Polymorphism in IrSi₃

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The iridium — silicon system has earlier been studied by Finnie,[1] Bhan and Schubert[2] and Engström and Zackrisson.[3,4] Finnie found a hexagonal compound $IrSi_{3\pm0.5}$, the structure of which was proposed to be of the anti-Na_3As-type. However, it was pointed out by Finnie and later by Pearson[5] that the c/a-ratio deviated considerably from what could be expected for an anti-Na_3As-type compound.

A single-crystal study of $IrSi_3$ by White and Hockings[6] showed that the compound was hexagonal, but the atomic arrangement did not correspond to the anti-Na_3As-type. The $Si-Si$-distances found were much shorter than those in other platinum-metal silicides;[3] the proposed structure is therefore probably only an approximative description of the real atomic arrangement.

The present paper describes an X-ray powder characterization of two new phases closely related

Table 1. X-Ray diffraction powder pattern of the orthorhombic modification of $IrSi_{\sim3}$.

hkl	d_{obs} (Å)	Q_{obs} (Å⁻²)	Q_{calc} (Å⁻²)	I_{obs}
200	3.782	.06992	.06992	18
110	3.769	.07038	.07040	16
002	3.312	.09114	.09117	30
201	3.284	.09272	.09272	100
111	3.276	.09318	.09320	100
202	2.492	.16110	.16109	45
112	2.488	.16155	.16157	40
310	2.181	.21023	.21025	30
020	2.174	.21169	.21169	15
203 ⎫ 113 ⎭	1.906	.27530	.27505 ⎫ .27553 ⎭	80
400	1.891	.27961	.27970	vw[a]
220	1.884	.28157	.28162	10
312	1.822	.30141	.30142	70
401 ⎫ 022 ⎭	1.817	.30276	.30249 ⎫ .30286 ⎭	45
221	1.812	.30448	.30441	45
004	1.656	.36479	.36467	vw[a]
402	1.641	.37126	.37086	vw[a]
222	overlap with Si-line		.37278	vw[a]

[a] Non-measurable intensity.

to the hexagonal $IrSi_{\sim3}$ discussed above [here denoted $IrSi_{\sim3}(h)$].

Experimental. Polycrystalline samples were made by arc-melting iridium sponge (Specpure J & M) and silicon powder (3N); unfortunately, it has not been possible to obtain single crystals. They were then heat-treated in evacuated silica tubes at various temperatures and quenched. The compositions of the samples given below are nominal.

X-Ray powder photographs were taken with Guinier-Hägg cameras (diam. = 100 mm) using $CuK\alpha_1$- ($\lambda = 1.540589$ Å) or $CrK\alpha_1$-radiation ($\lambda = 2.289753$ Å). Silicon was used as an internal calibration standard ($a = 5.431065$ Å). Some investigations were also made using the high-temperature Guinier-Hägg camera described in Ref. 7. Intensities were measured using a film-scanner. The powder data presented in Tables 1 and 2 were

Table 2. X-Ray diffraction powder pattern of the monoclinic modification of $IrSi_{\sim3}$.

hkl	d_{obs} (Å)	Q_{obs} (Å⁻²)	Q_{calc} (Å⁻²)	I_{obs}
200	3.848	.06753	.06756	10
110	3.806	.06904	.06909	18
2̄01	3.358	.08869	.08870	30
1̄11	3.310	.09130	.09133	55
201	3.277	.09314	.09312 ⎫	
002 ⎫ 1̄11 ⎭	3.270	.09349	.09340 ⎬ .09354 ⎭	100
2̄02	2.528	.15647	.15654	2
1̄12	2.498	.16025	.16028	10
112	2.464	.16468	.16470	14
202	2.459	.16535	.16538	6
310	2.213	.20418	.20421	25
020	2.188	.20881	.20879	14
400	1.924	.27026	.27024	16
1̄13 ⎫ 220 ⎭	1.903	.27603	.27593 ⎫ .27635 ⎭	30
113	1.881	.28258	.28256	20
2̄03	1.875	.28437	.28434	8
4̄01	1.860	.28920	.28917	10
3̄12	1.854	.29101	.29098	25
221	1.834	.29737	.29749 ⎫	35
401	1.832	.29795	.29801 ⎭	
2̄21 ⎫ 022 ⎭	1.820	.30202	.30191 ⎫ .30219 ⎭	45
312	1.813	.30426	.30424	25
4̄02	1.680	.35436	.35480	vw[a]
2̄22	1.655	.36513	.36534	vw[a]
4̄02 ⎫ 004 ⎬ 222 ⎭	1.635	.37393	.37248 ⎫ .37360 ⎬ .37417 ⎭	vw[a]

[a] Non-measurable intensity.

