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MELTING OF $PbBr_2$
A DSC investigation

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Abstract

The melting of $PbBr_2$ in sealed crucibles was investigated by means of DSC. Three factors were considered to affect melting point: i) impurities, ii) the bromine pressure over the $PbBr_2$, and iii) photolysis. Both crystals and powders were investigated. The peak of the melting changed after sample grinding. The bromine pressure over the $PbBr_2$ was found to cause a significant error in the determination of the melting point.

Lead bromide melts at 370.6±0.2°C. The heat of melting is 42.9±1.8 J g^{-1}.

Keywords: DSC, lead bromide, melting, systematic error

Introduction

Lead bromide ($PbBr_2$) is a material utilized for acousto-optical and electro-optical techniques. A reliable value of the melting temperature (T_m) is essential for growing single-crystals of high quality. However, handbooks of phase diagrams contain values that vary from 366 to 380°C [1]. Recent DTA measurements led to the thermodynamic melting point of $PbBr_2$ being reported as 360.4°C [2].

The two main objective of this work is to find out the sources of errors in measurements of T_m, and to use an experimental procedure without such errors in order to establish a reliable value of the melting point.

Experimental

Samples

Both single-crystals and powders of $PbBr_2$ were used. The starting material for all samples was $PbBr_2$ of Ch.P. reagent grade (sample P0). This was used for crystal growth as follows. Powder P0 was melted in a quartz ampoule. The melting was carried out under vacuum to evacuate moisture and gases. The next step was the purification of the sample from oxide phases by directional solidification repeated many times. $Pb_4O_3Br_2$ and Pb(OH)Br were crystallized as impurities [3] in ingot cover layers. These were cut off and clean ingots were used to synthesize single-crystals from the melt after the technique of Stockbarger [4].

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The procedure of modulated rotation of the growth container was used. Measurements were made on crystals synthesized at three values of Taylor's number (characterizing the intensity of forced convection) [5]: $T_a=1.6\cdot10^6$ (C1), $2.94\cdot10^6$ (C2) and $3.26\cdot10^6$ (C3). Impurity concentrations are shown in Table 1. Crystals were partly crushed for powder measurements. The notation is as follows: C1→P1, C2→P2, C3→P3.

Table 1 Results of atomic absorption analysis. Impurity concentrations in $PbBr_2$

Element	P0	P1	P2	P3
B	0.002	0.002	0.002	0.002
Ga	–	0.005	0.003	0.003
Mn	–	–	0.001	–
Ti	0.003	0.003	0.003	0.003
Cr	–	0.015–0.02	0.01	0.015–0.02
Ni	–	0.0005	0.0003	0.0001
Bi	0.001	–	–	–
Mo	0.0001	<0.0001	0.00015	0.0001
V	0.0005	0.0003	0.0005	0.0005
Zr	<0.001	<0.001	<0.001	<0.001
Cu	0.0005	0.0001	0.0003	0.0002
Co	<0.0001	<0.0001	<0.0001	<0.0001
Ag	0.0002	0.0002	0.0007	0.03
Ca	–	0.003	0.05–0.1	0.01
Fe	0.001	0.01	0.1	0.01
Mg	0.001	0.003	0.03	0.005
Si	<0.01	0.1	0.07	0.05
Al	0.0003	0.003	0.3	0.003

Ba, Be, P, Pt, Au, As, Sc, Zn, Sr, Y, Yb, K, Na and Tl were not detected

Powder PF and single-crystal CF were used to investigate how photolysis affects the melting point. Sample PF was prepared from sample P0. The latter was exposed to ultraviolet radiation for 1 h and then stored in a glass container under sunlight. Sample CF was a plate of single-crystal 1 mm thick. It was exposed to sunlight for a long time. Both PF and CF blackened.

Experiment

The measurements were carried out with a Setaram DSC-111. Samples were sealed in stainless crucibles. Sample masses are reported in Table 2. The heating rate for all

Table 2 Results of DSC measurements

Sample	Mass/ mg	T_m/ °C	ΔH_m/ J g^{-1}
Powders			
P0	55.58	365.9	39.0
P1	60.66	369.0	41.6
P2	83.39	369.3	42.8
P3	47.23	368.2	40.9
PF	59.11	365.2	40.4
Crystals			
C1	59.24	370.54	42.1
C2	84.41	370.62	43.2
C3	47.94	370.57	42.9
CF	36.64	370.40	43.4

runs was 20°C h^{-1}. A few runs were carried out in unsealed aluminum crucibles. When the calorimetric cell was opened after such an experiment, there was an evident odor of bromine.

