

SYNTHESES OF NEW LANTHANUM-SILICON-ARSENIC TERNARY COMPOUNDS

H. HAYAKAWA, A. SUZUKI and S. ONO

The National Chemical Laboratory for Industry, Yatabemachi, Tsukuba-gun, Ibaraki 305 (Japan)

(Received June 30, 1979)

Summary

A new ternary compound, the F-type phase, was synthesized from LaAs and silicon in a fused silica ampoule at 900 °C under controlled arsenic vapour pressures using a temperature-gradient furnace. This compound was orthorhombic with $a = 6.084(1)$ Å, $b = 5.986(1)$ Å and $c = 26.235(3)$ Å. Conditions for the formation of this ternary system were examined by X-ray techniques and the stoichiometric composition of the phase was found to be LaSiAs_3 . No reliable evidence was obtained to prove the existence of significant non-stoichiometry.

The F-type phase was formed at 900 °C under an arsenic pressure in the range 0.2 - 15 atm. Above this range LaAs_2 and SiAs_2 were formed, whilst below 0.08 atm LaAs and silicon remained unreacted. Under a constant arsenic pressure of 1 atm this phase was formed at temperatures between 750 and 940 °C. Above 950 °C it melted, whilst below 750 °C it decomposed to LaAs_2 and SiAs_2 .

1. Introduction

We have previously synthesized single crystals of some Ln-Si-P (Ln \equiv lanthanide) ternary compounds using the chemical transport method [1], have discussed their conditions of formation [2], and have performed a crystal structure analysis of CeSiP_3 (the P-type phase) [3].

During investigation of these ternary systems another ternary phase, designated F type and which has structural similarity to the P-type phase, was found to exist for the lanthanide elements lanthanum, cerium and praseodymium. The stoichiometric composition of this phase, however, was not determined, since X-ray examination showed that the F-type phase was apparently formed as the pure phase in the composition range from $[\text{LaSiP}_3]$ to $[\text{LaSi}_2\text{P}_4]$. Using quantitative electron probe microanalysis (EPMA) Torbov *et al.* [4] have reported $\text{La}_{1.25}\text{SiP}_{2.75}$ for a single crystal of the F-type phase.

Except for the aforementioned phosphides no IIIa–IVb–Vb ternary compound has ever been reported. In the present experiments similar syntheses by the temperature-gradient method were applied to the La–Si–As system. As a result the F-type phase was also formed in this ternary system, and the composition, non-stoichiometry and conditions of formation were examined experimentally and are discussed.

2. Experimental

2.1. Preparation of starting materials and La–Si–As ternary compounds

The method of synthesis was the same as that previously reported [2] unless otherwise specified. The elements used were lanthanum metal (nominally 99.9% pure from Shin-etsu Chemical Co., Ltd.), arsenic (99.999% grade from Mitsubishi Metal Mining Co., Ltd., Central Research Laboratory) and silicon (99.99% grade from Yamanaka Chemical Industries Ltd.).

The LaAs starting material was prepared by the direct reaction of lanthanum filings and crushed arsenic in a closed tube of fused silica at 700 °C.

Syntheses of the La–Si–As ternary compounds were carried out as follows. Weighed quantities of LaAs and silicon were well mixed in an agate mortar, pelleted, placed in a fused silica tube together with a small excess of arsenic and sealed under vacuum (less than 10^{-4} mmHg). The reaction tube was then placed in a two-temperature zone furnace as shown in Fig. 1. The sample was located at one end of the reaction tube maintained at a temperature T_p and the other end of the tube containing arsenic was kept at T_{As} . The arsenic vapour pressure in the tube was determined using the vapour pressure curve of arsenic given in ref. 5. The reaction was usually continued over 1 week.

2.2. Identification

The X-ray powder diffraction method, the arsenic weight method and density measurements were used as previously described [1].

The lanthanum and silicon were analysed as described in ref. 2. Arsenic was determined by the silver arsenate titration method [6].

