STUDIES ON SYNTHESES AND CONDITIONS OF FORMATION FOR $LnSiAs_3$ COMPOUNDS ($Ln \equiv La, Ce, Pr$)

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(Received March 2, 1988)

Summary

Syntheses of Ln-Si-As compounds (Ln = La, Ce, Pr, Nd, Sm) have been attempted using a temperature-gradient furnace by controlling the arsenic pressure. Several ternary compounds, with the composition LnSiAs₃ (Ln = La - Pr), were formed. In the case of lanthanum, two polymorphs, the LaSiAs₃ type and CeSiP₃ type, were found. By X-ray diffraction structure analysis using the Rietveld method the crystallographic data of the LaSiAs₃ type are obtained as space group *Pbca*, a = 6.0855(2) Å, b = 5.9837(2) Å, c = 26.2279(6) Å; and those of the CeSiP₃ type are found to be space group *Pn2*₁*a*, a = 6.0498(3) Å, b = 5.9545(3) Å, c = 26.383(1) Å. For Ln = Ce and Pr, only the CeSiP₃ type was found.

An apparatus for thermogravimetric experiments in a sealed silica tube under a controlled arsenic pressure using the temperature-gradient furnace was constructed for thermogravimetric measurements of conditions of formation for the Ln–Si–As systems between 700 and 1000 °C and arsenic pressures of 10^{-2} to 20 atm. From these results, together with other results from differential thermal and X-ray analyses, the conditions for the formation of these ternary compounds were obtained.

1. Introduction

Since research started on rare earth pnictides, with the expectation of producing magnetic semiconductors, a large number of new compounds have been synthesized within the binary systems [1]. Recently, primary interest seems to have shifted from binary systems to ternary systems. During our investigations on the rare earth pnictides a series of new ternary compounds containing silicon has been found and reported in previous papers [2 - 6]. These new compounds were confirmed by Mironov *et al.* [7].

The $III_A-IV_B-V_B$ ternary compounds which have been known hitherto are quite limited. In nitrides, $LaSi_3N_5$ [8], $Sm_3Si_6N_{11}$ [9] were reported. In phosphides, three polymorphs of $LnSiP_3$ composition and three compounds of $LnSi_2P_6$ composition for $Ln \equiv La$, Ce, Pr were synthesized [3]. The present investigation is on the synthesis of the ternary arsenides. Besides the F-type $LaSiAs_3$ compounds which were already reported [5, 6], several new compounds have been formed.

Conditions of formation for arsenides depend strongly on the vapour pressure of arsenic. In order to study the effect of arsenic pressure on the conditions of formation, a special thermogravimetric apparatus was constructed and used in the present experiments.

2. Experimental procedure

2.1. Syntheses

The starting elements were of nominal purity better than 99.9%. The materials were treated and kept in an argon dry box (less than 3 ppm oxygen) throughout these experiments. The rare earth metals used were La, Ce, Pr, Nd, Sm.

Syntheses of the ternary compounds have been carried out by the following two different ways. Firstly, an appropriate ratio of Ln and silicon was arc-melted to the rare earth silicide, which was then reacted with arsenic to form the ternary compound. In the second method, the rare earth metal ingot was filed and reacted directly with arsenic at 700 $^{\circ}$ C to give the NaCl-type monoarsenide, which was then mixed with a given amount of silicon and reacted further with arsenic to give the ternary compound. Details of the procedures were reported in the previous paper [5].

X-ray powder diffraction apparatus (Rigaku RAX-01) equipped with a graphite monochromator using Cu K α radiation (40 kV, 30 mA) was used for identification of the samples. The step-scanning diffraction data, which were measured with a stepwidth of 0.02° per step and a time constant 20 s per step, were subjected to the pattern fitting analysis (Rietveld method) in order to analyse the crystal structure of the phases. The program used in this analysis was *DBW 3.2* [10]. Refinement was made using the step-scan data in the range 20° to 100°.

Differential thermal analysis (DTA) was performed using a Mettler Analysis-1. The sample was sealed in a fused silica tube. The heating rates used were 4 $^{\circ}$ C min⁻¹ or 10 $^{\circ}$ C min⁻¹ and alumina powder sealed in a fused silica tube was used as the reference.

