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SYNTHESIS AND CRYSTAL DATA OF NEW Ln_3S_4 (Ln=La,Ce,Sm) AND LnS_2 (Ln=Nd) TYPE SULFIDES CONTAINING A SMALL AMOUNT OF ANTIMONY[1)]

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Single crystals of four new lanthanoid sulfides were prepared by the evacuated silica-tube method: $Ln_{3-x}Sb_xS_4$ with $0.02 \leqq x \leqq 0.1$, where Ln=La, Ce, and Sm; $Ln_{1-x}Sb_xS_2$ with $x \cong 0.02$, where Ln=Nd. They are all reddish black crystals with plate-like habits. The crystals belong to the orthorhombic system with space group $P2_122_1$.

Large number of studies has been made on the Ln_3S_4 (Ln stands for the lanthanoid elements) type compounds and related lanthanoid sulfides[2)] since superconducting property has been found in La_3S_4.[3)] During the investigation of Ln-Sb-S system,[4)] we have found unknown sulfides whose chemical formula are close to either Ln_3S_4 or LnS_2, but they contain antimony in appreciable amounts. In addition, X-ray diffraction studies have shown that their crystal lattices are different from those of corresponding binary sulfides. In the present communication we report a brief description of these new sulfides.

The crystals were synthesized by the conventional evacuated silica tube method. The synthesized compounds were originally obtained as by-products in the synthesis of $Ln_6Sb_8S_{21}$ type compounds. Therefore, the experimental procedure was the same as described in our previous paper.[4)] The starting materials were mixtures of Ln (Ln=La, Ce, Sm, and Nd), S, and Sb_2S_3 in a molar ratio of 6:9:4. They were pre-reacted for 2 h at 1000 °C (La- and Ce-systems) or at 1100 °C (Sm- and Nd-systems). Then, they were maintained for 5 d at 900 °C (La, Ce), 1000 °C (Sm), or 950 °C (Nd).

The products were analyzed with an electron microprobe analyzer using an

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accelerating voltage of 20 kV and a probe current of 0.02 μA. Synthetic Sb_2S_3 (Sb, S), La_2TiO_5 (La), $Nd_3Ga_5O_{12}$ (Nd), $Sm_3Ga_5O_{12}$ (Sm), and analyzed monazite (Ce) were used as the standards. The X-ray powder diffraction data were obtained using a 114.6 mm Gandolfi camera with Ni-filtered Cu Kα radiation. Crystal system and space group were determined by the precession photographs.

The crystals were obtained as reddish black mass with plate-like habits, maximum size about 1x0.5x0.2 mm. They are translucent and the colors are red by transmitted light. The results of chemical analysis are given in Table 1. According to the atomic ratio, their chemical formula are close to either Ln_3S_4 or LnS_2. However, they definitely contain antimony in appreciable amount. Chemical analyses of the various products have revealed that the amount of antimony is in the range of 1.3 to 2.3 wt%. The chemical formula for these compounds can be represented as $Ln_{3-x}Sb_xS_4$ (Ln=La, Ce, Sm: $0.02 \leqq x \leqq 0.1$) or $Ln_{1-x}Sb_xS_2$ (Ln=Nd: $x \cong 0.02$). Single crystals were selected under a binocular microscope to obtain the crystallographic data. The precession photographs of $Ce_{3-x}Sb_xS_4$ have indicated that the crystal is orthorhombic and the space group is $P2_122_1$. Table 2 shows the X-ray powder diffraction patterns for the four new sulfides. The powder pattern of $Ce_{3-x}Sb_xS_4$ was indexed with the aid of the single crystal photographs. As shown in Table 2, the powder patterns of other three sulfides are also successfully indexed with the same orthorhombic cell. The unit cell dimensions were calculated from the powder data by the use of the cell parameter least-squares program of Appleman and Evans[5] and are listed in Table 3.

Since the chemical composition of the starting materials substantially deviates from those of the synthesized compounds, the above syntheses have produced several by-products. The most frequently observed phase is Sb_2S_3 containing a small amount of the lanthanoid elements. Other major products are $La_6Sb_8S_{21}$,[4] $Ce_6Sb_8S_{21}$,[6] Nd_3SbS_6,[6] and an unknown phase, $SmSb_2S_4$, which will be described in detail in a

Table 1. Electron microprobe chemical analysis of the new sulfides.

	$La_{3-x}Sb_xS_4$		$Ce_{3-x}Sb_xS_4$		$Sm_{3-x}Sb_xS_4$		$Nd_{1-x}Sb_xS_2$	
	wt%	Atomic ratio[a]	wt%	Atomic ratio[a]	wt%	Atomic ratio[a]	wt%	Atomic ratio[a]
Ln	74.26	2.90	75.23	2.91	73.82	2.92	68.43	0.98
Sb	2.28	0.10	1.99	0.09	1.58	0.08	1.39	0.02
S	24.36	4.12	22.38	3.79	23.34	4.33	28.70	1.84
Total	100.90		99.60		98.74		98.52	

a) Calculated on the basis: Ln+Sb=3.0 (La, Ce, and Sm) and Ln+Sb=1.0 (Nd).

