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A DIFFERENTIAL SCANNING CALORIMETRIC STUDY ON PHASE TRANSFORMATIONS OF HgI_2

I The parameters that influence the α- to β-phase transition

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A quantitative study of the different factors that influence the $\alpha-\beta$ transformation of mercuric iodide was carried out with differential scanning calorimetry. The transformation temperature and the peak width during the heating of the material were followed. An attempt was made to explain the experimental results.

Mercuric iodide (HgI_2) undergoes a well-known phase transition at about 130°, from the red α-phase to the yellow β-phase.

Although the existence of this $\alpha-\beta$ transformation has been known since the nineteenth century, the transformation temperature has been reported at a great variety of values in the range 125° to 154°. This variation was the first indication that the transformation is affected by different factors. In a detailed study, Newkirk [1] optically determined the transformation temperature to be 127°. From a study of the kinetics of the transformation, he designated the purity and the grain size as factors that affect the $\alpha-\beta$ transformation.

A relation has been reported [2, 3] between the transformation temperature and the deviation from exact stoichiometry (I/Hg = 2.000). The growth procedure and the pretreatment of the material have also been reported [4] to be factors that influence the transformation temperature.

Finally, a more detailed and systematic study [5] proved that the factors that affect the $\alpha-\beta$ transformation are: 1. heating rate, 2. grain size, 3. purity, 4. heating pretreatment and 5. deviation from stoichiometry. It was found that the growth method indirectly affects the transformation through the impurities that are transported to the grown crystal and this is not considered to be an independent factor.

During cooling, the $\beta-\alpha$ transformation seems to be affected by the same factors, though the cooling rate and the heating pretreatment are the most significant.

A complete study of the phase transformations of mercuric iodide is now in progress. The purpose of the present work is to illustrate the quantitative influence of the above factors on the $\alpha-\beta$ transformation during heating.

Experimental

The α to β-HgI_2 transformation study was carried out with a differential scanning calorimeter (DSC-2, Perkin-Elmer). Calibration was performed with p-nitrotoluene (51.5°) and lead (327.47°), which allowed an accuracy better than $\pm 0.2°$ deg.

The reproducibility of the measurements was achieved by keeping the following factors constant in every set of measurements: heating rate, grain size, purity, heating pretreatment, stoichiometry and mass of the specimen. The mass must be 4.0–6.5 mg. Higher masses lead to reproducibility problems, and lower masses require a high instrumental sensitivity. It has been concluded experimentally that a sensitivity higher than 10 mcal/sec creates uncertainty in the determination of the beginning of the transformation. Accordingly, all the diagrams were recorded at a sensitivity of 10 mcal/sec. The values of the other factors will be mentioned explicitly below.

The α- to β-HgI_2 phase transformation appears in all DSC diagrams as a broad peak (Fig. 1), which indicates a first-order non-isothermal transformation without any change in c_p [6].

The specimens used were grown by the vertically moving vapour growth method [7]. The initial material was: a) powder of high-purity material[+] (99.9999%, Tousimis Research Corporation), b) powder of purity 99.985%[++] (Tousimis Research Corporation) and c) powder, commercial, pro analysis (Merck). The as-grown bulk material was powdered and sieves were used to achieve specimens with different particle sizes. Finally, the particle size was tested by means of optical microscopic observations.

The experimental work is divided into two sections (*A* and *B*), as concerns the topics under study, in order to have a complete view of the transformation. Each

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[+] Impurities, as determined spectrographically: Cu < 0.5 ppm, Mg < 0.1 ppm, Si < 0.1 ppm. No other metallic elements were detected.

[++] By spectroscopic analysis: Ca < 0.001%, Fe < 0.005%, Mg < 0.001%, Mn < 0.001%, Si < 0.007%.

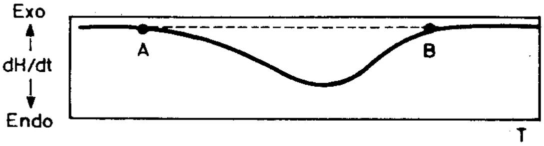

Fig. 1 Typical broad peak on a DSC diagram indicating the non-isothermal α to β-HgI_2 phase transformation. Points *A* and *B* indicate the beginning and the end of the transformation respectively

section is also divided into parts (1 to 5) that describe the influence of the different factors on the transformation.

