_2S_2$ is higher than 1000 °C.

$La_6Sb_8S_{21}$ is a columnar crystal of 0.4×0.1×0.05 mm^3 in maximum size. It is blackish-red with metallic luster. Thermal analysis showed that it melted incongruently at 985 °C into $La_3Sb_3S_{10}$ and liquid Sb_2S_3. The crystal is stable in air at room temperature and dissolved in diluted HNO_3 solution.

$La_3Sb_3S_{10}$ is a plate-like crystal of 0.3×0.3×0.01 mm^3. The crystal is bright-red and transparent. The melting point is higher than 1000 °C. Unfortunately,

TABLE 1. ELECTRON MICROPROBE CHEMICAL ANALYSIS OF THE THREE COMPOUNDS

	$LaSbO_2S_2$		$La_6Sb_8S_{21}$		$La_3Sb_3S_{10}$	
	wt%	Atomic ratio	wt%	Atomic ratio	wt%	Atomic ratio
La	38.26	1.01	31.85	5.95	37.26	2.97
Sb	33.21	1	37.54	8	32.93	3
S	17.39	1.99	25.89	20.95	29.60	10.23
O	8.85	2.03				
Total	97.71		95.28		99.79	

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the chemical formula of $La_3Sb_3S_{10}$ remains in question. The formula appears not to hold the electrical neutrality, if La and Sb are considered to be trivalant and S is divalent. Moreover, as mentioned later in this paper, $La_3Sb_3S_{10}$ has a superstructure. The limited amount of the specimen available precluded a precise wet chemical analysis. At the present stage, it is difficult to conclude whether it is $La_3{}^{3+}Sb_3{}^{3+}S_8(S_2)^{2-}$, or a mixed valence compound $La_3{}^{3+}Sb_2{}^{3+}Sb^{5+}S_{10}$ or a nonstoichiometric compound from the electron microprobe data.

Conditions of Formation. The experimental results of the silica tube method are summarized in Table 2. The purpose of maintaining the tube at the growth temperature is to obtain large crystals. However, in the case of $LaSbO_2S_2$, the crystal growth rate was slow and only polycrystalline materials were obtained. The results show that the appearance of a phase largely depends upon the temperature, but not on the ratio of the starting materials. For example, we could not obtain $La_3Sb_3S_{10}$ from the synthesis under conditions of the reaction temperature 1100 °C and the growth temperature 900 °C. Contrariwise, when the reaction temperature was 1200 °C and the growth temperature was 1000 °C, the crystals of $La_6Sb_8S_{21}$

TABLE 2. EXPERIMENTAL CONDITIONS AND RESULTS OF SYNTHESES BY SILICA TUBE METHOD

Run No.	Starting material/mol	Time / d	T/°C Reaction	T/°C Growth	Main product
1	La:S:Sb_2S_3=2:3:2	10	1200	1000	$La_3Sb_3S_{10}$
2	LaS_2[a]:Sb_2S_3=1:2	7	1200	1000	$La_3Sb_3S_{10}$
3	La:S:Sb_2S_3=1:2:2	10	1000	900	$La_6Sb_8S_{21}$
4	LaS_2[a]:Sb_2S_3=1:2	6	1000	900	$La_6Sb_8S_{21}$
5	La:S:Sb_2S_3=2:3:2	7	1000	900	$La_6Sb_8S_{21}$

a) LaS_2 was obtained by the silica tube method at 900 °C using a stoichiometric mixture of the elements.

