Studies on Lanthanoids-Antimony-Chalcogenides. III. Synthesis and Crystal Data of Nd_3SbS_6, $Ce_6Sb_8S_{21}$, and $Ce_3Sb_3S_{10}$

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Synopsis. Single crystals of three new sulfides were prepared in evacuated silica tubes heated in the temperature range 890—1200 °C. Nd_3SbS_6 is a red transparent crystal. Is is tetragonal, space group $I4_1/acd$ with lattice parameters a=15.54(1) and c=19.52(2) Å. $Ce_6Sb_8S_{21}$ and $Ce_3Sb_3S_{10}$ are isostructural with $La_6Sb_8S_{21}$, and $La_3Sb_3S_{10}$, respectively.

Lanthanoid sulfides have been the subject of intensive investigation for their interesting physical properties such as super-conducting property.[2] However, most of these investigations involved binary sulfides of lanthanoid. There has been little effort to prepare ternary sulfides containing antimony.[3,4] We have started this study to clarify the crystal chemistry of the ternary sulfides.

Recently, we studied a La–Sb–S system and obtained the three new compounds, $LaSbO_2S_2$, $La_6Sb_8S_{21}$, and $La_3Sb_3S_{10}$.[5] In the present work, we have extended our experiment to Ce–Sb–S and Nd–Sb–S systems, and found three more new compounds. This paper reports the synthetic conditions and crystal data of these compounds.

Experimental

The syntheses were made by applying the double silica tube method described in the previous paper.[5] The starting materials were cerium and neodymium metal chips (99.9%), sulfur powder (99.99%), and antimony trisulfide (99.99%). They were mixed in various molar ratios, sealed into an evacuated silica tube, and heated in an electric furnace. Temperature and heating period were decided by a trial and error method.

Reaction products were examined by X-ray powder diffraction patterns using a 114.6 mm Gandolfi camera with Ni-filtered Cu $K\alpha$ radiation. X-Ray single crystal measurements were performed on precession and Weissenberg cameras. The least-squares computer program of Appleman and Evans[6] was used to calculate the lattice parameters. Some of the products were chemically analyzed with an electron microprobe analyzer using an operating voltage of 20 kV, and a probe current of 0.02 μA. The standards used were analyzed monazite (Ce), synthetic $Nd_3Ge_5O_{12}$, (Nd) and Sb_2S_3 (Sb and S).

Results and Discussion

The powder diffraction patterns of the products showed the presence of three unknown compounds: two among the products in the Ce–Sb–S system, and one among those in the Nd–Sb–S system. The former two compounds were proved to be $Ce_6Sb_8S_{21}$ and $Ce_3Sb_3S_{10}$ because they exhibited isostructural powder diffraction patterns with those of $La_6Sb_8S_{21}$ and $La_3Sb_3S_{10}$, respectively.[5] On the other hand, the latter compound gave a powder pattern which has never been reported before. The subsequent electron microprobe analysis has revealed it to be Nd_3SbS_6, which is a new type of compounds in the Ln (lanthanoids)–Sb–S system. Table 1 gives the results of chemical analysis for $Ce_6Sb_8S_{21}$, and Nd_3SbS_6. The powder diffraction patterns for the three new sulfides are listed in Table 2.

Table 1. Electron microprobe chemical analysis of $Ce_6Sb_8S_{21}$ and Nd_3SbS_6

	$Ce_6Sb_8S_{21}$			Nd_3SbS_6	
	wt%	Atomic ratio		wt%	Atomic ratio
Ce	35.59	6.35	Nd	57.86	3.33
Sb	38.97	8	Sb	14.66	1
S	27.03	21.08	S	24.60	6.37
Total	101.59		Total	97.12	

$Ce_6Sb_8S_{21}$. The product is obtained as blackish-red crystals having metallic luster. It is isostructural with $La_6Sb_8S_{21}$:[5] orthorhombic, space group P222. The lattice parameters obtained from the powder data are a=14.27(1), b=15.23(1), and c=8.645(9) Å. These values are slightly smaller than those reported for $La_6Sb_8S_{21}$, a=14.317(2), b=15.239(4), and c=8.685(1) Å. This result is consistent with the lanthanoid contraction. The crystal has plate-like habits with well-developed (010) faces, and elongated along the c axis.

The best crystals were obtained in the following procedures. A mixture of Ce, S, and Sb_2S_3 in a molar ratio 6:9:4, was heated at the reaction temperature of 1000 °C for 1 h and kept at the growth temperature of 900 °C for 1 week. The maximum synthesized crystal is 0.5×0.2×0.1 mm^3 in size.