Table 3. Unit cell dimensions of IrSi$_{\sim 3}$-polymorphs (in Å and degr.).

	Unit cell	$a/\sqrt{3}b$	γ_P	V
IrSi$_{\sim 3}(m)$	$a = 7.6976(3)$	1.015	120.75	220.5
	$b = 4.3770(3)$			
	$c = 6.5467(4)$			
	$\beta = 91.594(4)$			
IrSi$_{\sim 3}(o)$	$a = 7.5634(11)$	1.0046	120.23	217.8
	$b = 4.3469(2)$			
	$c = 6.6238(10)$			
IrSi$_{\sim 3}(h)^a$	$a = 7.5410(16)$	1	120	217.6
	$b = 4.3538(9)$			
	$c = 6.6277(15)$			

[a] Unit cell dimensions from Ref. 4 transformed to an *ortho*-hexagonal unit cell.

obtained from investigations with CrKα$_1$-radiation. Least-squares refinements of unit cell dimensions were performed with the computer program CELNE.[8]

Phase-analytical results. In a sample of composition Ir$_{23}$Si$_{77}$ (*i.e.* 23 at % Ir), silicon was found as well as IrSi$_{\sim 3}$; and in a sample of composition Ir$_{30.5}$Si$_{69.5}$ a more Ir-rich phase was found as well as IrSi$_{\sim 3}$. A sample of composition Ir$_{26}$Si$_{74}$ consisted almost exclusively of IrSi$_{\sim 3}$.

In arc-melted samples, the IrSi$_{\sim 3}$ phase was found to be orthorhombic, IrSi$_{\sim 3}(o)$ but, after heat-treatment for one week at 900 °C, it had transformed to monoclinic, IrSi$_{\sim 3}(m)$. The phase transition could be reversed by a subsequent heat-treatment at 1000 °C. The phase transition could also be confirmed by an investigation of the sample in a high-temperature X-ray camera. The existence of the hexagonal form, IrSi$_{\sim 3}(h)$, could not be confirmed by this investigation, which was confined to the temperature region 900 – 1000 °C.

The unit cell dimensions (Table 3) of IrSi$_{\sim 3}(o)$ are very close to those of IrSi$_{\sim 3}(h)$ (ortho-hexagonal unit cell); the latter are also cited [4] for comparison. The unit cell dimensions of the monoclinic form deviate slightly more from those of IrSi$_{\sim 3}(h)$. The deviation from the hexagonal symmetry can also be illustrated by the ratio $a/\sqrt{3}b$ and $\gamma_P = 2\mathrm{arctg}(a/b)$, which is the γ-angle of the primitive cell. These two quantities given in Table 3 are, of course, interrelated.

The unit cell dimensions of the monoclinic modification were determined from a sample which was arc-melted and heat-treated for one week at 900 °C. The orthorhombic unit cell was determined from an arc-melted sample. The diffraction

photographs were taken with CrKα$_1$-radiation.

Both polymorphs of IrSi$_{\sim 3}$ show *C*-centering extinctions, as could be expected for *pseudo*-hexagonal phases. The observed *Q*-values for the powder patterns are given in Tables 1 and 2. In the least-squares refinement of the cell dimensions the reflections were given individual weights between 0 and 1 depending on the quality of the diffraction lines and the degree of overlap.

The figures of merit were calculated according to the rules in Ref. 9. For the powder diffraction data in Table 1 the result was $M_{17} = 89$ ($F_{17} = 88$) and for the data in Table 2 the result was $M_{20} = 82$ ($F_{25} = 87$). The *C*-centering, discussed above, was taken into account when the figures of merit were calculated. The high numerical values of the figures indicate that the indexing and thus the unit cell dimensions are reliable.

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