DIFFERENTIAL SCANNING CALORIMETRY AS A TOOL FOR EVALUATING PREPARATION TECHNIQUES, AND DETECTING IMPURITIES, METASTABLE STATES, ETC. IN SILVER MERCURY IODIDE (Ag₂HgI₄)

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ABSTRACT

Differential scanning calorimetry has been used for evaluating three different methods for the synthesis of Ag_2HgI_4 The information obtained from a DSC curve of the order–disorder transition at 52°C (temperature, enthalphy, shape of the DSC peak) is very sensitive to the purity of a sample Pure polycrystalline Ag_2HgI_4 can be obtained by a solid state reaction between stoichiometric amounts of powders of AgI and HgI_2 Precipitation from aqueous solutions of $AgNO_3$ and K_2HgI_4 is the most common way to prepare Ag_2HgI_4, but pure Ag_2HgI_4 is obtained only if an excess of K_2HgI_4 is present, while small amounts of AgI are coprecipitated as an impurity if stoichiometric solutions are used Two procedures for growing single crystals of Ag_2HgI_4 are described in detail, and it is demonstrated that minor deviations from the exact proportions of the constituents can result in a very impure product It is also shown that some preparation methods can result in metastable products, which can be converted into stable ones by thermal cycling

INTRODUCTION

Silver mercury iodide Ag_2HgI_4 has attracted much attention due to two changes in its properties in the vicinity of 52°C, namely a change in color from yellow to red, and a remarkable increase in its electrical conductivity The thermochromic event was first observed by Meusel in 1870 [1] In 1880 Bellati and Romanese [2] determined the transition temperature and enthalpy by means of thermal analysis and dilatometry They also found that the compound corresponded to Ag_2HgI_4 In 1903 Steger [3] established that this was the only compound formed in the system HgI_2–AgI

The first thorough investigation of the different forms of Ag_2HgI_4 and of the phase transition was made by Ketelaar [4–8] in the early 1930s He made

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TABLE 1

Transition temperature and enthalpy for the order–disorder phase transition in Ag_2HgI_4 reported by different authors

Reference	Preparation method	Analysis technique	Transition temperature (°C)	Transition enthalpy (kJ mol^{-1})
Bellati and Romanese [2]	Solid state reaction	Thermal analysis	45–50	8 05
Ketelaar [7]	Precipitation	Calorimetry	Homogeneous 40–50 7 Heterogeneous 50 7	1 21 5 23
Otsubo [13] et al	Precipitation	DTA	50 0	4 35
Brien and Palmer [14]	Precipitation	DTA	51 0	5 09
Akopyan and Novikov [15]	Solid state reaction	DSC	45 0	7 58

the first structure determination by means of X-ray powder diffraction [4,5], discovered the large change in electrical conductivity [6] and determined the latent heat [7] The low temperature β-phase was an ordered tetragonal, pseudocubic, structure with different sublattices for silver ions, mercury ions and vacancies distributed evenly, while the high temperature α-phase was instead a disordered cubic structure with silver ions, mercury ions and vacancies distributed at random Refinements of the structures made later on implied that the β-phase is tetragonal with the c dimension twice that of the a dimension, its space group is S_4^2 [9–11], while the α-phase is face centered cubic (zincblende type) with the space group T_d^2 [10–12]

Since the work of Ketelaar many studies of silver mercury iodide have been reported, utilizing a large variety of experimental techniques in order to study different properties Quite often the deviations between the results of independent investigations are larger than one would expect from the reported efforts A striking example is the transition enthalpy variation from 4 35 to 8 05 kJ mol^{-1} reported by different authors [2,7,13–15] as detailed in Table 1

Some years ago we started to study the phase diagram of Ag_2HgI_4 by means of differential scanning calorimetry (DCS) at high pressure [16] In our studies of the characteristics of the order–disorder phase transition [16–18] as well as of the electrical conductivity of the β-phase [19], we noticed a large influence of the preparation method as well as of the subsequent mechanical treatment such as grinding, hydrostatic or uniaxial pressure We have come to the conclusion that a reproducible investigation requires a systematic analysis of the different methods of preparation, and

are convinced that the basic reason for many of the discrepancies is that the histories of the samples used in the different investigations have not been identical The purpose of the present investigation is to compare different preparation methods and to give recommendations as to how pure samples with well-defined properties can be prepared

Three different methods can be distinguished for the preparation of silver mercury iodide

(1) The easiest and therefore most frequently used is a rapid precipitation from liquids, in which homogeneous solutions, usually aqueous, of suitable silver and mercury salts are put together Very fine precipitates are obtained and the details are described in several papers [20–30]

(2) Solid poly- or single crystals of silver and mercury iodides in direct contact are reacted, leading in suitable time and temperature conditions to homo- or heterogenous solids, determined by the phase diagram of the AgI–HgI_2 system [3,13,34] This is a straightforward method, used by many authors [2,3,9,31–37]

(3) The most tedious and complex method is the growth of single crystals from liquid solutions, since it is much easier to get crystals of the constituent salts than of the complex compounds The solutions can be based either on the complex K_2HgI_4 [38–40] or on hydriodic acid [41,42]

Further, a certain combination of the above three methods can be mentioned namely, one can transform polycrystalline silver iodide into silver mercury iodide by putting silver iodide in contact with an aqueous K_2HgI_4–HgI_2 solution [39] However this procedure is not advisable, because a heterogeneous mixture can easily result

For the examination of the prepared samples differential scanning calorimetry was found to be very informative [16–18], it includes both determining the transition temperature and enthalpy and studying the shape of the DSC peak To complement the analysis by DSC, X-ray powder diffraction patterns were taken for some samples

