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Subsolidus Phase Relations in the $ZnS–In_2S_3$ System: 600 to 1080° C

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Eleven ternary compounds were synthesised, of which nine are new. The seven most ZnS-rich compounds form a series. Each has a primitive hexagonal lattice with $a = 3.85 \pm 0.01$ Å. The c-dimension varies from 37.47 Å (39 ZnS:8 In_2S_3) to 18.63 Å (18 ZnS:8 In_2S_3) with a periodicity of 3.14 Å which can be related to a decrease in the ZnS content. One of the four remaining compounds (12 ZnS:8 In_2S_3) is triclinic, but at least two polytypes are present. The more common variety has the parameters: $a = 3.86$ Å, $b = 15.48$ Å, $c = 3.54$ Å, $\alpha = 90° 16'$, $\beta = 120° 02'$ and $\gamma = 89° 47'$. The structure of the other polytype and of compounds 17 ZnS:8 In_2S_3 and 10 ZnS:8 In_2S_3 have not been determined. Stoichiometric $ZnIn_2S_4$ has a rhombic hexagonal lattice ($a = 3.86$ Å, $c = 36.95$ Å). This ternary compound which has been synthesised previously is the only one to show appreciable solid solution. Approximately 2 mole % ZnS is soluble in $ZnIn_2S_4$ at 600° C; this increases to 8 mole % at 1080° C.

1. Introduction

Materials scientists have for some time been interested in compounds of zinc, indium and sulphur because of their optical and electrical properties [2, 13, 16, 17, 25]. Thus, while our studies have largely been confined to the composition of the naturally-occurring sulphides of zinc and indium [3], a growing interest in materials prompted us to investigate synthetic compounds on the $ZnS–In_2S_3$ binary and to establish the phase equilibria of these, many of which had not previously been prepared.

2. Previous Work

The $ZnS–In_2S_3$ binary falls within the Zn–In–S system and a review of part of the work in this system is summarised below.

2.1. Zn–S

Sphalerite, wurtzite and the intermediate sphalerite-wurtzite polytypes are the only binary phases in the Zn–S system. Allen and Crenshaw [1] proposed a first-order transition at 1020° C of sphalerite to wurtzite. Hill [9], on the other hand, suggested a higher order transition with ZnS polytypes stable over the range 960 to 1020° C. Scott and Barnes [15] recently indicated that phase changes in zinc sulphide are accompanied by a composition change. They suggested that wurtzite is sulphur-deficient relative to sphalerite, that the intermediate phases are not true polymorphs, and that wurtzite polytypism is a function of sulphur fugacity and temperature.

2.2. In–S

Stubbs *et al* [21] described four indium sulphides, βIn_2S_3, In_3S_4, In_5S_6, and InS, which they believed to be stable phases in the $In–In_2S_3$ system above 600° C. Miller and Searcy [12] disproved the existence of In_3S_4. The composition of In_5S_6 has since been changed to In_6S_7 [5, 10]. Zargarov and Gamidov [23] claimed to have synthesised a phase (In_3S_5) which is more sulphur-rich than In_2S_3. The melting point of pure In_2S_3 is reported to be between 1090 and 1100° C [21].

2.3. Zn–In

A simple eutectic between the Zn and In liquidus curves is located at 3.1 at. % Zn at

144 ± 1° C. The solid solution of Zn in In and of In in Zn at the eutectic temperature was estimated to be approximately 0.45 at. % and 0.65 at. % respectively [8].

2.4. Zn–In–S

Two compounds, $ZnIn_2S_4$ and $Zn_3In_2S_6$, both of which occur on the $ZnS-In_2S_3$ binary, have been synthesised by other workers [7, 24]. Lappe *et al* [11] showed that $ZnIn_2S_4$ has hexagonal symmetry with a rhombohedral lattice ($a = 3.85$, $c = 37.06$ Å). Donika *et al* [4] on a phase they indicated to be $Zn_3In_2S_6$, calculated a primitive hexagonal lattice with $a = 3.85$, and $c = 18.5$ Å.

3. Experimental

3.1. Preparation of Starting Materials

The ZnS and In_2S_3 end members were prepared by precipitation from aqueous solutions. Pure zinc (99.999 + %, ASARCO) and indium (99.999 + %, ASARCO) were dissolved in concentrated HCl. These solutions were evaporated and the chlorides redissolved in water. Hydrogen sulphide was then bubbled through each solution (pH 1.5 to 3.0) to precipitate In_2S_3 and ZnS. The precipitates were washed, dried, ground and rewashed several times to remove the excess chlorides. Finally each sulphide was heated in a vacuum at approximately 500° C for at least 1 h to eliminate traces of ammonium salts, water and most of the excess sulphur.

3.2. Furnace Runs

Charges for the experimental runs weighed 50 to 100 mg and were prepared from various mole ratios of the ZnS and In_2S_3 end members. These mixtures were placed in 6 mm OD (1.0 mm wall) vycor glass tubes which were evacuated at 25° C to a pressure of less than 1 torr before sealing.

All runs were equilibrated in electrically-heated vertical tube furnaces. The hot spot in each was located near the base and varied by less than 2° C over 75 mm. Temperatures were controlled to ± 10° C above 1000° C and to ± 5° C below 1000° C. The study was carried out below 1100° C so as to remain in the subsolidus region and above 600° C to facilitate rapid equilibration.

Runs were allowed to equilibrate for a minimum of 36 h at temperatures above 650° C. At the lowest temperature 602° C the charges were left in the furnace for up to 400 h to insure equilibration. At the termination of a run, each charge was quenched in cold water, and the product examined under a binocular microscope before diffractometer smear mounts and polished sections were prepared.

4. Analytical Procedure

4.1. X-ray Analyses

Diffractometer scans from 0 to 90° 2θ (iron filtered, cobalt $K\alpha$ radiation) were run on each charge to determine the co-existing phases. In addition, X-ray powder patterns (114.6 cm camera) were obtained for each of the eleven ternary compounds synthesised. Indexing and lattice parameter determinations were carried out using a least mean squares refinement in a computer program [6].

4.2. Microprobe Analyses

The analyses were performed on an Acton-Cameca MS 64 electron microprobe, and the data processed by a computer program [14] which applied corrections for drift, dead time, background, efficiency of excitation, absorption and fluorescence [19].

Compound 72L (fig. 4) was used as a standard for analyses of the ternary Zn–In–S compounds. This compound was initially analysed against pure αZnS and βIn_2S_3 and the composition corresponded, within the limits of error, to that of stoichiometric $ZnIn_2S_4$. The end member constituents were analysed against αZnS and βIn_2S_3.

The standards were run at the beginning and end of each set of analyses. A set consisted of from three to six grains for each sample with three repeated readings on each grain. The results were recast into mole % ZnS and the error quoted is the standard error of the mean at 97.6 % confidence. One hundred and thirty-one phases from 85 runs were analysed from a total of 227 runs.

