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Creation of metastable states during sample preparation as demonstrated for silver mercury iodide

Milan Friesel, Arnold Lundén, and Bogdan Baranowski*
Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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Sample-preparation techniques such as grinding, pressing of pellets, etc., can cause changes of the physical properties of a substance. With the choice of a suitable phase transition, differential scanning calorimetry (DSC) can be used as a very sensitive method to detect minor differences between samples, since DSC gives not only the temperature and latent heat of a phase transition but also additional information from the shape of the DSC plot. This is demonstrated for the order-disorder transition of Ag_2HgI_4 at 52 °C. The salt has been prepared in two different ways: precipitation from aqueous solutions and a solid-state reaction. The latent heat shows no significant difference depending on the preparation technique, but the DSC pattern is not the same. If the samples are remeasured after they have been treated by (hydrostatic or uniaxial) pressure, a lower latent heat is obtained, and changes can also be found in the DSC pattern. Both types of changes tend to reverse, at least partially, if the sample is cycled through the order-disorder transition, but the metastable condition remains for a long time if the sample is stored at ambient temperature. Concerning previous investigations of Ag_2HgI_4 it is obvious that existing discrepancies in the results can, at least in part, be due to undetected minor differences between the samples. This is the case also when the overall composition is very close to stoichiometric, which gives reason to suspect that similar phenomena occur also for materials other than Ag_2HgI_4.

Silver mercury iodide, Ag_2HgI_4, has an order-disorder transition at about 52 °C above which the electrical conductivity becomes of the order of 10^{-3} $(\Omega\,\text{cm})^{-1}$. Over a period of some 50 years, a large number of studies of Ag_2HgI_4 have been performed at normal pressure and there have also been some high-pressure investigations. On a whole the discrepancies between the results of various investigations tend to be larger than one might expect. We decided to apply differential scanning calorimetry (DSC) at high pressure[1] in order to improve the knowledge concerning the phase diagram of silver mercury iodide.[2]

DSC not only gives the temperature and the heat, but also additional information concerning a phase transition. Thus, the shape of a DSC peak can be influenced by pretransformation (which causes asymmetry), by partial overlapping of lying transitions, etc. In our first investigation[2] we prepared our salt by precipitation[3] using stoichiometric amounts of the solutions. Our DSC study gave two peaks, which were partly overlapping at normal pressure, a small one at 49 °C and a large one at 52 °C (given as 48 and 51 °C, respectively, in Ref. 2). The distance between the peaks became larger when the pressure was increased. However, in the range 400—460 MPa, only the large peak was obtained and this was also the case when we studied pieces of pellets that had been prepared in a uniaxial press.

DSC results that differ somewhat from ours have been obtained by Halmos and Wendlandt[4] and Akopyan and Novikov.[5] Both obtained two peaks, like we had, but their small peak was at a higher temperature than the large one. The former group, who had prepared their salt by a precipitation technique[6] very similar to ours, found that the small peak was not present when the sample was heated a second time, while our small peak is much more persistent (see below).

Akopyan and Novikov have recently reported a more extensive study[7] where they had prepared Ag_2HgI_4 by three different methods of which two were solid-state reactions and the third one concerned the growth of single crystals by evaporation of a solution. Their DSC scans of the phase transition gave one peak if the sample contained only Ag_2HgI_4, while two peaks were obtained if a second iodide was present. Extended two-component regions are formed during a solid-state reaction between single crystals of AgI and HgI_2, which is in agreement with Wagner's study of this type of diffusion-controlled reactions.[8,9]

It was thus evident both from our first study[2] and from the results of others[5] that a systematic investigation was required of how the properties of the salt depended on the chosen sample-preparation technique, on the composition of the mixture, and on the history of the sample. Obviously DSC was a sensitive and rapid method to identify the conditions of a sample. We have in this study used a Rigaku instrument. A complication is that the calibration factor of a sample holder can change by 5% or more during a period of some months. It is preferable to compare a measured latent heat both with previous measurements on the same sample and with measurements at the same occasion on some reference sample, if possible taken from the same batch. This report concentrates on the heating from room temperature of polycrystalline stoichiometric samples. A more detailed account, including cooling of samples and heating from about 35 °C, will be given elsewhere. Studies on nonstoichiometric samples, of single

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crystals, and at high pressures will also be reported separately.