Differential thermal analysis (DTA) of the specimens up to 1100 °C was carried out, using a Rigaku DTA apparatus, in a closed ampoule of fused silica at temperature scanning rates of 5 or 10 °C min⁻¹. α -Al₂O₃ was used as the reference material.

3. Results and discussion

3.1. Conditions of formation

Representative experimental results are summarized in Table 1 and the phase formation diagram of the ratio Si/(La + Si) against arsenic vapour pressure is shown in Fig. 2, in which the F-type phase is the only ternary com-

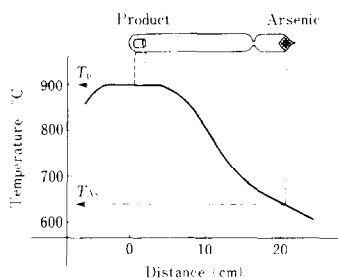


Fig. 1. A schematic diagram of the temperature-gradient furnace.

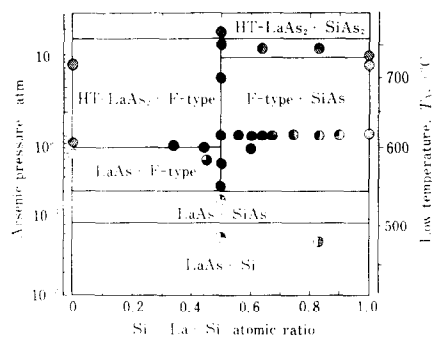


Fig. 2. A diagram of the phases formed at 900 °C for the La-Si-As system determined by X-ray diffractometry: ○, LaAs; ⊙, HT-LaAs₂; ●, F-type; ⊕, SiAs; ⊗, SiAs₂; ⊖, silicon.

pound. It was identified as a pure phase by X-ray examination in the Si/(La + Si) ratio range 0.5 - 0.63 and at arsenic pressures of 0.2 - 15 atm. Chemical analysis and the arsenic weight method revealed that the composition varied from LaSi_{1.0}As_{3.0} to LaSi_{1.7}As_{3.7}. The powder diffraction pattern was indexed on the basis of an orthorhombic unit cell with $a = 6.084(1)$ Å, $b = 5.986(1)$ Å and $c = 26.235(3)$ Å. The powder data are listed in Table 2. This compound is isostructural with the F-type phosphide reported previously [2].

This ternary compound is dark grey in colour and is reasonably stable in dry air; however, it reacts very slowly in moisture or water. It dissolves rapidly in HNO₃ solution to form a precipitate of SiO₂.

At 900 °C LaAs and silicon did not react under an arsenic vapour pressure lower than 0.08 atm (LSA-11) and silicon reacted to form SiAs at pressures of 0.08 - 0.2 atm. The value of 0.08 atm is in good agreement with the dissociation pressure of SiAs at 900 °C [7]. Between 0.2 and 15 atm an F-type ternary compound was formed. Above this pressure the high temperature (HT) modification of LaAs₂ [8] and SiAs₂ were formed (LSA-15) and no other high pressure ternary phase was observed.

When an arsenic vapour pressure above 5 atm was applied, the sample seemed to melt and attack the inside wall of the fused silica tube. From such samples plate-like single crystals with a metallic lustre were obtained and were identified as the F-type phase from precession photographs. Even under pressures greater than 15 atm single crystals with a metallic lustre grew in the melt. The precession photographs revealed that these crystals corresponded to the GeAs₂ structure type and were SiAs₂ [9]. The dimensions of the unit cell found from the powder pattern were $a = 14.545(3)$ Å, $b = 10.393(3)$ Å and $c = 3.636(1)$ Å. The powder data of SiAs₂ are listed in Table 3.

In the binary systems LaAs-As and SiAs-As the corresponding diarsenide phases were formed under high arsenic vapour pressures but they did not melt at 900 °C. DTA of the F-type ternary compound showed that it melted at 950 °C.