TABLE 3. EXPERIMENTAL CONDITIONS AND RESULTS OF SYNTHESES BY HYDROTHERMAL METHOD

Run No.	Solvent	T / °C	Pressure / kg cm^{-2}	Time / d	Main product
1	H_2O	500	1000	6	$LaSbO_2S_2$
2	H_2O	400	1000	9	$LaSbO_2S_2$
3	H_2O	350	900	7	$LaSbO_2S_2$
4	3% NaOH	500	1000	6	Sb_2S_3
5	5% Na_2S	350	800	8	Sb_2S_3

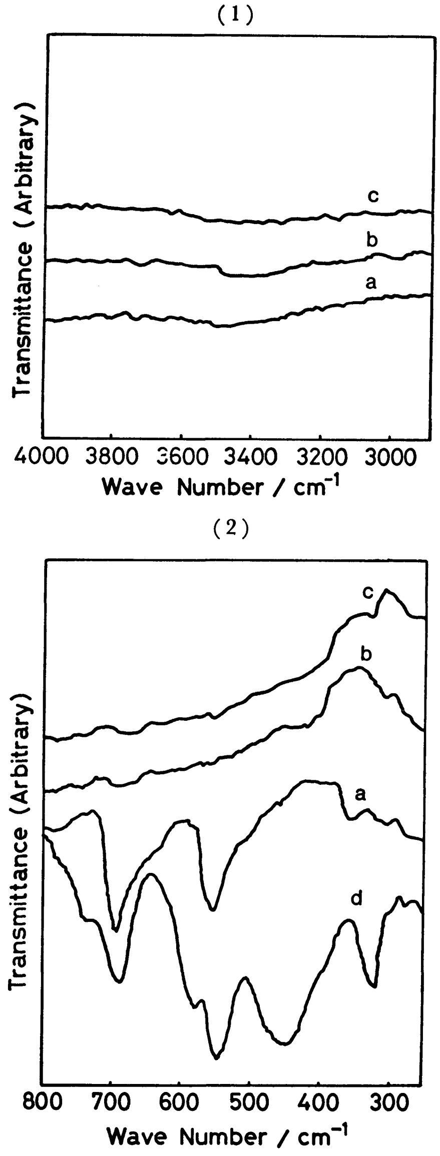

Fig. 1. Infrared spectra; a: $LaSbO_2S_2$, b: $La_6Sb_8S_{21}$, c: $La_3Sb_3S_{10}$, d: Sb_2O_3.

TABLE 4. CRYSTALLOGRAPHIC DATA

Compound	Crystal system	Space group	Lattice constants	Z	d_{obsd} / g cm^{-3}	d_{calcd} / g cm^{-3}
$LaSbO_2S_2$	hexagonal	$P6_3/m$	a=14.954(3)Å c=3.898(2)	6	4.84	4.71
$La_6Sb_8S_{21}$	orthorhombic	$P222$	a=14.317(2) b=15.239(4) c=8.685(1)	2	4.45	4.35
$La_3Sb_3S_{10}$	monoclinic		a=13.209(6) b=14.229(6) c=5.583(1) β=94.54(3)°	2	3.70	3.61

TABLE 5. X-RAY POWDER DIFFRACTION DATA OBTAINED USING A 114.6 mm DIAMETER GANDOLFI CAMERA. Cu/Ni RADIATION, INTENSITIES ESTIMATED VISUALLY

$LaSbO_2S_2$			$La_6Sb_8S_{21}$			$La_3Sb_3S_{10}$		
d/Å	I_{obsd}	$h\ k\ l$	d/Å	I_{obsd}	$h\ k\ l$	d/Å	I_{obsd}	$h\ k\ l$
7.51	vw	1 1 0	4.04	vw	3 2 0	3.76	s	$\bar{2}$ 2 1
4.92	s	2 1 0	3.69	w	1 4 0	3.56	s	0 4 0
3.61	s	1 3 0	3.63	w	2 1 2	3.29	m	4 0 0
3.35	w	2 0 1	3.48	s	3 3 0	3.03	vw	3 2 1
3.06	vs	2 1 1	3.34	m	2 2 2	2.780	s	0 0 2
2.983	w	2 3 0	3.24	m	4 2 0	2.732	w	0 1 2
2.902	w	3 0 1	2.962	w	3 2 2	2.679	m	1 0 2
2.836	w	4 1 0	2.811	s	1 4 2	2.629	w	5 0 0
2.653	m	3 1 1	2.716	w	3 3 2	2.439	vw	$\bar{3}$ 0 2
2.498	m	4 0 1	2.661	w	2 4 2	2.386	vw	3 5 0
2.371	m	3 2 1	2.459	w	1 5 2	2.271	m	3 0 2
2.229	s	4 1 1	2.365	m	5 1 2	2.232	w	2 6 0
2.139	w	3 4 0	2.178	m	0 0 4	2.196	m	5 2 1
2.084	w	5 2 0	2.074	w	4 6 0	2.078	w	5 3 1
1.952	w	0 0 2	1.998	vw	3 6 2	1.993	w	$\bar{5}$ 0 2
1.890	m	1 1 2	1.938	w	6 3 2	1.774	w	4 4 2
1.876	m	4 3 1				1.699	w	2 2 3
1.717	m	3 1 2				1.639	w	3 6 2

