The Crystal Structures of Zr_5Sn_3 and Zr_3Sn

GUNNAR GRAN AND STEN ANDERSSON

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

In the zirconium-tin system, four intermediate phases have been reported to exist, *viz.* Zr_4Sn, Zr_5Sn_3, ZrSn and $ZrSn_2$ (Refs. [1,2]). Crystal structures have been given only for $ZrSn_2$ (of $C54$ type) and for Zr_5Sn_3 (Ref. [2]). The latter is described as being of the $D8_8$ type but no structural details have hitherto been given.

In the present study, which was undertaken in order to complement the existing knowledge concerning this system, metallic zirconium and tin of 99.95 % purity were used as starting materials. Alloys of several compositions were prepared by melting pressed tablets of the metals in an electric arc furnace under argon atmosphere. The samples were then sealed in evacuated silica tubes and annealed for about two months at 900°C. Tantalum foils protected the alloys from reacting with the silica.

X-Ray powder patterns were registered in a Guinier focusing camera with strictly monochromatized CuKa_1 radiation. Single crystal data were obtained with a Weissenberg camera using CuK radiation.

Rod-formed single crystals were obtained from a sample of a composition close to $ZrSn_{0.5}$. Complete single-crystal data were registered while rotating the crystal around the rod axis, the unit length of which was found to be 5.8 Å. The symmetry proved to be hexagonal and the unit cell dimensions as obtained from the powder pattern were found to be:

$$a = 8.46 \text{ Å}, \qquad c = 5.78 \text{ Å}$$

It was confirmed that the structure was of the $D8_8$ type, as had previously been observed. The space group is thus $P6_3/mcm$ (No. 193) and all the atoms occupy positions 6 (g) (x, 0, ½ etc.). From the electron density projection (x, y, p), the following atomic parameters were obtained:

	Zr	Sn
x	0.245	0.609

Table 1. Powder pattern of the sample $ZrSn_{0.6}$ containing two phases of Zr_5Sn_3 type.

		$\sin^2\Theta$	
hkl	*I*	calc.	obs.
111	w	0.05042	0.05050
		0.05079	0.05077
002	m	0.07029	0.07020
		0.07093	0.07084
210	m	0.07633	0.07660
		0.07713	0.07710
012	w	0.08124	0.08122
		0.08195	0.08187
121	st	0.09420	0.09421
		0.09486	0.09494
030	m	0.09852	0.09857
		0.09916	0.09924
112	m	0.10314	0.10309
		0.10398	0.10397
022	w	0.11408	0.11419
		0.11500	0.11495
130	w	0.14231	0.14228
		0.14324	0.14328
221	w	0.14894	0.14886
		0.14995	0.15020

Table 2.

Composition	X-Ray evidence
$ZrSn_{0.4}$	$Zr_3Sn + Zr_5Sn'_3$
$ZrSn_{0.5}$	$Zr_5Sn'_3$
$ZrSn_{0.6}$	$Zr_5Sn'_3 + Zr_5Sn''_3$
$ZrSn_{0.7}$	$Zr_5Sn''_3 + ZrSn$

However, it was evident that this phase was not of the ideal composition Zr_5Sn_3. When the tin content was increased, extra lines appeared close to the original lines. The sample remained two-phasic after additional heat treatment. The new lines could be indexed in the same way as the former with the following unit cell parameters:

$$a = 8.50 \text{ Å}, \qquad c = 5.81 \text{ Å}$$

An indexed powder pattern of the sample $ZrSn_{0.6}$ is given in Table 1. The existence of two phases of Zr_5Sn_3 type has thus been found.

The symbols $Zr_5Sn'_3$ and $Zr_5Sn''_3$ used in Table 2 designate the ones low and high in tin, respectively. Further studies at the critical compositions of the two phases and concerning the type of defect are contemplated.

At a composition $ZrSn_{0.4}$, the Guinier powder pattern photograph showed, in addition to the pattern of the defective Zr_5Sn_3, a number of strong, extra lines. Assuming a cubic unit cell, these extra lines could be indexed with $a = 5.634$ Å. The structure was found to be of the well-known β-wolfram structure type and should thus be given the formula Zr_3Sn.

