ELSEVIER

18 April 1997

Chemical Physics Letters 268 (1997) 455–460

CHEMICAL
PHYSICS
LETTERS

# New differential thermal analysis study of lead halides

M. Rodová, A. Cihlář, Z. Málková, K. Nitsch

*Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Prague 6, Czech Republic*

Received 16 October 1996; in final form 17 February 1997

**Abstract**

Lead halides ($PbCl_2$, $PbBr_2$ and $PbI_2$) of various sources were examined by the DTA method in order to analyse polymorphism in these compounds. Only one peak corresponding to melting was found in the DTA curves of high-purity lead halides. This confirms that there is no phase transition in lead halides between room temperature and their melting point and therefore previous conclusions about the polymorphism in these compounds are incorrect.

## 1. Introduction

Differential thermal analysis (DTA) is a standard method used to determine phase transitions in solids. However, when using polluted samples, samples degraded by improper handling, as well as an improper measuring procedure, the results obtained lead to incorrect conclusions. The interpretation of the DTA measurements of lead chloride, bromide and iodide [1–6] is, in our opinion, such a case. In these compounds phase transitions were reported as early as 1956. In spite of the fact that their temperatures (in $PbCl_2$ at 422°C, in $PbBr_2$ at 344°C and in $PbI_2$ at 372°C) were close to the eutectic temperatures of $PbX_2 \cdot PbO–PbX_2$ mixtures (X = Cl, Br, I) (represented in the well-known phase diagrams of $PbX_2$–PbO systems [7–9]) the results are generally accepted and spread in the literature [10]. Lead halides hydrolyze partially forming lead hydroxide halides (PbOHX) both by crystallization from aqueous solution and when slightly heated in air [10,11]. Lead oxide halides ($PbX_2 \cdot PbO$) in $PbX_2$ samples are formed by the decomposition of PbOHX at an elevated temperature. Blachnik and Alberts [13], following their calorimetry measurement, considered the phase transition in $PbCl_2$ to be questionable. On the other hand, Modestova [13] proved polymorphism in $PbCl_2$ by X-ray diffraction while Berak and Dabrowiecka [4] used DTA and dilatometry. Some authors [11,14,15] have suggested that confusion exists between the phase transition and the eutectic temperature but this has met with no response.

Nevertheless, in the beginning of the nineties Posiadlo [5] again confirmed the phase transition in $PbCl_2$, and Eckstein et al. [6] that in $PbI_2$, while Singh et al. [16] even found another phase transition in $PbBr_2$, this time at a temperature of 365°C.

In our opinion the phase transitions in lead halides are suspect and the reports of their latest confirmation [5,6,16] are the reason why we decided to deal with these problems in detail. Some of our results concerning the phase transitions in $PbCl_2$ and $PbBr_2$ have already been presented elsewhere [17,18].

This Letter deals with the study of lead halides by means of the DTA method. Our aim is to determine whether the phase transitions are really present in

*PII* S0009-2614(97)00228-5

lead halides or whether confusion between the phase transition and the eutectic temperature has occurred and if so, why.

## 2. Experimental

The lead halides samples used in this study were as follows.

1. Samples C1 ($PbCl_2$), B1 ($PbBr_2$), I1 ($PbI_2$) – prepared by the precipitation of an aqueous solution of lead acetate with hydrogen halides. The precipitate was filtered, washed with distilled water and dried.

2. Samples C2, B2, I2 (high-purity materials) – prepared by the purification of materials obtained by the above mentioned method by halogenation with a gaseous mixture of halogenating agents in combination with subsequent zone-refining [19,20]. DTA samples of these refined materials were protected against any air or moisture contact.

3. Samples of commercially available materials: C3 ($PbCl_2$ for synthesis, Merck–Schuchard), B3 ($PbBr_2$, Fluka), I3 ($PbI_2$ p.a., Lachema).

4. Deliberately doped high-purity halides with PbO: C4 ($PbCl_2$ containing 2.42 wt% PbO), B4 ($PbBr_2$ containing 1.37 wt% PbO), I4 ($PbI_2$ containing 0.93 wt% PbO).

5. Sample I5 – $PbI_2$ prepared by the precipitation of an aqueous solution of lead acetate with a solution of potassium iodide.

DTA measurements of samples about 20 mg in weight were carried out using a Du Pont 990 thermal analyser in a flow of dried nitrogen in the temperature range of 200 K below and 50 K above the melting point of the halides. The heating rate was 10 K/min. The temperatures of the onsets of the peaks are presented in this Letter and were determined by means of the software for the DTA of the TA system. For the determination of the thermodynamic melting point heating rates of 0.5, 1, 2 and 5 K/min were also used.

