



ELSEVIER

Enthalpy increment measurements of PbI_2 : evidence for a reversible polytypic transition

R.J.M. Konings*, E.H.P. Cordfunke, R.R. van der Laan

Netherlands Energy Research Foundation ECN, P.O. Box 1, 1755 ZG Petten, Netherlands

Received 28 April 1995

Abstract

The enthalpy increment of solid and liquid PbI_2 have been measured by drop calorimetry from 528 to 763 K and the X-ray diffraction pattern has been recorded from 300 to 633 K. The calorimetric data show evidence for a reversible transition at ~ 580 K, the enthalpy difference between the two phases being small, 339 J mol^{-1} . The X-ray diffraction results show a transition of the 2H to the 4H polytype at ~ 440 K, for which the reverse reaction is not observed. The melting point of PbI_2 has been found at (679 ± 1) K by DSC, the enthalpy of fusion was obtained as $\Delta_{\text{fus}}H^\circ = 23471 \text{ J mol}^{-1}$ from the enthalpy increments of the solid and liquid phase.

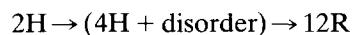
Keywords: PbI_2 ; Enthalpy increment; Drop calorimetry; Phase transition

1. Introduction

Lead diiodide shows a complex crystallographic behaviour. The compound can adopt various structures (polytypes) which consist of different stacking sequences of several basic layer units. Up to now, more than thirty different polytypes of PbI_2 have been identified of which three can be considered as basic structures [1]. These are indicated as the 2H, 4H and 12R, where H denotes hexagonal and R rhombohedral. The crystallographic data for these basic structures are summarized in Table 1.

In a previous enthalpy increment study of the isostructural CdI_2 [3] we confirmed the conclusions of Gierlotka and Palosz [4] that the energetic differences between the different polytypes of this compound are very small. In contrast to CdI_2 , in which the transformations seem to be irreversible, it has been claimed that reversible transformations occur between the different polytypes in PbI_2 . Salje et al. [1] reported that the 2H and 12R polytypes are in thermodynamic equilibrium near 367 K, although the time needed for the back-reaction 12R to 2H was of the order of weeks. Minaga [5] found that the 2H type transforms

into 12R after annealing at 423 K for 5 days, the back-transformation also taking considerable time. However, other studies [6,7] report that the 2H type transforms into the 4H type. Prasad and Srivastava [7] suggested that the transformation sequence in PbI_2 is:



Chaudhary and Trigunayat [8] concluded that the 2H type is thermodynamically stable at room temperature, that the 12R type is the stable high-temperature phase and that the 4H type is formed as a result of impurities. The available data on the phase transformations in PbI_2 are summarized in Table 2.

In the present study the thermal behaviour of PbI_2 has been investigated by enthalpy increment measurements, differential scanning calorimetry and high-temperature X-ray diffraction.

2. Experimental

The PbI_2 sample was purchased from Cerac and specified to be 99.999% pure (impurities Ca $1 \times 10^{-4}\%$, Mg $5 \times 10^{-4}\%$). X-ray diffraction analysis showed that the sample consisted of the 2H polytype only. Chemical analysis at our institute gave for the lead content $(44.75 \pm 0.15)\%$ (calculated 44.94%) and

* Corresponding author.

Table 1
Crystallographic data for the basic PbI_2 polytypes

Polytype	a (Å)	c (Å)	α	Z	V (Å ³)	Ref.
2H	4.5580	6.986		1	125.692	[1]
4H	4.5540	13.962		2	250.763	[1]
12R	14.2040		18.23	2	246.236	[2]

Table 2
The phase transformations in PbI_2

Authors	Method	T_{trs} (K)	
		2H → 4H	2H → 12R
Prasad and Srivastava [7]	annealing	533 ± 20	
Minaga [5]	annealing		423
Salje et al. [1]	annealing		367
	DSC		410–430
Palosz et al. [6]		423	
This study	XRD	440 ± 20	
	enthalpy increment		~580

for the iodine content ($55.03 \pm 0.18\%$) (calc. 55.06%). Lead was analysed by complexometric titration with standard EDTA, iodine by argentometric titration with standard AgNO_3 solution.