The temperature calibration of the calorimeter was carried out by using the standard melting points of In (156.6°C), Sn (231.93°C) and Zn (419.44°C). The standard samples were also measured in sealed stainless crucibles at a heating rate of 20°C h^{-1}.

Results

An endothermic peak of $PbBr_2$ melting was registered for all investigated samples. The peaks for crystal samples are triangular in shape and correspond to the well-known DTA peak of a first-order phase transition. There is a slight deflection at the very beginning of the peaks, caused by defects in the crystal lattice [6]. The melting point (T_m) was defined as the 'onset' of the peak (see Fig. 1 for the manner in which this was defined). The results are presented in Table 2. All the T_m values for single-crystals are situated close to one another (Fig. 2).

A different situation holds for powder samples. The differences in melting point between different crystals are much less than those between a given crystal and its powder. The peaks of powder melting do not correspond to a first-order phase transition (Fig. 3). This does not allow use of the 'onset' point correctly. T_m for powder samples of $PbBr_2$ should be accepted only as rough estimates of the melting point (Table 2). The scatter of T_m for powders is much greater than that for crystals (Fig. 4).

The heat of melting was evaluated for all samples (Table 2).

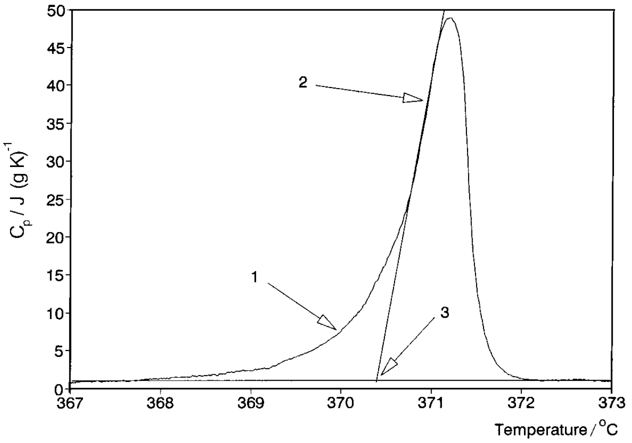

Fig. 1 DSC measurements on crystal: 1 – thermal effect of defects; 2 – linear part of the curve; 3 – 'onset' point

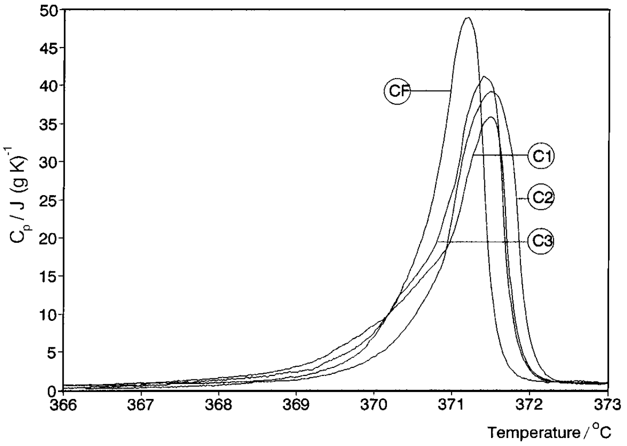

Fig. 2 Results of measurements on crystals

Discussion

The temperature of $PbBr_2$ melting measured in a DSC experiments depends, among other things, on three factors: i) impurities, ii) the Br_2 pressure over the $PbBr_2$, and iii) photolysis.

Impurities

Two samples, P0 and PF, contain oxide phases as impurities. The concentrations of these phases are difficult to measure. The phases are detected in noteworthy amount only after direct crystallization (see sample preparation). Oxide impurities

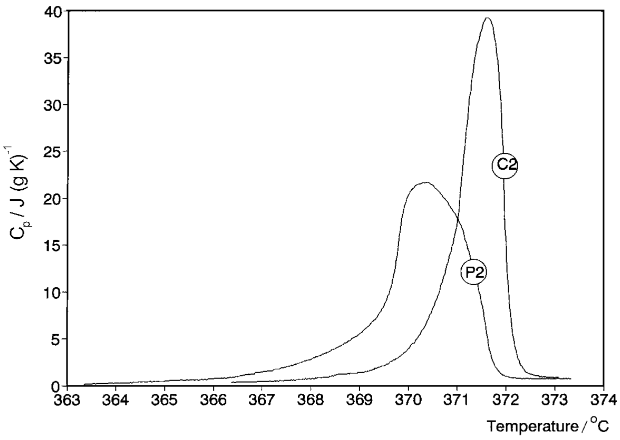

Fig. 3 Comparison between results for powder (P2) and crystal (C2)