The determination of the oxidic compounds content (represented by PbO) is based on their reaction with sulphur and iodometric titration of the $SO_2$ arising. Their absence in high-purity halides was also checked by adhesion removal of the melt to the wall of a quartz ampoule. The cation and metallic lead concentrations were determined by atomic absorption spectroscopy on a Varian model AA 30 spectrometer.

## 3. Results and discussion

Given that there is a suspicion that oxidic impurities in lead halides are the real cause of effects in DTA curves which have been interpreted as a phase transition, only high-purity lead halides without those impurities must be studied. This is why we concentrated on the purification of lead halide and the preparation of samples without oxidic compounds and protected from contamination by air moisture during manipulation. By such procedures were high-purity lead halides DTA samples prepared. The concentration of anionic impurities is so low that their melts do not wet the quartz ampoule. The PbO concentration determined by analysis is less than 0.15 wt%, but this value seems to be the sensitivity limit of the analytical method used [21]. The typical cation impurities and their concentration in the samples C1, B1, I1 (crystallized from aqueous solution)

Table 1
The results of the atomic absorption analysis

| | Impurity concentration (wt% $10^{-4}$) | | | | | |
|---|---|---|---|---|---|---|
| | Cu | Fe | Mg | Ag | Al | Pb metal |
| Sample C1 | 5 | 10 | 100 | – | 50 | – |
| Sample C2 | < 1 | 3 | < 1 | – | < 1 | 0 |
| Sample B1 | 24 | 19 | 4 | 0.5 | – | 50 |
| Sample B2 | 22 | < 1 | < 1 | 0 | – | 0 |
| Sample I1 | – | 10 | – | 3 | 5 | – |
| Sample I2 | – | 3 | – | 0 | < 1 | – |

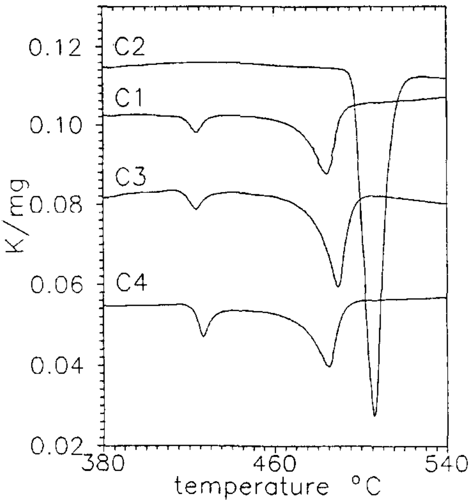

Fig. 1. The DTA curves of the $PbCl_2$ samples; C1 – $PbCl_2$ crystallized from aqueous solution; C2 – high-purity $PbCl_2$; C3 – commercial $PbCl_2$ (Merck–Schuchard); C4 – $PbCl_2$ mixed with 2.42 wt% PbO.

and the high-purity samples C2, B2, I2 are summarized in Table 1. The DTA curves of these high-purity lead halides are shown in Figs. 1–3 curves C2, B2 and I2. In these DTA curves only one sharp peak corresponding to the melting was registered – in $PbCl_2$ at 498°C, in $PbBr_2$ at 368°C and in $PbI_2$ at 407°C, and no signs of other effects are evident. Under repeated heatings at heating rates of 0.5, 1, 2 and 5 K/min additional peaks did not appear either. From these measurements the thermodynamic melting points of $PbCl_2$ and $PbI_2$ were determined as 486.4 and 396.5°C, respectively, while that of $PbBr_2$ of 360.4°C has already been reported [17]. From these results the conclusion follows that there are no phase transitions in lead halides in the temperature range studied.

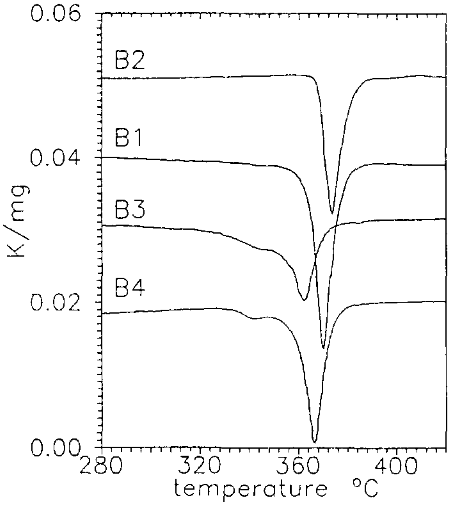

Fig. 2. The DTA curves of the $PbBr_2$ samples; B1 – $PbBr_2$ crystallized from aqueous solution; B2 – high-purity $PbBr_2$; B3 – commercial $PbBr_2$ (Fluka); B4 – $PbBr_2$ mixed with 1.37 wt% PbO.