High-temperature X-ray diffraction measurements in air and in helium were made with a Guinier–de Wolf camera (Cu $K\alpha$ radiation) using a few milligrams of sample pressed on a platinum grid. The heating rate was 1 K min^{-1} .

The enthalpy increments were measured in an isothermal diphenyl ether drop-calorimeter, as previously described by Cordfunke et al. [9]. The sample was purified before use by heating at 400 K in purified argon. For the experiment 8.02939 g of PbI_2 was enclosed in a quartz capsule of 1.02939 g. The capsule was then heated in a three-zone furnace whose temperature is measured to $\pm 0.1 \text{ K}$ with a calibrated Pt to (Pt + 10 mass% Rh) thermocouple. After a thermal equilibration time, the capsule is dropped into the calorimeter where the energy of the sample plus the quartz melts solid diphenyl ether which is in equilibrium with its liquid in a closed system. The resulting volume increase of the ether is measured by weighing the displaced mercury. The enthalpy contribution of the capsule material was determined separately. The ratio of heat input to mass of mercury making the volume increase is a constant which is obtained by calibration with sapphire (NBS standard reference material No. 720).

Differential scanning calorimetry (DSC) measurements were made in a modified Mettler apparatus (type TA 2000) using a stainless steel container. The temperature scale of the apparatus was calibrated

using the melting points of indium, tin, cadmium, lead and silver.

3. Results

3.1. X-ray diffraction

The high-temperature X-ray diffraction measurements show that the thermal behaviour of PbI_2 in air and in helium is identical: upon heating from room temperature to 633 K a change in the X-ray pattern occurs at $(440 \pm 20) \text{ K}$, where a new phase appears. The most distinct d values of this phase were found at about 3.80, 3.00 and 1.875, indicating that this phase is the 4H polytype. However, lines due to the 2H type do not disappear completely. During heating of the sample for 5 h at 633 K the fraction of 4H further increased. Subsequent cooling to room temperature shows that the intensities of the 2H type slightly increase but the 4H type remains abundantly present.

These observations indicate that the 2H → 4H transition, in forward as well as backward direction, is very slow and that the crystalline state after rapid cooling to room temperature, as is applied in the enthalpy-increment measurements, is probably a mixture of the 2H and 4H polytypes.

3.2. Calorimetric measurements

The results of the drop calorimetric measurements are listed in Table 3. The plot of the enthalpy increment versus temperature (Fig. 1) shows only one discontinuity which is due to the melting of PbI_2 . Fig. 2 shows a plot of the reduced enthalpy increment of solid PbI_2 from which it is evident that the results for the solid phase fall into two groups, irrespectively of the thermal history of the sample. This implies that a reversible transformation occurs for which the transition temperature is estimated at about 580 K. Since the X-ray diffraction data show that the 2H → 4H occurs at much lower temperature, it is most likely that the nature of the transition is a transformation to the 12R polytype.

The enthalpy increment data below 580 K have been fitted to the polynomial:

Table 3
The experimental enthalpy increments of $\text{PbI}_2(\text{s,l})$

T (K)	$\{H^\circ(T) - H^\circ(298.15 \text{ K})\} (\text{J mol}^{-1})$		δ (%)
	Experimental	Calculated	
496.4	15499	15452	0.30
511.6 ^{a,c}	16433	16643	-1.23
527.8	17866	17913	-0.27
547.7 ^{b,c}	19525	19475	0.26
557.8	20254	20268	-0.07
567.8	21160	21054	0.50
588.8	23082	23083	-0.01
619.5	25539	25521	0.07
639.2 ^c	27042	27111	-0.26
649.0	27977	27910	0.24
666.0	29294	29308	-0.05
685.0	31954	-	-
702.4	56157	56309	-0.27
721.4	58596	58437	0.27
743.0	60992	60858	0.22
762.5	62903	63043	-0.22

^a Mean of two determinations; ^b thermal equilibration time 20 h; ^c measured after melting of the sample.