Polycrystalline Ag_2HgI_4 has been prepared by precipitation[3] as well as by a solid-state reaction (SSR) between AgI and HgI_2 powder. The precipitated salt gave two peaks, while only one peak was obtained for the SSR material. This always occurred independent of the chosen temperature, i.e., independent of whether disordered α-Ag_2HgI_4 or ordered β-Ag_2HgI_4 was the primary reaction product. Stoichiometric amounts of reagent-grade chemicals were used for both procedures, and there was no significant difference to be detected between the two cases concerning the total latent heat of the order-disorder transition. X-ray powder diffraction gave the same Ag_2HgI_4 pattern, but in the case of precipitated salt one or two weak lines (002 and 110) characteristic of AgI were also present. (It might be mentioned that DSC at high pressures gives the same phase diagram for SSR salt as that for precipitated salt, with two exceptions, namely that neither the 1 J/g transition at about 49 °C nor the 0.1 J/g transition at around 380 MPa occur for the SSR salt, cf. Ref. 2.)

A large number of stoichiometric samples prepared either by precipitation or by SSR have been subject to various thermal treatments including cycling in the DSC apparatus (typical heating rates of 1 to 5 K/min and cooling rates of about 0.1 K/min), a large number of rapid temperature changes ("thermal shocks"), and prolonged storage at an elevated temperature. Both fresh and old samples have been used. On a whole, both the shape of the DSC pattern and the total latent heat are very resistant to temperature changes as well as to long storage times, but in some cases the DSC pattern did change at last.

Significant changes were observed for all samples that have been treated by either a hydrostatic (2 to 3 GPa) or a uniaxial (110 to 380 MPa) pressure. In the former case a liquid was used as pressure-transmitting medium. While the pressure was increased slowly in steps, the release to normal pressure was rapid. The most thorough study was made for four samples. They were first compared with the equal number of reference samples, of about the same weight, and a ratio of 1.00±0.02 was obtained for the enthalpies of the order-disorder transition. These series of DSC measurements were repeated after the four samples had been treated by hydrostatic pressure. Table I gives both the ratio between the pairs of samples and the ratio between measurements on the same sample after and before the treatment. The latter ratios were corrected for a certain drift of the proportionality factor of the DSC instruments during the time that had elapsed (a couple of months) since the first series of DSC measurements. The enthalpy is significantly lower for the first heating cycle after the pressure treatment, but the deficit decreased gradually for the next cycles. After a couple of cycles the average of the enthalpy was perhaps somewhat lower than what it had been before the pressure treatment, but the difference is not significant. Similar or even larger initial deficits of the latent heat were found for eight other samples of which five had instead been prepared by means of a uniaxial pressure.

In all eight cases where precipitated salt was used, the small DSC peak was not detectable for the initial heating after the pressure treatment, but it reappeared after a couple of cycles, see Fig. 1. One of the four SSR samples actually had two peaks at first, with the small one on the high-temperature side, but it vanished gradually when the sample was cycled a few times, see Fig. 2.

It is obvious from the two figures that the position of the large peak is shifted downward by the pressure treatment. Altogether four precipitated and three SSR samples have been treated by hydrostatic pressure. For the first heating cycle after the pressure treatment the displacement was -2.1 ± 0.4 K for the precipitated samples and -1.5 ± 0.3 K for the SSR ones. After a few cycles the transition temperature seemed to be stable at a level that might be slightly lower than what it had been before the pressure treatment. Thus, the remaining deficit was estimated to be of the order of -0.6 K for the four precipitated samples and perhaps -0.3 K for the three SSR samples. Neither of these "remaining deficits" is significant.

