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QUATERNARY CHALCOGENIDE-HALIDE SYSTEMS

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SUMMARY

Mixtures of silver- or copper(I)-halides with mercury(II)-chalcogenides were investigated by X-ray and thermal methods.

The phase relations of the systems AgCl-HgS and CuCl-HgS were determined. In the first system the new quaternary chalcogenide-halides $AgHg_2S_2Cl$ and AgHgSCl were found. AgHgSCl crystallizes in the orthorhombic system with the lattice parameters $a = 1024(1)$, $b = 1273(3)$ and $c = 902{,}3(5)$ pm. $CuHg_2S_2Cl$ was observed in the system CuCl-HgS. The compound crystallizes in the tetragonal system with the lattice parameters $a = 2644{,}4(3)$ and $c = 409{,}2(1)$ pm.

INTRODUCTION

Few quaternary chalcogenide-halides with group Ib and IIb metals as one component were reported in the literature. Suchov et al. (ref. 1) described the formation of Ag_2HgSI_2 in the system Ag_2S-HgI_2. Karateva et al. (ref. 2) observed "Ag_2HgSBr_2" by X-ray and thermal methods. The existence of the first compound was confirmed by Dreisbach (ref. 3), however, the compound is a metastable intermediate, at longer annealing times it decomposes into AgHgSI and AgI. Dreisbach showed also that "Ag_2HgSBr_2" of Karateva was a mixture of AgHgSBr and AgBr.

Investigations of quaternary copper(I)-chalcogenide-halides were more successfully. Guillo et al. (ref. 4,5) solved the structures of CuHgSCl and CuHgSeCl. Blachnik et al. (ref. 6) found the compounds CuHgSI and $Cu_2Cd_3S_2I_4$. However, the structures of the latter compounds and of the quaternary silver compounds have not yet been determined.

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Phase diagrams of the systems M(I)X - M(II)Y [M(I)X = Ag ,Cu; M(II) = Hg,Cd; X = Cl, Br, I; Y = S, Se, Te] are unknown, though these diagrams would reveal the best experimental conditions for the growth of single crystals of the compounds, which would allow the determination of the crystal structures.

EXPERIMENTAL

The constituent binaries AgCl, CuCl and HgS (Merck, p.a.) were dried in vacuo at 400 K. The samples for the investigation of the phase diagrams were prepared with a step width of 1 to 5 mole-% in the concentration ranges 0 - 100 mole-%. The components were mixed in an agate mortar and pressed to pills. These were sealed in evacuated silica ampoules, which were annealed for 14 days at 570 K. Annealing temperatures above the solidi were avoided to prevent decomposition of HgS. X-ray data of the reaction products confirmed that complete equilibrium could be reached by this procedure.

The apparatus and the DTA method, used in this investigation, have been described elsewhere (ref. 7). A differential scanning calorimeter (DSC) (990 thermal analyzer, Du Pont) was used for the determination of temperature effects below 900 K. The temperatures were calibrated with indium, lead and tellurium as standards. The accuracy of the thermal effects is ± 3 K and the heating rate 10 K min^{-1}.

X-ray data of powdered samples were obtained with a Guinier camera (620 Huber). High temperature X-ray data were measured with a Simon-Guinier camera, using $Cu-K_1$ radiation and SiO_2 as reference in both cases.

RESULTS

The phase diagram AgCl-HgS is shown in Fig. 1. Two compounds, $AgHg_2S_2Cl$ and AgHgSCl were observed. $AgHg_2S_2Cl$ decomposes peritectically at 715 K. A thermal effect at 680 K may indicate a phase transition of this compound, however, it was not detected in high temperature X-ray photographs. $AgHg_2S_2Cl$ exists between 33 and 40 mole-% AgCl at 500 K. This homogeneity range increases up to 640 K.