EXPERIMENTAL

A commercial differential scanning calorimeter from Rigaku (Japan) was used This instrument is of the power-compensation type. Figure 1 shows schematically the sample and reference holder The temperature of the sample and the DSC signal are recorded simultaneously with a two-pen recorder. A detailed description of the instrument is given elsewhere [43] Both the sample and the aluminum oxide used as reference are enclosed in platinum cups Following the standard procedure of DSC, the transition temperature is defined as the intersection between the extrapolated leading edge of a transition peak and the base line The area of the transition peak is measured with a planimeter and the transition enthalpy is then calculated
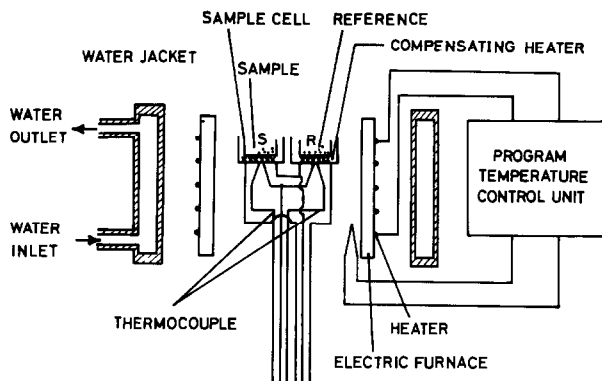
Fig 1 Schematic view of the Rigaku sample and reference holder

Proper calibration and maintenance of a DSC instrument is, of course, essential for the accuracy of the determined temperatures and enthalpies, see for example refs 44–46 and references cited therein In recent years much work has been devoted to finding materials suitable as calibration standards for DSC [45,47] For the calibration for temperature and enthalpy measurements nine high purity materials were used Figure 2 shows the temperature correction curve and Fig 3 the instrument constant for the temperature range 20–700 ° C

All chemicals used for the preparation of silver mercury iodide were of reagent grade No additional purification was carried out Essential preparation details will be mentioned for each method in the different sections below
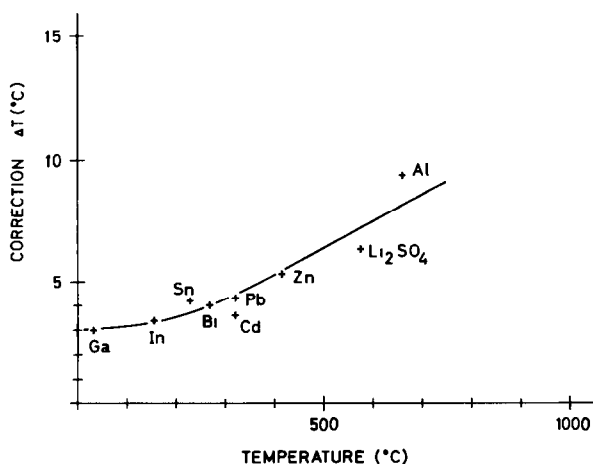

Fig 2 Temperature correction ΔT as a function of temperature for a sample and reference holder
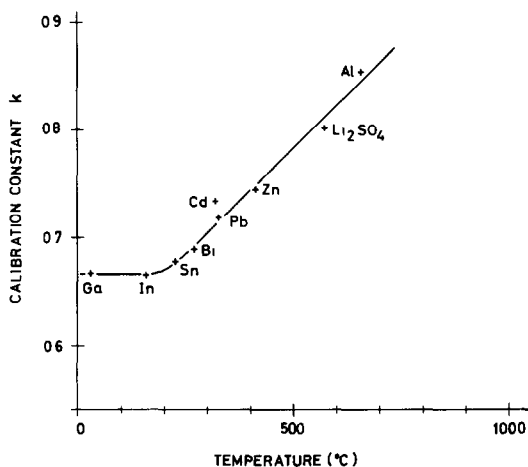
Fig 3 Instrument constant, k, as a function of temperature for a sample and reference holder

Samples of some 10–150 mg of silver mercury iodide were sealed in platinum cups Heating and cooling rates were kept at moderate values from 0 6 to 5 K min^{-1} and from 0 5 to 2 5 K min^{-1} respectively A Philips X-ray powder diffractometer provided with a conventional goniometer (PW 1050/25) and a high-temperature attachment (PW 1158) was used when searching for impurities in a limited number of samples

RESULTS AND DISCUSSION

Solid state reaction between AgI and HgI$_2$

Koch and Wagner [31,32] studied the formation of Ag$_2$HgI$_4$ from AgI and HgI$_2$ by pressing pellets against each other and leaving them in contact for sufficient time They determined the reaction constant, and that the diffusion of silver and mercury ions controls the rate with which Ag$_2$HgI$_4$ is formed by the solid state reaction Hahn et al [9] tried various other methods in vain before they succeeded in producing pure Ag$_2$HgI$_4$ by melting a stoichiometric mixture of AgI and HgI$_2$ in a glass vessel Leute and Schroder [34] pressed together single crystals of AgI and HgI$_2$ within a matrix of AgI powder They studied the kinetics of the solid state reaction by measuring the thickness of the layer of the produced α-Ag$_2$HgI$_4$ phase Leute and Rusche [33] pressed pellets of a mixture of the two salts and annealed them for a long period of time. They studied the electrical conductivity and determined the composition range of β-Ag$_2$HgI$_4$ Also Akopyan and Novikov [15,35,36] prepared Ag$_2$HgI$_4$ by pressing together single crystals of AgI and HgI$_2$. Some of the samples they obtained were not
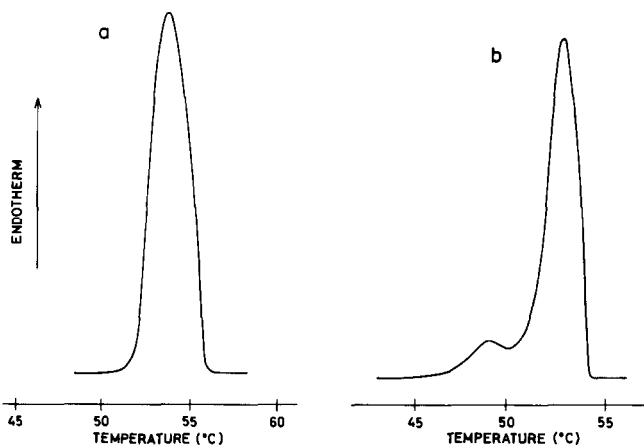
Fig 4 DSC curves of the order–disorder phase transition in Ag_2HgI_4 prepared by solid state reaction (a) Stoichiometric composition, 66 67 mol% AgI, heating rate, 1 25 K min^{-1}, DSC range, 2 mcal s^{-1}, sample mass, 118 67 mg, chart speed, 10 mm min^{-1}, transition temperature, 52 0 °C, transition enthalpy, 8 77 kJ mol^{-1} (b) An excess of 0 63 mol% of AgI (67 3 mol% of AgI), heating rate, 1 25 K min^{-1}, DSC range, 2 mcal s^{-1}, sample mass, 109 39 mg, chart speed, 10 mm min^{-1}, transition temperatures, 47 0 °C and 51 5 °C, transition enthalpy, 8 52 kJ mol^{-1}