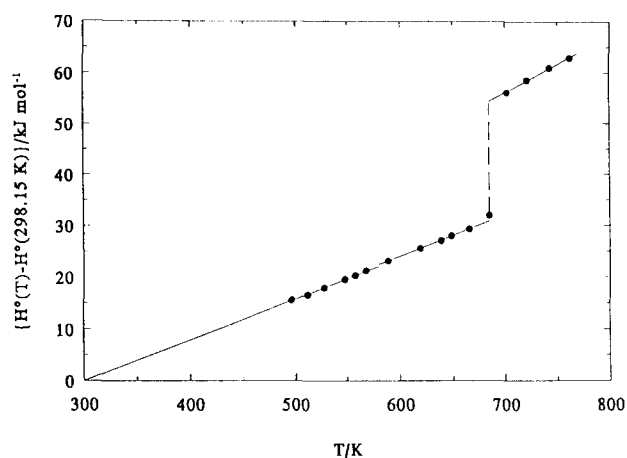


Fig. 1. The enthalpy increment of PbI_2 .

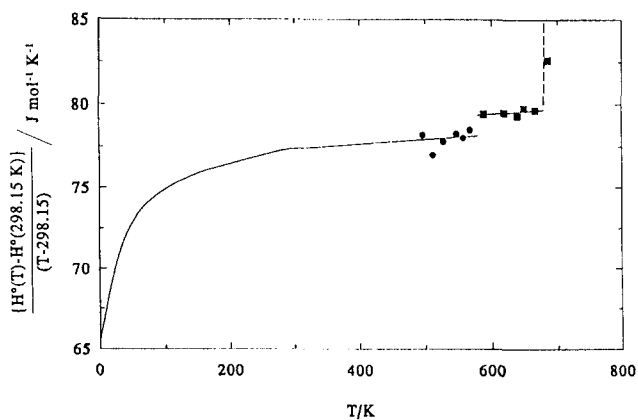


Fig. 2. The reduced enthalpy increment of $\text{PbI}_2(\text{s})$.

Table 4
The melting point of PbI_2

Run	heating rate (K s^{-1})	T_{onset}	T_{top}
1	5	679	690
	5	678	695
2	15	679	691
	15	678	688
3	10	680	688
	10	680	688
	15	681	691

$$\{H^\circ(T) - H^\circ(298.15 \text{ K})\} / \text{J mol}^{-1} = 75.7235(T/\text{K}) + 2.74446 \cdot 10^{-3}(T/\text{K})^2 - 22820.9$$

applying $C_p^\circ(298.15 \text{ K}) = 77.36 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\{H^\circ(T) - H^\circ(298.15 \text{ K}) = 0$ at 298.15 K as boundary conditions. The value for C_p° at 298.15 K has been derived from the low-temperature heat capacity measurements by McBride [10], which were kindly supplied to us by Prof. Edgar F. Westrum Jr.

The data between 588.8 and 666.0 K have been fitted to:

$$\{H^\circ(T) - H^\circ(298.15 \text{ K})\} / \text{J mol}^{-1} = 76.3237(T/\text{K}) + 3.42420 \cdot 10^{-3}(T/\text{K})^2 - 23060.3$$

By combining the above equations we obtain for the enthalpy of transition $\Delta_{\text{trs}}H^\circ(580 \text{ K}) = 339 \text{ J mol}^{-1}$.