5. Results

Eleven ternary compounds were synthesised in addition to the end members (Zn,In)S and $(In,Zn)_2S_3$, denoted A and M respectively. These eleven have been designated B, C, D, E, F, G, H1, H2, J, K, and L (figs. 1 and 4). Compounds G and L have been previously prepared but the remainder are new.

In those runs which contained only indium and sulphur and where more than 60 at. % of the mixture was sulphur, βIn_2S_3 and sulphur vapour were stable over our experimental temperature

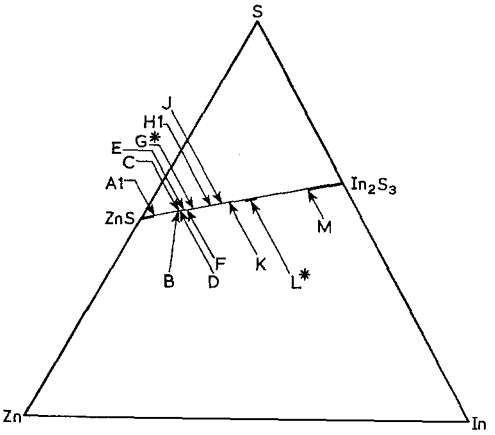

Figure 1 Compounds on the ZnS–βIn_2S_3 join in the Zn–In–S system at 950° C; synthesised by previous workers.

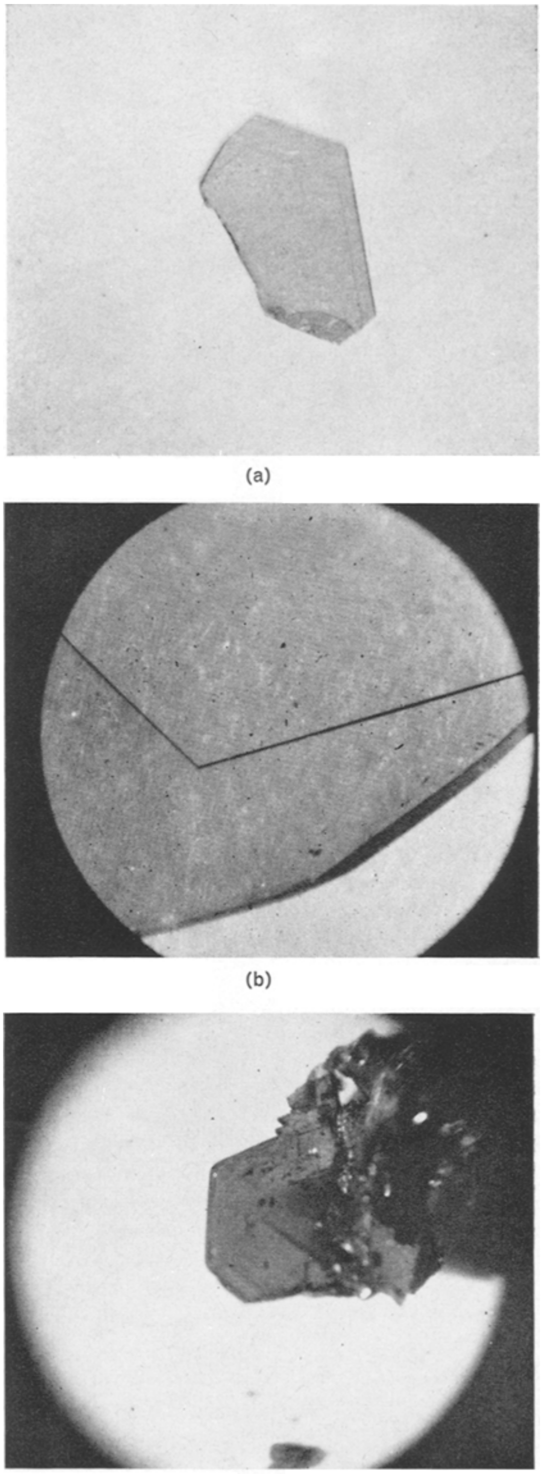
(a)
(b)
(c)

Figure 2 Photomicrographs: (a) crystal of compound H1 (× 8); (b) crystal of compound H1 (× 56) showing growth line at approximately 120°; (c) hexagonal plate of compound L with octahedron of $\beta(In,Zn)_2S_3$ (× 8).

range. Zargarov and Gamidov's In_3S_5 [23] was not observed.

All charge products were coarsely crystalline, ranging in size from 0.1 mm in runs at 600° C to 5 mm and larger at temperatures above 900° C. The ternary phases and $\alpha(Zn,In)S$ exhibited hexagonal plates with platey cleavage, while $\beta(In,Zn)_2S_3$ formed octahedrons (fig. 2).

Phases B, C, D, and E are yellow; F and G also are yellow but with a greenish tint; H1 is brownish yellow. H2 and J are also brownish yellow when formed above 800° C but are green at lower temperatures. Compound K has a bronze cast while crystals of L vary from red-brown to brown.

5.1. Crystallography

X-ray powder data from the recrystallised αZnS, βZnS and βIn_2S_3 starting materials compare favourably with previously published data (table I).

The unit cell size of $\beta(Zn,In)S$ increases with increasing indium solubility from 5.4102 ± 0.0003 Å at 600° C to 5.4135 ± 0.0003 Å at 862° C, the sphalerite-wurtzite inversion temperature. Reflections from co-existing ternary compounds interfere with wurtzite lines and hence accurate lattice parameters for the hexagonal $\alpha(Zn,In)S$ phase could not be determined. However, both *a* and *c* appear to increase with increasing indium solubility. The effect of zinc substitution in In_2S_3 on the cell parameters was not measured.

The different ternary phases have character

TABLE I Lattice parameters of the end members

End member	System	Space group	Lattice parameters Å This study	 Other studies	 Reference
α ZnS	hexagonal	$P6_3mc$	$a = 3.820 \pm 0.005$, $c = 6.249 \pm 0.005$	$a = 3.820$, $c = 6.260$	[22]
β ZnS	isometric	$F\bar{4}3m$	$a = 5.4098 \pm 0.0003$	$a = 5.4093 \pm 0.0002$	[18]
βIn_2S_3	tetragonal	$14_1/amd$	$a = 7.606 \pm 0.001$, $c = 31.8 \pm 0.1$	$a = 7.623$, $c = 32.36$	[20]

istic diffraction patterns. As the ZnS content increases, the 2θ position of the principal reflection is shifted to a higher angle (fig. 3). The X-ray powder data for these phases are shown in the appendix (tables AI and AII). Compounds B, C, D, E, F, G, and H2 have hexagonal symmetry with primitive-type lattices. The length of the a and b axes is 3.85 Å, whereas c changes from 37.47 Å for phase B to 18.63 Å for crystals of compound H2, with a periodicity (increments)

