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THE PHASE DIAGRAM AgI-SnI_2

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SUMMARY

The phase diagram AgI - SnI_2 was investigated by x-ray and difference thermoanalytical methods. The system contains the three compounds Ag_3SnI_5, $AgSn_2I_5$ and $AgSn_4I_9$. The high-temperature phase Ag_3SnI_5 exists between 395 and 637 K and has the NaCl-structure (a = 630 pm at 430 K). $AgSn_2I_5$ decomposes at 438 K peritectoidally, $AgSn_4I_9$ at 563 K peritectically. $AgSn_4I_9$ has probably a cell of monoclinic symmetry with the lattice parameters a = 1429.3 pm, b = 446.6 pm, c = 1332.8 pm and ß = 105.48°.

INTRODUCTION

In recent years the chemistry and physics of some double salts of AgI have been intensely studied because some of these salts are good silver ion conductors. However, a systematic survey of the phase diagrams of mixtures of AgI with other main group element iodides is missing, though new phases can be expected in these systems. This paper is part of a series of investigations we have started on these systems.

First informations about the system AgI-SnI_2 were given by Alberts (ref. 1). He assumed similar phase relations as in the system AgI-CdI_2 and reported the phases Ag_3SnI_5 and $AgSnI_3$, both should decompose peritectically at 629 K resp. 576 K. Wojakowska and Terpilowski (ref. 2) obtained a phase diagram of AgI-SnI_2 from cooling curves. They observed the compounds Ag_4SnI_6, $AgSn_2I_5$ and $AgSn_4I_9$. According to their results $AgSn_2I_5$ decomposes peritectoidally at 513 K. The two other compounds are of the peritectic type with peritectic temperatures of 636 K (Ag_4SnI_6) and 566 K ($AgSn_4I_9$).

In order to clarify these differences the system AgI-SnI_2 was investigated by means of difference thermal analysis and X-ray methods.

METHODS

SnI_2 was prepared by sealing and melting stoichiometric amounts of the components (Sn, Preussag 99.999%; I_2, Merck, sublimed twice) in an evacuated silica ampoule. In the system Sn-I the phase SnI_2 is surrounded by two miscibility gaps (ref. 3), thus it was very difficult to achieve complete reaction of the components. The raw product was for that reason purified by removing SnI_4 and I_2 with a vacuum destillation at 650 K.

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Pure SnI_2 was obtained from the residue by sublimation. AgI (Degussa p.a.) was used after drying in vacuum at 400 K. Both iodides were mixed in the desired amounts for steps of 5 mole% and the mixtures sealed under vacuum in silica ampoules. The mixture were molten, homogenized by shaking and then annealed for six weeks. The annealing temperatures were chosen from preliminary experiments, usually at about 50 K below the temperatures of the eutectic or peritectic lines.

The apparatus and the method (ref. 4) of the difference thermal analysis have already been described. The heating rate was 10 K min^{-1}, the accuracy of the liquidus temperatures is $\pm$ 5 K, that of the three phase equilibria lines $\pm$ 2 K. A differential scanning calorimeter (DSC) (990 thermal analyzer, DuPont) was used for the investigation of the low temperature reactions. X-ray data of the powders were obtained with a Guinier camera (620, Fa. Huber). High-temperature X-ray data were measured by a Simon-Guinier-camera, in both cases the $CuK\alpha_1$-radiation was used.

RESULTS

The phase diagram AgI-SnI_2 (fig. 1) shows the three compounds Ag_3SnI_5, $AgSn_2I_5$ and a third phase, probably with the stoichiometry $AgSn_4I_9$.

"Ag_3SnI_5" is a high temperature phase which forms by a eutectoid reaction between ß-AgI and $AgSn_2I_5$ at 395 K and decomposes peritectically into α-AgI and melt at 637 K. The phase shows a broad region of solid solubility which terminates at lower temperatures at the stoichiometry Ag_3SnI_5. It was not possible to obtain this phase metastable at room temperature by quenching. The X-ray reflections of a high temperature photograph were indexed with the assumption of a cubic face-centered lattice and the lattice parameter a = 630 pm at 430 K. The X-ray data of this compound are given in table 1. The phase seems to be related to the high-pressure modification of AgI, which has according to Schock and Jamieson (ref. 5) NaCl-structure.

A second phase $AgSn_2I_5$ is found at lower temperatures and increased SnI_2-concentrations. The high-temperature x-ray photographs reveal that it decomposes at 438 K by a peritectoid reaction into Ag_3SnI_5 and $AgSn_4I_9$.

In the DTA experiments this peritectoid temperature could be observed between 70 and 30 mole% AgI. We concluded from this observation that a third phase exists in the AgI-SnI_2 system. This assumption is verified by the appearance of thermal effect at 563 K in the DTA experiments. The X-ray reflections of $AgSn_4I_9$ could be indexed with a cell of monoclinic symmetry and the lattice parameters of a = 1429.3 pm, b = 446.6 pm, c = 1332.8 pm and ß = 105.48°. The X-ray data of the compound are given in table 2.

