Thermochimica Acta, 145 (1989) 93–99
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE PHASE DIAGRAM AgI–ZnI_2

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(Received 9 August 1988)

ABSTRACT

The system AgI–ZnI_2 was investigated using thermal and X-ray methods. It contains the compound Ag_2ZnI_4 which exists in two temperature ranges. Low-temperature Ag_2ZnI_4 decomposes peritectoidally at 477 K. It crystallizes in the orthorhombic system with a = 1173.1(6), b = 1334.4(3) and c = 730.4(3) pm. At 538 K a high-temperature compound is formed by an eutectoid reaction. It probably has the composition Ag_2ZnI_4 again, and decomposes in a peritectoid reaction at 553 K.

INTRODUCTION

In recent years the research on ternary silver iodides has increased, since some of these iodides are superionic conductors at elevated temperatures. However, systematic studies of phase diagrams based on AgI are rare. This paper is part of an investigation of these systems [1].

The first complete AgI–ZnI_2 phase diagram was given by Fourcroy et al. [2] (Fig. 1). It contains the compound Ag_2ZnI_4 which decomposes peritectoidally at 469 K. The authors observed two further endothermic effects: the first at 545 K was attributed to the sublimation of ZnI_2 and the second at 595 K to the eutectic temperature of the system.

Ammlung et al. [3] stated, from conductivity and Raman spectroscopic measurements, that Ag_2ZnI_4 undergoes a phase transition at 418 K and melts incongruently at 429 K.

Recently Brightwell et al. [4] investigated samples in the AgI–ZnI_2 system by difference thermal analysis, X-ray, and electrical conductivity measurements and obtained the phase diagram given in Fig. 2. The existence of Ag_2ZnI_4 was confirmed and the temperature of the peritectic decomposition was found to be 440 K.

EXPERIMENTAL

ZnI_2 was prepared by sealing and melting stoichiometric amounts of the components (Zn, Preussag 99.999%; I_2, Merck, sublimed twice) in an

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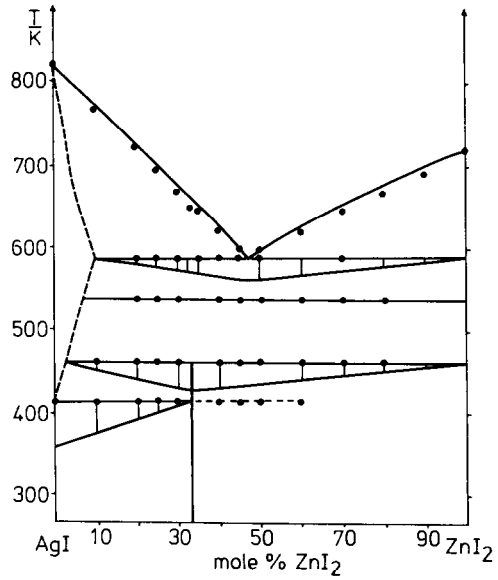

Fig. 1. The AgI–ZnI_2 system, according to ref. 2.

evacuated silica ampoule. AgI (Degussa, p.a.) was used after drying in vacuo at 400 K. For the preparation of the binary samples both iodides were mixed in the desired amounts in steps of 5 mol%, and sealed in evacuated silica

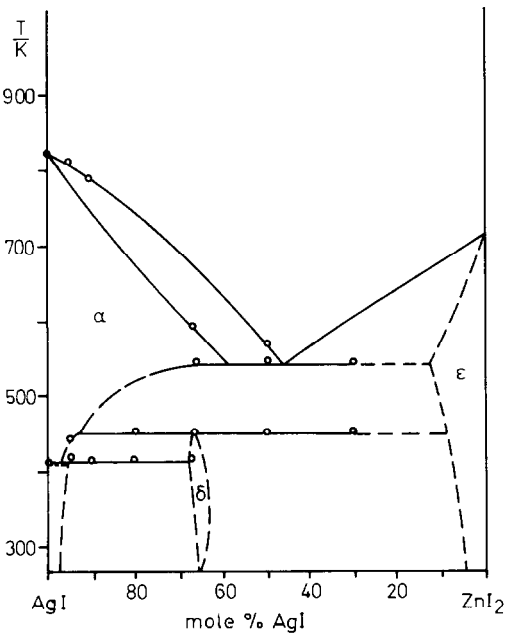

Fig. 2. The AgI–ZnI_2 system, according to ref. 4.

ampoules. The molten mixtures were homogenized by shaking, and then annealed in three series at 373, 500 and 573 K respectively for 6 weeks. Since the starting materials were very hygroscopic all operations were carried out in a glove box.

Our apparatus and the DTA method employed have been described elsewhere [5]. The heating rate was usually 10 K min^{-1}. The accuracy of the liquidus temperatures is ± 5 K and that of the three phase equilibria lines ± 2 K. A differential scanning calorimeter (DSC) (990 thermal analyser, DuPont) was used for the investigation of the low temperature reactions. X-ray data of the powdered samples were obtained with a Guinier camera (620, Huber). High-temperature X-ray data were measured with a Simon–Guinier camera, using Cu $K\alpha_1$ radiation in both cases.