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Synthesis of Benzyl 4-*O*-Methyl-β-D-Xylopyranoside

PER J. GAREGG

Svenska Träforskningsinstitutet, Träkemiska avdelningen, Stockholm Ö, Sweden

Previous studies of a naturally occurring acetylated xylan [1] in birch wood have raised the question of whether the *O*-acetyl groups are attached to the most readily acetylated free hydroxyl groups in the β-1,4-linked anhydroxylose chains. In an attempt to investigate which of the two free hydroxyl groups at the 2- and 3-position is the most readily acetylated, benzyl 4-*O*-methyl-β-D-xylopyranoside was selected as a suitable model for partial acetylation. The synthesis of this substance, by a sequence of reactions given below is analogous to that described by Hough and Jones [2] for the synthesis of the corresponding methyl glycoside, is reported in the present paper. The final product and all the intermediates were obtained in a crystalline form and the overall yield from D-arabinose was 10 % of the theoretical.

Experimental. All melting points are corrected. Evaporations were done under reduced pressure at a bath temperature below 40°.

Benzyl 3,4-isopropylidene-2-tosyl-β-D-arabinopyranoside, II. Benzyl-3,4-*iso*propylidene-β-D-arabinopyranoside (81 g, m. p. 55—57°, $[\alpha]_D^{20}$ —195°), prepared from 100 g D-arabinose according to Ballou [3] was dissolved in pyridine (500 ml) and treated with *p*-toluenesulphonyl chloride (112 g). The solution was allowed to stand at room temperature during 48 h and then poured on ice. The mixture was extracted with chloroform and the chloroform solution was dried over anhydrous sodium sulphate, filtered and concentrated to dryness. The syrup obtained was used directly in the next step; a small quantity which was set aside crystallised from 96 % aqueous ethanol, m.p. 62—64° unchanged on further recrystallisation, $[\alpha]_D^{20}$ —194° (*c* 1.0 in chloroform). (Found: C 61.14; H 5.96; O 26.20; S 6.84. Calc. for $C_{22}H_{26}O_7S$: C 60.81, H 6.03; O 26.78; S 7.38.)

Benzyl 2-tosyl-β-D-arabinopyranoside, III. The above product was dissolved in boiling acetone (900 ml) and 0.1 N formic acid (1 800 ml) was added over a period of 20 h under reflux. Concentration yielded a syrup which crystallised from aqueous ethanol. Recrystallisation from ethanol/*iso*propyl ether yielded benzyl 2-tosyl-β-D-arabinopyranoside (70 g) with m. p. 120—123°. The pure substance had m. p. 123.5—124.5°, $[\alpha]_D^{20}$ —156° (*c* 0.8 in chloroform). (Found: C 57.40; H 5.52; O 27.94; S 7.88. Calc. for $C_{19}H_{22}O_7S$: C 57.86; H 5.62; O 28.39: S 8.13.)

Benzyl 2,3-anhydro-β-D-ribopyranoside, IV. Benzyl 2-tosyl-β-D-arabinopyranoside (70 g) was dissolved in methanolic sodium methoxide (1 l, made from 13 g sodium) and allowed to stand overnight. The solution was diluted with water (500 ml) and neutralised with sulphuric acid, the methanol was removed by vacuum distillation and the aqueous solution was extracted with chloroform. The combined chloroform solutions were dried over anhydrous sodium sulphate, filtered and the filtrate was concentrated to dryness. Spontaneous crystallisation occurred giving benzyl 2,3-anhydro-β-D-ribopyranoside (29 g) with m. p. 64—76°. Recrystallisation from *iso*propyl ether gave 25 g with m. p. 74—76°. The pure substance had m. p. 76—77°, $[\alpha]_D^{20}$ —67° (*c* 0.8 in chloroform). (Found: C 64.60; H 6.13; O 29.04. Calc. for $C_{12}H_{14}O_4$: C 64.85; H 6.35; O 28.80.)

Benzyl 4-O-methyl-2,3-anhydro-β-D-ribopyranoside, V. Benzyl 2,3-anhydro-β-D-ribopyranoside (25 g) was methylated with methyl iodide (38 ml) and silver oxide