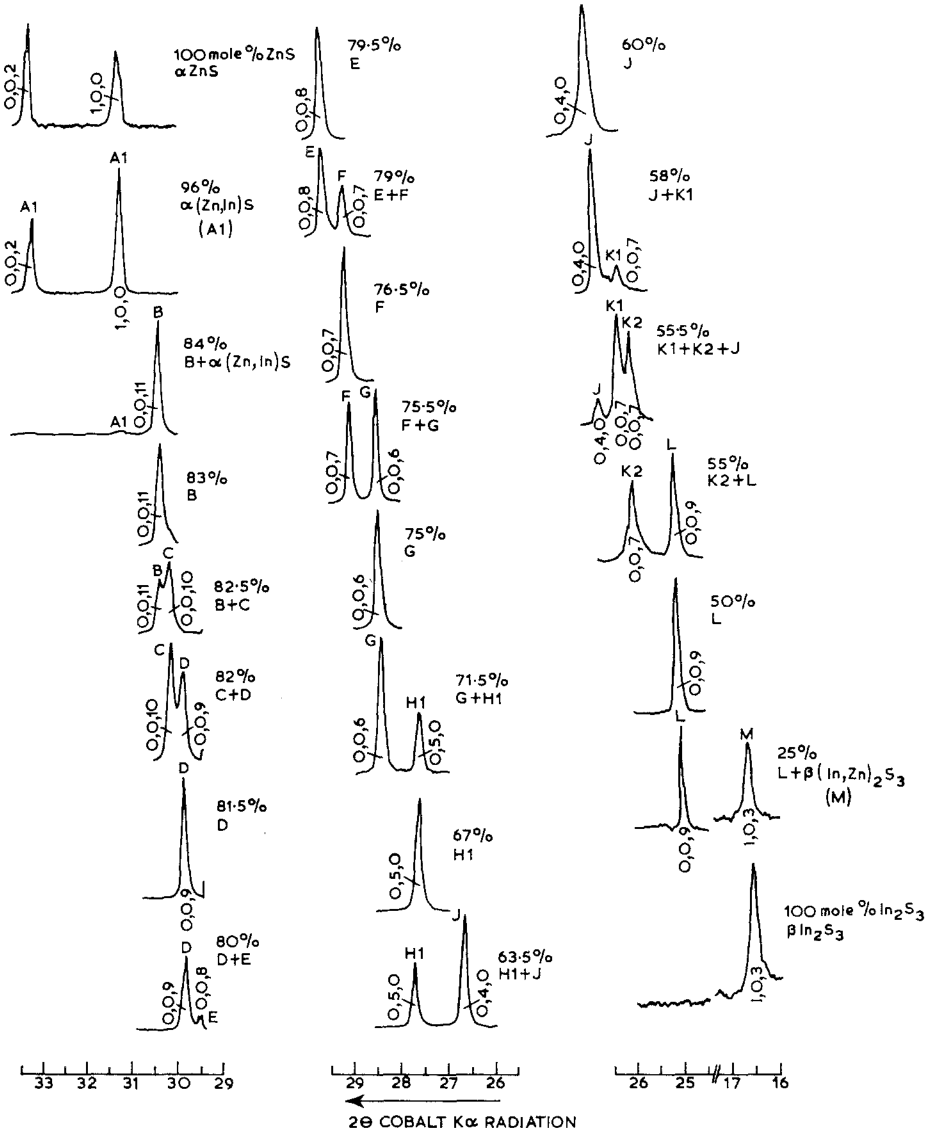

Figure 3 X-ray diffractometer profiles illustrating 2θ angular positions for the principal reflection from each phase along the 950° C isotherm.

TABLE II Phases present on the ZnS–In_2S_3 binary

Phase		Temperature	Composition				Crystallography			
Analysed	Co-existing	°C	Mole % ZnS	Approx. formula	System	Lattice	Principal reflection	a (± 0.01 Å)	b (± 0.01 Å)	c (± 0.01 Å)
α (Zn, In)S		> 862	92.4 (min)	(Zn, In)S	Hex.	P	101	3.82	3.82	6.26 (αZnS)
β (Zn, In)S		< 862	99.0 (min)	(Zn, In)S	Iso.	F	111	5.4135 ± 0.0003		
B	A1/C	> 942	82.9 ± 0.2	$39ZnS.8In_2S_3$	Hex.	P	0011	3.84	3.84	37.47
C	B/D	< 942	82.6 ± 0.1	$38ZnS.8In_2S_3$	Hex.	P	0010	3.85	3.85	34.35
	A1/D	927–942	82.9 ± 0.2	$39ZnS.8In_2S_3$						
D	C/E	> 927	81.2 ± 0.2	$35ZnS.8In_2S_3$	Hex.	P	009	3.85	3.85	31.18
	A1/E	892–927	82.1 ± 0.4	$37ZnS.8In_2S_3$						
E	D/F	> 892	79.4 ± 0.2	$31ZnS.8In_2S_3$	Hex.	P	008	3.85	3.85	28.02
	A1/F	862–892	80.1 ± 0.1	$32ZnS.8In_2S_3$						
F	E/G	> 862	77.6 ± 0.1	$28ZnS.8In_2S_3$						
	A2/G	847–862	78.1 ± 0.3	$29ZnS.8In_2S_3$	Hex.	P	007	3.85	3.85	24.92
G	F/H1 F/H2	> 914 847–914	75.0 ± 0.1	$24ZnS.8In_2S_3$	Hex.	P	006	3.85	3.85	21.79
	A2/H2	803–847	75.3 ± 0.1	$24ZnS.8In_2S_3$						
H1	G/J	> 914	67.9 ± 0.2	$17ZnS.8In_2S_3$	Tricl.	?	050			
H2	G/J A2/J	803–914 600–803	69.3 ± 0.1	$18ZnS.8In_2S_3$	Hex.	P	005	3.85	3.85	18.63
J	H1/K	> 914								
	H2/K	775–914	60.7 ± 0.1	$12ZnS.8In_2S_3$	Tricl.	P	040	3.86	15.48	3.54
	H2/L	600–775								
K	J/L	> 775	56.0 ± 0.2	$10ZnS.8In_2S_3$	Hex.	?				
L	K/M	> 775	49.6 ± 0.2 (max)	(6–8) $ZnS.8In_2S_3$	Hex.	R	009	3.86	3.86	36.95
	J/M	600–775	50.2 ± 0.2 (max)							
β $(In,Zn)_2S_3$		600–1080	23.0 (max)	$(In,Zn)_2S_3$	Tetra.	I	213	7.61	7.61	31.76

of approximately 3.14 Å (table II). Some preliminary work (L. Trembath, personal communication) with oscillation and rotation films on single crystals of phases F and G gave *c* dimensions one-half and twice those calculated from powder data. This suggests that polytypism may be present.

Compound H1 has strong intensity reflections in the same 2θ positions as the $00l$ lines from H2 but, in addition, H1 also has reflections which could not be indexed in the hexagonal system. The powder data for the compound which has not been indexed are shown in table AII.

