Thermochimica Acta, 86 (1985) 291-294
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

REEXAMINATION OF THE SYSTEM Bi_2S_3-In_2S_3 AND CRYSTAL DATA OF INDIUM BISMUTH SULPHIDE $InBiS_3$

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(Received 23 October 1984)

ABSTRACT

The phase diagram of the system Bi_2S_3–In_2S_3 was redetermined by annealing appropriate mixtures of the binary components at 600°C followed by X-ray phase analysis and DTA heating runs. Three intermediate compounds were found: a probable high-temperature phase of approximate composition $In_2Bi_4S_9$, as well as $Bi_2In_4S_9$ and $InBiS_3$. The latter crystallizes in an orthorhombic form with lattice parameters $a = 9.297(3)$, $b = 3.889(2)$, and $c = 13.222(4)$ Å; its X-ray powder diffraction data are listed.

INTRODUCTION

In 1976, the present author reported on the system Bi_2S_3–In_2S_3 [1] and its investigation by means of differential thermal analysis (DTA), chemical vapour transport (CVT), and X-ray phase analysis (XPA). By DTA the liquidus curves of the system could be established but in the subsolidus region considerable kinetic barriers prevent the evaluation of the phase relationships. Therefore CVT experiments were performed to explore the subsolidus equilibrium phases. Thereby the tendency of bismuth was observed to form various thermally stable sulphide halides [1]; after studies on their stability [2] in order to circumvent their formation during CVT (with chlorine and iodine as transport agents) three phases near the compositions 2 : 1 (**II**), 1 : 1 (**IV**) and 1 : 2 (**I**) could be prepared which were believed to represent halogen-free ternary In–Bi sulphides. To prove this assumption long-time annealing experiments were performed which should elucidate whether these phases form under halogen-free conditions. Crystal structure analyses should confirm or determine their composition.

EXPERIMENTAL

The binary components Bi_2S_3 and In_2S_3 were synthesized from high-purity elements in evacuated quartz ampoules at 600 and 800°C, respectively; their homogeneity was tested by XPA and DTA. Mixtures of the compo-

0040-6031/85/$03.30

nents in steps of 2.5 mol% were pressed into pellets (1 g), sealed into small quartz ampoules and annealed at 600°C for three months. The sintered products were then examined by XPA for phase identification and by DTA heating runs (for details compare refs. 1 and 2) to detect the thermal effects reliable for solidus and liquidus temperatures. Combined with the earlier results of CVT, an improved phase diagram could be constructed.

RESULTS

Figures 1a–c schematically illustrate the experimental steps which led to the phase diagram of Fig. 2.

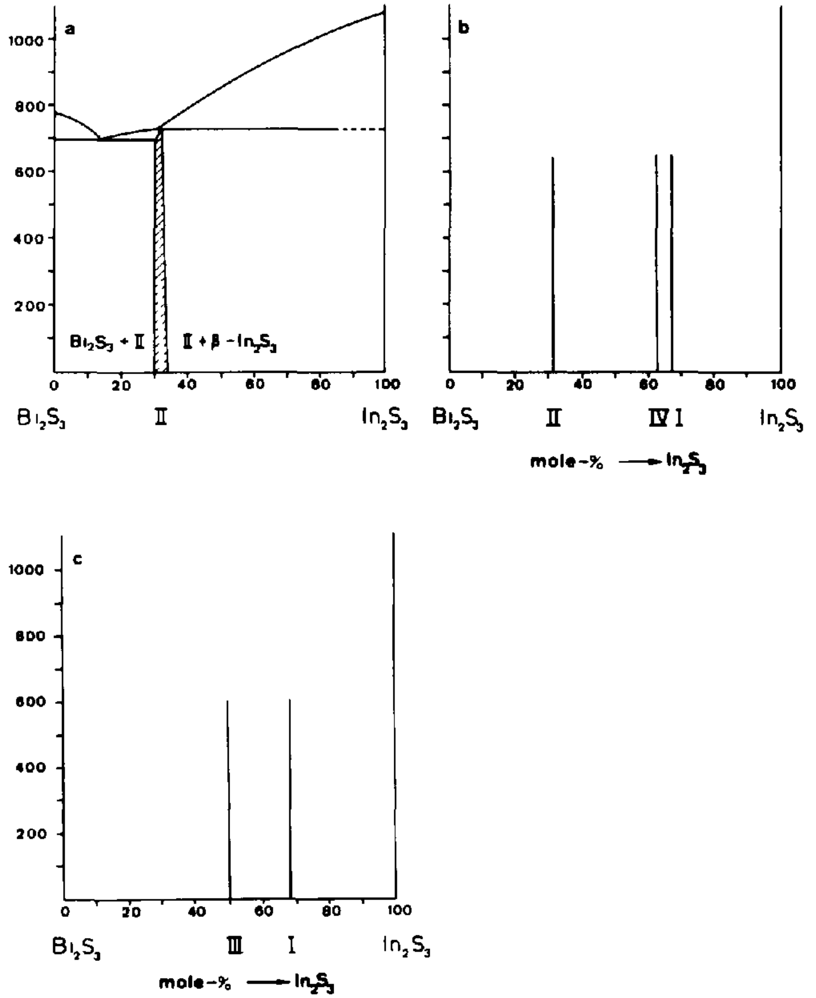

Fig. 1. Phases found by (a) DTA, (b) CVT (temperature region 680/620°C), and (c) annealing (at 600°C) experiments. (I) $Bi_2In_4S_9$, (II) $In_2Bi_4S_9$ (approx.), (III) $InBiS_3$, (IV) $Bi_3In_5S_{12}$: X.

