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THE PHASE DIAGRAM AgI–PbI_2

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ABSTRACT

The phase diagram AgI–PbI_2 was investigated by X-ray and difference thermoanalytical methods. Two high-temperature compounds, one based on Ag_3PbI_5 the other on $AgPb_4I_9$, were observed. The temperature of transformation of PbI_2 into the high-temperature 12R-PbI_2 modification is decreased by the addition of AgI.

INTRODUCTION

In recent years ternary silver iodides have become of increasing interest because some are good silver-ion conductors. However, systematic studies of the phase diagrams of AgI with other main group element iodides are rare, although new compounds are to be expected in these systems. This paper continues investigations begun on these systems [1].

The first information about the system AgI–PbI_2 was given by Tubandt and Eggert [2]. They reported a compound Ag_4PbI_6 which decomposes peritectically at 671 K. Frank et al. [3] obtained the AgI–PbI_2 phase diagram by taking thermal arrests from cooling curves. They detected the compound Ag_5PbI_7 and two regions of solid solubility, one lying between 81.5 and 42.5 mol.% AgI and the other being a mixed crystal, based on PbI_2, with a maximum solubility of 15 mol.% AgI. According to their results, Ag_5PbI_7 decomposes peritectoidally at 675 K.

Recently, Brightwell investigated thoroughly the AgI–PbI_2 system [4–6] using difference thermal analysis, X-ray and electrical conductivity measurements. In the most recent version of the phase diagram he reported the formation of a high-temperature compound δ based on Ag_4PbI_6. The compound has a f.c.c. lattice with $a = 633.5$ pm. On cooling it decomposes to β-AgI and PbI_2, accompanied by the transient formation of a compound with the approximate composition Ag_2PbI_4.

In order to clarify the differences between the above results, the system AgI–PbI_2 was investigated by means of difference thermal analysis and various X-ray methods.

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EXPERIMENTAL

PbI_2 was prepared by sealing and fusing stoichiometric amounts of the components (Pb, Preussag, 99.999%; I_2, Merck, sublimed twice) in an evacuated silica ampoule. AgI (Degussa, p.a.) was used after drying in vacuo at 400 K. Both iodides were mixed in the desired amounts, in steps of 5 mol.%, and the mixtures were sealed under vacuum in silica ampoules. The mixtures were fused, homogenized by shaking and then annealed in three series at 373, 500 and 573 for six weeks.

The apparatus and the method [7] of the difference thermal analysis have already been described. The heating rate was 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 (Dupont 990 thermal analyser) was used for the investigation of the low-temperature reactions. X-ray data of the powders were obtained with a Guinier camera (Huber 620) and high-temperature X-ray data were measured using a Simon–Guinier camera. In both cases Cu $K\alpha_1$ radiation was used.

RESULTS

The phase diagram AgI–PbI_2 is shown in Fig. 1. It contains two high-temperature compounds.

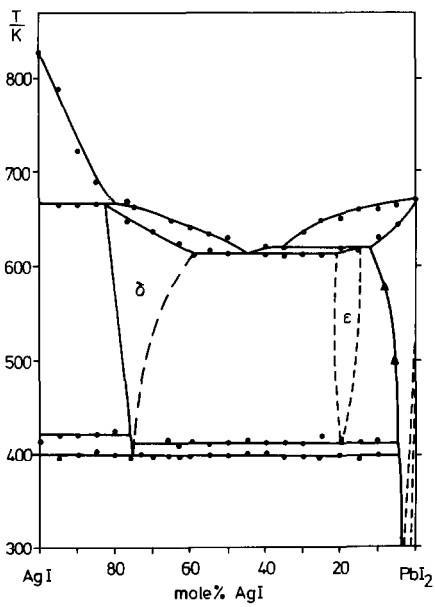

Fig. 1. The system AgI–PbI_2.

The first compound (δ) is formed by a eutectoid reaction between β-AgI and PbI_2 at 405 K and decomposes peritectically into α-AgI and melt at 671 K. The maximum area of the decomposition peak was found to be approximately 75 mol% AgI. High-temperature X-ray photographs of samples with 80 mol% AgI showed the presence of AgI between 408 and 423 K. In contrast to Brightwell's assumption we assume that the homogeneity range is centred around the composition Ag_3PbI_5. This is in agreement with the phase relations in the system AgI–SnI_2. The phase has a broad homogeneity region which stretches from Ag_4PbI_6 at higher temperatures to Ag_3PbI_5 at the lower decomposition temperature. It was not possible to quench this phase to room temperature. The reflections of a high-temperature X-ray photograph were indexed using the assumption of a f.c.c. lattice and a lattice parameter a of 628.9 pm at 423 K (compared with a value given by Brightwell [6] of 633.5 pm).

A second high-temperature compound (ϵ) was found at higher PbI_2 concentrations. The high-temperature X-ray photographs reveal that it is formed by a eutectoid reaction between δ and PbI_2 at 423 K. The compound decomposes peritectically at 625 K into melt and a mixed crystal with a 12R-PbI_2 structure. It cannot be quenched to room temperature. The reflections of the high-temperature X-ray photograph were too diffuse for

TABLE 1

X-ray data of $AgPb_4I_9$, Ag_2PbI_4 [5] and Ag_3PbI_5

$AgPb_4I_9$ (523 K)		Ag_2PbI_4	Ag_3PbI_5			
d (pm)	I/I_0	d (pm)	d_{exp} (pm)	d_{calc} (pm)	I/I_0	hkl
696.8	60		363.0	363.0	10	111
384.1	40	385.4	314.0	314.4	100	200
315.2	100	314.7	222.4	222.3	100	220
288.1	40	286.5	181.5	181.5	70	222
239.9	10		157.4	157.2	10	400
234.6	20		140.9	140.6	40	420
228.2	70		128.3	128.4	20	422
219.2	70	218.5				
217.2	30					
197.3	10					
185.5	30	184.5				
176.1	20					
164.1	20					
158.7	20	157.6				
150.3	10	148.4				
144.3	20	143.7				
139.6	30					
132.2	10					
130.4	10					

indexing of the pattern. A shift in the position of the X-ray reflections in the photographs with decreasing PbI_2 concentration indicates the existence of a homogeneity range for the compound; however, no exact width and position of this range can be given. By analogy to the system $AgI–SnI_2$ we suggest a composition based on $AgPb_4I_9$. The X-ray data of the compound at 523 K are given in Table 1.

All samples with more than 10 mol.% AgI, annealed at 373 K, consisted of β-AgI and PbI_2. The solubility of AgI in PbI_2 is low at 373 K (β-AgI was still found in samples with 95 mol.% PbI_2). It increases to approximately 5 mol.% at 500 K and 7 mol.% at 573 K. The X-ray data of PbI_2 in the mixtures, annealed at 373 K, revealed fewer lines than pure PbI_2. This effect could have been caused by long grinding of PbI_2, although we did not observe this effect in PbI_2 treated in the same way as the $AgI–PbI_2$ mixtures. A high-temperature X-ray photograph of pure PbI_2 indicates a phase transformation at 530 K, in agreement with the reported change into the 12R polytype [8–10]. There was a striking similarity between the X-ray pattern of this 12R-PbI_2 polytype and the X-ray pattern of PbI_2 mixtures annealed at 373 K. Only the 12R-PbI_2 pattern was observed in samples with AgI concentrations of between 2 and 10 mol.%, quenched from 573 and 500 K to room temperature. The transformation temperature of PbI_2 is thus substantially decreased by the incorporation of small amounts of Ag^+ in the PbI_2 structure.

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