Compound J has a number of reflections ($00l$, $h00$, $h0l$) which can be indexed in the hexagonal system. As $0k0$ or hkl lines could not be indexed, the length of the *b*-axis must differ from *a*. By making *b* the principal axis approximately perpendicular to the hexagonal-like plates, all reflections have triclinic symmetry (table AI). The *b*-axis for this crystal is 15.48 Å, hence the 3.14 Å periodicity along *c*, which is present in the hexagonal crystals, has been transferred to the *b*-axis in the triclinic crystals. In addition to this form, a few crystals of the same composition were synthesised in which only the basal reflections could be indexed in the hexagonal system. This suggests that these crystals might also be triclinic, but that neither *a* nor *b* is 3.86 Å (J2; table AII).

The majority of our runs with starting mixtures in the vicinity of the composition of compound K were carried out at temperatures under 950° C. Large single crystals of K were not obtained and the powder patterns of the charge products were always complicated by lines from either compounds L or J. In some instances the basal reflections of compound K appeared as doublets, as shown on fig. 3. K1 with a principal basal reflection at approximately 26.0° 2θ appears to be more stable with compound L whereas K2 with its principal reflection at approximately 26.2° 2θ is more stable with compound J.

The lattice parameters determined from our powder data for stoichiometric $ZnIn_2S_4$ (compound L, table II) are in agreement with those given by Lappe *et al* [11]. The other previously synthesised phase has been described as having the composition $Zn_3In_2S_6$ [24]. Donika *et al* [4] calculated lattice parameters of $a = 3.85 \pm 0.02$ and $c = 18.5 \pm 0.03$ Å for a phase which they believed to have the composition $Zn_3In_2S_6$. However, in our work we found that a compound with this composition, phase G, has a *c* of 21.79 Å. Phase H2 which co-exists with G over the range 803 to 914° C (fig. 4) has lattice parameters ($a = 3.85 \pm 0.01$ and $c = 18.63 \pm 0.01$ Å) similar to those given by Donika *et al.* It is possible that the synthetic product studied by these workers yielded two co-existing phases, phase G which they analysed and phase H2 on which they did their structural analyses, thinking it to be phase G.

5.2. Chemistry

The chemistry of the binary system is summarised in table II and in figs. 4 and 5.

Phase boundaries were fixed from the weighted average of all the analyses of a phase on either side of the boundary at various temperatures. With the exceptions of compound L and the end members (Zn,In)S and $(In,Zn)_2S_3$, all boundaries are vertical. Solid solution in each phase is within the limits of analytical error.

On the (Zn, In)S solvus, the solubility of indium in sphalerite increases from less than 0.15 wt % at 600° C to approximately 2.3 wt % at 862° C, the temperature of the sphalerite-wurtzite inversion. The solubility of indium in wurtzite increases from 5.5 wt % at the inversion to approximately 17.7 wt % at 1055° C.

Approximately 23 mole % ZnS is soluble in In_2S_3 at 600° C; this decreases to 15 mole % at 1080° C. The slope of the boundary between compounds L and M is approximately parallel to that of the $(In,Zn)_2S_3$ solvus (fig. 4). Approximately 8 mole% In_2S_3 is soluble in $ZnIn_2S_4$ at 1080° C, this decreases to 2 mole % at 600° C. Where compound L co-exists with the more zinc-rich compounds, J and K, at 50.2 and 49.6 mole % ZnS respectively, there is no measurable solid solution effect and the boundaries are vertical.

Table II shows the stability range of each phase along the $ZnS–In_2S_3$ binary. As compounds C, D, E, F and G become stable with a (Zn,In)S phase, there is a slight shift in their composition towards increased ZnS (fig. 5; table II). The compositions of H2 and J are apparently not affected by changes in their co-existing assemblage.

Of the nine samples which contained compound K and were analysed, six showed doublets on the major X-ray reflection. 27K (56.29 ± 0.76 mole % ZnS), 35K (54.82 ± 1.38) and 48K (55.75 ± 0.24) produced only single reflections. 27K co-existed with compound J, while the other two were in equilibrium with L.

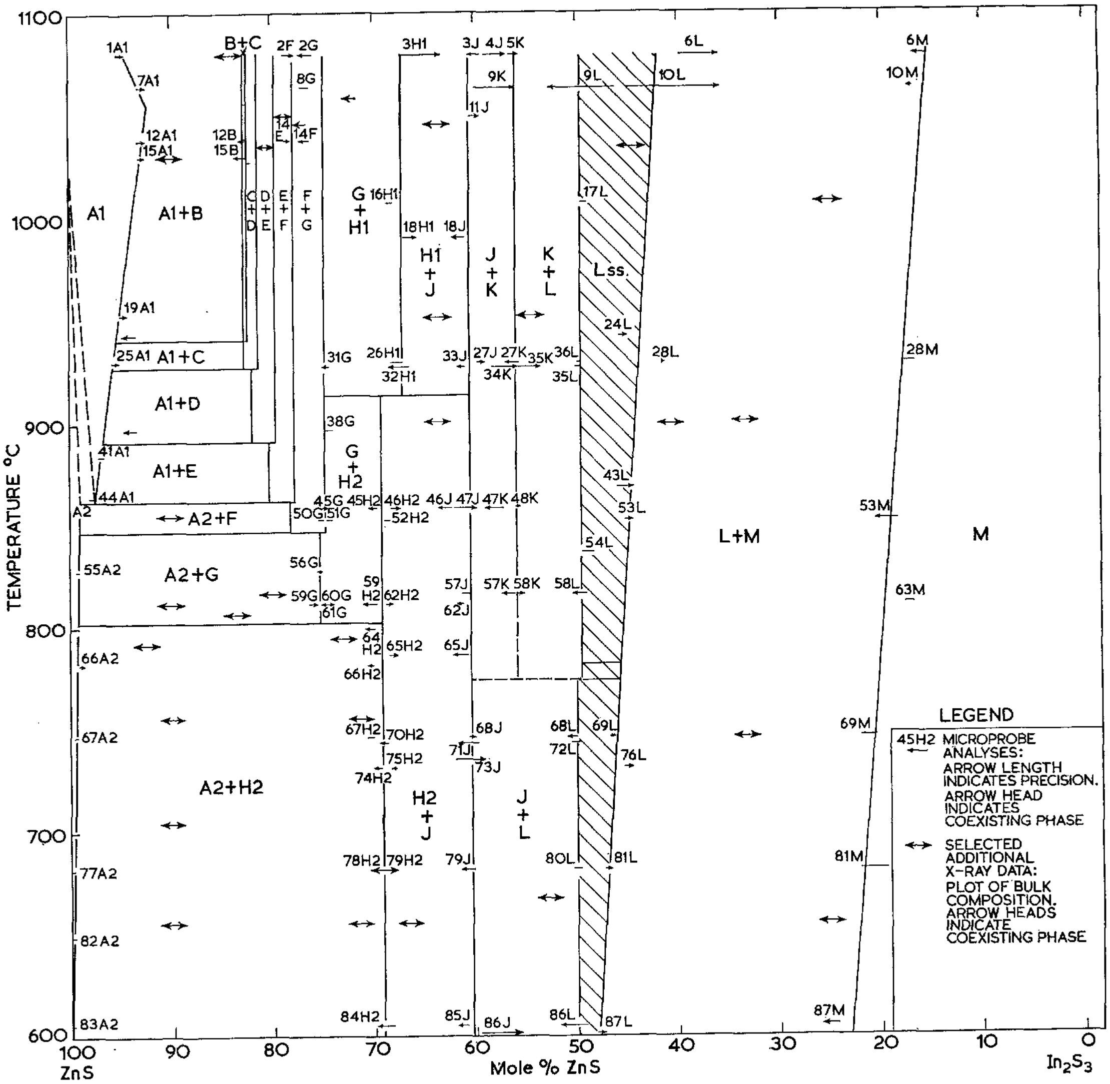

Figure 4 Phase diagram of ZnS-In_2S_3 binary (600 to 1080° C). Numerical data for figs. 4 and 5 are available in a table listing the temperature, starting mixture, length of run and the phases both identified and analysed. Copies of these tables can be obtained by writing to the authors.