Dilatometric measurements were performed using a Bähr Instrument (802 Automatik) with α-Al_2O_3 as a reference and heating rates of 5 K min^{-1}.

RESULTS

The phase diagram AgI–ZnI_2 is shown in Fig. 3. Ag_2ZnI_4 exists in two temperature intervals. At 477 K, the end of the first one, the low tempera-

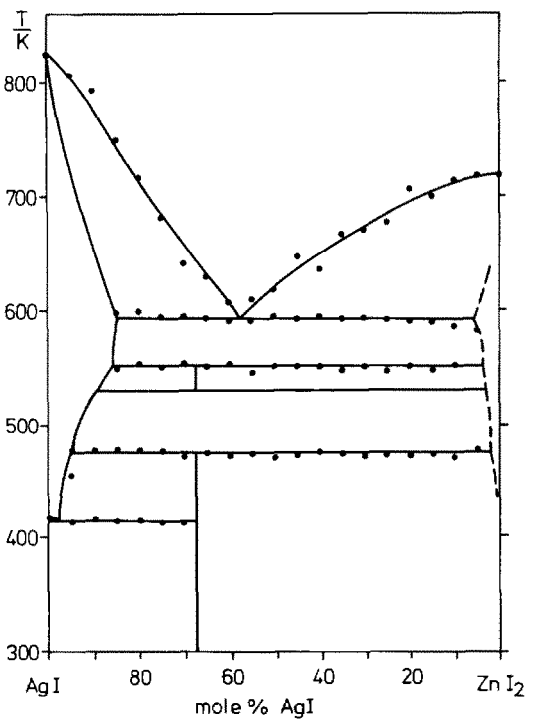

Fig. 3. The AgI–ZnI_2 system, according to this work.

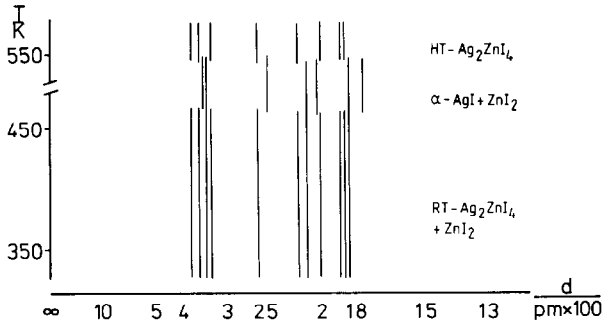

Fig. 4. High-temperature X-ray photograph of Ag_2ZnI_4.

ture form decomposes in a peritectoid reaction into β-AgI and ZnI_2. The maximum area of this decomposition peak was found at approximately 75 mol% AgI. High-temperature X-ray photographs (Fig. 4) of these samples confirmed the decomposition to AgI and ZnI_2 between 477 and 538 K.

All reflections of the low-temperature modification were indexed with the assumption of an orthorhombic lattice and lattice parameters of $a =$ 1173.1(6) pm, $b = 1334.4(3)$ pm and $c = 730.4(3)$ pm at 293 K. In the earlier investigations on Ag_2ZnI_4, only the strongest reflections were indexed by assuming a wurtzite-like structure. Fourcroy et al. [2] thus reported lattice parameters of $a = 439$ pm and $c = 733$ pm, and Brightwell et al. [4] of $a = 438$ pm and $c = 720$ pm for Ag_2ZnI_4 (Table 1).

At higher temperatures in the X-ray photographs a slightly shifted X-ray pattern of Ag_2ZnI_4 reappeared. It was not possible to quench this phase to room temperature. The compound decomposes peritectoidally into α-AgI and ZnI_2 at 553 K (Table 2).

The solubility of ZnI_2 in α-AgI is approximately 15 mol% at 573 K, the α–β AgI transition temperature is slightly decreased. The solubility of AgI

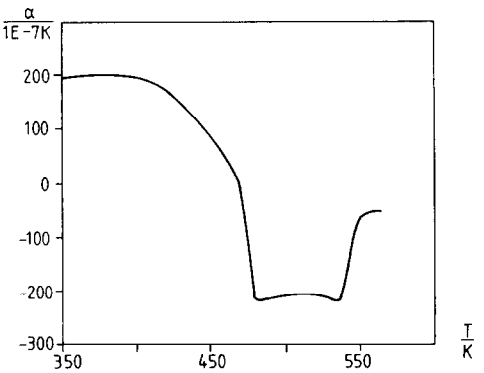

Fig. 5. Linear thermal expansion coefficient of a sample with 68 mol% AgI, annealed at 453 K.