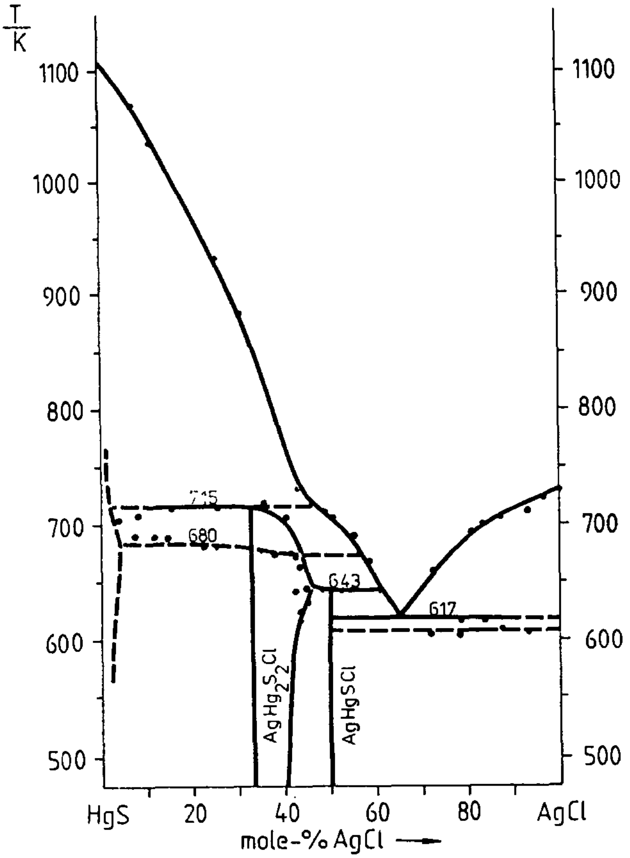

Fig. 1. The AgCl-HgS system (samples annealed at 570 K).

The second compound AgHgSCl (Table 3) decomposes peritectically into $AgHg_2S_2Cl$ and melt at 643 K. The eutectic was found at 66 mole-% AgCl and 617 K. Below the eutectic temperature weak thermal effects (dashed line) were observed in the concentration range between 50 and 97 mole-% AgCl with a maximum at 93 mole-% AgCl. Electron microprobe analysis indicated that these effects are related to an unidentified AgCl-rich compound.

The phase diagram CuCl-HgS is shown in Fig. 2. HgS (sphalerite-type) dissolves CuCl; the largest solubility is found at 750 K with 10 mole-% CuCl. $CuHg_2S_2Cl$ (Table 4) decomposes peritectically into HgS-based solid solution and melt at 751 K. The eutectic point was found at 75 mole-% CuCl and 595 K. On the halide-rich side of the phase diagram no solid solutions were observed.

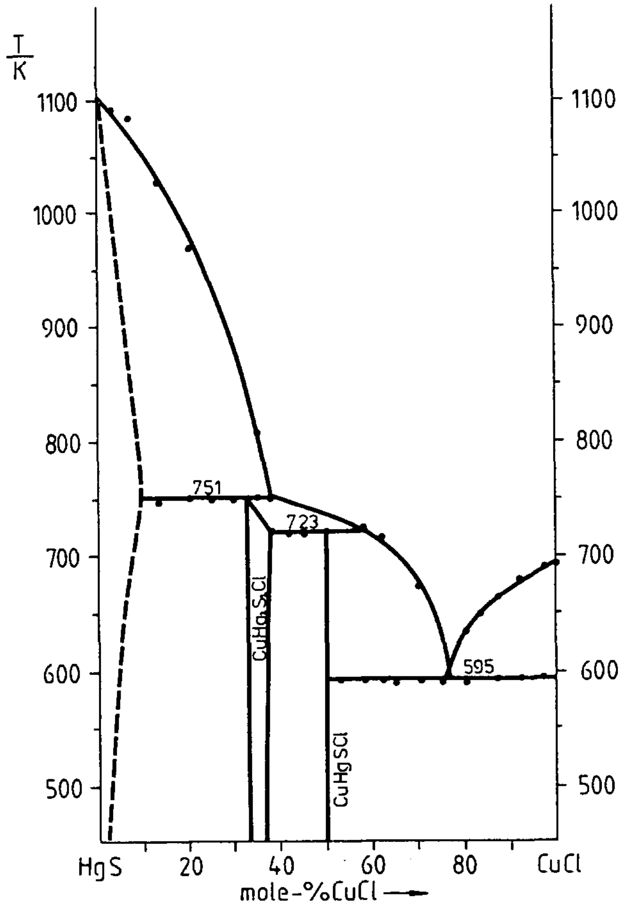

Fig. 2. The CuCl-HgS system (samples annealed at 570 K)

From X-ray experiments during the preparations we concluded, that the constituent compounds reacted rapidly to the quaternaries though the preparations were performed in the solid state. To explain this unusual fact the behaviour of unreacted mixtures was investigated by means of a differential scanning calorimeter.

The first curve given in Fig. 3 (50%) is produced by a DSC-measurement of a AgHgSCl sample prepared from AgCl and HgS by reacting the components at 570 K for 14 days. It has one endothermic thermal effect, due to the peritectic decomposition of AgHgSCl at 643 K.