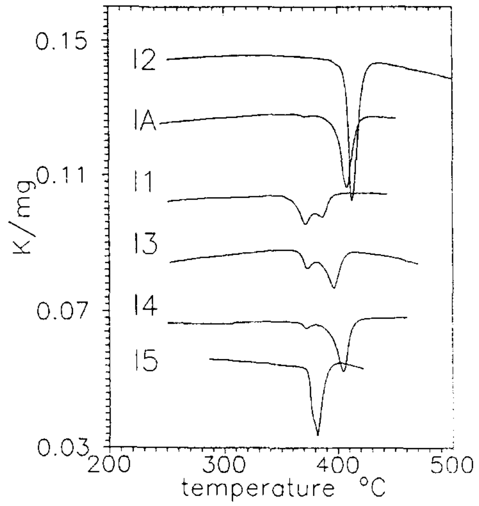

Fig. 3. The DTA curves of the $PbI_2$ samples; I1 – $PbI_2$ prepared by precipitation with hydroiodic acid; I2 – pure $PbI_2$; I3 – commercial $PbI_2$ (Lachema); I4 – $PbI_2$ mixed with 0.93 wt% PbO; I5 – $PbI_2$ prepared by precipitation with a solution of potassium iodide; IA – $PbI_2$ handled in air.

However, what are the reasons for the origin of another peak routinely found in the DTA curves of lead halides? When looking at other authors' methods of sample preparation and purification, the following was found. Modestova and Sumarokova [1,2,13] refined commercial $PbCl_2$, $PbBr_2$ and $PbI_2$ (purum) by crystallization from an aqueous solution. In our previous study [18] analysing Modestova's results [13], we demonstrated that there were some impurities in the $PbCl_2$ samples. By chemical analysis in our Samples C1, B1 and I1 (crystallized from aqueous solution), a PbO concentration of about 1% was found. The same concentration of PbO can also be expected in all $PbX_2$ prepared by this method. Berak and Dabrowiecka [4] and Posiadlo [5] dried only commercial $PbCl_2$ in a vacuum desiccator in

Table 2
Thermal data and PbO content in the samples

| Sample | Low-temperature peak (°C) | High-temperature peak (°C) | Concentration of PbO (wt%) |
|---|---|---|---|
| C1 | 418 | 469 | 1.5 |
| C2 | – | 498 | < 0.15 |
| C3 | 418 | 478 | 1.76 |
| C4 | 422 | 471 | 2.42 |
| B1 | 340 | 364 | 0.8 |
| B2 | – | 368 | < 0.15 |
| B3 | 336 | 356 | 1.2 |
| B4 | 336 | 359 | 1.37 |
| I1 | 365 | 382 | 0.45 |
| I2 | – | 407 | < 0.15 |
| I3 | 367 | 387 | 0.97 |
| I4 | 369 | 395 | 0.93 |
| I5 | 366 | – | 7.03 |

the presence of $P_2O_5$. A similar method was also used by Blachnik and Alberts [12]. Commercial lead halides (our Samples C3, B3, I3) also contain oxidic compounds. According to our chemical analyses, the concentration of PbO in these samples was 1.76, 1.2 and 0.97 wt%, respectively. By drying, the residual water can be removed from the halides but the hydrolysis products remain there. Based on this analysis an assumption was formed that the samples of the previously mentioned authors [1–5,12,13] were polluted by oxidic impurities arising from the hydrolysis of $PbX_2$ during its preparation.

Therefore, in order to confirm this assumption samples of lead halides crystallized from aqueous solution, commercial samples and deliberately prepared mixtures of $PbX_2$ with PbO were measured. The DTA curves obtained are shown in Figs. 1–3, the temperatures of the onsets of peaks and PbO content in the samples are summarized in Table 2.

Fig. 1 shows the DTA curves of $PbCl_2$ samples. While in the DTA curve of the C2 sample there is only one sharp peak, in the curves of the other samples (C1, C3, C4) there are always two peaks. The higher temperature peaks correspond to the melting and their temperature, area and shape of onset are changed depending upon the origin of the sample. The temperature of the second peak in curves C1, C3, C4 is approximately constant for all the measured samples.

