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Note

On the phase diagrams of the systems Pb–PbI_2, PbI_2–NaI and PbI_2–ZnI_2

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Abstract

The phase diagrams of the systems Pb–PbI_2, PbI_2–NaI and PbI_2–ZnI_2 have been determined by differential scanning calorimetry. PbI_2–NaI and PbI_2–ZnI_2 are simple eutectic systems; the system Pb–PbI_2 shows an immiscibility of two liquids.

Keywords: DSC; Lead iodide; Phase diagram

1. Introduction

As part of a systematic study of the physicochemical properties of lead diiodide, we have investigated the phase diagrams of the systems Pb–PbI_2, NaI–PbI_2 and ZnI_2–PbI_2 for which the results are presented here. The high-temperature enthalpy increment measurements and the study of the vaporization behaviour of the pure compound PbI_2 are described in separate publications from our group [1, 2].

2. Experimental

The starting materials PbI_2 (99.999% purity), Pb (99.9999%) and NaI (99.999%) were purchased from Cerac. The ZnI_2 sample was prepared previously at ECN. X-ray diffraction analysis proved the samples to be pure. The samples were prepared by intimately mixing the compounds in molar ratios between 0 and 1, and encapsulating

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Table 1
The experimental results

PbI_2 in mol%	T_1 in K	T_2 in K	T_3 in K	PbI_2 in mol%	T_1 in K	T_2 in K	PbI_2 in mol%	T_1 in K	T_2 in K
$Pb–PbI_2$				$NaI–PbI_2$			$ZnI_2–PbI_2$		
0	600			0		935	0		713
2.438	600			15.066		905	14.441	607	694
4.994	600			30.175	644	857	29.864	608	666
9.973	600	638		45.243	647		44.252	606	634
20.086	601	643	658	49.930	643	764	53.239	610	
40.131	600	641	667	60.380	648		59.580	609	
60.091	600	640	674	76.427	647		68.356	610	
78.892	600	640	679	89.260	644	652	73.166	608	637
84.999	600	642	679	95.028		672	89.635	608	670
89.095	600		679	100		679	100		681
100			679						

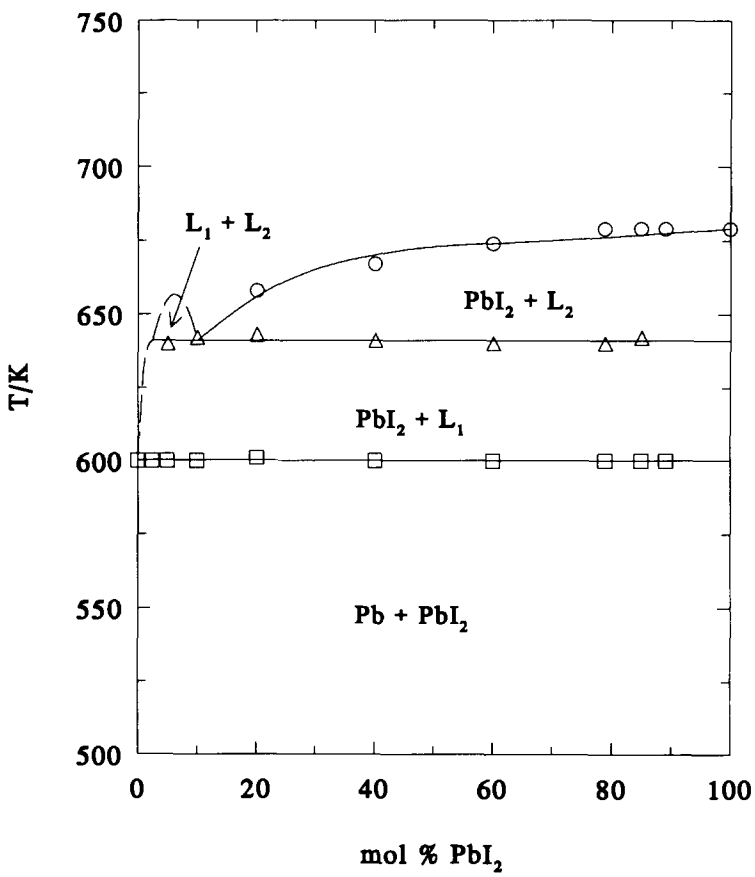

Fig. 1. The phase diagram of the $Pb–PbI_2$ system.

them in stainless steel containers. All handlings were done in an argon-filled glove-box.

The differential scanning calorimetric (DSC) measurements were made in a modified Mettler TA 13-2000 apparatus. The temperature scale of the apparatus was calibrated using the melting points of indium, tin, cadmium, lead and silver. Almost all measurements were reproducible within 2 K. The measurements were performed with heating rates of 5 or 10 K min^{-1}. The experimental results, listed in Table 1, are given as the onset temperatures in all cases.