homogeneous [36] (also see below regarding single crystals). It is of special interest to note that they studied the order–disorder phase transition by means of DSC, and that one peak was obtained if the sample had the stoichiometric composition, but two peaks if it was non-stoichiometric Schon and Schmidt [37,48] studied the kinetics of the solid state reaction between AgI and HgI_2 by means of dielectric spectroscopy and differential microcalorimetry Pellets of the two salts, corresponding to stoichiometric amounts, were pressed against each other and left to react The conductivity of the sample and the peak area of the order–disorder phase transition obtained by means of differential microcalorimetry, were measured at certain time intervals

We have prepared our samples by mixing powders of AgI and HgI_2 (reagent grade, Merck, Darmstadt) in the desired proportions The mixture was ground in a mortar and then placed in a desiccator. The normal procedure was to allow the salt to react for about one week at 60 °C, but on one occasion we instead chose room temperature and a much longer time As expected, this variation did not affect the properties of the samples

Samples obtained from the stoichiometric mixture gave only one DSC peak, upon both heating and cooling, as can be seen from Fig 4(a) and Table 2 The values obtained for the transition enthalpy and temperature are taken as reference values for our measurements

Non-stoichiometric mixtures have been prepared with an excess of either 0 7–11 7 mol% HgI_2 or 0 6–13 3 mol% AgI The transition temperatures

TABLE 2

Transition temperatures and enthalpies of the phase transition at $52\,^{\circ}C$ in Ag_2HgI_4 for samples prepared by solid state reaction (SSR) and by precipitation

Preparation	Phase transition	T_L [a] ($^{\circ}C$)	T_H [b] ($^{\circ}C$)	ΔH (kJ mol^{-1})	n [c]
SSR stoichiometric	Order–disorder	None	$52\,0\pm0\,5$	$8\,72\pm0\,07$	30
66 67 mol% AgI	Disorder–order	None	$47\,0\pm1$	$8\,39\pm0\,18$	30
Prec stoichiometric	Order–disorder	$47\,5\pm0\,5$	$51\,5\pm0\,5$	$8\,23\pm0\,14$	45
	Disorder–order	31	$45\,0\pm3$	$7\,86\pm0\,26$	30
Excess of K_2HgI_4	Order–disorder	None	$51\,5\pm0\,5$	$8\,55\pm0\,14$	10
Excess of 2 mol% $AgNO_3$	Order–disorder	$46\,5\pm0\,5$	$51\,5\pm0\,5$	$8\,07\pm0\,14$	9
Excess of 10 mol% $AgNO_3$	Order–disorder	None	$48\,0\pm0\,5$	$7\,13\pm0\,11$	5
Excess of 50 mol% $AgNO_3$	Order–disorder	None	$47\,5\pm0\,5$	$3\,31\pm0\,19$	4

[a] Small peak
[b] Large peak
[c] Number of measurements

obtained for these samples are plotted in Fig 5 as a section of the phase diagram of the system AgI–HgI$_2$ in the vicinity of the stoichiometric composition, and Fig 6 shows the measured enthalpies Each point in the figures is an average calculated for five to ten measurements made on a sample The standard deviation of the temperature measurements is $\pm0\,5$ K, and for the enthalpy it is 1–2% The transition enthalpies of Fig 6 are for heating, while those obtained for cooling are some 1–3% lower, but show the
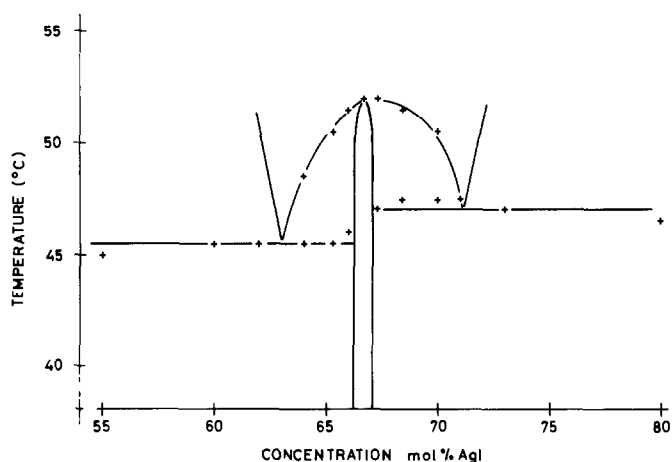

Fig 5 Phase diagram, x mol% of AgI vs T, of the system AgI–HgI$_2$ in the vicinity of the stoichiometric composition, 66 67 mol% AgI
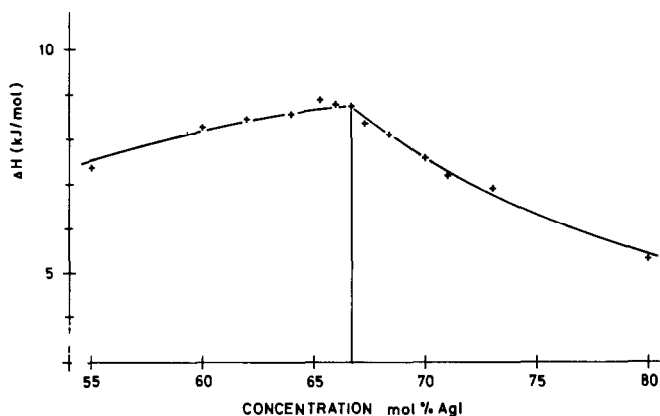
Fig 6 Enthalpy as function of concentration of AgI for the order–disorder phase transition in Ag_2HgI_4 prepared by solid state reaction

same dependence on composition The enthalpies were calculated from the area enclosed by both peaks, because it was not possible to separate them in DSC curves The transition enthalpy of the small peak was estimated to be about $0\,7$ kJ mol^{-1} of Ag_2HgI_4 for a sample with an excess of $0\,67$ mol% of HgI_2 Approximately the same value was obtained for a sample with an excess of $0\,63$ mol% of AgI

