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The Phase AB_2 in the Ternary Systems La–Sb–Te and La–Sn–Sb[1]

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Received January 16, 1967

Ternary alloys of the sections $LaSb_2$–$LaTe_2$ and "$LaSn_2$"–$LaSb_2$ were investigated by X-ray diffraction techniques. The substitution of Te by Sb in the first system produces an orthorhombic distortion of the tetragonal $LaTe_2$ structure. The maximum solubility of Sb in $LaTe_2$ leads to the terminal composition $LaSb_{1.5}Te_{0.5}$. In the "$LaSn_2$"–$LaSb_2$ section no alloy of the type $LaSn_{2-x}Sb_x$ for $0 \leq x < 2$ exists. A phase $LaSnSb_2$ was found, and it is isostructural with $NdTe_3$.

Introduction

During the investigation of AB_2 compounds formed by rare earths with group Va and VIa elements, several new crystal structures were found. Elements from La to Sm formed diantimonides having the $LaSb_2$-type structure;[2] $YbSb_2$ was found to crystallize in the $ZrSi_2$-type structure;[3] rare earth ditellurides crystallize with the Cu_2Sb-type structure;[4,5] rare earth diselenides build two different types of superstructures based on the Cu_2Sb-type structure.[2] Lanthanum and samarium do not form a distannide compound. All of these structures display a close relationship and a discussion of the crystal chemistry of these phases is given by Wang, *et al.*[2]

After the crystal structures of the diantimonides, ditellurides, and diselenides of the rare earths had been determined, it was considered desirable to investigate the changes which result from the partial substitution of the B elements in order to ascertain the stabilities of the various structures, their abilities to form solid solutions, and, if possible, the mechanism of transformation from one structure into another. The ternary alloys of the sections "$LaSn_2$"–$LaSb_2$ and $LaSb_2$–$LaTe_2$ were investigated in order to study the above-mentioned effects.

Experimental Method

The alloys studied were prepared by allowing the elements to react in Vycor tubes. The La–Sb–Te alloys were preheated below 500° for 24 hr and kept later at 700° for about 1 week. The La–Sn–Sb alloys were prepared in tantalum tubes since the mixture reacted with the Vycor tubes. The preheated samples were finally allowed to react at 750° for 15 days. The material was judged to be single phase if no extraneous X-ray diffraction lines were seen on powder photographs. The X-ray diffraction powder patterns of the samples were obtained in a Guinier camera using Cu Kα radiation, λ 1.5405 A. The lattice parameters of the different phases were calculated by minimizing the differences between the experimental and calculated $\sin^2 \theta$ values to less than 0.0005 and are considered accurate to 0.005 A for a_0 and b_0 and to 0.01 A for c_0.

Results

(1) $LaSb_2$–$LaTe_2$ Section.—Five ternary alloys with compositions denoted by the formulas $LaSb_{0.2}Te_{1.8}$, $LaSb_{0.3}Te_{1.7}$, $LaSb_{0.5}Te_{1.5}$, LaSbTe, and $LaSb_{1.5}Te_{0.5}$ were investigated.

$LaTe_2$ has the Cu_2Sb (C38) tetragonal structure[4] with lattice parameters a_0 = 4.507 A, c_0 = 9.128 A. $LaSb_2$ has an orthorhombic structure, space group Cmca, with lattice parameters a_0 = 6.314 A, b_0 = 6.175 A, and c_0 = 18.56 A.[2]

The ternary alloys form a solid solution from the composition $LaTe_{2.0}$ to $LaSb_{1.5}Te_{0.5}$. The powder pattern of the homogeneous alloy $LaSb_{1.5}Te_{0.5}$ could be indexed on a tetragonal unit cell with lattice parameters a_0 = 4.383 A and c_0 = 9.438 A. Alloys richer in Te content gave diffraction photographs in which some of the lines are split and which can be indexed on the basis of an orthorhombic cell with slight differences in a_0 and b_0 values, Table I. As the concentration of the Sb atoms increased, the a_0 parameter decreased almost linearly from the value 4.507 A in $LaTe_2$ to 4.38 A in $LaSb_{1.5}Te_{0.5}$. The b_0 parameter, which is equal to a_0 for $LaTe_2$, rapidly dropped when about 25% of the Te atoms were replaced by Sb atoms and then remained approximately constant at 4.39 A from $LaSb_{0.5}Te_{1.5}$ to $LaSb_{1.5}Te_{0.5}$. The c_0 parameter increased linearly from 9.128 A in $LaTe_2$ to 9.438 A in $LaSb_{1.5}Te_{0.5}$. The variations of the lattice parameters and the mean atomic volumes are shown in Figure 1. An indexed powder pattern of the ternary phase $LaSb_{0.5}Te_{1.5}$ is given in Table II. The discontinuity of this solid solution occurred when the Sb content increased beyond 50 atom % in the alloys. The alloys with more than 50 atom % Sb exhibited equilibrium between the two phases $LaSb_2$ and $LaSb_{1.5}Te_{0.5}$.