$Ce_3Sb_3S_{10}$. The crystal is bright red and transparent having the same appearance as $La_3Sb_3S_{10}$.[5] The X-ray single crystal photographs have indicated that $Ce_3Sb_3S_{10}$ and $La_3Sb_3S_{10}$ are isomorphous. It belongs to the monoclinic system. However, as reported for $La_3Sb_3S_{10}$,[5] the presence of very weak superstructure reflections and very diffuse nature of the diffraction spots precluded the determination of the true cell and space group. The lattice parameters of the average lattice were calculated as a=13.15(1), b=14.20(2), c=5.568(6) Å, and β=95.17(8)°, which are slightly smaller than those of $La_3Sb_3S_{10}$: a=13.209(6), b=14.229(6), c=5.583(1) Å, and β=94.54(3)°.[5]

Thin plate crystals of 0.25×0.1×0.02 mm^3 in maximum size were synthesized by heating the mixture of Ce, Sb, and Sb_2S_3 in a molar ratio, 6:9:4. The suitable

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TABLE 2. INDEXED X-RAY POWDER DIFFRACTION DATA FOR THE THREE NEW SULFIDES[a)]

$Ce_6Sb_8S_{21}$				$Ce_3Sb_3S_{10}$				Nd_3SbS_6			
hkl	d_c/Å	d_o/Å	*I*	*hkl*	d_c/Å	d_o/Å	*I*	*hkl*	d_c/Å	d_o/Å	*I*
320	4.034	4.03	vw	$\bar{2}21$	3.760	3.76	m	400	3.885	3.89	vw
140	3.680	3.67	vw	040	3.550	3.54	s	402	3.609	3.60	s
212	3.593	3.60	m	400	3.273	3.27	s	314	3.463	3.48	m
330	3.471	3.46	s	231	3.079	3.09	vw	332	3.429	3.44	m
222	3.326	3.33	m	002	2.773	2.77	s	422	3.273	3.28	vw
420	3.231	3.22	m	500	2.619	2.62	m	431	3.069	3.06	vw
232	2.989	3.00	vw	$\bar{5}11$	2.419	2.43	w	206	3.001	2.99	vw
322	2.949	2.96	w	350	2.380	2.37	w	440	2.747	2.74	vw
142	2.802	2.80	s	302	2.250	2.25	w	523	2.638	2.64	s
332	2.707	2.71	w	$\bar{4}12$	2.190	2.19	m	600	2.590	2.59	vs
242	2.653	2.64	w	$\bar{5}02$	1.996	1.993	w	406	2.494	2.51	w
350	2.566	2.57	w	071	1.905	1.907	vw	336	2.432	2.43	vw
152	2.453	2.45	m	442	1.761	1.759	vw	444	2.394	2.40	w
512	2.353	2.35	m	$\bar{7}31$	1.701	1.700	vw	604	2.288	2.284	w
004	2.161	2.16	m					1.1.10.	1.922	1.926	vw
460	2.069	2.07	w					617	1.884	1.885	m
362	1.989	1.988	m					547	1.831	1.829	m
632	1.928	1.928	m					833	1.752	1.752	w
561	1.853	1.854	w								
712	1.830	1.830	w								
372	1.799	1.800	w								

a) Intensities were visually estimated: vs(very strong) > s > m(medium) > w(weak) > vw.

reaction and growth temperatures were 1200 °C and 1000 °C, respectively. Both $Ce_6Sb_8S_{21}$ and $Ce_3Sb_3S_{10}$ were able to be synthesized from the starting materials of the same composition. It was found that the appearance of each phase largely depends upon the growth temperature.

Nd_3SbS_6. The crystal is red and transparent. It has short prismatic shape with the maximum size of 0.15×0.05×0.05 mm³. The X-ray single crystal photographs have indicated that it belongs to the tetragonal system. The space group was determined as $I4_1/acd$ by the extinction rule. The elongation axis of the crystal is *c*. The indexing of the X-ray powder pattern was made with the aid of the single crystal photographs. As shown in Table 2, they are successfully indexed on the basis of the tetragonal cell. The lattice parameters were calculated as a=15.54(1) and c=19.52(2) Å from the powder data.

The optimum synthetic condition for the preparation of single crystal is as follows. A mixture of Nd, S, and Sb_2S_3 in a molar ratio, 6:9:4, was heated at 1100 °C for 2 h, and the temperature was dropped to 1040 °C. Then, it was slowly lowered to 890 °C at a rate of 6.25 °C/h. The temperature was raised again to 1040 °C, kept for 1 h, and slowly lowered in the same manner. This process was repeated four times in all. The run was terminated by turning off the furnace power to allow natural cooling. Attempts to synthesize at a fixed temperature, *i.e.* 1000 °C, did not yield any good crystals.

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