TABLE 1

X-ray powder data of room-temperature Ag_2ZnI_4 [a]

No.	d_{exp} (pm)	d_{calc} (pm)	I/I_0	h	k	l
1	581.8	580.0	10	1	2	0
2	566.9	562.3	10	1	1	1
3	452.0	454.2	5	1	2	1
4	440.4	440.5	5	2	2	0
5	415.8	415.9	5	1	3	0
6	380.8	379.9	90	0	3	1
7	361.4	361.3	40	1	3	1
8	336.4	337.3	100	3	2	0
9	313.1	310.0	5	2	0	2
10	305.8	306.2	20	3	2	1
11	261.5	261.7	30	3	1	2
12	250.9	250.6	10	0	5	1
13	219.5	220.3	100	5	1	1
		220.2		4	4	0
14	218.7	218.5	5	1	6	0
15	204.2	204.1	20	3	1	3
16	203.5	203.3	30	4	3	2
17	190.7	190.6	20	0	7	0
		190.5		4	5	1
18	188.2	188.1	60	1	7	0
19	184.3	184.4	5	0	7	1
20	180.9	180.9	5	0	1	4
21	168.8	168.9	5	0	3	4
22	149.9	150.1	5	0	7	3
23	149.4	149.4	5	1	5	4
24	144.3	144.2	5	6	3	3
		144.2		1	9	1
		141.6		1	2	5
25	141.4	141.4	5	3	8	5
26	135.6	135.4	15	8	1	2
27	135.1	135.1	15	7	2	3
		135.0		2	3	5
28	133.8	133.8	10	0	4	5
29	127.1	127.2	5	4	6	4
		123.9		6	4	4
30	123.7	123.7	30	2	9	3
		123.5		5	9	1
31	123.4	123.4	5	8	2	3
		119.7		0	2	6
32	119.6	119.6	5	0	11	1

[a] $a = 1173.1 \pm 0.6$ pm; $b = 1334.4 \pm 0.3$ pm; $c = 730.4 \pm 0.3$ pm.

in ZnI_2 is very low. The eutectic point was found to be at 59 mol% AgI and 595 K.

The unusual temperature behaviour of Ag_2ZnI_4 was confirmed by dilatometric measurements. The linear expansion coefficient of a sample with 68

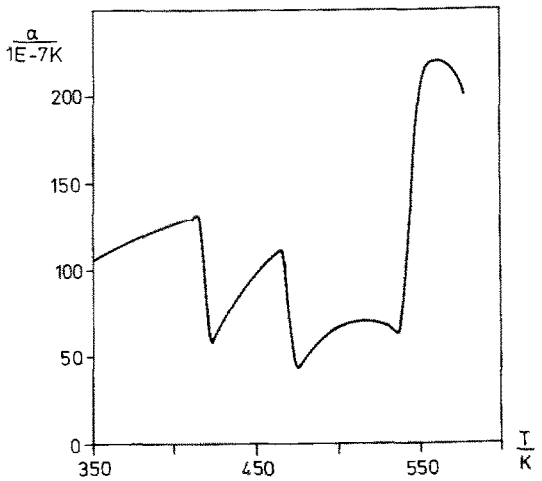

Fig. 6. Linear thermal expansion coefficient of a sample with 68 mol% AgI, heated to 550 K and cooled.

TABLE 2

X-Ray powder data of high-temperature Ag_2ZnI_4 at 550 K

No.	d (pm)	I/I_0
1	387.9	100
2	359.7	10
3	341.1	100
4	212.0	40
5	205.4	20
6	193.4	10
7	189.9	20
8	186.9	10

mol% AgI annealed for three weeks at 453 K is given in Fig. 5. The first decomposition of Ag_2ZnI_4 starts at 460 K. Between 477 and 538 K the two-phase region (α-AgI + ZnI_2) is observed. At 538 K Ag_2ZnI_4 appears again. A consecutive run of the same sample (Fig. 6) shows that on cooling to ambient temperature the rate of formation of Ag_2ZnI_4 from AgI and ZnI_2 is low; hence the back reaction is incomplete. In a subsequent heating experiment in the dilatometer the heating curve thus reveals the α–β transformation of AgI at 417 K.

DISCUSSION

The thermal effects measured in this work are identical to those of Fourcroy et al. [2]. We disagree in the interpretation of the effect at 533 K

which is not the temperature of sublimation of ZnI_2, since such an interpretation is not in accordance with the phase rule. 533 K is the temperature of decomposition of high-temperature Ag_2ZnI_4. The low-temperature form of Ag_2ZnI_4 is not a metastable modification of the high-temperature form. Samples, quenched from the melt, were annealed for 25 days at 398 K to prove this statement. Only after this period the sample showed the X-ray reflection of Ag_2ZnI_4 in X-ray experiments.

The phase transition in Ag_2ZnI_4 at 417 K, reported by Ammlung et al. [3], is easily explained by the presence of traces of unreacted AgI in his material.

In the main, all previously reported phase diagrams are in good agreement with our results. The principal difference is the existence of high-temperature Ag_2ZnI_4 which was observed for the first time.

ACKNOWLEDGEMENT

We wish to express our gratitude to the Fonds der chemischen Industrie for financial support.

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