Antimony and tellurium have nearly the same X-ray scattering factors and therefore the substitution of one for the other in the structure will leave the intensities unaffected. However, there are small differences in bond lengths between RE–Te and RE–Sb and a slight change in the coordination polyhedron around RE occurs, from nine atoms in the former to ten in the latter. Both the $YbSb_2$[3] and the $LaSb_2$[2] structures are orthorhombic and are closely related to the $LaTe_2$ structure. The splitting of the lines, *i.e.*, change to an orthorhombic cell, may be due to a transition to the $LaSb_2$-type structure with increasing antimony substitution. The "tetragonal" pattern for the com-

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[1] Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR Grant No. 806-65.

[2] R. Wang and H. Steinfink, to be published.

[3] R. Wang, R. E. Bodnar, and H. Steinfink, *Inorg. Chem.*, **5**, 1468 (1966).

[4] R. Wang, H. Steinfink, and W. F. Bradley, *ibid.*, **5**, 142 (1966).

[5] M. P. Pardo, J. Flahaut, and L. Domange, *Bull. Soc. Chim. France*, 3267 (1964).

Table I

Lattice Parameters, Unit Cell Volumes, and Mean Atomic Volumes of the Phases in $LaSb_2$–$LaTe_2$ Section

Alloy compn	Structure	*a*	*b*	*c*	Vol, A^3	Mean atomic vol, A^3/atom
$LaTe_{2.0}$	Tetragonal	4.507	...	9.128	185.4	30.90
$LaSb_{0.2}Te_{1.8}$	Orthorhombic	4.503	4.451	9.168	183.7	30.62
$LaSb_{0.3}Te_{1.7}$	Orthorhombic	4.493	4.414	9.232	183.2	30.52
$LaSb_{0.5}Te_{1.5}$	Orthorhombic	4.474	4.398	9.263	182.2	30.37
$LaSb_{1.0}Te_{1.0}$	Orthorhombic	4.440	4.388	9.330	181.8	30.30
$LaSb_{1.5}Te_{0.5}$	Tetragonal	4.383	4.383	9.438	181.3	30.22
$LaSb_{2.0}$	$LaSb_2$	6.314 (4.465 × $\sqrt{2}$)	6.175 (4.367 × $\sqrt{2}$)	18.56 (9.280 × 2)	721.7	30.07

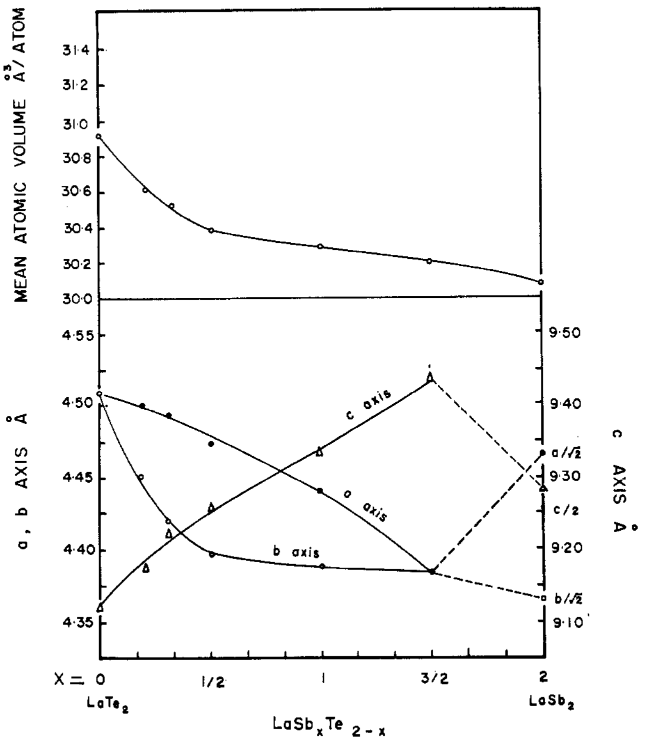

Figure 1.—Variation of lattice parameters and mean atomic volume in the solid solution $LaSb_xTe_{2-x}$, $0 \leq x \leq 1.5$.

position $LaSb_{1.5}Te_{0.5}$ may be just the composition in the solid solution series at which accidental equivalence between a_0 and b_0 exists for the orthorhombic cell. This postulated process for the solid solution formation could probably be tested from single crystal X-ray data, but until such crystals become available no firm conclusion can be reached.