TABLE 1
Experimental conditions and results of syntheses for the La-Si-As system

Experiment number	Starting material	Si/(La + Si) ratio	Temperature (°C)		Arsenic pressure (atm)	Time (days)	X-ray results ^a		Arsenic weight method	Chemical analysis
			High	Low						
LSA-1	LaAs	0.00	900	570	0.4	9	LaAs		LaAs _{1.0}	
LSA-2	LaAs	0.00	900	600	0.7	7	HT-LaAs ₂		LaAs _{2.1}	
LSA-3	LaAs + Si	0.44	900	580	0.5	12	F-type + LaAs		LaSi _{0.8} As _{2.4}	LaSi _{0.83} As _{2.44}
LSA-4	LaAs + Si	0.50	900	620	1.0	12	F-type		LaSi _{1.0} As _{3.0}	LaSi _{0.99} As _{2.99}
LSA-5	LaAs + Si	0.56	900	620	1.0	12	F-type		LaSi _{1.3} As _{3.2}	LaSi _{1.28} As _{3.17}
LSA-6	LaAs + Si	0.60	900	620	1.0	12	F-type		LaSi _{1.5} As _{3.4}	
LSA-7	LaAs + Si	0.64	900	620	1.0	12	F-type + SiAs		LaSi _{1.8} As _{3.6}	LaSi _{1.71} As _{3.65}
LSA-8	LaAs + Si	0.83	900	630	1.3	13	SiAs + F-type		LaSi _{5.1} As _{6.9}	
LSA-9	Si	1.00	900	730	8.5	9	SiAs		SiAs _{1.0}	
LSA-10	Si	1.00	900	740	10.	7	SiAs ₂		SiAs _{2.1}	
LSA-11	F-type	0.50	900	490	0.06	7	LaAs + Si		LaSi _{1.0} As _{1.0}	
LSA-12	F-type	0.50	900	540	0.18	7	LaAs + SiAs		LaSi _{1.0} As _{2.0}	
LSA-13	F-type	0.50	900	550	0.25	11	F-type		LaSi _{1.0} As _{2.9}	
LSA-14	F-type	0.50	900	740	10.	9	F-type		LaSi _{1.0} As _{3.1}	
LSA-15	F-type	0.50	900	800	28.	7	HT-LaAs ₂ + SiAs ₂		LaSi _{1.0} As _{4.2}	
LSA-16	F-type	0.50	800	685	4.	8	HT-LaAs ₂ + SiAs ₂		LaSi _{1.0} As _{4.0}	
LSA-17	F-type	0.50	940	620	1.0	5	F-type			
LSA-18	F-type	0.50	800	620	1.0	10	F-type		LaSi _{1.0} As _{3.1}	
LSA-19	F-type	0.50	750	620	1.0	7	F-type + SiAs ₂ + HT-LaAs ₂		LaSi _{1.0} As _{3.5}	
LSA-20	F-type	0.50	725	620	1.0	6	SiAs ₂ + HT-LaAs ₂		LaSi _{1.0} As _{4.0}	

^a HT-LaAs₂, high temperature form of LaAs₂.