Hence, there is no compositional difference between K1 and K2 (fig. 3) within the limits of analytical error. The doublets may indicate polytypism.

6. Conclusions

Eleven ternary compounds, nine of which are new, were synthesised in the ZnS-In_2S_3 system over the range 600 to 1080° C. X-ray powder patterns for compounds B, C, D, E, F, G and H2 can be indexed on primitive lattices within the hexagonal system. Compound L is also hexagonal but has the rhombic lattice. Single crystal X-ray work is required to study polytypism in these compounds and to resolve the structures of compounds J2, H1 and K.

The lattice parameters for compound L ($ZnIn_2S_4$) calculated in this study agree with those previously determined [20]. However, the length of the *c*-axis of the other previously synthesised compound, G($Zn_3In_2S_6$), as determined by Donika *et al* [4] differs from our cell size. Their result corresponds more closely to our value for H2, a compound ($Zn_9In_8S_{21}$) which contains less zinc.

The new compounds and compound G have compositions that change progressively in a step-like manner between $ZnIn_2S_4$ and ZnS.

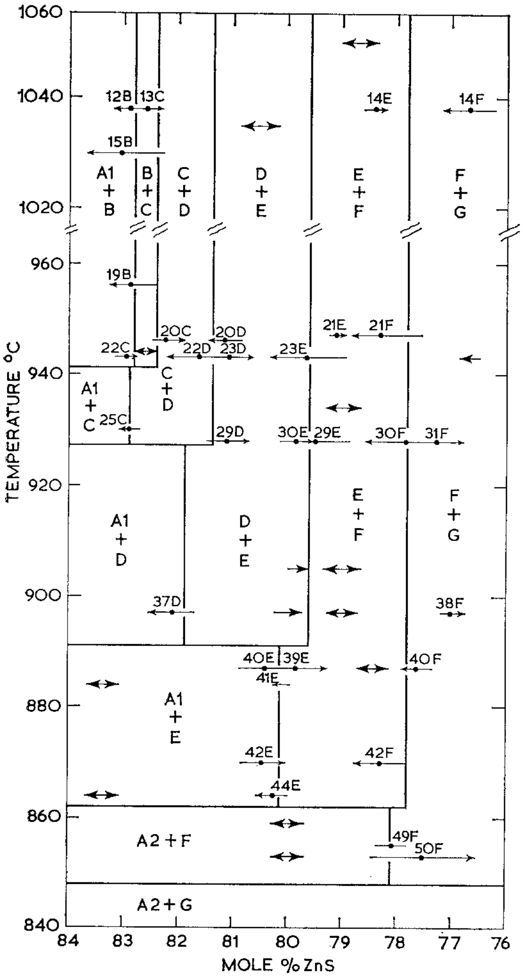

Figure 5 Enlargement of the more congested portion of the ZnS–In_2S_3 binary.

Similar variations in the electrical and optical properties can be expected and investigation of these might lead to some interesting findings.

Although the fundamental optical, electrical and luminescence properties of $ZnIn_2S_4$ have previously been studied [16, 17], the solid solution of In_2S_3 in this compound has hitherto not been observed. In the light of this new information, the influence of chemical variation on properties should also be determined. The substitution of zinc in In_2S_3 and indium in the ZnS phase will also affect the semiconducting properties of these compounds.

This study has been confined to the ZnS–In_2S_3 binary, and additional work is still required to complete the phase relationships within the three component system zinc-indium-sulphur. Once the chemistry of the system is known, efforts can be concentrated on the synthesis of ultra pure single crystals which will be needed before an extensive study can be made of their optical and electrical properties.

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Appendix

The X-ray crystallographic data for all phases synthesised are given in the following tables.

TABLE AI X-ray power diffraction data. Cobalt radiation ($K\alpha = 1.79021$ Å)

B; 39 $ZnS.8In_2S_3$ (approx.); hexagonal;
$a = 3.84 \pm 0.01$ Å; $c = 37.47 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 3	1	12.743	12.489
0 0 5	3	7.473	7.494
0 0 7	3	5.357	5.353
0 0 9	3	4.149	4.163
0 0 11	10	3.406	3.406
1 0 0	3	3.331	3.330
1 0 2	1	3.273	3.278
1 0 3	1	3.211	3.217
0 0 12	1	3.126	3.122
1 0 5	6	3.046	3.043
1 0 6	1	2.938	2.938
0 0 13		†	2.882
1 0 7	3	2.826	2.827
1 0 8	2	2.711	2.714
0 0 14		†	2.676
0 0 15		†	2.498
1 0 10	2	2.488	2.489
1 0 11	1	2.383	2.381
0 0 16	1	2.340	2.342
1 0 12	3	2.279	2.278
1 0 13	4	2.178	2.179
0 0 18	2	2.084	2.082
1 0 15	1	1.996	1.998
0 0 19		†	1.972
1 0 16	8	1.917	1.915
0 0 20		*	1.873
1 0 17		*	1.838
1 1 7		*	1.809
0 0 21		†	1.784
1 0 18	8	1.765	1.765
1 1 9		*	1.745
0 0 22		†	1.703
1 1 11	4	1.675	1.674
0 0 23	2	1.629	1.629
1 1 13	2	1.599	1.599
2 0 8		*	1.569
2 0 10		*	1.521
2 0 12		*	1.469
0 0 26	3	1.441	1.441
1 0 24	1	1.413	1.413
0 0 28	1	1.338	1.338