(2) **"$LaSn_2$"–$LaSb_2$.**—A thermal analysis study reported by Canneri[6] indicated the existence of the phases La_2Sn, La_2Sn_3, and $LaSn_2$. The phase La_2Sn is probably La_5Sn_3, which has the Mn_5Si_3-type structure, $D8_8$,[7] while $LaSn_2$ was proved to be $LaSn_3$ having the Cu_3Au-type structure.[6,8] An alloy $La_{33.3}Sn_{66.7}$ prepared as described in the Experimental Section contained some unreacted Sn. Besides the $LaSn_3(Cu_3Au)$ phase a cubic CsCl-type phase with a = 4.086 A was detected and assigned a formula, LaSn. This CsCl-type phase has perhaps a small homogeneity range on the Sn-rich side and may include the composition La_2Sn_3. The La–Sb system has been studied by thermal and microscopic analyses and the phases La_2Sb, La_4Sb_3, LaSb, and $LaSb_2$ have been reported.[6] The phase La_4Sb_3 was shown to have the inverse Th_3P_4-type structure[9] and LaSb was found to crystallize in the NaCl-type structure.[6]

Table II

Powder Patterns of $LaSb_{0.5}Te_{1.5}$ and $LaSnSb_2$ Obtained in a Guinier Camera with Cu Kα Radiation[a]

$LaSb_{0.5}Te_{1.5}$			$LaSnSb_2$		
hkl	d_{obsd}, A	Rel intens	*hkl*	d_{obsd}, A	Rel intens
101	4.027	w	101	4.145	s
011	3.983	w	006	3.814	w
102	3.211	w	014	3.528	vs
012	3.184	w	105	3.099	vs
110	3.129	s	111	3.039	s
003	3.087	s	016	2.900	s
111	2.966	vs	008	2.873	vs
112	2.593	vs	113	2.848	vvs
103	2.540	s	107	2.586	vvs
013	2.527	s	115	2.514	vvs
200	2.236	vs	018	2.417	vs
020 113	2.197	vs	020 117	2.236	vvs
114	1.861	s	022	2.199	w
212	1.829	vvw	200	2.107	vs
203 122	1.812	s	024	2.089	vvw
023	1.789	s	01,10	2.045	vw
105	1.710	w	121	1.963	w
015	1.705	w	026	1.932	w
213	1.674	m	123 00,12	1.913	w
123	1.662	m	10,11	1.873	w
204	1.607	vvw	214	1.812	s
115 024	1.594	w	028	1.760	s
220	1.567	s	127	1.697	s
106 016	1.456	w	218	1.589	w
310	1.414	vvw	220	1.534	w
311 130	1.394	s			
116	1.383	vvw			
131	1.375	vw			
215	1.355	vw			
125 312	1.349	vw			
132	1.332	vw			

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Four samples with compositions corresponding to the stoichiometries $LaSn_2$, $LaSn_{0.5}Sb_{1.5}$, LaSnSb, and $LaSn_{1.5}Sb_{0.5}$ were studied. In the sample of composition LaSnSb and $LaSn_{0.5}Sb_{1.5}$ a new phase was found. This phase was observed also in the alloy of composition $SmSn_{0.5}Sb_{1.5}$. A single crystal of this new ternary phase was selected and the lattice constants measured from X-ray precession diagrams were a_0 = 4.228 A, b_0 = 4.478 A, and c_0 = 22.99 A. The powder pattern of this phase was indexed using these lattice parameters and is given in Table II. The extinctions observed from the X-ray single crystal photographs are

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[6] M. Hansen, "Constitution of Binary Alloys," McGraw-Hill Book Co., Inc., New York, N. Y., 1958.

[7] W. Jeitschko and E. Parthe, *Acta Cryst.*, **19**, 275 (1965).

[8] R. Harris and G. V. Raynor, *J. Less-Common Metals*, **9**, 7 (1965).

[9] D. Hohnke and E. Parthe, *Acta Cryst.*, **21**, 435 (1966).

consistent with the diffraction symbol mmmB--b. The phase $NdTe_3$[10] shows the same extinctions and has the same space group and similar lattice parameters, $a = b = 4.35$ A, $c = 25.80$ A. A comparison of the relative intensities of corresponding reflections leads to the conclusion that the new phase probably has a structure similar to $NdTe_3$. A tentative formula $LaSnSb_2$ was assigned to this phase, but the exact atomic positions in the structure were not determined.

The LaSb, Sn, and $LaSn_3$ phases were found in the alloy of composition $LaSn_{1.5}Sn_{0.5}$; SmSb, Sn, and $SmSn_3$ phases were likewise found in equilibrium in the alloys of composition SmSnSb and $SmSn_{1.5}Sb_{0.5}$. The alloy of composition LaSnSb showed the equilibrium between LaSb, Sn, and the new ternary phase, while in $LaSn_{0.5}Sb_{1.5}$ the new ternary phase was predominant.