TABLE 2

X-ray powder diffraction data for the LaSiAs_3 (F-type) ternary compound

h	k	l	d_{obs}	d_{calc}	I_{obs}^a
0	0	2	13.1	13.118	vw
0	0	4	6.57	6.5588	vvw
0	0	6	4.379	4.3726	vw
1	1	1	4.212	4.2115	w
1	1	5	3.31	3.3104	vw
0	0	8	3.279	3.2794	w
2	0	0	3.043	3.0419	m
0	2	0	2.993	2.9929	m
2	0	2	2.966	2.9633	vw
0	2	2	2.918	2.9179	vw
1	1	7	2.815	2.8159	vs
2	0	4	2.759	2.7595	m
0	2	4	2.723	2.7228	m
0	0	10	2.624	2.6235	s
2	0	6	2.498	2.4971	m
0	2	6	2.470	2.4698	m
1	1	9	2.41	2.4070	vvw
2	2	0	2.133	2.1334	s
2	2	2	2.11	2.1057	vvw
1	1	11	2.082	2.0819	w
2	2	4	2.03	2.0288	vw
2	0	10	1.987	1.9867	vw
0	2	10	1.971	1.9729	vw
2	2	6	1.918	1.9174	w
3	1	1		1.9156	
1	3	1	1.89	1.8910	vw
3	1	3	1.873	1.8760	vw
0	0	14		1.8740	
1	1	13	1.824	1.8243	vw
2	2	8	1.78	1.7883	vw
1	3	5		1.7831	
2	0	12		1.7753	
0	2	12		1.7654	
3	1	7	1.709	1.7093	w
1	3	7	1.692	1.6918	w
2	2	10	1.653	1.6552	w
0	0	16	1.64	1.6397	vvw
1	1	15	1.619	1.6183	vw

^avs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak.

Throughout these runs by the temperature-gradient method, it was always observed that brown-coloured thin-ribbon or sword-like crystals were grown at the central zone of the fused silica tube. The quantity of these crystals increased with the amount of silicon added. Deviation from the pre-

TABLE 3

X-ray powder diffraction data for SiAs₂ (GeAs₂-type structure) recorded using MgO ($a = 4.2114 \text{ \AA}$) as an internal standard

h	k	l	d_{obs}	d_{calc}	$I_{\text{obs}}^{\text{a}}$
2	0	0	7.278	7.272	vw
2	1	0	5.960	5.958	w
3	1	0	4.397	4.394	vw
2	2	0	4.225	4.228	vvw
4	0	0	3.636	3.636	m
3	2	0	3.548	3.545	w
4	1	0	3.433	3.432	vs
1	3	0	3.371	3.370	w
1	1	1			
2	3	0	3.128	3.128	vw
0	2	1	2.979	2.979	s
4	2	0			
1	2	1	2.918	2.919	m
3	1	1	2.801	2.801	w
5	1	0			
2	2	1	2.758	2.757	vw
0	4	0	2.59	2.598	vvw
1	4	0	2.558	2.558	vw
3	2	1	2.538	2.538	m
5	2	0			
4	3	0	2.508	2.508	vw
1	3	1	2.471	2.472	vvw
2	4	0	2.449 ^b	2.447	vvw
6	0	0	2.424 ^b	2.424	vvw
6	1	0	2.361	2.361	vw
4	2	1	2.304	2.305	vw
3	3	1	2.228	2.228	vvw
5	3	0			
6	2	0	2.196	2.197	vw
0	4	1	2.113 ^b	2.114	vvw
4	4	0			
2	4	1	2.030	2.030	vw
6	3	0	1.982	1.986	vw
6	1	1			
3	4	1	1.938	1.938	vw
5	4	0			
7	2	0	1.929	1.929	vw
5	3	1	1.900	1.900	vw
4	4	1	1.828	1.828	vw
0	0	2	1.818	1.818	w
8	0	0			
4	5	0	1.803	1.805	m
8	1	0	1.791	1.791	w
1	5	1			

^avs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak.

^bOverlapped by a magnesium oxide line.

determined compositions by silicon separation due to this phenomenon was not serious, as is shown by the chemical analysis results in Table 1. The crystals have cleavage planes parallel with the flat faces of the sword-like crystals. Because the crystals were only several microns thick, the precession photographs were not good enough to obtain crystallographic data. Since the amount of these unknown crystals was not sufficient for chemical analysis, they were subjected to EPMA. The results revealed that this compound is an Si-As binary phase. No exact composition was obtained but, judging from the information of the Si-As system previously reported [7, 10], it seems to be an SiAs crystal.

From experiments on the binary systems La-As and Si-As by the temperature-gradient method, the equilibrium arsenic pressures of HT-LaAs₂ and SiAs₂ were determined to be 0.7 atm (at 600 °C) and about 9 atm (at 720 - 740 °C) respectively, as can be seen in Fig. 2.