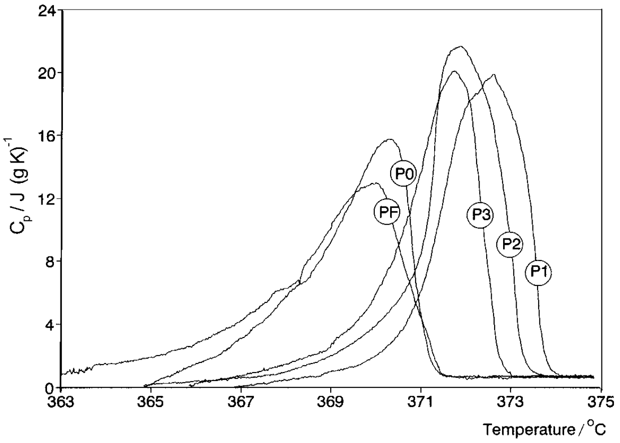

Fig. 4 Results of measurements on powders

decompose during heating in vacuum. On the other hand, heating in air can increase the oxide content. The concentration of PbO was controlled in [7]. It was found that the temperature of melting for lead halides ($PbCl_2$, $PbBr_2$ and PbI_2) decreases with increase of the PbO concentration. 1% of PbO lowers T_m by approximately 10°C.

The oxide impurities in our samples P0 and PF lowered T_m by 4–5°C.

Only impurities that form individual phases change the temperature of $PbBr_2$ melting. Element impurities do not affect the melting point. They give rise to ‘pre-melting’. Table 1 shows that the total amount of such impurities is 0.02% for P0, 0.15% for P1 and C1, 0.60% for P2 and C2, and 0.14% for P3 and C3. There is no evident relation between the total quantity of element impurities and the temperature of melting.

Br_2 pressure over $PbBr_2$

Crushing a crystal into powder changes the peak of melting significantly. The thermal conductivity of a powder is less than that of a crystal. An increase in the temperature of the peak might be expected. Our experimental results indicate just the opposite. The peak decreases in temperature and changes in shape.

We presume that the reason is an increase in the equilibrium Br_2 pressure over the $PbBr_2$. There are two arguments in support of this assumption. Firstly, after $PbBr_2$ is melted in an open crucible, an evident odor of Br_2 is detected. Secondly, during the growing of crystals, the air over the hot ingots just synthesized is reddish in colour. Unfortunately, we have found no literature data on the equilibrium Br_2 pressure over $PbBr_2$.

The partial decomposition of $PbBr_2$ is described by the reaction

$$PbBr_2 \rightarrow (1-x)\, PbBr_2 + xPb + xBr_2\uparrow$$

Such decomposition causes the $PbBr_2$ to become impure, and lowers the temperature of its melting. The greater the surface area of a sample, the higher the decomposition rate. The reaction is therefore faster for a powder than for a crystal. In [2], DTA measurements of $PbBr_2$ melting were carried out in a flow of dried nitrogen. These are very suitable conditions for decomposition. The duration of the decomposition varies with the heating rate. When the heating rate was decreased from 10 to 0.5°C min^{-1}, the temperature of melting decreased from 368 to 360.5°C. The value 360.4°C was accepted as the temperature of $PbBr_2$ melting. This is the lowest value ever published.

Our measurements show that T_m for the powder is approximately 1.5°C less than that for the crystal.

Photolysis

On exposure to light, $PbBr_2$ decomposes according to the reaction

$$PbBr_2 + h\nu \rightarrow Pb + Br_2\uparrow$$

If the bromine is released, the residual $PbBr_2$ becomes impure. Photolysis proceeds better in vacuum than in air [8]. Bromine is released only from the surface. Photolysis in the central part of a crystal is reversible. Colloidal lead is a product of photolysis. It is formed in the thin region near the surface of a crystal [9]. Photolysis evidently affects a powder much more strongly than a single-crystal. Photolysis lowers the temperature of melting by 0.7°C for PF powder, but by only 0.15°C for CF crystal.

Conclusions

Three factors that lower the melting point of $PbBr_2$ have been investigated. When these factors were avoided, the temperature of melting of $PbBr_2$ crystals was to be 370.6±0.2°C. The heat of melting is 42.0 ± 1.8 J g^{-1}.

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