C; 38 $ZnS.8In_2S_3$ (approx.); hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 34.35 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 3	1	11.598	11.449
0 0 5	1	6.924	6.869
0 0 6	1	5.719	5.724
0 0 8	3	4.290	4.293
0 0 10	10	3.438	3.435
1 0 0	6	3.330	3.334
1 0 2	1	3.276	3.273
1 0 3	2	3.205	3.201
1 0 4	2	3.111	3.108
1 0 5	1	3.003	3.000
0 0 12	5	2.869	2.862
1 0 7	1	2.755	2.758
0 0 14	1	2.448	2.453
1 0 10	2	2.390	2.392
1 0 11	3	2.275	2.279
1 0 12	4	2.173	2.172
1 1 0	8	1.924	1.925
0 0 19		†	1.808
1 0 16	1	1.804	1.805
1 1 10	4	1.676	1.679
2 0 1		*	1.665
1 1 12	2	1.597	1.597
0 0 22	1	1.561	1.561
2 0 12	1	1.441	1.441
1 0 22	1	1.413	1.414
2 1 1	2	1.2587	1.2594
2 1 7	2	1.2179	1.2206
2 1 12	2	1.1527	1.1534
3 0 2	3	1.1093	1.1091
3 0 8	4	1.0773	1.0760
3 0 10	1	1.0561	1.0574
0 0 33	1	1.0412	1.0408
1 0 32	2	1.0223	1.0217
0 0 35	2	0.9826	0.9813
3 0 17	1	0.9750	0.9738
2 2 2	2	0.9612	0.9610
1 1 33	2	0.9154	0.9155
2 0 32	3	0.9025	0.9025

D; 37 $ZnS.8In_2S_3$ (approx.); hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 31.18 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 1		†	31.185
0 0 2		†	15.592
0 0 3	3	10.393	10.395
0 0 5	6	6.243	6.237
0 0 6		†	5.197
0 0 7	6	4.444	4.455
0 0 9	10	3.456	3.465
1 0 0	5	3.331	3.332
1 0 1		†	3.313
1 0 2	3	3.258	3.258
1 0 3	1	3.175	3.173
0 0 10		3.119†	3.118
1 0 4	8	3.062	3.064
1 0 5		*	2.939
0 0 11	6	2.841	2.835
1 0 6	5	2.804	2.805
0 0 12	1	2.597	2.599
1 0 8	2	2.531	2.533
1 0 9 }	2	2.400	2.402
0 0 13 }			2.399
1 0 10	1	2.274	2.277
0 0 14	1	2.227	2.227
1 0 11	6	2.157	2.159
0 0 15		†	2.079
1 0 12		*	2.049
0 0 16 }	3	1.947	1.949
1 0 13 }			1.947
1 1 0 }	8	†	1.924
1 1 1 }		1.921	1.920
0 0 17	1	1.833	1.834
1 0 15	10	1.763	1.764
0 0 18	1	1.732	1.732
1 0 16 }	7	1.681	1.682
1 1 9 }			1.682
2 0 0 }	1	1.663	1.666
2 0 1 }			1.663
0 0 19	4	1.640	1.641
2 0 4	1	1.628	1.629
2 0 6	1	1.589	1.586
2 0 7 }	1	1.560	1.560
0 0 20 }			1.559

†Detected with diffractometer
*Intensity < 1

TABLE AI continued

B; 39 ZnS.8In$_2$S$_3$ (approx.); hexagonal;
$a = 3.84 \pm 0.01$ Å; $c = 37.47 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
2 0 18	2	1.301	1.300
2 1 0	2	1.2593	1.2584
2 1 3	1	1.2507	1.2521
2 1 5	2	1.2405	1.2411
2 1 7		*	1.2250
1 0 29	5	1.2043	1.0245
1 0 30	2	1.1687	1.1694
2 1 13	2	1.1532	1.1533
1 0 31	3	1.1361	1.1361
0 0 33		†	1.1354
3 0 1	2	1.1096	1.1093
2 1 18	4	1.0765	1.0769
1 1 30		*	1.0473
0 0 36	2	1.0409	1.0408
2 0 29	2	1.0208	1.0207
1 1 32		*	1.0000
2 0 30		*	0.9990
1 0 36	3	0.9934	0.9934
2 0 31	1	0.9782	0.9781
2 2 1	3	0.9610	0.9608
2 2 11	2	0.9250	0.9250

C; 38 ZnS.8In$_2$S$_3$ (approx.); hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 34.35 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)

D; 37 ZnS.8In$_2$S$_3$ (approx.); hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 31.18 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
2 0 8		*	1.532
2 0 11		*	1.436
0 0 22		†	1.417
2 0 13		*	1.368
1 0 21		1.357	1.356
0 0 23			1.356
2 0 15	2	1.299	1.300
0 0 24			1.299
2 1 0		*	1.2593
1 0 24		†	1.2106
0 0 26		†	1.1994
2 0 19		†	1.1692
1 0 26	1	1.1294	1.1285
0 0 28	1	1.1138	1.1137
1 0 28		*	1.0563
0 0 30	2	1.0395	1.0395
3 0 24	1	1.0243	1.0246
0 0 31		†	1.0060
1 0 30	2	0.9926	0.9923
2 0 26		*	0.9734
0 0 33		†	0.9450
1 0 32		†	0.9353
1 1 30		0.9148	0.9145
3 0 20		0.9043	0.9043
2 1 24			

E; 32ZnS.8In$_2$S$_3$ (approx.) hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 28.02 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 1		†	28.020
0 0 2		†	14.010
0 0 3		†	9.340
0 0 4		†	7.005
0 0 5	4	5.591	5.604
0 0 7	7	4.000	4.003
0 0 8	10	3.500	3.503
1 0 0		3.334†	3.330
1 0 1	6	3.314	3.307
1 0 2	2	3.241	3.240
1 0 3	2	3.131	3.137
1 0 4	2	3.004	3.008
0 0 10	3	2.806†	2.802

F; 29ZnS.8In$_2$S$_3$ (approx.) hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 24.92 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 1		†	24.916
0 0 2		†	12.458
0 0 4	8	6.232	6.229
0 0 6	6	4.160	4.153
0 0 7	10	3.557	3.559
1 0 0		3.336†	3.331
1 0 1	4	3.308	3.302
1 0 2	2	3.222	3.218
1 0 3	7	3.087	3.092
1 0 4	1	2.932	2.937
0 0 9	7	2.766	2.768
1 0 6	1	2.595	2.598
1 0 7	1	2.431	2.432

G; 24ZnS.8In$_2$S$_3$ (approx.); hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 21.79 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 1		†	21.791
0 0 2	1	10.945	10.895
0 0 3	2	7.223	7.264
0 0 4	3	5.433	5.448
0 0 5	2	4.355	4.358
0 0 6	10	3.627	3.632
1 0 0	9	3.326	3.335
1 0 2	1	3.184	3.189
0 0 7	5	3.112	3.113
1 0 3	8	3.033	3.031
1 0 4	4	2.841	2.844
0 0 8	4	2.722	2.724
1 0 6	4	2.459	2.456

†Detected with diffractometer
*Intensity < 1

TABLE AI continued

E; 32ZnS.8In$_2$S$_3$ (approx.) hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 28.02 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
1 0 6	3	2.713	2.711
0 0 12	1	2.335	2.335
1 0 9	3	2.274	2.274
1 0 10	5	2.143	2.144
1 0 11	2	2.022	2.023
0 0 14		†	2.001
1 1 0	8	1.921	1.923
0 0 15		*	1.868
1 0 13		*	1.809
1 1 8	5	1.684	1.685
0 0 17	1	1.649	1.648
1 1 10	1	1.585	1.585
1 0 17		†	1.477
2 0 10		1.431	1.431
1 0 18		1.411	1.410
0 0 21		1.336	1.334