As can be seen in the phase diagram all non-stoichiometric samples in the range $64\,0$–$70\,0$ mol% AgI gave DSC curves with two peaks This also happened for cooling Figure 4(b) shows such a DSC curve obtained upon heating a sample with an excess of $0\,63$ mol% AgI The DSC curve obtained upon heating a sample with an excess of $0\,67$ mol% HgI_2 was nearly identical, the difference being that the transition temperature of the small peak was $1\,5°C$ lower That even such a small excess of AgI or HgI_2 gives two peaks means that the composition range of the ordered β-phase of Ag_2HgI_4 is extremely narrow This was pointed by Leute and Rusche [33], who observed that the lattice constants of the β-phase are independent of the overall composition of the sample They studied mixtures with different deviations from stoichiometry by X-ray diffraction An excess of $1\,67$ mol% HgI_2 was the smallest deviation investigated by them The present investigation indicates that the allowed deviation from stoichiometry is less than $0\,5$ mol% of AgI or HgI_2

All the samples with an excess of HgI_2 were investigated by X-ray diffraction In addition to the lines characteristic of the β-phase of Ag_2HgI_4, the (101), (102) and (200) lines of the room-temperature phase (red, tetragonal) of HgI_2 were also obtained For the smallest excess ($0\,67$ mol%) these lines were hardly detectable, while two peaks were evident in the DSC curve Thus, in this case, DSC might be a more sensitive technique than X-ray powder diffraction to detect minor amounts of impurity Some samples with
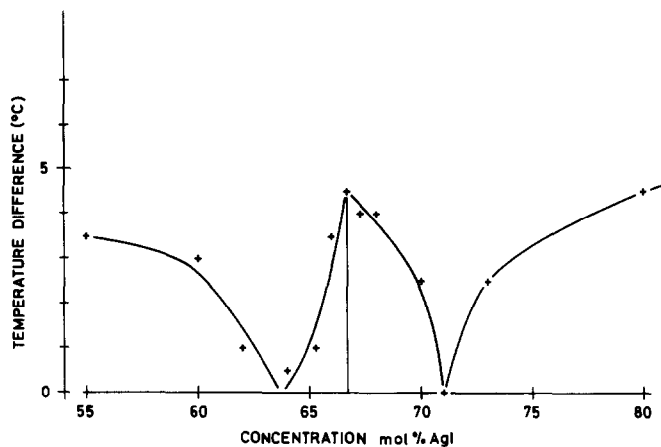
Fig 7 Hysteresis in temperature as a function of concentration of AgI for the phase transition in Ag_2HgI_4 prepared by solid state reaction

an excess of AgI were also investigated by X-ray diffraction for comparison with the patterns obtained for precipitated samples

The phase diagram shown in Fig 5 might be an improvement on that of Leute and Ruche [33], which was based on conductivity measurements The transition temperature for the stoichiometric composition is the same ($52°C$) but the temperatures of the eutectoid points are approximately $25°C$ lower in our phase diagram However, it is not always relevant to compare transition temperatures obtained from electrical conductivity measurements with those from DSC measurements DSC allowed us to do more detailed investigations of the transition temperature of the small peak in the range 64–70 mol% AgI and of the deviation from non-stoichiometry, than the electrical conductivity did in the investigation by Leute and Rusche

The temperature hysteresis of the large peak was studied as a function of AgI content The results are presented in Fig 7 The hysteresis is dependent on cooling rate and therefore all runs were made at a cooling rate of 0 5 K min^{-1} The hysteresis decreases to zero at approximately 63 and 71 mol% AgI, which are the eutectoid compositions

Polycrystalline Ag_2HgI_4 prepared by precipitation

An overwhelming number of the investigations so far of different properties of Ag_2HgI_4 have been made on samples prepared by precipitation from aqueous solutions It is sometimes explicitly stated that the authors consider this method more satisfactory than a solid state reaction [26] In many of the earlier studies a chemical analysis is performed in order to compare the amount of silver in the precipitate with what is expected for a stoichiometric composition [4,20–23,26–30,39]. Titova [24] takes the color of the precipitate
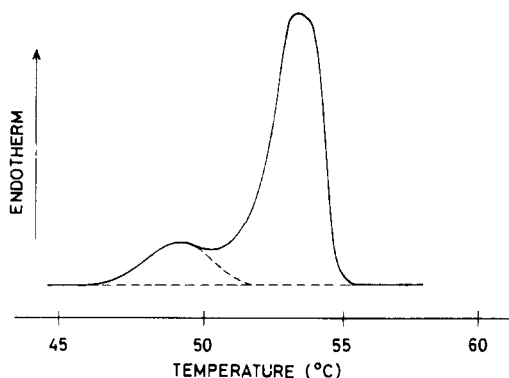
Fig 8 DSC curve of the order–disorder phase transition in Ag_2HgI_4 prepared by precipitation from stoichiometric solutions (method of Suchow and Keck [26]) Heating rate, 5 K min^{-1} DSC range 2 mcal s^{-1} sample mass 22 00 mg chart speed, 40 mm min^{-1}, transition temperature 47 0 °C and 51 5 °C transition enthalpy 8 40 kJ mol^{-1}

as evidence as to whether AgI, HgI_2 or Ag_2HgI_4 is obtained under the different conditions studied by her For a number of investigations X-ray diffraction was used to verify that the precipitate consisted of Ag_2HgI_4 [16,25,26,30,42,49] Ketelaar [4] found an excess of 3% AgI in most of his samples, Neubert and Nichols [28] reported an excess of 0 9% Ag, while Suchow and Keck [26] say that the analytical results were "very close" to the stoichiometric composition Gallais [21,50] found when working with aqueous solutions that some AgI was always coprecipitated, but he claimed that a procedure where 20 vol% alcohol was present in the solution gave pure Ag_2HgI_4