2.2. Thermogravimetric measurements

The thermogravimetric apparatus shown in Fig. 1 was used for measurements on the LnAs-As, Si-As and LnSiAs₃-As systems at temperatures from 700 to 1000 °C and arsenic pressures of 10^{-3} to 20 atm. The uniform temperature region $(T_{\rm P})$ of 5 cm length was obtained with a three-point silicon-controlled rectifier (SCR) temperature control (Fig. 1(b)). Gravimetric data were measured with a microstrain gauge and collected on a micro-computer, together with data on the temperatures of the reaction and arsenic regions. The measurements were made mainly at a constant reaction temperature.



Fig. 1. Specially designed thermogravimetric apparatus. (a) Block diagram: (1) electronic furnace, (2) SCR temperature controller, (3) spring, (4) micro-computer, (5) fulcrum, (6) sample, (7) thermocouple (PR13), (8) thermocouple (CA), (9) cold junction, (10) arsenic, (11) strain gauge, (12) bridge, (13) cooling water, (14) amplifier, (15) data logger, (16) recorder. (b) Temperature profile. (c) Dimensional relation.

ature $(T_{\rm P})$, changing the temperature $(T_{\rm As})$ of the arsenic region. This is called the "constant temperature method". The heating or cooling rate was 10 to 60 °C h⁻¹. The sample weighed 1.5 to 2 g and was encapsulated in a fused silica tube of inner diameter of 7.5 mm and length 280 mm. A weight change of ±0.5% was measurable on this apparatus.

The apparent weight change (Δg) can be represented as follows,

$$\Delta g = \Delta g_1 + \Delta g_2 + \Delta g_3 \tag{1}$$

where Δg_1 is the change in the amount of arsenic reacted into the sample, Δg_2 is the weight change in the arsenic vapour, and Δg_3 is the apparent change in buoyancy, convection, thermal expansion etc.

The total amount of vaporized arsenic (m_0) is shown as

$$m_0 = m_1 + m_2 \tag{2}$$

where m_1 is the amount of reacted arsenic and m_2 is that of arsenic vapour. m_1 can be obtained from the following equations

$$m_1 = \frac{L}{L_a} \left(\Delta g - \Delta g_2 - \Delta g_3 \right) \tag{3}$$

$$\Delta g_2 = \left(\frac{L_3 - L_2}{L}\right) m_2 \tag{4}$$

where L is the length of beam, L_a is the length of the fused silica tube, and L_1 , L_2 , L_3 are the distances from the fulcrum to m_1 , m_2 , m_0 respectively. Under the conditions of the present experiments, the vapour composition of arsenic can be assumed to be As₄ molecules [11]. The amount of arsenic vapour was calculated from the vapour pressure data of arsenic [12] assuming As₄ molecules in the gas phase. The compensation parameter Δg_3 was obtained experimentally from an experimental run with only arsenic.

3. Results and discussion

3.1. Ln-Si-As ($Ln \equiv La$ - Sm) ternary compounds

In the La-Si-As system, two phases of LaSiAs₃ composition have been found. One of them has already been reported [5, 6] and has a structure which belongs to space group *Pbca*. The sample was synthesized with an [Si]/[La] ratio of 1.0, a temperature of 900 °C and an arsenic pressure of 1.0 atm. This sample was subjected to X-ray examination by Rietveld's method. The results are shown in Fig. 2(a). The sample was almost single phase. The crystallographic data are orthrorhombic, *Pbca*, a = 6.0855(2) Å, b = 5.9837(2) Å, c = 26.2279(6) Å. The final "goodness-of-fit" indicators are $R_{WP} = 10.3\%$, $R_P = 7.9\%$, $R_E = 4.9\%$ and $R_B = 7.1\%$. Definitions of these indicators are given in refs. 10, 13 and 14. The atomic parameters and powder diffraction data are listed in Tables 1 and 2. In the following discussion this structure is called the LaSiAs₃ or F-type structure.