A Transformation temperature

As a non-isothermal procedure is involved, in order to have the same reference in all the following measurements, the beginning of the transformation (point *A* in Fig. 1) was taken as the transformation temperature.

A1 Heating rate

Heating rates from 0.31 deg/min to 2.5 deg/min all showed the transformation at the same temperature when the specimen was treated for the first time. At heating rates of 5 deg/min and 10 deg/min, there were shifts to temperatures higher by 0.5 deg and 2.0 deg, respectively. At higher heating rates, the shift increased rapidly and the transformation temperature was no longer reproducible.

A2 Grain size

All the above findings concerning the heating rates were valid for specimen grain sizes of 150 ± 50 μm and 100 ± 50 μm. Specimens with a grain size of 10 ± 5 μm also displayed a temperature shift, but at lower heating rates: 1.25 deg/min and above. Specimens of single-crystal grain exhibited the same behaviour as the 100 ± 50 μm and 150 ± 50 μm powders. All the results relating to the heating rate and grain size dependence are tabulated in Table 1.

A3 Purity

Although it has already been mentioned that the purity affects the transformation temperature, it was not possible to express this in a quantitative relation. It is known [2] that the impurities in crystals that have already been purified show a variation of about 100–300 ppm. The variation in the stoichiometry of the grown crystal, when starting materials with the same purity are used, is about 750–4000 ppm. Further, the different stoichiometry determination methods also display considerable variation in their results. Thus, apart from the uncertainty in the measurements, there is a superimposition of the purity and stoichiometry values, a fact that prevents correlation of the transformation temperature with

Table 1 Influence of heating rate and grain size on transformation temperature. θ is the constant transformation temperature

Heating rate, deg/min	Transformation temperature, °C			
	Grain size			
	10 ± 5 μm	100 ± 50 μm	150 ± 50 μm	bulk
0.31	θ	θ	θ	θ
0.62	θ	θ	θ	θ
1.25	θ	θ	θ	θ
2.5	$\theta+0.4$	θ	θ	θ
5.0	$\theta+1.0$	$\theta+0.5$	$\theta+0.5$	$\theta+0.4$
10.0	$\theta+4.0$	$\theta+2.0$	$\theta+2.0$	$\theta+2.1$
20.0	$\theta+8.0$	$\theta+6.0$	$\theta+6.5$	$\theta+6.5$

exact values of stoichiometry and purity. However, specimens with higher purities generally have lower transformation temperatures.

A4 Heating pretreatment

The experimental results revealed the great influence of the heating pretreatment on the transformation temperature. To approach the problem, the specimens were heated up to 150° at a heating rate of 1.25 deg/min, followed by one of the following treatments:

a) The specimen was cooled rapidly to 100° and immediately reheated at a rate of 1.25 deg/min.

b) The specimen was cooled at a rate of 5 deg/min to 100° and immediately reheated at a rate of 1.25 deg/min.

c) The specimen was cooled rapidly to room temperature. After 5 days it was reheated at a rate of 1.25 deg/min.

d) The specimen was cooled at a rate of 5 deg/min to room temperature. After 5 days it was reheated at a rate of 1.25 deg/min.

e) The specimen after procedure (b) was cooled again at a rate of 20 deg/min to 100° and then reheated at a rate of 1.25 deg/min.

From the above heating procedures, the DSC diagrams gave the following information: Procedure (a) did not indicate any transformation, which means that the β-phase does not have enough time to transform to the α-phase during cooling. Procedure (b) showed the transformation at a lower temperature then during the first heating of the same specimen. Procedures (c) and (d) indicated the same temperature as during the first heating of the same specimen. Procedure (e) showed a broad peak with many maxima (Fig. 2). This may indicate that the cooling rate of 20 deg/min is so high that only a portion of the material is transformed to the α-