TABLE I. Influence of a treatment by hydrostatic pressure (2.3 GPa for 1 h at 25 °C) on the latent heat of the order-disorder transition. The latent heat of the treated sample is compared both with that of an untreated reference sample and with the latent heat measured for the sample before it was subject to the pressure treatment. The samples had been prepared either by a solid-state reaction (SSR) or by precipitation (prec.). The comparison is done for the first heating cycle after the treatment as well as for the average of several later cycles. The number of DSC peaks is given for the cycles before the treatment, for the first cycle afterward and for the final ones.

Preparation method	SSR	SSR	Prec.	Prec.	Average
Sample weight (mg)	18.9	75.2	18.5	66.2	
Latent-heat ratios					
First cycle (treated)/(reference)	0.915	0.879	0.910	0.867	0.90±0.02
(after)/(before)	0.914	0.905	0.896	0.902	
Later cycles (treated)/(reference)	0.963	0.953	0.953	0.983	0.97±0.03
(after)/(before)	0.961	0.982	0.938	1.023	
Peaks					
Before	1	1	2	2	
Afterward, first	2	1	1	1	
Afterward, final	1	1	2	2	

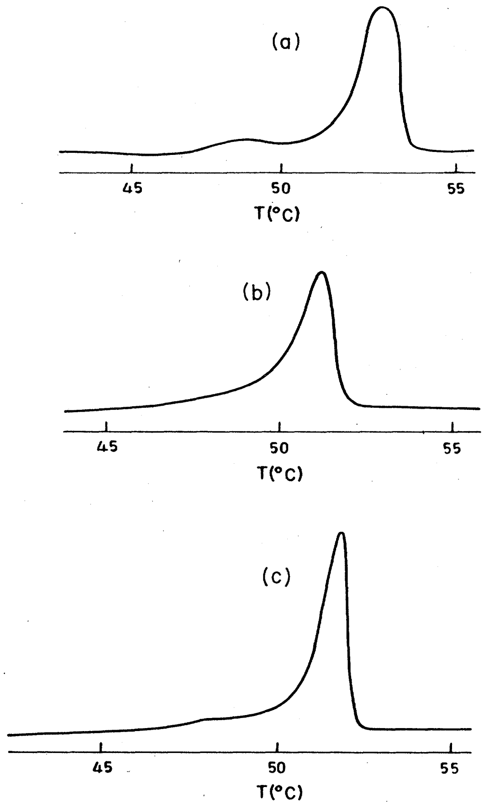

FIG. 1. DSC heating curves for an 18.5-mg sample prepared by precipitation. (a) Before treatment with hydrostatic pressure (2.3 GPa for 1 h at 25 °C). (b) First heating after the pressure treatment. (c) Fourth heating after the pressure treatment.