The other LaSiAs₃ compound, which was synthesized for the first time in the present experiments, was found to be isostructural with CeSiP_3 [4]. Its crystallographic data are orthorhombic, $Pn2_1a$, a = 6.0498(3) Å, b =5.9545(3) Å, c = 26.383(2) Å. From the fact that this phase was formed under conditions of 780 °C, 1 atm or 700 °C, 0.1 atm and has a higher density than that of the F-type by 0.4%, this can be designated as the lowtemperature, high-pressure stable phase. However, since conditions of lower temperature and higher pressure decompose this ternary compound to $(LaAs_2 + SiAs_2)$ and its stable region is narrow, the pure phase was difficult to obtain. The best sample, which was obtained with [Si]/[La] = 1.2, 780 $^{\circ}$ C and 1 atm, was subjected to Rietveld's analysis and the results are shown in Fig. 2(b). The sample contains a small amount of SiAs₂. The final "goodnessof-fit" indicators were $R_{WP} = 10.0\%$, $R_P = 7.7\%$, $R_E = 4.6\%$, $R_B(LaSiAs_3) =$ 6.1%, $R_{\rm B}({\rm SiAs}_2) = 10.4$. The crystallographic data and powder diffraction data are listed in Tables 3 and 4 respectively. In the following discussion, this phase is called the $CeSiP_3$ or P-type structure.

In the case of the Ce-Si-As system, only the CeSiP₃ type compound was formed. Its crystallographic data are orthorhombic, $Pn2_1a$, a = 5.988(1) Å, b = 5.906(1) Å, c = 26.231(3) Å.

In the case of the Pr-Si-As system, the synthesis based on increasing arsenic pressure gradually was unsuccessful, resulting in direct reaction from (SiAs + PrAs) to (SiAs₂ + PrAs₂). However, the mixture of diarsenides was





TABLE 1

Atom	Site	x	У	z	$B_{\rm iso}({\rm \AA}^2)$
La(1)	8c	-0.0007(5)	0.0041(8)	0.0922(1)	0.88(3)
As(1)	8c	-0.0016(9)	0.5021(16)	0.1239(1)	0.71(6)
As(2)	8c	-0.0385(7)	0.0097(14)	0.2116(1)	1.26(7)
As(3)	8c	0.2750(10)	0.2333(11)	0.0007(2)	4.07(11)
Si(1)	8c	-0.0700(18)	0.4271(18)	0.2057(3)	2.70(32)

Final positional and isotropic thermal parameters with standard deviations in parentheses for $LaSiAs_3$ type $LaSiAs_3$

TABLE 2

X-ray powder data for F-LaSiAs₃ (Pbca) λ = 1.54056 (Å)

Number	hkl	d _{calc} (Å)	Icalc	Iobs	
1	002	13.11395	34	30	
2	004	6.55698	8	6	
3	102	5.52010	2	4	
4	104	4.46047	4	3	
5	006	4.37132	10	9	
6	11 1	4.21129	32	27	
7	106	3.55031	2	3	
8	11 5	3.30998	5	6	
9	008	3.27849	10	12	
10	200	3.04275	38	41	
11	020	2.99185	38	40	
12	202	2.96401	11	10	
13	022	2.91690	13	13	
14	11 7	2.81536	100	100	
15	204	2.76005	44	46	
16	024	2.72189	41	40	
17	210	2.71223	1	1	
18	0010	2.62279	47	54	
19	214	2.50628	1	1	
20	206	2.49732	39	37	
21	026	2.46895	39	37	
22	11 9	2.40645	5	5	
23	220	2.13333	60	59	
24	222	2.10565	2	3	
25	1111	2.08140	28	27	
26	224	2.02866	4	5	
27	2010	1.98661	9	8	
28	0210	1.97224	9	8	
29	304	1.93788	2	2	
30	226	1.91720	5	6	
31	31 1	1.91598	4	5	

(continued)