were not observed.

The results of hydrothermal experiments are given in Table 3. Single crystals of $LaSbO_2S_2$ have been obtained from the synthesis. $La_6Sb_8S_{21}$ and $La_3Sb_3S_{10}$ were found to be unstable under the hydrothermal conditions. Three kinds of liquids, *i.e.* H_2O, 3% NaOH, 5% Na_2S solutions, were examined as solvents. In the case of 3% NaOH or 5% Na_2S solutions, only La_2O_3 and Sb_2S_3 were observed as the products.

Crystallographic Data. Crystallographic data for the three compounds are summarized in Table 4. The crystal systems and space groups were determined by Weissenberg and precession photographs. X-Ray diffraction spots of $La_3Sb_3S_{10}$ were very diffuse, probably due to the thermal strain and very thin thickness of the crystal. Oscillation photographs (rotation axis =c) exhibited very weak super structure reflections with c=3c′. However, the super lattice could not be determined because of the diffuse nature and the weakness of the diffraction spot intensities. The average lattice is given in Table 4.

Unit cell dimensions were first determined from the photographs. The final cell parameters were calculated by a least-squares treatment of 2θ values centered automatically on the automatic four-circle diffractometer using monochromated Mo $K\alpha$ radiation (λ=0.70926Å). X-Ray powder diffraction data were obtained with the Gandolfi camera using Ni filtered Cu $K\alpha$ radiation and are given in Table 5.

Morphology of the single crystal of $LaSbO_2S_2$ is a hexagonal column elongated along c axis. $La_6Sb_8S_{21}$ is a plate crystal having well developed (010) faces. The elongation axis is c. $La_3Sb_3S_{10}$ is a very thin plate with well developed (100) faces and the elongation axis is c.

Infrared Spectroscopy. IR spectra were measured by the conventional KBr method in the region from 4000 to 250 cm^{-1} to examine the absorption bands of H_2O, OH, and Sb–O bonds. Figure 1-(1) shows the spectra of the three compounds in the region from 4000 to 2900 cm^{-1}, in which these spectra indicate the absence of any hydroxide ion or water of hydration. Figure 1-(2) shows the spectra of the three compounds and Sb_2O_3 for comparison. Two rather strong absorption bands at 695 and 555cm^{-1} were observed in $LaSbO_2S_2$. These bands are attributed to the Sb–O vibration from analogy with the spectrum of Sb_2O_3. From these results, $LaSbO_2S_2$ is considered to be oxide-sulfide but not to be hydrated sulfide nor sulfate of La and Sb. Both $La_6Sb_8S_{21}$ and $La_3Sb_3S_{10}$ exhibit featureless spectra even in the low wave number regions.

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Note added in proof: The crystal structure of $LaSbO_2S_2$ has been determined from Patterson and Fourier syntheses using intensity data collected on the four-circle diffractometer. The structure was refined by a full-matrix least-square method to a conventional R of 0.065 for 738 observed reflections. The structure consists of the $[La_3O_6]_\infty$ hexagonal prism and $[Sb_2S_4]_\infty$ double chain. They are parallel to the c-axis and linked each other by the weak La–S bonds.