F; 29ZnS.8In$_2$S$_3$ (approx.) hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 24.92 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
1 0 8		2.276†	2.275
0 0 11		2.268†	2.265
1 0 9	6	2.128	2.129
0 0 12		†	2.076
1 0 10		†	1.995
1 1 0	7	1.926	1.923
1 1 1		*	1.917
1 1 3		*	1.874
1 0 11			1.873
1 1 4		*	1.838
0 0 14		1.779†	1.780
1 0 12	8	1.761	1.762
1 1 7	2	1.692	1.692
2 0 1	2	1.662	1.662
2 0 3	1	1.634	1.633
2 0 4		*	1.609
2 0 5	1	1.580	1.580
1 1 9		†	1.579
1 0 14		†	1.570
1 0 16	1	1.410	1.411
2 0 10	1	1.386	1.385
0 0 18			1.384
0 0 19		†	1.311
2 0 13		†	1.2572
2 1 5	1	1.2199	1.2207
1 0 19			1.2202
0 0 21	1	1.1859	1.1865
1 0 20	1	1.1664	1.1669
2 1 9	1	1.1459	1.1461
0 0 22		†	1.1325
1 0 21	1	1.1168	1.1177
3 0 1		†	1.1093
2 1 12	2	1.0763	1.0766
0 0 24	1	1.0375	1.0382
2 0 19	1	1.0293	1.0303
1 0 23			1.0302
1 1 21	1	1.0092	1.0098
2 0 20	1	0.9973	0.9976
3 0 11			0.9970
1 0 24	1	0.9902	0.9911

G; 24ZnS.8In$_2$S$_3$ (approx.); hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 21.79 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 9		*	2.421
1 0 7	2	2.276	2.276
0 0 10		†	2.179
1 0 8		*	2.110
0 0 11		1.980	1.981
1 0 9	5	1.960	1.959
1 1 0	9	1.925	1.925
1 0 10	8	1.823	1.824
1 1 5	3	1.762	1.761
1 0 11	5	1.702	1.703
1 1 6			1.701
0 0 13	1	1.677	1.676
2 0 0	1	1.667	1.667
2 0 1			1.663
2 0 3	1	1.626	1.625
1 0 12	1	1.596	1.595
2 0 4			1.594
1 1 8	1	1.573	1.572
2 0 6	1	1.516	1.515
1 0 13	1	1.496	1.498
2 0 7		*	1.470
0 0 15		*	1.453
2 0 9	1	1.375	1.373
0 0 16		*	1.362
2 0 10	2	1.324	1.324
1 0 16	4	1.2619	1.2608
2 1 3	2	1.2416	1.2419
2 0 12	2	1.2283	1.2282
2 1 4			1.2280
0 0 18		1.2102	1.2106
1 1 14			1.2104
0 0 19		*	1.1469
2 1 9		*	1.1180
3 0 1	3	1.1107	1.1102
2 1 10	2	1.0918	1.0911
1 0 19	2	1.0846	1.0845
3 0 5	1	1.0777	1.0771
3 0 6	1	1.0628	1.0630
2 0 16	1	1.0550	1.0548
1 0 20	1	1.0363	1.0357
1 1 19		*	0.9853
2 2 0	1	0.9627	0.9627
3 1 0	1	0.9249	0.9249

†Detected with diffractometer
*Intensity < 1

TABLE AI continued

H2; $18ZnS.8In_2S_3$ (approx.) hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 18.63 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 1		†	18.626
0 0 2		†	9.313
0 0 3	8	6.191	6.209
0 0 4		†	4.656
0 0 5	10	3.725	3.725
1 0 0	2	3.339	3.338
1 0 1	3	3.282	3.285
1 0 2	8	3.140	3.142
1 0 3	4	2.940	2.940
1 0 4	7	2.715	2.713
0 0 7	7	2.660	2.661
1 0 5	5	2.485	2.486
0 0 8	5	2.328	2.328
1 0 6	5	2.276	2.273
1 0 7	8	2.080	2.081
0 0 9		†	2.070
1 1 0	7	1.929	1.927
0 0 10	1	1.865	1.863
1 1 3	1	1.843	1.840
1 0 9	8	1.760	1.759
1 1 5	3	1.715	1.712
0 0 11	3	1.693	1.693
2 0 1	1	1.661	1.662
2 0 2	2	1.643	1.643
1 0 10	1	1.629	1.626
2 0 4		*	1.571
2 0 5		*	1.523
1 1 8		*	1.485
2 0 6		*	1.470
0 0 13		*	1.433
2 0 7		*	1.414
0 0 14	1	1.332	1.330
1 1 11	1	1.273	1.272
2 1 0		*	1.262
2 1 2		1.2509	1.2502
2 0 10		†	1.2429
2 1 3		†	1.2363
1 0 14	7	1.2357	1.2359
2 1 4	1	1.2168	1.2177
2 1 5	1	1.1940	1.1949
0 0 16		†	1.1641
1 0 15	6	1.1636	1.1638

J; $12ZnS.8In_2S_3$ (approx.); triclinic;
$a = 3.86 \pm 0.01$ Å; $b = 15.48 \pm 0.01$ Å;
$c = 3.54 \pm 0.01$ Å; $\alpha = 90° 16'$; $\beta = 120° 02'$; $\gamma = 89° 47'$

hkl	I(est.)	d(meas.)	d(calc.)
0 1 0	2	15.433	15.475
0 2 0	4	7.736	7.738
0 3 0	6	5.155	5.159
0 4 0	10	3.872	3.869
1 0 0	1	3.335	3.340
1 1 0	4	3.264	3.266
−1 0 1	5	3.181	3.191
0 5 0	2	3.097	3.095
0 0 1	3	3.070	3.068
1 2 0			3.068
0 1 1			3.008
−1 2 1	1	2.937	2.945
1 3 0	5	2.805	2.805
0 3 1	2	2.667	2.663
0 6 0	4	2.580	2.579
1 4 0	1	2.531	2.530
0 4 1	4	2.396	2.400
1 5 0	5	2.272	2.272
0 7 0	4	2.210	2.211
0 5 1	4	2.153	2.175
1 6 0	8	2.043	2.043
0 8 0	9	1.931	1.935
1 7 0	1	1.845	1.845
−2 −3 1	1	1.808	1.807
−1 1 2	8	1.758	1.757
−1 2 2	8	1.726	1.724
1 8 0	1	1.674	1.675
−1 3 2			1.672
−1 8 1	1	1.651	1.651
0 8 1	1	1.635	1.634
2 2 0			1.633
−2 5 1			1.633
−2 0 2	1	1.600	1.595
2 3 0	1	1.590	1.589
−2 2 2		*	1.561
0 10 0		*	1.548
1 9 0		*	1.530
0 2 2	1	1.504	1.504
−2 4 2	2	1.472	1.472
2 5 0			1.471
0 3 2			1.469
−1 6 2	1	1.454	1.456