Number	hkl	d _{calc} (Å)	I _{calc}	I _{obs}	
32	13 1	1.89043	4		
33	0014	1.87342	3	4	
34	306	1.84003	2	3	
35	$1\ 1\ 13$	1.82390	10	10	
36	$2\ 2\ 8$	1.78810	6	6	
37	2 0 12	1.77515	4	5	
38	$0\ 2\ 12$	1.76488	5	6	
39	308	1.72501	1	1	
40	317	1.70950	18	18	
41	137	1.69128	21	20	
42	2 2 10	1.65499	29	26	
43	324	1.62650	1	1	
44	$1\ 1\ 15$	1.61793	9	9	
45	319	1.60395	1	1	
46	139	1.58887	2	2	
47	326	1.56734	1	1	
48	400	1.52138	7	6	
49	3 1 11	1.49596	10	9	
50	040	1.49593	8	8	
51	328	1.49441	1	1	
52	1 3 11	1.48370	9	9	
53	404	1.48201	2	2	
54	044	1.45845	1	1	
55	1 1 17	1.45088	$1\overline{7}$	18	
56	2016	1.44314	4	5	
57	0 2 16	1.43760	5	5	
58	406	1.43684	1	2	
59	331	1.42013	1	1	
60	046	1.41534	1	1	
61	$2\ 2\ 14$	1.40768	2	2	
62	3113	1.39127	3	3	
63	$1\ 3\ 13$	1.38139	3	3	
64	408	1.38003	1	1	
65	048	1.36095	1	1	
66	420	1.35611	5	5	
67	240	1.34246	5	5	
68	337	1.32965	8	9	
69	424	1.32801	7	8	
70	4010	1.31600	4	4	
71	2 4 4	1.31518	6	6	
72	1119	1.31339	3	3	
73	2216	1.29983	1	1	
74	0410	1.29943	5	4	
75	426	1.29522	6	6	
76	$3\ 1\ 15$	1.29311	4	3	
77	$1\ 3\ 15$	1.28517	3	3	
78	246	1.28330	6	6	
79	3311	1.22143	4	3	
80	4 2 10	1.20462	2	2	
81	3117	1.20293	8	9	

 TABLE 2 (continued)

TABLE 3

Atom	Site	x	У	z	$B_{\rm iso}({\rm \AA}^2)$
La(1)	4a	0.016(1)	0.750	0.0900(1)	0.80(11)
La(2)	4a	0.512(1)	0.241(3)	0.0978(1)	0.71(11)
As(1)	4a	0.511(2)	0.732(3)	0.1210(3)	0.70(5)
As(2)	4a	0.005(2)	0.240(4)	0.1233(3)	0.70(5)
As(3)	4a	0.279(2)	0.499(3)	0.0003(7)	0.70(5)
As(4)	4a	0.699(2)	0.543(2)	-0.0013(6)	0.70(5)
As(5)	4a	0.550(1)	0.228(3)	0.2144(3)	0.70(5)
As(6)	4a	0.976(2)	0.719(2)	0.2084(3)	0.70(5)
Si(1)	4a	-0.028(4)	0.326(4)	0.2063(7)	1.00
Si(2)	4 a	0.630(3)	0.811(5)	0.2074(10)	1.00

Final positional and isotropic thermal parameters with standard deviations in parentheses for CeSiP_3 -type LaSiAs_3

TABLE 4

X-ray powder data for P-LaSiAs₃ ($Pn2_1a$) $\lambda = 1.54056$ (Å)

Number	hkl	d _{calc} (Å)	I _{calc}	Iobs	
1	002	13.19150	32	30	
2	004	6.59575	11	12	
3	10 1	5.89673	4	3	
4	102	5.49905	2	2	
5	10 3	4.98429	4	2	
6	104	4.45838	7	5	
7	006	4.39717	12	11	
8	11 2	4.03985	54	51	
9	015	3.94915	1	1	
10	114	3.56886	22	24	
11	106	3.55689	3	3	
12	11 5	3.30693	3	3	
13	008	3.29788	18	20	
14	10 7	3.19898	4	5	
15	017	3.18465	1	1	
16	11 6	3.05358	32	32	
17	200	3.02489	62	65	
18	201	3.00520	4	4	
19	020	2.97726	66	70	
20	202	2.94836	17	17	
21	022	2.90421	23	24	
22	10 8	2.89559	2	2	
23	11 7	2.81805	1	1	
24	204	2.74953	69	76	
25	024	2.71361	66	71	
26	121	2.65771	3	3	
27	212	2.64221	3	4	
28	0010	2.63830	70	80	

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(continued)