We have produced a large number of samples by the procedure of Suchow and Keck [26] where a solution of 0 4 M $AgNO_3$ is added to a 0 1 M boiling solution of K_2HgI_4 which means that α-Ag_2HgI_4 is precipitated A couple of times we chose to work at room temperature which gives β-Ag_2HgI_4 instead If stoichiometric amounts of the two solutions had been used, heating the precipitated samples from room temperature always gives DSC curves with two partly overlapping transition peaks a large one and a small one a few degrees lower (see Fig 8) Typically, the small peak occurs at about 49°C the first time the sample is heated and near 47°C for the later heatings while the transition temperature for the large peak is about 52°C all the time Many measurements have been made on precipitated samples, for heating as well as for cooling and some results of such measurements are given in Table 2 Because it was not possible to separate the two peaks, only the sum of their transition enthalpies was calculated Halmos and Wendlandt [51] observed a large endothermic peak at 47°C and a small shoulder peak at 49°C in their DTA curve for the first heating This small peak was not present in the curve for the second heating They had prepared the sample by precipitation according to Meyer [22]

The occurrence of two peaks follows from the phase diagram for the AgI–HgI$_2$ system in the vicinity of 66 67 mol% of AgI shown in Fig 5 Below the eutectoid temperatures there are two-phase regions with stoichiometric β-Ag$_2$HgI$_4$ and an excess of either AgI or HgI$_2$

It was found by X-ray powder diffraction that AgI had been coprecipitated during the preparation of Ag$_2$HgI$_4$ X-Ray patterns taken at room temperature showed two weak lines, neither of which had been reported by Hahn et al [9], nor could be found for stoichiometric samples prepared by a solid state reaction However, both types of sample gave identical patterns for the α-phase The additional lines were identified as the (002) and (110) lines of β-AgI, which thus was present as an impurity In our earlier X-ray studies only precipitated samples were investigated [16], and it was only when we could compare the results with those of samples prepared by a solid state reaction that the two additional lines were identified to be due to a slight excess of AgI Concerning previous X-ray studies of the β-phase one author reports additional lines [4], while others did not observe any [25,26,30,49] From a study where commercial reagent grade Ag$_2$HgI$_4$ was used, it is reported that neither AgI nor HgI$_2$ could be detected by X-ray diffraction [52], but in this case it is not known how the salt was prepared

As mentioned above the two peaks are always overlapping The only way to estimate the transition enthalpy of the small peak is to separate the peak areas graphically in the DSC curve as is shown in Fig 8, where the dashed line marks the approximate shape of the small peak Doing so, the transition enthalpy for the small peak, calculated from ten measurements, is approximately equal to 1 12 ± 0 17 kJ calculated for one mol of Ag$_2$HgI$_4$, which can be compared with 0 69 kJ mol^{-1} found for non-stoichiometric samples prepared by a solid state reaction with an excess of 0 63 mol% of AgI (see the preceding section). This should indicate that the samples prepared by precipitation have an excess of about 1 5 mol% AgI This assumption is supported by comparisons with non-stoichiometric samples prepared by a solid state reaction concerning the intensities of the additional AgI X-ray diffraction lines as well as the transition enthalpy as a function of AgI content This function, shown in Fig 6, gives an AgI content of 68 mol% for an enthalpy value of 8 23 kJ mol^{-1} It is also interesting to note that our 1 12 kJ mol^{-1} for the small peak is of the same order as the 1 21 kJ mol^{-1} found by Ketelaar [7] for the "homogeneous transformation"

For the transition temperature of the large peak it was observed that the temperature hysteresis is dependent not only on the cooling rate but also on the thermal and mechanical treatment of the sample (Both grinding and pellet pressing can produce traces of metastable high pressure phases [17]) Furthermore, the hysteresis can differ from one sample to another, the cause is probably that not exactly the same amount of AgI is coprecipitated each time the salt is prepared (see Fig. 7) The hysteresis of the small peak is about 16 °C and was studied only in some measurements, a large cooling rate is necessary to obtain a distinct peak

The proportions between the solutions were also varied In one series there was an excess of 2, 10 or 50 mol% of Ag^+, and in another one there was instead an excess of 2, 5 or 50 mol% of Hg^{2+} The precipitates obtained were studied by DSC and X-ray diffraction The results are very different for the two alternatives Independent of how large the excess was of K_2HgI_4 solution, the precipitate showed no diffraction lines in addition to those of Ag_2HgI_4, and the DSC curve showed only one peak for heating as well as for cooling For these samples the average values of transition temperature and enthalpy are presented in Table 2

If instead an excess of the $AgNO_3$ solution was added, a couple of lines characteristic of AgI were always detectable in the X-ray pattern, and the results of the DSC study depended on how large the excess was For an excess of 2 mol% the situation was about the same as when stoichiometric solutions had been used, i e there was a small peak appearing a few degrees below the big one For an excess of 10 or 50 mol% only one transition peak was detected in DSC heating curves No cooling runs were studied

As mentioned above, Gallais [21,50] claimed that pure Ag_2HgI_4 can be obtained if a mixture of water and alcohol is used at room temperature instead of only water Following the description in ref 21 a mixture of 80 vol% H_2O and 20 vol% C_2H_5OH was used as the solvent for 0 1 M solutions of K_2HgI_4 and of $AgNO_3$ 500 ml silver nitrate solution was added to 250 ml of the potassium mercury iodide solution. The precipitate was then washed twice with the hydroalcoholic solution and once with water before it was dried in a desiccator During heating two endothermic peaks were observed in DSC curves, one large peak at the temperature of $51 \pm 0\,5°C$ and a second small one at $47 \pm 0\,5°C$ with a total transition enthalpy $7\,70 \pm 0\,09$ kJ mol^{-1} An X-ray pattern taken at room temperature showed two additional weak lines belonging to β-AgI. A precipitate produced from a solution with 50 vol% alcohol still gave two endothermic peaks in DSC curves, but this time at $46°C$ and $49°C$ with transition enthalpy $7\,73$ kJ mol^{-1} The X-ray pattern showed one additional line which could neither be referred to silver iodide nor mercury iodide

Growth of single crystals from aqueous solution

The only method used so far for the preparation of single crystals of stoichiometric Ag_2HgI_4 is crystallization from a suitable liquid solution [10,39–41] It is not possible to grow single crystals from a melt, since decomposition takes place at temperatures far below the melting point [13]. Single crystals of AgI and HgI_2 have been used to produce Ag_2HgI_4 [15,35,36], but one cannot expect to obtain single crystals of the double salt in this way We shall discuss these studies later on.