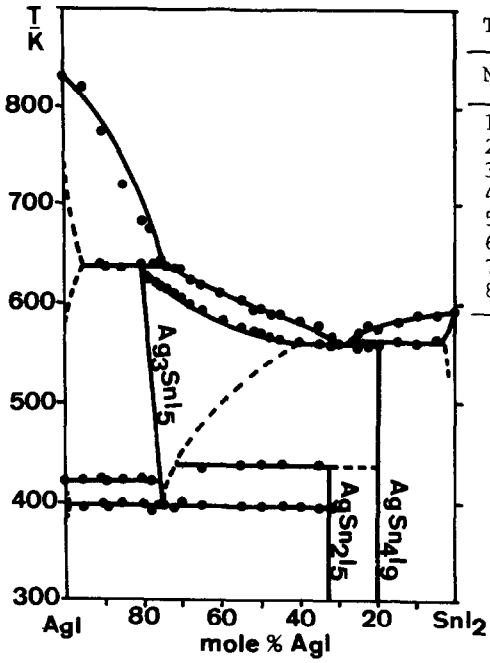

Fig. 1: The phase diagram AgI-SnI_2

TABLE 1: X-ray data of Ag_3SnI_5 at 430 K

Nr.	d_{exp}[pm]	d_{calc}[pm]	I/I_o	hkl
1	363.1	363.9	30	111
2	315.5	315.2	90	200
3	222.8	222.9	100	220
4	190.2	190.1	20	311
5	182.9	182.0	40	222
6	158.6	157.6	20	400
7	140.9	140.9	40	420
8	128.9	128.7	30	422

TABLE 2: X-ray data of $AgSn_4I_9$

Nr.	d_{exp}[pm]	d_{calc}[pm]	I/I_o	hkl
1	6.886	6.892	40	-201
		6.876		200
2	6.404	6.411	20	002
3	5.475	5.471	50	201
4	4.282	4.275	20	003
5	4.181	4.176	20	-203
6	4.132	4.137	20	-111
7	3.683	3.687	10	-112
8	3.572	3.573	30	-401
9	3.441	3.446	20	-402
		3.438	20	400
10	3.415	3.411	60	112
11	3.266	3.266	100	-204
12	3.248	3.252	100	-311
13	3.199	3.198	80	-310
14	3.143	3.148	10	-113
15	3.105	3.108	100	-312
16	2.975	2.974	80	311
17	2.825	2.832	40	-313
18	2.744	2.748	50	-404
		2.735		402
19	2.669	2.669	60	-114
		2.667		312
20	2.651	2.651	50	-205
21	2.569	2.656	10	005
22	2.465	2.461	30	114
23	2.402	2.404	5	-511
24	2.387	2.385	10	-512
25	2.360	2.355	20	313
26	2.344	2.342	10	510
27	2.293	2.297	5	-603
		2.292		600
28	2.225	2.224	40	015
29	2.217	2.217	50	-315
30	2.160	2.164	40	-604
		2.157		601
31	2.139	2.137	30	006
32	2.123	2.124	20	-221
		2.118		115
33	2.066	2.068	5	-222
		2.067		221
34	2.055	2.052	20	512
35	2.000	2.001	5	-605
36	1.967	1.967	20	222
37	1.908	1.899	5	206
		1.904		-207
38	1.892	1.894	5	-421
39	1.871	1.874	5	-422
		1.873		-420
40	1.854	1.856	5	-712

a = 1429.3 pm; b = 446.6 pm; c = 1332.8 pm; ß = 105.48°

DISCUSSION

It is known that the polarizibility of the ions play an important part in the formation of structures. Thus TiO_2 and CdI_2 have nearly the same radii ratio, but due to the different polarizibilities of the anions they crystallize in different structural types. This effect is also shown by the topology of the phase diagrams silver-halide-tin halide. Whereas the system $AgCl-SnCl_2$ (fig. 2, ref. 6) is of the eutectic type, the system $AgI-SnI_2$ contains three compounds.

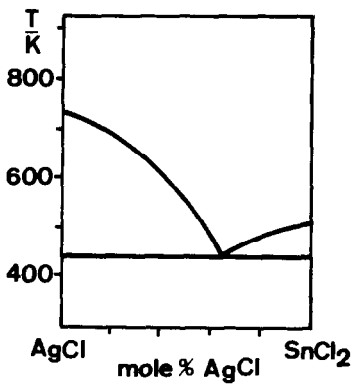

Fig. 2: The phase diagram $AgCl-SnCl_2$

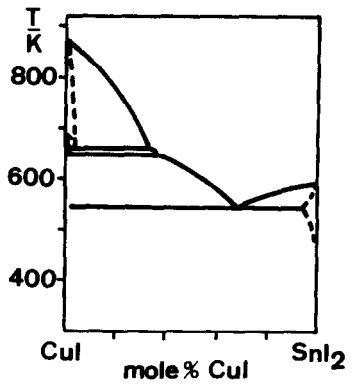

Fig. 3: The phase diagram $CuI-SnI_2$

The existence of phases in these salt mixtures is also influenced by the monovalent cation. The substitution of Ag^+ by Cu^+ leads to eutectic type phase diagrams (fig. 3, ref. 7). The formation of complex SnI_{n+2} anions by the transfer of I^- ions from Cu^+ to Sn^{2+} is not possible, because the Cu-I and Sn-I bonds are of comparable covalent character. The increased ionic character of the Ag-I bond allows such transfer in the $AgI-SnI_2$ system which explains why compounds appear in this system.

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