Number	h k l	d_{calc} (Å)	Icalc	Iobs	
29	10 9	2.63806	4	5	
30	019	2.63001	2	2	
31	11 8	2.60402	91	93	
32	$12 \ 3$	2.55599	1	1	
33	206	2.49215	56	57	
34	124	2.47595	1	1	
35	026	2.46531	58	61	
36	125	2.38329	2	1	
37	$1\ 2\ 6\ 2.28303\ 1$		1	1	
38	1 1 10	2.24060	15	14	
39	0.2 8 2.24000 10		3	2	
40	220	2,12188	100	100	
41	221	2 11505	2	200	
42	222	2.09495	5	5	
43	224	2.01993	8	ğ	
44	30 1	2.01070	3	3	
45	2010	1 98828	11	11	
46	0 2 10	1 97457	19	19	
47	1 1 1 9	1 95916	12	5	
48	30 4	1 99847		9	
40	20 4 22 6	1 91101	7	8	
50	220	1.01101	1	1	
51	219	1 80039	L F	6	
59	0014	1.89/50	3	3	
53	30 5	1 88971	5	5	
50	121	1.00071	1	0	
55	13 9	1 86605	1 7	2	
56	13 2	1.80095	1	1	
57	100	1.04401	1	1	
58	306	1 83302	2	3	
50	134	1.81297	2	5	
60	204	1 70999	4	5	
61	4 I II 1 9 11	1.19444	1	1	
62	2211	1.70400	19	10	
63	220	1.70440	12	12	
64	2012	1.77040	10	10	
04 65	0414	1.76100	10	10	
66	126	1.70100	10	10	
67	100	1,70024	10	14	
69		1.72232	28	31	
60	01 / 00 1	1.70374	1	1	
70	02 I 0010	1.00031	1	1	
70	2210	1.0004/	44	47	
· 1 79	20 2 0 T O	1.00200	41 2	42	
72	040 190	1.04034	ំ ក វ	4	
74	20 A	1.00/14	44 0	25	
1 ± 75	04 4 1919	1.01000	2	2	
76	1 4 1 O 9 9 1	1 60000	1	1	
(0)	Z 3 4	1.60933	1	1	

 TABLE 4 (continued)

(continued)

Number	hkl	d _{calc} (Å)	I _{calc}	I _{obs}	
77	2014	1.59949	1	1	
78	0214	1.59233	1	1	
79	326	1.56090	1	1	
80	3110	1.54714	4	5	
81	$1\ 1\ 16$	1.53699	1	1	
82	1 3 10	1.53425	4	4	
83	327	1.52656	4	4	
84	400	1.51244	11	10	
85	1017	1.50327	1	1	
86	328	1.48962	1	1	
87	040	1.48863	13	13	
88	042	1 47924			
89	404	1 47418	3	3	
90	1 2 15	1 46903	2	2	
91	04 4	1 45211	2	2	
99	39 0	1 45082	2	29	
92 02	0 2 9 0 1 6	1 44780	6	6	
04	2010	1 44949	7	9	
94	0 4 10	1.44240	1	0	
90	3112	1.44190	2	2	
96	1312	1.43145	2	2	
97	3013	1.43048	1	1	
98	406	1.43020	Z	2	
99	046	1.41002	2	2	
100	2214	1.40902	2	2	
101	332	1.40652	2	2	
102	1 1 18	1.38542	20	20	
103	408	1.37476	2	2	
104	048	1.35681	2	3	
105	1019	1.35339	1	1	
106	420	1.34843	7	8	
107	336	1.34662	3	3	
108	$3\ 1\ 14$	1.34148	10	10	
109	24 0	1.33565	8	10	
110	$1\ 3\ 14$	1.33305	10	12	
111	3015	1.32552	3	3	
112	424	1.32110	11	12	
113	0 0 20	1.31915	1	1	
114	0218	1.31500	1	1	
115	4010	1.31213	6	7	
116	244	1.30908	11	12	
117	338	1.30004	8	9	
118	0410	1.29649	6	6	
119	426	1.28917	8	8	
120	246	1.27799	10	11	
121	427	1.26962	1	1	
122	1120	1.25970	1	1	
123	3 3 10	1.24669	2	2	
124	1316	1.24136	1	1	
125	4 2 10	1.20060	3	4	
			-	-	

TABLE 4 (continued)

found to form $PrSiAs_3$ by decreasing pressure. Its crystallographic data are orthorhombic, $Pn2_1a$, a = 5.949(2) Å, b = 5.877(2) Å, c = 26.149(9) Å.