Following the quoted reports, we started from aqueous solutions of potassium mercury iodide, K_2HgI_4 [10,39], or hydriodic acid, HI [40,41].

TABLE 3

Results from DSC investigation of crystals prepared by slow dilution of 5 cm^3 3 M K$_2$HgI$_4$ solution with 0 21 g AgI and an increasing amount of HgI$_2$

Solution number	Added HgI$_2$ (g)	Molar ratio	Characteristics of the order–disorder phase transition in Ag$_2$HgI$_4$ obtained in DSC curves
1	0 40	0 98	One small peak at 48°C Majority not Ag$_2$HgI$_4$
2	0 74	1 82	Same pattern
3	1 30	3 20	Same pattern
4	1 40	3 44	One peak at 48°C ΔH about 25% of the transition enthalpy for Ag$_2$HgI$_4$
5	1 50	3 69	First heating one peak at 52°C $\Delta H = 8\ 01$ kJ mol^{-1} Second heating two peaks $\Delta H = 7\ 37$ kJ mol^{-1}
6	1 78	4 38	First heating one peak at 52°C $\Delta H = 8\ 25$ kJ mol^{-1} Second heating two peaks $\Delta H = 7\ 53$ kJ mol^{-1}

Most of our work concerned aqueous solutions of K$_2$HgI$_4$ Unfortunately, information concerning the starting concentrations of all components was either very general [39] or insufficient [10] for a quick reproduction of the reported results For instance, in ref 10 it is proposed to "nearly" saturate a 3.0 M aqueous solution of K$_2$HgI$_4$ first by HgI$_2$ and later by AgI Following this description, one precipitates big yellow crystals from the K$_2$HgI$_4$ solution very easily when adding increasing amounts of HgI$_2$ To what extent has the starting solution to be saturated by HgI$_2$? In ref 39 not even the starting concentration of the K$_2$HgI$_4$ solution is given, but in both cases the necessity of a large (but never quantitatively described) excess of HgI$_2$ is underlined

Thus one can spend a long time before a proper proportion of all components involved, i e of KI, HgI$_2$, AgI and H$_2$O, is found which guarantees the crystallization of Ag$_2$HgI$_4$ from a homogeneous solution. Hereby one can make use of the property that Ag$_2$HgI$_4$ crystallizes from a suitable solution of the above mentioned components either by cooling or by slow dilution with water [39]

To demonstrate how crucial it is to use a sufficient excess of HgI$_2$, we present some results in Table 3 In 5 cm^3 of a 3 M aqueous solution of K$_2$HgI$_4$ different amounts of HgI$_2$ were dissolved and after that the same amount of AgI (0 21 g) was added to each solution Each time a homogeneous solution was prepared by heating to 50–70°C About 4 cm^3 of this solution was later kept in contact with water vapor in a sealed chamber. This was realized by putting the above solution on a parabolic glass plate which
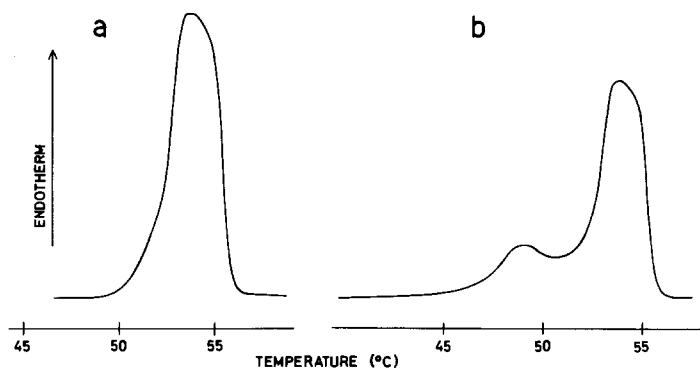
Fig. 9. DSC curves for the order–disorder phase transition obtained upon heating crystals of Ag_2HgI_4 prepared from solution number 5 by water vapour uptake at room temperature (see Table 6). Heating rate, $2.5\,^{\circ}C$ min^{-1}; DSC range, 2 mcal s^{-1}, chart speed, 20 mm min^{-1}; sample mass, 55.10 mg. (a) First heating run: transition temperature, $52.0\,^{\circ}C$; transition enthalpy, 8.01 kJ mol^{-1}. (b) Second heating run: transition temperature, $46.5\,^{\circ}C$ and $52.0\,^{\circ}C$; transition enthalpy, 7.37 kJ mol^{-1}.

was surrounded by water in a sealed chamber. As the water activity was higher above the pure component, water was taken up by the concentrated solution, leading to a continous dilution. This resulted in precipitation of crystals from the solution: these were later filtered, washed successively with 0.1 M K_2HgI_4 and distilled water, and after drying the characteristic of the order–disorder phase transition peak was checked with DSC. As can be seen in Table 3, solutions 1–3 gave only a small peak with the transition temperature equal to $48\,^{\circ}C$. This means that the most of the crystals obtained were not Ag_2HgI_4. The temperature of the transition was about $4\,^{\circ}C$ lower than the value for the stoichiometric compound (see Table 2). From the phase diagram shown in Fig. 5, one can conclude that these samples are certainly non-stoichiometric. Sample 4, with the molar ratio HgI_2/AgI about 3.45 already had some 25% Ag_2HgI_4 in the crystals obtained, as estimated from the fact that the measured transition enthalpy was only about 1.8 kJ mol^{-1}.

Pure crystals of Ag_2HgI_4 precipitated from solutions 5 and 6, i.e. for molar ratios HgI_2/AgI above 3.7. The samples were cycled several times through the order–disorder transition. In both cases only one DSC peak was detected for the first heating run. But two peaks appeared for the second heating and this structure of the DSC curve was also obtained in the further heating cycles. Figure 9(a, b) illustrates this behavior. The appearance of the second peak is accompanied by a decrease of the total transition enthalpy, which is in accordance with the dependence of transition enthalpy on the composition (see Fig. 6).