The enthalpy increment of liquid PbI_2 can be represented by:

$$\{H^\circ(T) - H^\circ(298.15 \text{ K})\} / \text{J mol}^{-1} = 112.059(T/\text{K}) - 22401.9$$

Combining the above equations we obtain for the enthalpy of melting $\Delta_{\text{trs}}H^\circ(685 \text{ K}) = 23344 \text{ J mol}^{-1}$.

The melting point has been found in the DSC runs as a sharp and reproducible peak. The results for three different runs are summarized in Table 4. We select the mean onset temperatures, $T_{\text{fus}} = (679 \pm 1) \text{ K}$. No solid-state phase transitions were observed.

4. Discussion

Salje et al. [1] concluded from DSC measurements that the enthalpy change associated with the $2\text{H} \rightarrow 12\text{R}$ transformation is $\sim 350 \text{ J mol}^{-1}$, which is in fair agreement with the value found in the enthalpy increment measurements. However, they found the transition at a much lower temperature, $T_{\text{trs}} = 400\text{--}430 \text{ K}$ in DSC measurements and near 367 K in kinetic experiments for the annealing process. The temperature in the DSC measurements is almost identical with that found by us for the $2\text{H} \rightarrow 4\text{H}$ in the X-ray diffraction study. As the starting material in both

experiments was the 2H modification, serious doubts can be raised about the interpretation by Salje et al., and it seems very likely that their data from the DSC measurements refer to the 2H→4H transformation.

The fact that the transition to the 12R modification is not observed in the X-ray diffraction experiments can be explained as follows. It is well known that the growth of polytypes is not only determined by thermodynamic rules but also by kinetic rules and the effects of impurities, stoichiometry, defect structure etc. Salje et al. [1] and Minaga [5] have shown that kinetics of the 2H→12R transformation are slow. In the enthalpy increment study a reasonable equilibration time has been applied whereas in the high-temperature X-ray study a heating rate of 1 K min⁻¹ was used, which is probably too high.

The differential scanning calorimetric experiments did not show evidence for phase transitions below the melting temperature. As shown in Table 1, the crystallographic structures of the 2H and 4H polytypes are almost identical, and, as a consequence, the difference in molar volume is small: $V/Z = 125.69 \text{ \AA}^3$ for the 2H and 125.38 \AA^3 at room temperature [1]. Such a small difference in volume is most likely to be associated with a very small energetic difference, which is probably below the detection limit of the technique as previously found for the 2H→4H transition in CdI₂ [3]. The molar volume of the 12R polytype is $V/Z = 123.12 \text{ \AA}^3$ at room temperature, about 2 \AA^3 smaller

than that of the hexagonal types. However, as discussed above, the kinetics of this transition are slow and at the heating rates applied here, the phase change is not likely to occur.

Acknowledgement

The authors wish to thank Mr. P. van Vlaanderen for the recording of the X-ray powder diffraction patterns.

References

- [1] E. Salje, B. Palosz and B. Wruck, *J. Phys. C., Solid State Phys.*, 20 (1987) 4077.
- [2] R.S. Mitchell, *Z. Kristallogr.*, 111 (1959) 372.
- [3] R.J.M. Konings, E.H.P. Cordfunke and R.R. van der Laan, *J. Alloys Comp.*, 179 (1992) 195.
- [4] S. Gierlotka and B. Palosz, *Acta Crystallogr.*, B42 (1986) 350.
- [5] T. Minagawa, *Acta Crystallogr.*, A31 (1975) 823.
- [6] B. Palosz, W. Steurer and H. Schulz, *J. Phys.: Cond. Matter*, 2 (1990) 5285.
- [7] R. Prasad and O.N. Srivastava, *Acta Crystallogr.*, B30 (1974) 1748.
- [8] S.K. Chaudhary and G.C. Trigunayat, *Acta Crystallogr.*, B43 (1987) 225.
- [9] E.H.P. Cordfunke, R.P. Muis and G. Prins, *J. Chem. Thermodyn.*, 11 (1979) 819.
- [10] J.J. McBride, *PhD Thesis*, University of Michigan, 1955.