In the case of the Nd-Si-As and Sm-Si-As systems, no ternary compound was formed in the present experiments.

The crystallographic data for the ternary compounds are summarized in Table 5. A lanthanide contraction is observed for the data of the $CeSiP_3$ -type phases. The degree of contraction is largest along the *a* axis, as in the case of the ternary phosphides already reported [4]. This can be explained from the structural characteristics that the arsenic layers perpendicular to the *c* axis form covalent As—As chains in the direction of the *b* axis, while they have only Van der Waals bonds between the chains in the direction of the *a* axis.

TABLE 5

Compound	Structure	a (Å)	b (Å)	c (Å)	V (Å ³)	7.	$d_{\rm x}$ (g cm ⁻³)
LaSiAs ₃	LaSiAs ₃ (Pbca)	6.0855(2) 6.084(1)	5.9837(2) 5.986(1)	26.2279(6) 26.235(5)	955.06(3) 955.4(3)	8 8	5.447 ^a 5.445 ^b
	$CeSiP_3$ (<i>Pn2</i> ₁ <i>a</i>)	6.0498(3)	5.9545(3)	26.383(1)	950.4(1)	8	5.475 ^a
${\rm CeSiAs}_3$	(5.988(1) 5.981(4)	5.906(1) 5.899(4)	26.231(3) 26.256(5)	927.7(2) 926.3(9)	8 8	5.625 5.633 ^b
PrSiAs ₃		5.949(2)	5.877(2)	26.149(9)	914.2(5)	8	5.721

Crystal data of LnSiAs3 ternary compounds

^aObtained from X-ray powder pattern fitting analysis. ^bObtained from the single-crystal structure analysis.

3.2. Conditions for the formation of LnSiAs₃ phases

Thermogravimetric measurements have been carried out for the $LnSiAs_3$ -As, LnAs-As and Si-As systems to obtain their dynamic pressurecomposition isotherms. Figure 3 shows the results for the $LaSiAs_3$ -As system at 798, 854, 895, 923 and 1014 °C. In the figure, solid curves were obtained by increasing pressure, corresponding to absorption runs, and dotted curves, by decreasing pressure, corresponding to desorption runs.

In this figure, three plateaux are clearly distinguished corresponding to phase transitions from 1 to 2, 2 to 3 and 3 to 4 in the [As]/[La] ratio. Judging from the X-ray examinations, the reactions corresponding to these transitions are shown to be

$$\begin{aligned} \operatorname{Si}(s) + 1/4\operatorname{As}_4(g) &\longrightarrow \operatorname{SiAs}(s) \\ \operatorname{SiAs}(s) + \operatorname{LaAs}(s) + 1/4\operatorname{As}_4(g) &\longrightarrow \operatorname{LaSiAs}_3(s) \\ \operatorname{LaSiAs}_3(s) + 1/4\operatorname{As}_4(g) &\longrightarrow \operatorname{LaAs}_2(s) + \operatorname{SiAs}_2(s) \end{aligned}$$



Fig. 3. Pressure-composition isotherms for the $LaSiAs_3-As$ system: solid line taken by increasing pressure, dotted line by decreasing pressure; figures in the diagram represent temperatures (°C).

Each isotherm shows a large hysteresis in these dynamic measurements. Since the unit cell parameters of the F-type phase are not changed by the [Si]/[La] ratio [5] and Fig. 3 shows very clear plateau regions, LaSiAs₃ seems to have little non-stoichiometry. It is observed in Fig. 3 that above 830 °C the plateau shifts to lower pressure and does not end at [As]/[La] = 4. Moreover above 950 °C the pressure rise at [As]/[La] = 3 also disappears. These phenomena can be explained by the formation of a liquid phase and arsenic solution into the liquid.