Figure 9(a, b) can explain the controversy between the work of Olsen and Harris [39] and Browall et al. [10]. Olsen and Harris [39] found that after a

first transition from the ordered β-phase to the disordered α-phase and back to the β-phase, the single crystals of the β-phase were different In other words, fresh untransferred β-phase single crystals, termed β'-phase by Olsen and Harris [39], are not identical with those of the same phase even after the first recovery from the α-phase Schematically this sequence of events can be presented as [39]

$$\beta' \quad \rightarrow \quad \alpha \quad \rightleftharpoons \quad \beta$$
initial phase　disordered　equilibrium
 ordered　 phase　 ordered phase
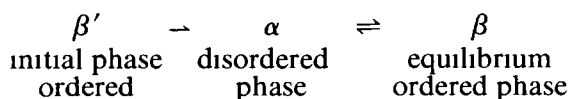
A difference in crystallographic structure was assumed by Olsen and Harris [39] as being responsible for the difference between the β and β' phases This conclusion was rejected by Browall et al [10], who claimed that a multidomain arrangement of the β-phase (after the reverse transition from the α-phase) is responsible for the difference between the β and β'-phases in terms of ref 39 From our DSC analysis it is obvious that after the first transition to the α-phase we do not get the same β-phase A phase separation process, or in other words the removal of an initial metastability of the crystals, has taken place This phase separation is not reversible, thus we support the conclusions of both Browall et al [10] and Olsen and Harris [39] about a unique behaviour of fresh crystals, but we propose here a new interpretation based on the DSC analysis of the order–disorder phase transition Let us further remark that it is far from certain that the single crystals used in the studies [10] and [39] were identical Because no detailed description of the preparation method was given in either paper, the above question cannot be answered with certainty We can also refer to the results summarized in Table 3, indicating how sensitively the concentrations of all components determined the properties of the crystals obtained

During the crystallization from all solutions summarized in Table 3, a crucial point was to avoid the appearance of crystals originating from K_2HgI_4 On this basis big crystals can very easily be prepared or they can confuse a simultaneous precipitation of the Ag_2HgI_4 crystals To avoid this difficulty we increased the amount of water in the starting solution After many tedious attempts we can recommend two solutions, A and B, which can be used for crystallization of pure Ag_2HgI_4

Solution A In 5 cm^3 of an aqueous 3 M K_2HgI_4 solution 1 8 g HgI_2 was first dissolved To increase both the kinetics and the solubility, the solution was heated to about 50°C Next, 0 21 g of AgI were dissolved, whereby a much longer time was required to obtain a homogeneous solution (again with the heating up to about 50°C) To this solution 2 cm^3 of distilled water were added, and the solution became homogeneous around 65°C From such a solution crystals of Ag_2HgI_4 precipitate if a slow uptake of water takes place This can easily be realized as described above by putting solution A into contact with water vapour when separated dishes of solution
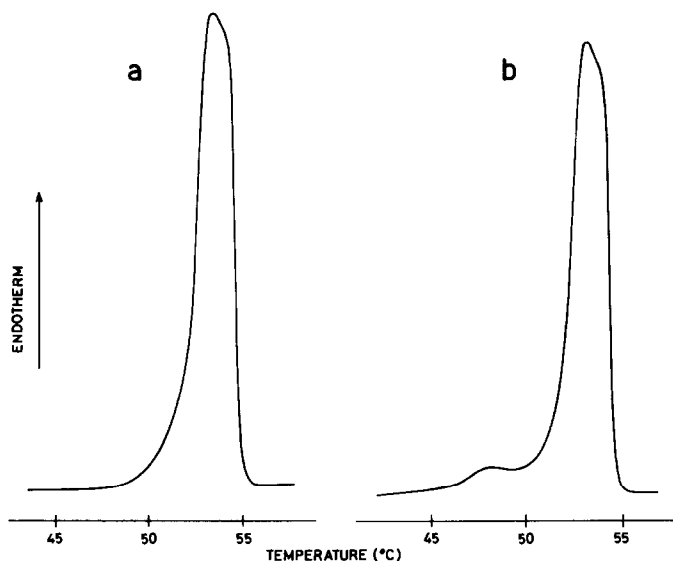
Fig 10 DSC curves for the order–disorder phase transition obtained upon heating crystals of Ag_2HgI_4 prepared from solution A by water vapor uptake at room temperature Heating rate, 2 5 °C min^{-1}, DSC range, 1 mcal s^{-1}, chart speed, 20 mm min^{-1}, sample mass, 36 20 mg (a) first heating run transition temperature, 52 0 °C, transition enthalpy, 8 05 kJ mol^{-1} (b) Second heating run transition temperature, 45 5 °C and 51 5 °C, transition enthalpy, 7 91 kJ mol^{-1}

A and pure water are kept together in a closed space at room temperature If thermal crystallization started before an evident uptake of water, solution A had to be homogenized by slight heating After filtration the crystals were washed in 0.3 M K_2HgI_4 solution and later in distilled water The crystals were dried in air at room temperature The DSC curves of the order–disorder phase transition of the first two heating runs are shown in Fig 10(a, b)

Similarly as for solution number 6 of Table 3 we get one peak for the first heating and a small second peak for the next heating Again, the phase separation (see Fig 10(b)) is accompanied by a slight reduction of the transition enthalpy Thus we again meet here a metastability of freshly prepared crystals which disappears after repeated transition to the α-phase

Solution B All the steps described for the preparation of solution A are repeated with the difference that the amount of HgI_2 is increased to 1 9 g and the volume of water added is increased to 2 5 cm^3. The temperature of homogenization of the final solution is higher by about 15° C

A solution prepared in this way is especially suitable for preparation of Ag_2HgI_4 crystals by lowering the temperature Thus the homogenized solution (80 °C) is simply cooled to room temperature and the precipitated crystals are washed and dried in the same way as described above for the crystals obtained by the dilution method from solution A Figure 11 shows a
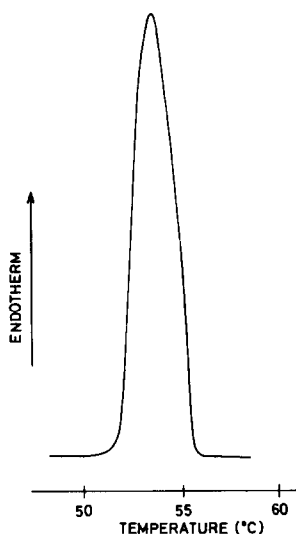
Fig 11 DSC curve for the order–disorder phase transition obtained upon heating crystals of Ag_2HgI_4 prepared from solution B by cooling the homogeneous solution from about 80 °C to room temperature Heating rate, 1 25 °C min^{-1}, DSC range, 2 mcal s^{-1}, chart speed, 10 mm min^{-1}, sample mass, 114 50 mg First heating run transition temperature, 52 0 °C, transition enthalpy, 8 51 kJ mol^{-1}

DSC curve for the order–disorder phase transition

We obtained here a single transition peak, which was repeated in its structure during the following five heating runs. Thus no phase separation takes place in this sample The only difference stated was a slight increase of the transition enthalpy for the second and further heating runs, probably due to equilibration of the defect concentration in the successive runs.