The measured DTA curves of the $PbBr_2$ samples are shown in Fig. 2. Only one sharp peak was found in the DTA curve of pure $PbBr_2$ (B2), unlike the curves of the other samples where two effects can be distinguished. The higher temperature peaks correspond to the liquidus, and their parameters are different in the individual samples. The peaks are broader and they also move to lower temperature. The temperatures of the additional peaks in curves B3 and B4 were determined as 336°C for both samples measured. The lower temperature peak of sample B1 is nearly imperceptible and its onset was determined as 340°C.

The obtained DTA curves of the $PbI_2$ samples are shown in Fig. 3. The DTA curve of pure $PbI_2$ (I2) exhibits only one peak, corresponding to melting, while in the I1, I3, and I4 DTA curves two peaks are evident. Also in this case, the temperature of the liquidus depends on the origin of the samples whereas the temperature of the additional peaks is approximately the same. In the curve of sample I5 due to the high concentration of oxidic compounds (7.03 wt% of PbO) only one peak expressing both effects – eutectic temperature and liquidus, is evident. For some samples, especially pure ones (more than fifty zone passes), we found that the peak of melting is broader with a more gradual start (Fig. 4, curve I-HP) than that with about thirty zone passes (I2). An attempt at separating this peak and distinguishing

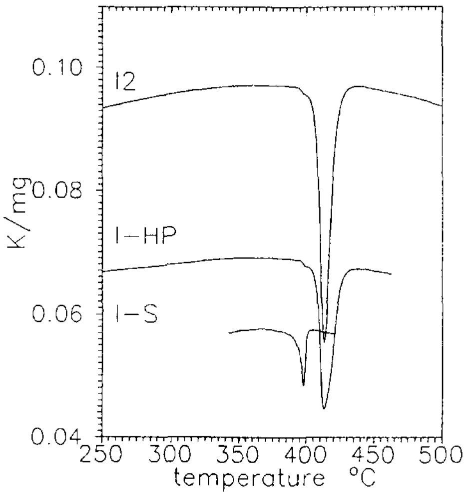

Fig. 4. The DTA curves of the $PbI_2$ samples; I2 – pure $PbI_2$ (thirty zone passes); I-HP – pure $PbI_2$ (fifty zone passes); I-S – sample I-HP measured at a heating rate of 2 K/min.

two effects by reducing the heating rate into 2 K/min failed – curve I-S. Nevertheless, further investigation of this problem is in progress.

Additional peaks appear only in the DTA curves of the samples, surely mixtures of $PbX_2$ and their oxidic compounds, formed either naturally by hydrolysis or artificially by doping. The onset temperatures of the lower-temperature peaks of the individual halides studied are nearly the same and this allows us to state that they are caused by the same reason: they represent the eutectic temperatures of the $PbX_2$–$PbX_2 \cdot PbO$ mixture and not phase transitions.

The existence of the phase transition in $PbBr_2$ at 365°C has already been tested; it has not been confirmed [17].

As only little is well-known about the hygroscopicity of high purity lead halides the influence of air moisture on these compounds was also studied. The measurements of $PbCl_2$ and $PbI_2$ showed that the little traces of moisture and air adsorbed have a strong influence on the DTA measurement. The DTA curve of high-purity $PbCl_2$ coming in contact with air shows one sharp peak on the first heating, but on the second heating another smaller peak appears and the peak of melting changes its area and moves to a lower temperature (Fig. 5, curve A1). These DTA curves as well as those of $PbCl_2$ samples kept from one day to two weeks in air are shown in Fig. 5. Increasing the time during which the $PbCl_2$ sample was kept in air, the DTA curve becomes more complicated; other peaks can be recognized in the curves of samples kept in air for 8 days or more. Posiadlo [5] also found three peaks in the DTA curves of $PbCl_2$ and its mixture with PbO. However, according to our results, this does not confirm the presence of the phase transition in $PbCl_2$, it only suggests a poor purity of the $PbCl_2$.

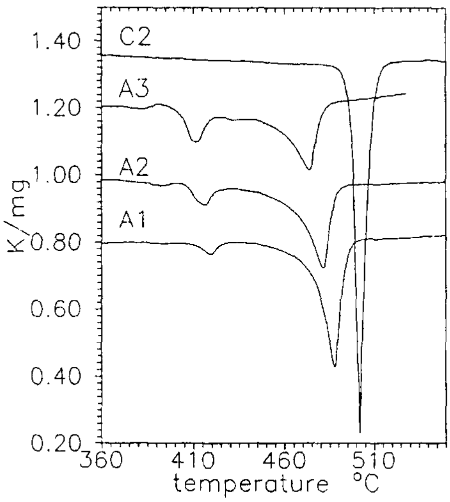

Fig. 5. The influence of moisture and air on $PbCl_2$; C2 – high-purity $PbCl_2$; A1 – pure $PbCl_2$ handled in air; A2 – sample A1 after 8 days in air; A3 – sample A2 after 6 days in air.