From Fig 3, the pressure-temperature diagram for conditions of formation shown in Fig. 4 was obtained. Black circles are absorption plots and white circles are desorption plots. Although there exist large hystereses between them, the reactions are reversible. In the absorption experiments, by increasing pressure at a given temperature, 945 °C, 1.1 atm is the highest temperature limit where the formation line intersects the liquid line. This temperature is in agreement with the large endothermic peak observed in Fig. 5 showing DTA results of LaSiAs₃. For higher pressure LaSiAs₃ decomposes to LaAs₂ and SiAs₂. This decomposition line intersects the liquid line at 830 $^{\circ}$ C, 6 atm. The region of formation for LaSiAs₃ is concluded to exist between the liquid line and the decomposition line. There are two polymorphs for LaSiAs₃. From X-ray examination, it is concluded that the Ftype is the high-temperature low-pressure stable phase and the P-type, the low-temperature high-pressure stable phase. In the present experiments, however, accurate conditions of the transformation between these were not measured.

Figure 6 shows the pressure-composition isotherm at 797, 845, 896 and 922 °C for the CeSiAs₃-As system. There is a large hysteresis observed as for lanthanum, but the boundaries of each plateau appear very clearly at



Fig. 4. Pressure-temperature diagram for the LaSiAs₃-As system: \bullet , by increasing pressure; \circ , by decreasing pressure; \blacktriangle , by increasing temperature; \triangle , by decreasing temperature.

values $1.0 \rightarrow 2.0$, $2.0 \rightarrow 3.0$, $3.0 \rightarrow 4.0$ of the [As]/[Ce] ratio. Similar to the La-Si-As system, the corresponding reactions are

$$Si(s) + 1/4As_4(g) \longrightarrow SiAs(s)$$

 $SiAs(s) + CeAs(s) + 1/4As_4(g) \longrightarrow CeSiAs_3(s)$

$$CeSiAs_3(s) + 1/4As_4(g) \longrightarrow CeAs_2(s) + SiAs_2(s)$$

A similar phenomenon relating to liquid formation was also observed in Fig. 6, *i.e.* above 8 atm at 845 °C the rapid rise at [As]/[Ce] = 4.0 disappears, and above 3 atm at 890 °C the increase at [As]/[Ce] = 3.0 also disappears. From Fig. 6, the conditions of formation in the Ce-Si-As ternary system were obtained, as shown in Fig. 7. As in the case of Fig. 4, black circles represent absorption plots and white circles desorption plots. In the absorption run, the formation curve of CeSiAs₃ intersects the liquid formation curve at 930 °C, 3 atm, which is in agreement with the large endothermic peak in Fig. 5(a). Under higher arsenic pressure the ternary phase decomposes



Fig. 5. DTA results: (a) $LnSiAs_3$ phases ($Ln \equiv La$, Ce, Pr); (b) La-Si-As system for changing [Si]/[La] ratio.



Fig. 6. Pressure-composition isotherms for the CeSiAs₃-As system: solid line taken by increasing pressure, dotted line by decreasing pressure; figures in the diagram represent temperatures (°C).



Fig. 7. Pressure-temperature diagram for the CeSiAs₃-As system: \bullet , by increasing pressure; \circ , by decreasing pressure; \blacktriangle , by increasing temperature; \diamond , by decreasing temperature.

to CeAs₂ and SiAs₂. The decomposition curve intersects the liquid formation curve at 845 $^{\circ}$ C, 8 atm.

The isotherms of the $PrSiAs_3$ -As system are shown in Fig. 8. The thermogravimetric data measured by varying the arsenic pressure at a fixed temperature of 820 °C is shown in Fig. 9. The apparent weight change in this figure corresponds to Δg in eqn. (1). While no inflection was observed in the absorption curve between [As]/[Pr] = 2.0 and 4.0, an inflection was observed in the desorption curve. That means that the PrSiAs₃ phase was formed only by desorption, which was also confirmed by X-ray diffraction analysis. Figure 10 is the diagram for the formation conditions for the Pr-Si-As system. The formation and decomposition lines in the absorption run intersect the liquid line at 890 °C, 6 atm, which is in agreement with the endothermic peak in Fig. 5(a).

Figure 5 shows DTA data measured using the samples sealed in a silica tube for the Ln-Si-As system. F-type $LaSiAs_3$, $CeSiAs_3$ and $PrSiAs_3$ showed large endothermic peaks at 945, 930 and 890 °C respectively, which can



Fig. 8. Pressure-composition isotherms for the $PrSiAs_3$ -As system: solid line taken by increasing pressure, dotted line by decreasing pressure; figures in the diagram represent temperatures (°C).