A certain advantage of solution B and the thermal (cooling) precipitation of the Ag_2HgI_4 crystals is the possibility of a repeated use of the filtrate for new preparation Thus the solution left after filtration of the crystals at room temperature can be mixed with a powder of stoichiometric Ag_2HgI_4 (in amounts not higher than the mass of the separated crystals) and after homogenization at around 80 °C the crystallization of a new batch of Ag_2HgI_4 can be repeated. In other words, solution B remaining after crystallization of Ag_2HgI_4 at room temperature is in stable equilibrium with these crystals and will dissolve them in a congruent way when heated up to at least 80 °C

Instead of K_2HgI_4 we also tried to apply a 57% aqueous solution of HI as the starting basis for Ag_2HgI_4 crystallization Two successful attempts of this kind are reported in the literature [41,42] We did not work as systematically as in the case of the K_2HgI_4 solution, but let us mention here one example which may be instructive in connection with a previous comparison of our results [16] with some others [15,35,36]
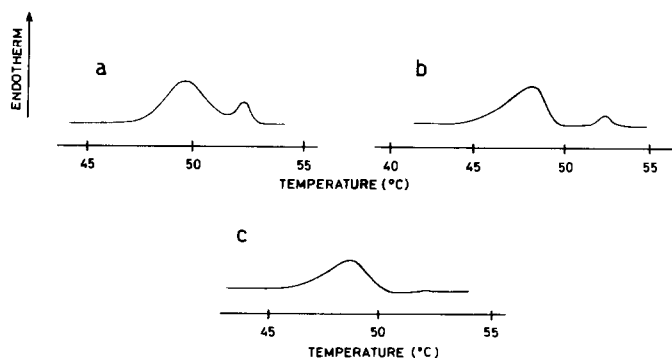
Fig 12 DSC curves for the order–disorder phase transition obtained on heating crystals of Ag_2HgI_4 prepared from HI (57%) aqueous solution saturated with HgI_2 Heating rate, $2\,5\,^{\circ}C$ min^{-1}, DSC range, 2 mcal s^{-1}, chart speed, 20 mm min^{-1}, sample mass, 70 40 mg (a) First heating run transition temperature, 47 5 $^{\circ}C$ and 51 5 $^{\circ}C$, transition enthalpy, 0 8 kJ mol^{-1} (b) second heating run transition temperature, 45 0 $^{\circ}C$ and 51 5 $^{\circ}C$ (c) Sixth heating run transition temperature, 46 0 $^{\circ}C$

An aqueous solution of HI (57%) was saturated with HgI_2 at about $50\,^{\circ}C$ and later with Ag_2HgI_4 powder After filtration around $35\,^{\circ}C$ a red precipitate was obtained by cooling to room temperature The DSC curves obtained in a sequence of heating runs are shown in Fig 12 Upon heating the sample for the first time, the order–disorder phase transition exhibits two peaks in the DSC curve, of which the small one on the high-temperature side is characteristic for a stoichiometric sample (see Fig 12(a)) The transition enthalpy, calculated from the area of both peaks, is small (about 0 8 kJ mol^{-1}) thus indicating that the majority of the crystals prepared are pure HgI_2 In the second, subsequent, heating the transition temperature of the large peak decreases $2\,5\,^{\circ}C$, thus being $45\,0\,^{\circ}C$, which indicates that the large peak is characteristic for a non-stoichiometric composition with an excess of HgI_2, (see Figure 5) The area of the small peak is now quite small, (see Fig 12(b)) Finally, in the sixth heating of the sample the small peak disappeared (see Fig 12(c)) A similar two-peak structure was reported in ref 15 This was striking for us, since an opposite sequence of peaks (a small one at a lower and a large one at a higher temperature) was observed for our Ag_2HgI_4 samples precipitated from solution (see the previous section) It is worth mentioning that both Akopyan and Novikov [15] and we used the same DSC device (Rigaku) It is obvious from our results reported here, as well as from later investigations by the same authors [36], that this sequence of peaks, a small one at a higher temperature and a large one at a lower temperature, is due to an inappropriate method of preparation, and that the peak structure reported by us [16] corresponded to a nearly stoichiometric sample (see previous section) The sequence of runs presented in Fig 12 proves that such a structure of the DSC peak is far from being stable and

may be changed considerably by repeated transitions This was probably also the case for the sample described by Akopyan and Novikov [15]

FINAL CONCLUSIONS

This investigation confirms that the stability range of Ag_2HgI_4 is very small for the ordered phase, while the composition of the disordered phase can deviate considerably from stoichiometric. We have shown that DSC cycling through the order–disorder transition is a very efficient method not only to test whether a sample is pure but also to remove initial metastability (In a previous investigation we studied metastability due to mechanical treatment of a sample such as pellet pressing [17]) We have also described how pure Ag_2HgI_4 can be prepared in three different ways a solid state reaction between stoichiometric amounts of AgI and HgI_2, precipitation from aqueous solutions of $AgNO_3$ and K_2HgI_4 with an excess of the latter salt, and by the growth of single crystals according to a carefully described procedure

Both from the present DSC investigation of pure Ag_2HgI_4 samples, and from our separately reported studies of conductivity [19], it can be concluded that the order–disorder phase transition in stoichiometric Ag_2HgI_4 is a first-order phase transition Over the years observations concerning a λ-shaped specific heat curve, pretransformation etc , have been interpreted as a two-step phase transition [25,28,37–39] or as a combination of two different phase transitions [8,53] However, these are probably only apparent effects which can be related to the non-stoichiometry of the investigated samples

ACKNOWLEDGMENTS

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