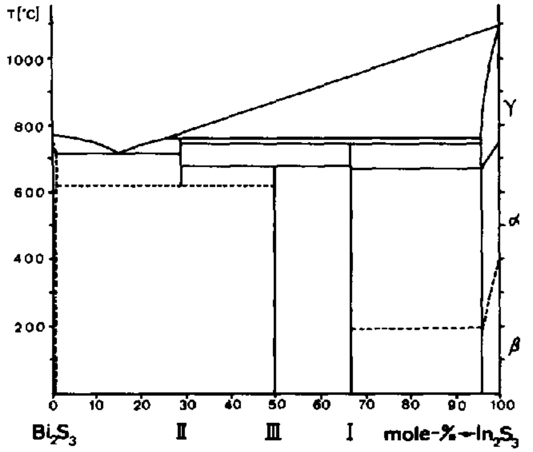

Fig. 2. Tentative phase diagram of the system Bi_2S_3–In_2S_3.

Figure 1a shows the former results of the DTA and XPA investigation: an incongruently melting compound (**II**) near the composition 2 : 1 with a phase width of about 4 mol%, the liquidus curves and two solidus lines at 705 and 725°C.

Figure 1b shows the phases **I**, **II** and **IV** which were grown single-crystalline by CVT. The crystal structures of **I** [3] and **IV** [4] were determined, the resulting compositions being $Bi_2In_4S_9$ (**I**) and $Bi_3In_5S_{12}$ (**IV**); the latter was originally envisaged as $InBiS_3$ [1]. **II** exhibits a twelvefold superstructure in the [010] direction which has not been solved so far. Its composition may lie

TABLE I

Powder diffraction data of $InBiS_3$

hkl	d_{calc}	d_{obs}	I/I_0	*hkl*	d_{calc}	d_{obs}	I/I_0
101	7.6053	7.6096	7	212	2.7189	2.7178	15
002	6.6111	6.6367	12	204	2.6939	2.6935	43
102	5.3878	5.3837	29	303	2.5351	2.5351	6
200	4.6486	4.6581	19	213	2.4702	2.4717	6
201	4.3855	4.3877	< 3	114	2.4310	2.4309	4
103	3.9826	3.9699	100	400	2.3243	2.3237	< 3
202	3.8026	3.7910	12	205	2.2986	2.2989	17
011	3.7309	3.7300	13	312	2.2755	2.2778	5
111	3.4625	3.4581	7	006	2.2037	2.2026	13
004	3.3056	3.2955	9	402	2.1927	2.1919	42
203	3.1984	3.1975	17	106	2.1443	2.1463	5
112	3.1533	3.1546	35	115	2.1287	2.1294	4
301	3.0173	3.0130	21	403	2.0559	2.0570	< 3
210	2.9828	2.9808	16	206	1.9913	1.9913	< 3
211	2.9097	2.9086	46	215	1.9788	1.9785	8
302	2.8061	2.8056	6				

TABLE 2

Crystal data of the ternary indium bismuth sulphides

		$InBiS_3$	$Bi_2In_4S_9$ [1,3]	$In_2Bi_4S_9$ [1]
Lattice parameters	a (Å)	9.297(3)	16.167(12)	12.62(3)
	b (Å)	3.889(2)	3.917(2)	3.93(1)×12
	c (Å)	13.222(4)	11.111(6)	11.67(6)
	β (°)	90	94.1(1)	105.8(2)
Cell volume	V (Å^3)	478.1	701.9	6683
Formula units/cell	Z	4	2	18
Density (pycn)	(g cm^{-3})	–	5.53(5)	6.09(9)
(calc)	(g cm^{-3})	5.85	5.52	6.10
Possible space groups		$Pnma$ $Pn2_1a$	$P2_1/m$	$C2$, Cm $C2/m$

in the 2 : 1/5 : 2 region ($In_2Bi_4S_9/In_4Bi_{10}S_{21}$).

Figure 1c shows the XPA results after the annealing procedure. Besides the CVT phase **I**, the new phase **III** with 1 : 1 composition has formed which has so far been completely overlooked. Its powder diffraction and crystal data are listed in Tables 1 and 2, respectively. Obviously the missing DTA and CVT phase **II** suggests a high-temperature phase above 600°C. Annealing of crystals of **II** just below this temperature resulted in their decomposition confirming the deduction to be stable only at high temperatures. Furthermore the missing CVT phase **IV** indicates a halogen-stabilized compound; X-ray fluorescence and microprobe analyses yielded halogen contents in the order of magnitude of S : X = 100 : 3 (X = Cl, I) thus leading to the formula $Bi_3In_5S_{12}:X$.

The annealed mixtures were subjected to DTA heating runs which revealed the solidus and liquidus temperatures of Fig. 2.

Numerous experiments to grow single crystals of $InBiS_3$ (**III**) by CVT have not yet been successful because of the predominant formation of sulphide halides.

ACKNOWLEDGEMENT

Financial support of the Deutsche Forschungsgemeinschaft is highly appreciated.

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