Fig. 9. Thermogravimetric data for the $PrSiAs_3$ -As system at 820 °C: •, absorption run; \circ , desorption run.

be ascribed to the liquid formation as already mentioned in the previous section.

In the La-Si-As system, this endothermic peak shows the simplest form at [Si]/[La] = 1.0 and the F-type showed no peak before 945 °C. However, the P-type showed a very broad endothermic peak above 840 °C. This seems to correspond to the transformation between the P-type and F-type.

From the present experimental results, it is concluded that the following reversible reactions exist and the non-stoichiometry of the ternary compounds is negligibly small, if any. Their stoichiometric formula is LnSiAs₃. PrSiAsz - As System



Fig. 10. Pressure-temperature diagram for the $PrSiAs_3$ -As system: •, by increasing pressure; \circ , by decreasing pressure; **A**, by increasing temperature; \triangle , by decreasing temperature.

$$\begin{aligned} &\text{Si}(s) + 1/4\text{As}_4(g) \longrightarrow \text{SiAs}(s) \\ &\text{SiAs}(s) + \text{LnAs}(s) + 1/4\text{As}_4(g) \longrightarrow \text{LnSiAs}_3(s) \\ &\text{LnSiAs}_3(s) + 1/4\text{As}_4(g) \longrightarrow \text{LnAs}_2(s) + \text{SiAs}_2(s) \end{aligned}$$

It is also concluded from the above results, together with those of thermogravimetric measurements for the LnAs-As and Si-As systems, that the ternary phase ([Si]/[Ln] = 1.0) is formed in the region common to the formation regions of LnAs₂ and SiAs, and furthermore that there is a relationship between the structures of LnSiAs₃ and LnAs₂, that the F-type LnSiAs₃ coexists with the LaP₂-type LnAs₂ [15], and that the P-type LnSiAs₃ coexists with the NdAs₂-type LnAs₂ [16].

References

1 F. Hülliger, Rare Earth Pnictides, in K. A. Gschneidner, Jr. and L. R. Eyring (eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 4, North-Holland, Amsterdam, 1979, p. 153.

- 2 H. Hayakawa, T. Sekine and S. Ono, J. Less-Common Met., 41 (1975) 197.
- 3 S. Ono, H. Hayakawa and K. Nomura, Nippon Kagaku Kaishi, (1976) 1700.
- 4 H. Hayakawa, S. Ono, A. Kobayashi and Y. Sasaki, Nippon Kagaku Kaishi, (1978) 1214.
- 5 H. Hayakawa, A. Suzuki and S. Ono, J. Less-Common Met., 71 (1980) 235.
- 6 H. Hayakawa, A. Suzuki and S. Ono, Nippon Kagaku Kaishi, (1984) 697.
- 7 K. E. Mironov and R. V. Abdullin, Russ. J. Inorg. Chem., 25 (1980) 1142.
- 8 Z. Inoue, M. Mimoto and N. Ii, J. Mater. Sci., 15 (1980) 2915.
- 9 G. Jean, J. Jean and L. Daniel, Rev. Chem. Miner., 20 (1983) 523.
- 10 D. B. Wiles and R. A. Young, J. Appl. Cryst., 14 (1981) 149.
- 11 H. Rau, J. Chem. Thermodyn., 7 (1975) 27.
- 12 Gmelin, Handbuch der Anorganischen Chemie, No. 17, Arsen, Verlag Chemie, Weinheim, 8th edn., 1952, p. 134.
- 13 R. A. Young and D. B. Wiles, J. Appl. Cryst., 15 (1982) 430.
- 14 W. I. F. David and J. C. Matthewman, J. Appl. Cryst., 18 (1985) 461.
- 15 H. G. von Schnering, W. Wichelhaus and M. Schulze Nahrup, Z. Anorg. Allg. Chem., 412 (1975) 193.
- 16 Yu. Wang, R. D. Heyding, E. J. Gabe, L. D. Calvert and J. B. Taylor, Acta Crystallogr., Sect. B, 34 (1978) 1959.