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[10] B. K. Norling and H. Steinfink, *Inorg. Chem.*, **5**, 1488 (1966).

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The Systems Xenon Hexafluoride–Germanium Tetrafluoride and Xenon Hexafluoride–Silicon Tetrafluoride

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Received December 20, 1966

Xenon hexafluoride and germanium tetrafluoride, when mixed in the proper proportions, produce the compounds $4XeF_6 \cdot GeF_4$, $2XeF_6 \cdot GeF_4$, and $XeF_6 \cdot GeF_4$. Xenon hexafluoride appears not to react with silicon tetrafluoride.

Formation of compounds by the combination of xenon hexafluoride with stannic fluoride[1] suggests that fluorides of group IV elements other than tin may also combine with xenon hexafluoride. It has now been found that the reaction of excess XeF_6 with GeF_4 proceeds readily at room temperature to yield the white solid $4XeF_6 \cdot GeF_4$. The substance has a dissociation pressure of the order of 1 mm at 22°. When the complex is pumped at 0°, XeF_6, but practically no GeF_4, is slowly lost. After half of the combined XeF_6 has been removed, further loss is very slow. The substance remaining in the reactor, $2XeF_6 \cdot GeF_4$, is a white, crystalline solid. When $2XeF_6 \cdot GeF_4$ is pumped at 22°, XeF_6 and GeF_4 are removed in a 2:1 molar ratio at a rate of about 100 mg/hr in the system employed. At 0° the rate is much slower. The low rate of sublimation of $2XeF_6 \cdot GeF_4$ indicates that its dissociation pressure at 22° is only a small fraction of that of $4XeF_6 \cdot GeF_4$.

The reaction of excess GeF_4 with XeF_6 proceeds at room temperature to form the white, crystalline solid $XeF_6 \cdot GeF_4$. When pumped at 22°, a sample of this compound decomposed under vacuum in a somewhat complicated manner. The XeF_6 and GeF_4 were lost at a molar ratio of about 3:4 until about 61% of the sample had been removed. While the next 23% was removed, the XeF_6 to GeF_4 molar ratio in the sublimate rapidly increased to 2:1. During removal of the last 16% of the sample, the XeF_6 and GeF_4 were lost at a constant molar ratio close to 2:1. This behavior indicates that pumping from a mixture of $XeF_6 \cdot GeF_4$ and $2XeF_6 \cdot GeF_4$ gives the gases GeF_4 and XeF_6 in a ratio of about 4:3. As the process continues more $2XeF_6 \cdot GeF_4$ is formed. When the proportion of $XeF_6 \cdot GeF_4$ in the solid becomes low, the composition of the gas being removed changes and becomes 2:1 for the XeF_6 to GeF_4 ratio after only $2XeF_6 \cdot GeF_4$ remains in the solid phase. Equilibria which probably are involved are represented by

$$[4XeF_6 \cdot GeF_4] = [2XeF_6 \cdot GeF_4] + 2XeF_6(g)$$

$$[2XeF_6 \cdot GeF_4] = 2XeF_6(g) + GeF_4(g)$$

$$2[XeF_6 \cdot GeF_4] = [2XeF_6 \cdot GeF_4] + GeF_4(g)$$

The physical and chemical properties of the GeF_4 complexes are in many ways similar to those of the SnF_4 complexes. The compounds react violently with water to give a nearly quantitative yield of Xe(VI) in solution. Neither $2XeF_6 \cdot GeF_4$ nor $XeF_6 \cdot GeF_4$ melts under an atmosphere of nitrogen up to temperatures of 98 and 135°, respectively.

Attempts to prepare adducts of xenon hexafluoride with silicon tetrafluoride have been unsuccessful.

Experimental Section

Reagents.—Xenon hexafluoride was prepared by the combination of the elements under pressure at about 225°. Germanium tetrafluoride was prepared by passing fluorine over germanium dioxide at 300°. Ten grams of GeO_2 contained in a nickel boat was placed inside a nickel tube that could be heated electrically. A flow rate of about 1 l./hr of fluorine was used, and the GeF_4 was collected in a copper trap cooled to $-183°$. Silicon tetrafluoride was prepared by the reaction of silica with sodium fluoride and sulfuric acid.

Equipment.—Prefluorinated Monel and stainless steel reactors equipped with brass Hoke valves were used for the reactions. The reactors could be opened to allow the solid adducts to be re-

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[1] K. E. Pullen and G. H. Cady, *Inorg. Chem.*, **5**, 2057 (1966). Further detail will be included in the thesis of the junior author, to be published in 1967.