L; $8ZnS.8In_2S_3$ (approx.); hexagonal (rhomb.);
$a = 3.86 \pm 0.01$ Å; $c = 36.95 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
0 0 3	3	12.245	12.318
0 0 9	10	4.107	4.106
1 0 1	5	3.335	3.332
0 1 2	3	3.286	3.292
1 0 4	8	3.148	3.146
0 1 5	2	3.049	3.048
1 0 7	1	2.827	2.826
0 1 8	8	2.709	2.710
1 0 10	2	2.484	2.480
0 0 15	2	2.467	2.464
0 1 11	1	2.371	2.371
1 0 13	8	2.168	2.166
0 1 14	3	2.072	2.072
0 0 18	4	2.053	2.053
1 1 0	7	1.932	1.932
1 0 16	1	1.904	1.901
0 1 17	8	1.821	1.823
0 0 21	3	1.761	1.760
1 1 9	4	1.749	1.748
0 2 4	1	1.646	1.646
2 0 8	1	1.574	1.573
0 2 10	4	1.523	1.524
1 0 22	1	1.502	1.501
0 1 23	1	1.449	1.448
0 2 13	1	1.442	1.442
1 1 18	1	1.406	1.407
0 0 27	2	1.368	1.369
0 2 16	1	1.354	1.355
2 0 17	2	1.325	1.326
0 1 26	3	1.308	1.308
1 0 31	1	1.1230	1.1229

†Detected with diffractometer
*Intensity < 1

TABLE AI continued

H2; $18ZnS.8In_2S_3$ (approx.) hexagonal;
$a = 3.85 \pm 0.01$ Å; $c = 18.63 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)
2 1 7	3	1.1390	1.1399
3 0 1	3	1.1110	1.1106
1 0 16		*	1.0992
0 0 17		†	1.0956
3 0 3			1.0952
2 1 9	3	1.0772	1.0772
3 0 5	1	1.0661	1.0661
2 0 14	2	1.0403	1.0403
0 0 18	1	1.0353	1.0348
1 1 16	4	0.9967	0.9964
2 0 15			0.9962
1 0 18	3	0.9889	0.9884
0 0 19	3	0.9808	0.9803
3 0 9			0.9800
2 2 0	3	0.9632	0.9635
3 0 10	3	0.9553	0.9552
1 0 19	1	0.9413	0.9406
2 2 5	1	0.9333	0.9328
3 1 2	1	0.9212	0.9212
2 0 17	6	0.9159	0.9159
3 1 3			0.9156
1 1 18	1	0.9122	0.9117
3 1 4	1	0.9080	0.9080

J; $12ZnS.8In_2S_3$ (approx.); triclinic;
$a = 3.86 \pm 0.01$ Å; $b = 15.48 \pm 0.01$ Å;
$c = 3.54 \pm 0.01$ Å; $\alpha = 90° 16'$; $\beta = 120° 02'$; $\gamma = 89° 47'$

hkl	I(est.)	d(meas.)	d(calc.)
0 11 0	6	1.406	1.407
1 10 0			1.405
2 6 0			1.403
−2 −8 1	1	1.368	1.368
1 8 1		*	1.335
−1 8 2	3	1.300	1.303
1 11 0			1.297
−2 7 2	2	1.292	1.291
0 12 0			1.290
−3 −2 1	7	1.2517	1.2538
2 1 1	1	1.2266	1.2268
−1 12 1	2	1.1923	1.1937
0 13 0			1.1905
−2 0 3	1	1.1690	1.1715
−2 1 3			1.1677
−1 10 2	3	1.1622	1.1624
2 10 0	2	1.1360	1.1359
−1 13 1	1	1.1135	1.1136
3 0 0			1.1133
−3 −7 2	1	1.0863	1.0865
−1 5 3	2	1.0786	1.0786
2 7 1	1	1.0763	1.0752
−1 6 3	5	1.0506	1.0506
1 14 0			1.0499
−2 −13 1	4	1.0150	1.0144
3 7 0	2	0.9960	0.9949
0 4 3	4	0.9870	0.9879

L; $8ZnS.8In_2S_3$ (approx.); hexagonal (rhomb.);
$a = 3.86 \pm 0.01$ Å; $c = 36.95 \pm 0.01$ Å

hkl	I(est.)	d(meas.)	d(calc.)

†Detected with diffractometer
*Intensity < 1

TABLE AII X-ray diffraction data for unindexed phases. Cobalt radiation ($K\alpha = 1.79021$ Å)

H1; 17 $ZnS.8In_2S_3$ (approx.)			J2; 12 $ZnS.8In_2S_3$ (approx.)			K; 10 $ZnS.8In_2S_3$ (approx.)			
2θ	d	I(est.)	2θ	d	I(est.)	2θ	d	I(est.)	Comment
16.57	6.215	9	6.68	15.360	3	7.19	14.280	1	
27.76	3.732	10	13.31	7.725	4	7.40	13.880	2	
31.19	3.331	10	19.99	5.1505	7	11.10	9.250	1	
*32.52	3.197	1	26.79	3.864	10	16.66	6.185	1	
*33.79	3.080	4	31.14	3.335	3	21.49	4.800	2	
*34.55	3.015	4	31.89	3.259	3	22.27	4.634	1	
*36.40	2.865	4	†32.32	3.217	2	25.20	4.101	2	L
*37.40	2.792	2	†33.07	3.146	9	26.00	3.980	10	K1
39.25	2.665	4	33.60	3.098	1	26.00	3.950		K2
*43.51	2.415	9	†34.85	2.985	1	26.70	3.877	4	J
45.18	2.385	3	†35.95	2.899	1	31.21	3.328	7	
*52.54	2.365	1	†38.52	2.714	8	32.09	3.239	8	
*54.17	1.9661	3	†39.90	2.624	1	34.72	3.001	1	
55.40	1.9257	6	40.58	2.582	2	36.20	2.880	1	
57.50	1.861	3	†43.03	2.441	1	38.60	2.708	8	
58.23	1.8395	1	†44.78	2.351	1	41.11	2.550	1	
*59.38	1.8075	5	47.80	2.2058	1	43.46	2.418	1	
63.06	1.7116	5	†48.20	2.1904	1	48.87	2.164	1	
63.73	1.6960	1	†50.08	2.087	6	49.62	2.1306	1	
			†53.93	1.974	1	55.31	1.929	7	
			55.23	1.931	8	59.80	1.7955	9	
			55.88	1.910	1	62.22	1.7323	8	
			59.36	1.808	1	63.05	1.712	8	
			†60.19	1.785	7	65.98	1.644	1	
			62.49	1.7252	8	69.36	1.573	2	
			†65.97	1.644	1	70.54	1.5501	3	
			†69.29	1.5746	2				

*Could not be indexed as Phase H2
+Could not be indexed as Phase J