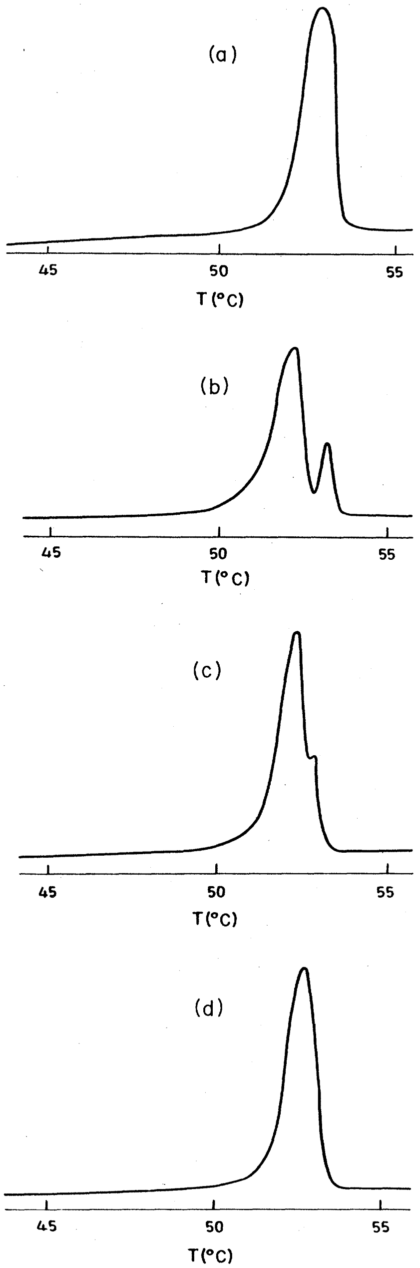

FIG. 2. DSC heating curves for an 18.9-mg sample prepared by a solid-state reaction. (a) Before treatment with hydrostatic pressure (2.3 GPa for 1 h at 25 °C). (b) First heating after the pressure treatment. (c) Third heating after the pressure treatment. (d) Seventh heating after the pressure treatment.

Also grinding in a mortar can cause a reduction in the enthalpy detected at the phase transition. We have, however, not yet studied this phenomenon in detail. A well-known example of coexistence of two phases is silver iodide at normal pressures and temperatures, and in this case grinding transfers stable β-AgI to metastable γ-AgI. These two phases can be distinguished by x-ray powder diffractrography since the stable phase is hexagonal and the metastable one is cubic. Even if we have not yet been able to identify a second component in any sample it is difficult to avoid the conclusion that treatments like pressing and grinding produce a component that remains metastable for a very long time under ordinary conditions, and which does not undergo the order-disorder transition at 52 °C. However, the transformation between the two components present in Ag_2HgI_4 is enhanced at this transition. Such an enhancement of the reaction rate at a solid-solid phase transition is often called the Hedvall effect.[10] The observed difference between the DSC patterns of precipitated and SSR samples of Ag_2HgI_4 might be due to coprecipitation of small amounts of AgI together with slightly nonstoichoimetric $Ag_{2-x}HgI_{4-x}$, where the latter lies within the small solubility range determined by Leute and Rusche.[11] This interpretation is supported by our observation that the transition temperature is about 0.5 K lower for our precipitated samples than for the SSR ones. According to Leute and Rusche the transition temperature is slightly higher for stoichiometric Ag_2HgI_4 than for nonstoichiometric salt.

We have thus found that pressing or grinding changes the properties of Ag_2HgI_4. A large number of studies of Ag_2HgI_4 are reported in the literature where pressed pellets were used, and single crystals have been used in a few cases. As examples we can take three often quoted papers on the electrical conductivity.

In his pioneering paper Ketelaar[12] gives no details of how he prepared his pellets, while Suchow and Pond[13] used 70 MPa as well as 165—275 MPa. They found that higher pressures gave pellets with higher conductivities. Neubert and Nichols[14] who used 140—275 MPa for preparing their pellets, found that both the sample history and the time schedule of measurement were very important. They found that their results agreed with neither of the mentioned earlier studies. Browall and Kasper[15] have made the only study so far of the electrical conductivity of single crystals of Ag_2HgI_4. Considerable effort has been given to identifying phases and phase transitions of Ag_2HgI_4, see, e.g., the recent study by Paić and Paić.[16] We suggest that undetected minor differences between the samples used by previous investigators can explain much of the disagreement between the results. Both the preparation technique and the heating rate during the investigation can contribute to the differences between the samples. This might well be the case also for a number of other materials than silver mercury iodide.

Note added in proof. We have above suggested the coprecipitation of small amounts of AgI and slightly nonstoichiometric $Ag_{2-x}HgI_{4-x}$. Further studies support the alternative interpretation that below 52 °C we have a mixture of AgI and stoichiometric β-Ag_2HgI_4 while above 52 °C we have disordered, nonstoichiometric α-$Ag_{2+2x}Hg_{1-x}I_4$.

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*Permanent address: Institute of Physical Chemistry, Polish Academy of Sciences, ul Kasprzaka 44/52, 01-224 Warszawa, Poland.

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