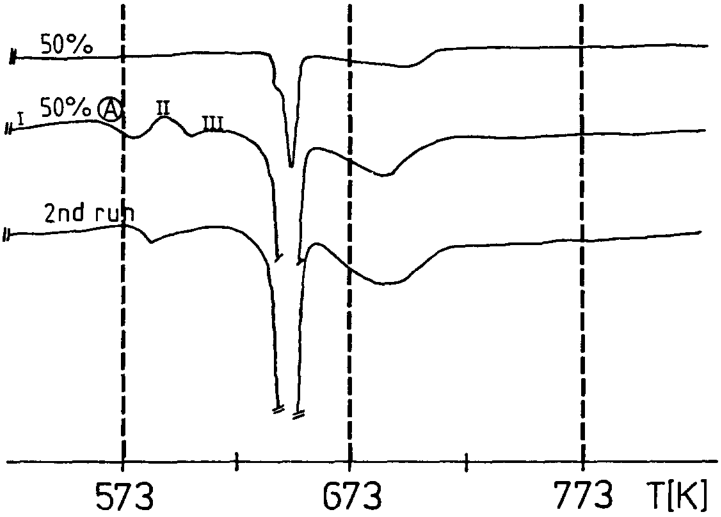

Fig. 3. DSC-curves of AgHgSCl samples

TABLE 1

Results of DSC-experiments with AgCl-HgS mixtures in a 1:1 ratio.

	T [K]	colour	X-ray pattern
I	530	red, small yellow areas	AgCl, HgS, few AgHgSCl
II	593	yellow, small red areas	AgHgSCl, traces of HgS and AgCl
III	610	yellow	AgHgSCl

The second curve shows the thermal behaviour of unreacted AgCl-HgS mixture of the same composition. In order to identify the thermal effects of this curve, separate samples of this powder were heated in independent experiments to the temperatures, given in Fig. 3 and quenched to ambient temperature. X-ray experiments were performed after this procedure (Table 1).

The X-ray data reveal that after heating to 550 K (I) the powder consists of unreacted AgCl, HgS and some yellow AgHgSCl. The latter compound and traces of AgCl and HgS are observed after heating to 590 K (II). At 610 K (III) the reaction is finished. The X-ray patterns of AgCl and HgS have disappeared.

With the aid of these data the DSC-curve of the unreacted sample can be interpreted. The endothermic peaks at 575 and 610 K belong both to the same endothermic effect whith a maximum at 585 K. The endothermic peak is generated by the metastable eutectic between unreacted AgCl and HgS. Its equilibrium line can be constructed by extrapolating the liquidi, starting at HgS, respectively AgCl. The temperature of their intersection (575 K) is approximately identical to the temperature of the endothermic effect in the DSC-experiment (585 K). This eutectic leads to the formation of melt, which increases the velocity of the reaction. The formation of AgHgSCl is exothermic, the connected thermal effect superposes the eutectic effect between the unreacted AgCl and HgS, leading to the dublett in the DSC-run.

After the first run of the unreacted powders was observed, a second DSC-experiment was performed. This measurement is shown in the third curve, which is nearly identical with curve 1. The weak endothermic effect at 585 K indicates that the reaction between AgCl and HgS is not completely finished after the first heating.

Similar effects are revealed by the DSC-curves of $AgHg_2S_2Cl$ mixtures, shown in Fig. 4. The first run (33 %) is produced by $AgHg_2S_2Cl$, prepared from the powdered components at 570 K for 14 days. The second curve (33 % A) shows the thermal behaviour of a powdered, unreacted AgCl-2HgS mixture. The third curve (2nd run) is the result of heating this same sample in a second DSC-run. The reaction is nearly finished after the first heating.

The results of X-ray experiments, performed in the same way as those of the previous samples, are summarized in table 2.

Again a rapid exothermic reaction is observed after the appearance of metastable eutectic melt.

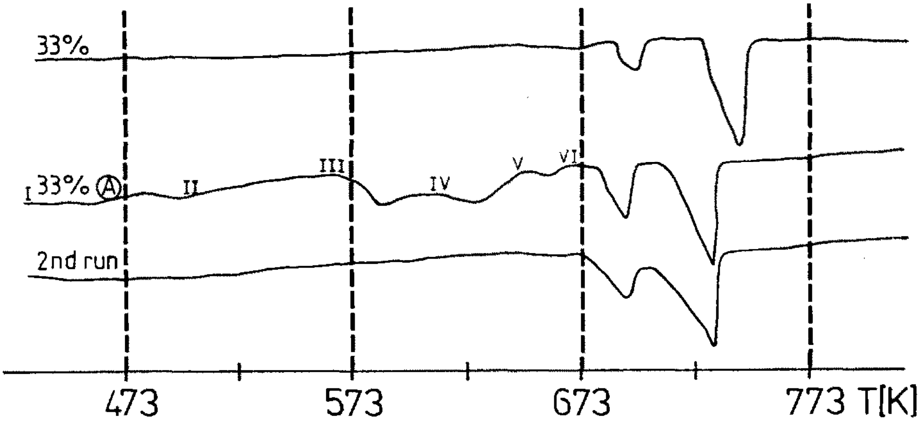

Fig. 4. DSC-curves of $AgHg_2S_2Cl$ samples.