3.2. Stability of the F-type phase

The stability of F-type LaSiAs₃ was examined under an arsenic vapour pressure of 1 atm and at varying temperatures in the range 700 - 1000 °C (LSA-17 - LSA-20 in Table 1). Below 750 °C the F-type phase decomposed to HT-LaAs₂ and SiAs₂ and it melted at 1000 °C. DTA measurements of the F-type phase showed a large endothermic peak at 950 °C on heating which can be ascribed to the melting point. On cooling, however, it gave two exothermic peaks. Additional DTA experiments are necessary before this problem can be resolved.

The F-type phase is stable between 750 and 940 °C for an arsenic vapour pressure of 1 atm. Its stability region is shown in Fig. 3. The boundary conditions were ascertained by experiments both on the formation and on dissociation reactions of the F-type phase. The stability region of the F-type phase is within that of the SiAs phase. The lower boundary can be regarded as the dissociation pressure curve for each phase. The heat of dissociation of the F-type phase, calculated from the slope in Fig. 3, is approximately 10 kcal mol⁻¹.

3.3. The composition of the F-type phase

Torbov *et al.* [4] have reported that they obtained single crystals of the F-type phase by chemical transport reactions of the LaP-I₂ system in a fused silica tube. Their semiquantitative EPMA revealed that the crystals had an approximate composition La_{1.25}SiP_{2.75}, although the lanthanum and the other two elements were distributed homogeneously within ranges of 5 wt.% and 3 wt.% respectively.

We have previously synthesized [1] an F-type La-Si-P ternary compound from LaP and silicon. X-ray examination showed that it was formed as a pure phase in the composition range Si/La of 1.0 - 2.0. Precise determination of the unit cell parameters revealed that they were constant irrespective of the Si/La ratio; we concluded that determination of the precise composition of this phase by X-ray techniques was not possible.

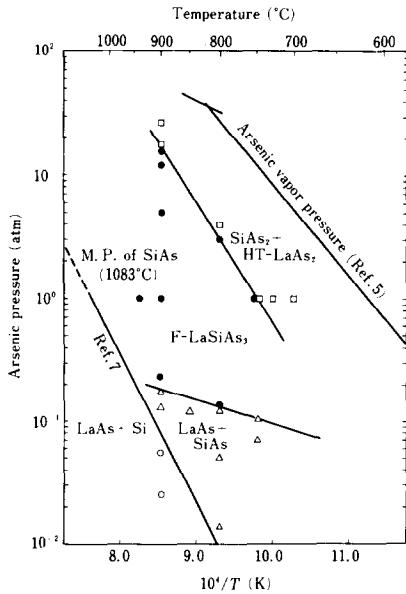


Fig. 3. P - T state diagram of the La-Si-As system at an atomic ratio Si/La of 1.0: \circ , LaAs + Si; \triangle , LaAs + SiAs; \bullet , F-LaSiAs₃; \square , HT-LaAs₂ + SiAs₂.

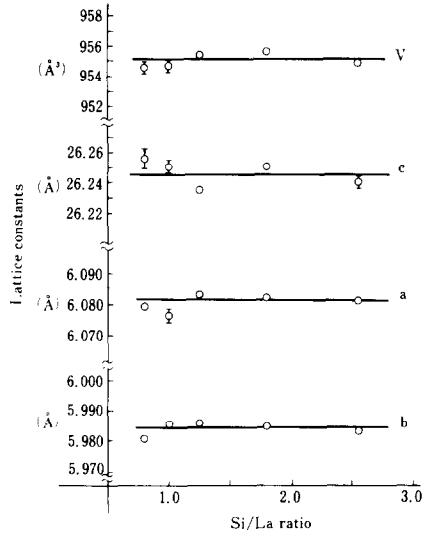


Fig. 4. Relation between the lattice constants and the Si/La atomic ratio for the F-type La-Si-As ternary compound: reaction temperature, 900 °C; arsenic pressure, 1 atm.