3. The phase diagrams

3.1. $Pb–PbI_2$

The phase diagram of the $Pb–PbI_2$ system is shown in Fig. 1. Three different peaks were identified in the DSC runs which are indicated by T_1, T_2 and T_3 in Table 1. The

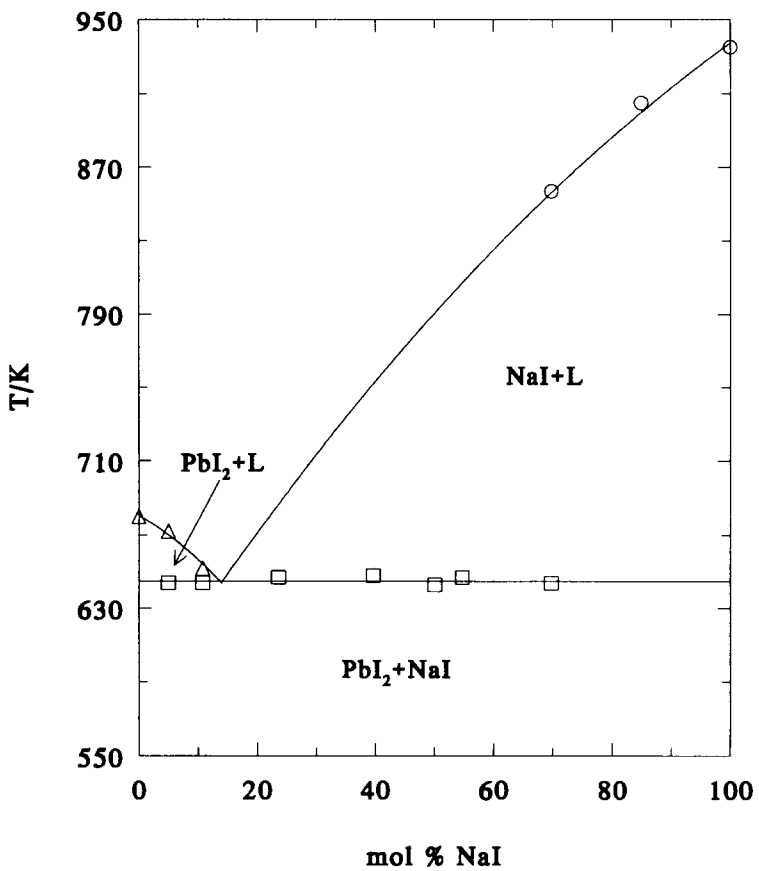

Fig. 2. The phase diagram of the $NaI–PbI_2$ system.

first peak was found at $T_1 = 600$ K, independently of the composition, and corresponds to the melting of Pb (600.652 K). T_2 corresponds to the eutectic point, which is found at 641 K and approximately 10 mol% PbI_2. The third peak, T_3, is the liquidus of the PbI_2-side of the diagram. It is evident that lead diiodide is almost immiscible with molten lead and two immiscible liquids are formed at 641 K. The immiscibility region for these liquids shown in Fig. 1 is estimated and not based on experimental observation.

3.2. NaI–PbI_2

The NaI–PbI_2 phase diagram, shown in Fig. 2, is a simple eutectic characterized by two peaks in the DSC runs. T_1 is the eutectic temperature and T_2 is the liquidus temperature; the eutectic point is found at 645 K and about 84 mol% PbI_2. This system was studied by Il'yasov and Bostandzhiyan [3] who found the eutectic at 651 K and 17 mol% Na_2I_2. Although the eutectic temperature is in fair agreement with that found

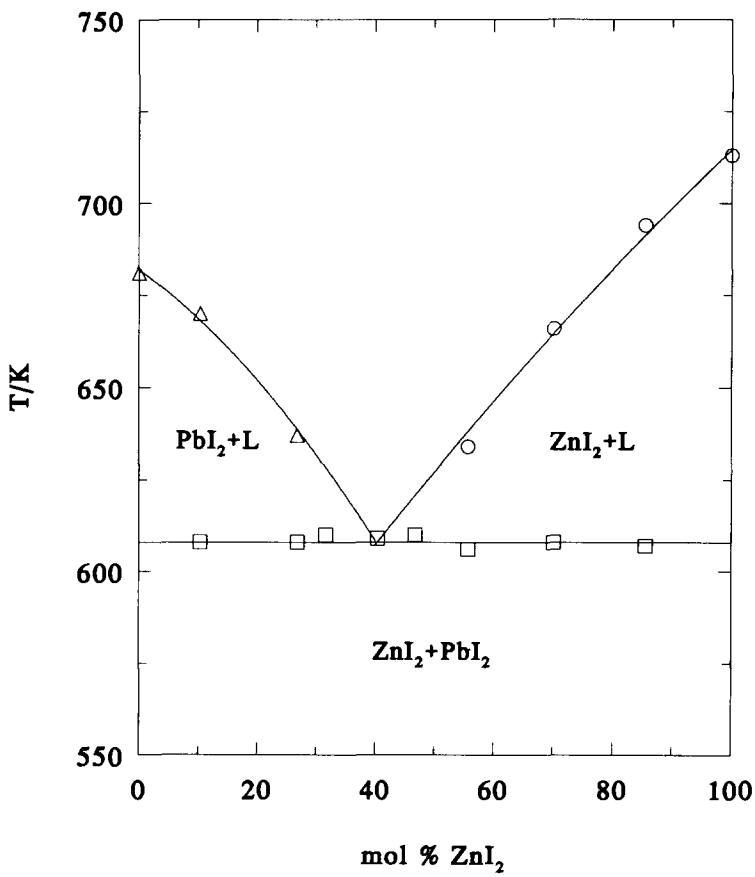

Fig. 3. The phase diagram of the ZnI_2–PbI_2 system.

here, the eutectic composition, 70.9 mol% PbI_2 when recalculated to the molecular formula NaI, differs considerably.

3.3. ZnI_2–PbI_2

The ZnI_2–PbI_2 phase diagram is shown in Fig. 3. It is also a simple eutectic. Again, two peaks were identified in the DSC runs (Table 1) where T_1 is the eutectic temperature and T_2 is the liquidus temperature. The eutectic point is found at 608 K and about 60 mol% PbI_2.

References

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