TABLE 2

Results of DSC-experiments with AgCl-HgS mixtures in a 1:2 ratio.

	T [K]	colour	X-ray pattern
I	428	red	AgCl, HgS (wurtzit)
II	500	red, small yellow areas	AgCl, HgS (wurtzit), traces of AgHgSCl
III	563	red-orange, small yellow areas	AgCl, HgS (wurtzit), few AgHgSCl and $AgHg_2S_2Cl$
IV	610	orange	$AgHg_2S_2Cl$, HgS (wurtzit), few AgCl and AgHgSCl
V	648	orange	$AgHg_2S_2Cl$, HgS (wurtzit), traces of AgCl, HgS (sphalerite)
VI	670	orange, black areas, traces of Hg	$AgHg_2S_2Cl$, less HgS (wurtzit) as V, few HgS (sphalerite)

TABLE 3

X-ray powder data of AgHgSCl [a]

h	k	l	d_{calc} [pm]	d_{obs} [pm]	I/I_0 vis.	h	k	l	d_{calc} [pm]	d_{obs} [pm]	I/I_0 vis.
0	2	0	636 64	636.02	9	1	4	1	288.07	288.16	6
1	1	1	597.80	596.89	2	2	4	0	270.35	270.54	5
1	2	1	463.81	463.57	3	3	1	2	266.23	266.28	8
0	0	2	451.14	450.59	4	2	3	2	264.65	264.69	9
0	3	1	384.06	381.58	10	1	2	3	262.83	263.07	8
1	3	1	359.61	359.58	10	2	4	2	231.90	231.50	3
2	0	2	338.53	338.43	4	3	4	1	225.44	225.41	4
2	1	2	327.16	327.04	7	1	5	2	216.74	215.89	3
0	4	0	318.32	318.28	7	0	6	0	212.21	212.19	2
2	2	2	298.90	298.89	4	2	5	2	203.50	203.44	5

[a] *a* = 1024(1); *b* = 1273(3); *c* = 902,3(5) pm

The partial formation of AgHgSCl at the beginning of the reaction is due to the reaction of HgS with the AgCl-rich eutectic melt; the metastable eutecticum is lying at 58 mole-% AgCl.

The endothermic effect at 660 K can be explained by a partial decomposition of HgS, because at 670 K elementary mercury was detected. The endothermic effect between 610 and 650 K can probably be explained by a phase transition of HgS from the hexagonal into the cubic modification (ref. 8).

TABLE 4

X-ray powder data of $CuHg_2S_2Cl$ [b]

h	k	l	d_{calc} [pm]	d_{obs} [pm]	I/I_o vis.
2	2	0	935.06	934.94	4
3	1	0	836.35	837.54	2
4	0	0	661.19	661.23	2
4	2	0	591.38	591.02	2
5	1	0	518.68	519.58	2
4	4	0	467.53	467.50	1
5	3	0	453.57	453.99	3
6	2	0	418.17	418.39	9
0	0	1	408.86	409.25	9
2	0	1	390.62	390.68	3
2	2	1	374.62	375.03	10
6	4	0	366.76	366.76	4
4	0	1	347.75	348.20	2
3	3	1	341.89	342.06	2
8	0	0	330.59	330.49	6
5	1	1	321.10	320.91	3
6	6	0	311.68	311.38	10
4	4	1	307.77	307.70	4
7	1	1	275.97	276.11	3
6	4	1	273.01	273.09	3
8	6	0	264.47	264.49	5
10	2	0	259.34	259.39	5
8	0	1	257.07	257.03	10
8	2	1	252.35	252.35	3
6	6	1	247.87	247.83	4
8	4	1	239.60	239.59	5
8	8	0	233.76	233.78	5
10	6	0	226.78	226.65	5
8	6	1	222.06	222.15	5
12	0	0	220.39	220.33	4
10	2	1	219.00	219.11	3
10	4	1	210.51	210.55	3
0	0	2	204.43	204.36	4
11	7	0	202.84	202.73	8
2	2	2	199.71	199.65	3

[b] *a* = 2644,4(3); *c* = 409,2(1) pm

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