Table 2. Indexed X-ray powder diffraction data for the new sulfides.[a)]

$La_{3-x}Sb_xS_4$

hkl	d_c/Å	d_o/Å	*I*
020	4.103	4.10	vs
120	3.671	3.69	s(br[b)])
220	2.904	2.91	m(br)
211	2.738	2.74	vs
221	2.371	2.37	vs
230	2.277	2.28	m
400	2.055	2.07	m
231	1.991	1.990	w
420	1.837	1.838	w
141	1.791	1.791	w
032	1.642	1.639	w
232	1.525	1.525	m
402	1.452	1.454	mw
251	1.429	1.429	mw
422	1.369	1.370	w
600	1.300	1.298	w

$Sm_{3-x}Sb_xS_4$

hkl	d_c/Å	d_o/Å	*I*
020	3.976	3.98	m
011	3.517	3.52	vs(br)
220	2.781	2.78	m
030	2.650	2.65	w
221	2.268	2.27	s
230	2.191	2.19	m
002	1.961	1.961	mw
122	1.715	1.715	mw
341	1.464	1.467	vw
440	1.391	1.391	vw

$Ce_{3-x}Sb_xS_4$

hkl	d_c/Å	d_o/Å	*I*
020	4.085	4.08	s
120	3.650	3.65	vs(br)
220	2.881	2.90	w
211	2.705	2.70	s
221	2.347	2.35	m
230	2.263	2.26	m
400	2.033	2.03	mw
231	1.974	1.976	vw
420	1.820	1.816	mw
141	1.779	1.780	mw
232	1.508	1.507	m
251	1.420	1.418	w
601	1.285	1.285	w

$Nd_{1-x}Sb_xS_2$

hkl	d_c/Å	d_o/Å	*I*
020	3.979	3.98	m
120	3.566	3.56	vs
201	2.811	2.81	m
211	2.650	2.66	mw
130	2.519	2.51	vw
221	2.296	2.30	s
230	2.214	2.21	m
040	1.990	1.982	mw
231	1.929	1.929	w
240	1.783	1.778	w
141	1.734	1.733	mw
050	1.592	1.593	vw
431	1.483	1.483	mw
402	1.405	1.405	w

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

b) br: broad peak.

Table 3. Unit cell parameters for the new sulfides.

	$La_{3-x}Sb_xS_4$	$Ce_{3-x}Sb_xS_4$	$Sm_{3-x}Sb_xS_4$	$Nd_{1-x}Sb_xS_2$
a/Å	8.220(6)	8.130(6)	7.784(9)	8.034(9)
b/Å	8.206(7)	8.170(7)	7.951(7)	7.958(3)
c/Å	4.105(8)	4.043(8)	3.921(2)	3.934(6)

further publication.

Crystal chemistry of the rare earth binary sulfides is very complicated and a quite large number of compounds are known.[2] However, the sulfides reported here are not simple solid solutions of any corresponding binary sulfides.

Although Ln_3S_4 type sulfides are compositionally related to the synthesized sulfides, their lattices are cubic with lattice parameters $a \cong 8.6$ Å,[7] which has little similarity to those of the present compounds. The synthesized sulfides might have some structural relation to the LnS_2 type sulfides because their lattice parameters are about integral multiple of 4 Å: *e.g.* LaS_2 is orthorhombic with a=8.131(5), b=16.34(1), and c=4.142(2) Å[8]; NdS_2 is tetragonal with a=4.022(3) and c=8.031(3) Å.[9] After all, however, none of them corresponds well with the present compounds.

The role of antimony in those compounds is interesting, but it remains as a question at the present stage. We cannot rule out the possibility of the Sb⇄S substitution since an alloy of $SmSb_xS_{1-x}$ with cubic NaCl structure is known to exist.[10] The electron microprobe analysis is not very sensitive to determine the delicate difference in composition and to know the deviation from stoichiometry. Precise wet chemical analyses and X-ray crystal structure analyses are essential for the better understanding of the synthesized compounds. Further investigations are now underway to characterize their electrical properties as well as to solve the above problems.

References

1) Studies on Lanthanoids-Antimony-Chalcogenides. II.
2) J. Flahaut, "Sulfides, selenides and tellurides," in "Handbook on the Physics and Chemistry of Rare Earths," ed by K.A. Gschneidner, Jr., and L.R. Eyring, North-Holland, New York (1979), Vol. 4. Chap. 31, pp. 3-18.
3) R.M. Bozorth, F. Holtzberg, and S. Mathfessel, Phys. Rev. Lett., 14, 952 (1965).
4) J-zh. Gao, I. Nakai, and K. Nagashima, Bull. Chem. Soc. Jpn., 56, 2615 (1983).
5) D.E. Appleman and H.T. Evans, Jr., U.S. Department of Commerce, Tech. Inform. Serv. NTIS Document No. PB-216188 (1973).
6) J-zh. Gao, I. Nakai, and K. Nagashima, Bull. Chem. Soc. Jpn., having been submitted (1983).
7) "Crystal Data," 3rd ed, ed by H.M. Ondik and A.D. Mighell, U.S. Department of Commerce, National Bureau of Standards and the JCPDS-International Center for Diffraction data (1978), Vol. 4, C 136-144.
8) J. Dugué, D. Carré, and M. Guittard, Acta Crystallogr., Sect. B, 34, 403 (1978).
9) A.A. Eliseev, S.I. Uspenskaya, and A.A. Federov, Zh. Neorg. Khim., 16, 1485 (1971).
10) R.B. Beeken, Wm.R. Savage, and J.W.Schweitzer, J. Appl. Phys., 49, 2093 (1978).

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