X-ray examination showed that, in the La-Si-As ternary system, the F-type compound was also obtained apparently as a pure phase in the Si/La range 1.0 - 1.7. In order to ascertain the existence of a non-stoichiometric or a stoichiometric composition, the dependences of the amount of absorbed arsenic, of the unit cell parameters and of the density on the Si/La atomic ratio were examined. The results were similar to those obtained for the La-Si-P ternary phase, *i.e.* no change was observed in the unit cell parameters (Fig. 4) and the amount of absorbed arsenic increased with the amount of silicon at the equiatomic ratio.

Assuming that the products are two-phase mixtures of F-type LaSiAs₃ and SiAs, the X-ray intensity ratio of SiAs in the mixtures to pure SiAs can be estimated as

$$\frac{I_{\alpha}}{I_{\alpha(\text{pure})}} = \frac{\omega_{\alpha}(\mu_{\alpha}/\rho_{\alpha})}{\omega_{\alpha}(\mu_{\alpha}/\rho_{\alpha} - \mu_{\beta}/\rho_{\beta}) + \mu_{\beta}/\rho_{\beta}}$$

where μ/ρ is the mass absorption coefficient, ω is the percentage weight, α represents SiAs and β represents LaSiAs₃. From this equation $I_{\alpha}/I_{\alpha(\text{pure})}$ is only 5% at an Si/La ratio of 1.5. This is nearly beyond the detection limit of the X-ray powder technique. Furthermore, within the limits of experimental error, the measured densities of the powdered samples changed continuously with the Si/La ratio in accordance with calculated values for mixtures of LaSiAs₃ and SiAs.

From these results, together with the fact that the F-type phase is structurally related to P-type CeSiP_3 , the crystal structure of which has been determined previously [3], we conclude that the F-type phase has the stoichiometric composition LaSiAs_3 . Even if it exists, no evidence of non-stoichiometry was obtained, and therefore it cannot be as significant as indicated in Fig. 2.

Acknowledgments

The authors thank Mr. T. Sekine, Energy Chemistry Division, National Chemical Laboratory for Industry, for his advice and cooperation with the EPMA measurements. We also acknowledge the help of Mr. A. Fukami, student of Kogakuin University (at that time).

References

- 1 H. Hayakawa, T. Sekine and S. Ono, *J. Less-Common Met.*, **41** (1975) 197.
- 2 S. Ono, H. Hayakawa and K. Nomura, *Nippon Kagaku Kaishi*, (1976) 1700.
- 3 H. Hayakawa, S. Ono, A. Kobayashi and Y. Sasaki, *Nippon Kagaku Kaishi*, (1978) 1214.
- 4 V. I. Torbov, V. I. Chukalin, V. N. Doronin, L. G. Nikolaeva and Z. S. Medvadeva, *Zh. Neorg. Khim.*, **19** (1974) 39.
- 5 *Gmelin, Handbuch der Anorganischen Chemie*, No. 17, *Arsen*, Verlag Chemie, Weinheim, 8th edn., 1952, p. 134.
- 6 Methods for determination of arsenic in ores, *Jpn. Ind. Std.*, **M8132**, Japanese Standard Association, Tokyo, 1977.
- 7 T. L. Chu, R. W. Kelm, Jr., and S. S. C. Chu, *J. Appl. Phys.*, **42** (1971) 1169.
- 8 S. Ono, J. G. Despault, L. D. Calvert and J. B. Taylor, *J. Less-Common Met.*, **22** (1970) 51.
- 9 T. Wadsten, *Acta Chem. Scand.*, **21** (1967) 593.
- 10 W. Klemm and P. Pirscher, *Z. Anorg. Allg. Chem.*, **247** (1941) 211.
T. Wadsten, *Acta Chem. Scand.*, **19** (1965) 1232; **23** (1969) 331.