High-purity $PbBr_2$ is not hygroscopic and no changes in the DTA curves of $PbBr_2$ kept in air were observed in comparison with $PbCl_2$.

The same study performed with high purity $PbI_2$ shows that it is also hygroscopic. In the DTA curves of $PbI_2$ coming in contact with air (Fig. 4, curve IA) an additional peak was registered. This can explain the effect at a temperature of 372°C found in the DTA curves of $PbI_2$ by Eckstein et al. [6] provided that their samples came in contact with air.

## 4. Conclusions

This Letter presents new results achieved in the investigation of lead halide phase transitions by means of the DTA method. Only one peak corresponding to the melting point was found in the DTA curves of all the samples of the high-purity lead halides prepared and measured under conditions of the absolute elimination of both moisture and air contact. On the contrary, two peaks were found in the curves of samples polluted by adsorbed air moisture or the products of hydrolysis of lead halides. The same peaks were also found in the DTA curves of samples deliberately polluted by PbO. The results obtained in this study confirm that there are no phase transitions in lead halides in the temperature range studied and the additional lower temperature peaks express an actual eutectic temperature of the $PbX_2 \cdot PbO$–$PbX_2$ mixture. In the past some authors [1–6] confused this eutectic temperature with a phase transition. A negligent approach to the preparation and purification of the lead halides and the samples used, an insufficient purity check of the samples and lack of verification of the results by independent methods were reasons for this confusion. The use of improper methods of lead halide preparation and purification resulted in a situation where no pure samples but rather mixtures of lead halides and products of its hydrolysis, were measured. The hygroscopicity of $PbCl_2$ and $PbI_2$ and the influence of moisture on samples were not sufficiently taken into account by these authors.

## Acknowledgements

The work was supported by grant 203/95/0202 from the Grant Agency of the Czech Republic.

## References

[1] T. Sumarokova, T. Modestova, Zh. Neorg. Khim. 1 (1956) 2027.
[2] T. Modestova, T. Sumarokova, Zh. Neorg. Khim. 3 (1958) 1635.
[3] A.P. Palkin, Ju.P. Afinogenov, Zh. Neorg. Khim. 2 (1963) 379.
[4] J. Berak, H. Dabrowiecka, Pol. J. Chem. 56 (1982) 1223.
[5] H. Podsiadlo, J. Therm. Anal. 37 (1991) 613.
[6] J. Eckstein, B. Erler, K.W. Benz, Cryst. Res. Technol. 27 (1992) 897.
[7] A. Baroni, Atti Reale Accad. Lincei 20 (1934) 384.
[8] L.M. Knowles, J. Chem. Phys. 9 (1951) 1128.
[9] H.S. van Klooster, R.M. Owens, J. Am. Chem. Soc. 57 (1935) 670.
[10] Gmelins Handbuch der anorganischen Chemie, Blei, System Nummer 47, Verlag Chemie, Weinheim, 1969.
[11] H.L. Keller, J. Solid State Chem. 48 (1983) 346.
[12] R. Blachnik, J.E. Alberts, Z. Anorg. Allg. Chem. 469 (1980) 22.
[13] T.P. Modestova, Zhur. Neorg. Khim. 5 (1960) 1655.
[14] N. Ryšavá, J. Trnka, J. Novák, D. Schultze, J. Therm. Anal. 26 (1983) 101.
[15] H.L. Keller, D. Haueis, W. Naujokat, Rev. Chem. Minéral. 18 (1981) 178.
[16] N.B. Singh, M. Gotlieb, T. Henningsen, R.H. Hopkins, R. Mazelsky, M.E. Glicksman, S.R. Coriell, G.J. Santoro, W.M.B. Duval, J. Cryst. Growth 123 (1992) 221.
[17] K. Nitsch, M. Rodová, J. Cryst. Growth 134 (1993) 386.
[18] K. Nitsch, K. Knížek, M. Rodová, Solid State Commun. 91 (1994) 611.
[19] K. Nitsch, A. Cihlář, Z. Málková, M. Rodová, M. Vaněček, J. Cryst. Growth 131 (1993) 612.
[20] K. Nitsch, V. Hampolová, M. Nikl, K. Polák, M. Rodová, Chem. Phys. Lett. 258 (1996) 518.
[21] Z. Málková, K. Nitsch, J. Novak, Anal. Chim. Acta submitted.