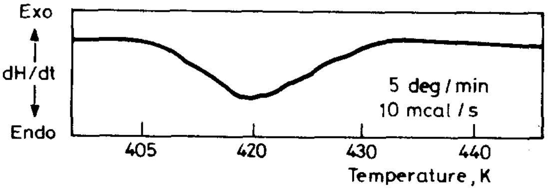

Fig. 2 Typical broad peak with many maximums. This kind of peak appears when the specimen is reheated after a fast enough cooling at a rate of 20 deg/min

Table 2 Influence of heating pretreatment on transformation temperature

Grain size, μm	Transformation temperature, °C					
	Heating pretreatment					
	First heating	*a*	*b*	*c*	*d*	*e*
100 ± 50	133.2	—	131.0	133.1	133.2	;
150 ± 50	133.4	—	131.3	133.6	133.4	;
bulk	133.4	—	129.8	133.0	133.0	;

phase. Thus, the material is in a non-equilibrium state and during heating it undergoes transformation in a non-uniform way. All the results are tabulated in Table 2.

A5 Stoichiometry

Deviation from stoichiometry affects the transformation temperature. Work leading to the phase diagram of the material will be described in a separate publication.

B Peak width

Although the beginning of the transformation has so far been used for the temperature determination, the DSC diagrams indicate that the $\alpha-\beta$ transformation takes place in a wide range of temperatures. As the transformation is non-isothermal, we shall now study the parameters that influence the transformation peak width. The peak width is taken as the temperature difference between the end and the beginning of the transformation (points *B* and *A* in Fig. 1).

B1 Heating rate

As the heating rate is decreased from 20 deg/min to 1.25 deg/min, the peak width decreases. For heating rates below 1.25 deg/min, the peak width remains constant. Table 3 shows the dependence of the peak width on the heating rate for various specimens.

Table 3 Dependence of peak width on heating rate for various specimens. Mass of specimens 5.0 ± 0.5 mg. The influence of grain size and purity on peak width is also shown

Heating rate, deg/min	Peak width, °C								
	Purity								
	99.9999%			99.985%			Merck		
	Grain size, μm								
	10 ± 5	100 ± 50	bulk	10 ± 5	100 ± 50	bulk	10 ± 5	100 ± 50	bulk
0.31	2.5	2.7	2.7	2.8	3.1	3.1	3.2	3.5	3.4
0.62	2.5	2.7	2.7	2.8	3.1	3.1	3.2	3.5	3.5
1.25	2.5	2.7	2.7	2.8	3.1	3.1	3.2	3.5	3.5
2.5	3.2	3.5	3.4	3.8	4.2	4.1	4.3	4.9	5.0
5.0	4.5	5.1	5.0	5.3	6.0	5.9	6.2	7.8	7.8
10.0	6.8	8.0	7.8	8.5	10.0	10.0	10.4	17.0	18.0
20.0	12.0	14.0	14.0	15.0	17.0	17.0	17.0	23.0	23.0

B2 Grain size

The grain size also affects the peak width. As the grain size increases, the peak width increases. Table 3 additionally shows the influence of the grain size on the peak width.

B3 Purity

The influence of the purity on the peak width is that expected for the DSC diagrams, i.e. specimens with higher purity display a narrower peak width (Table 3). Figure 3 also shows this effect. The three zones correspond to specimens with purity 99.9999% and 99.985%, and commercial powder. The appearance of a zone instead of a line is explained by the influence of the grain size. For specimens with the same purity, the available maximum and minimum grain size values that define the zone are 150 ± 50 μm and 10 ± 5 μm. The absence of any superimposition of the zones is accidental and is due to the purity values available.

The influence of the purity of the material on the peak width means that it is possible to study the impurity distribution in the grown crystal. It has already been proved [7] that the mechanism of growth of HgI_2 crystals from the melt is the vapour-melt-solid (VMS) mechanism. According to this, the growth takes place under diffusion-controlled steady-state conditions, during which the impurity distribution in the grown crystal has the shape shown in Fig. 4 [8]. This means that there is a plateau (region BC) in which the impurity concentration is constant, while there is a considerable increase in the impurity concentration at the end of the grown crystal (region CD). Specimens taken from the end of the crystals give broader peaks and at higher temperatures in comparison to those taken from the middle of the crystals (Table 4).

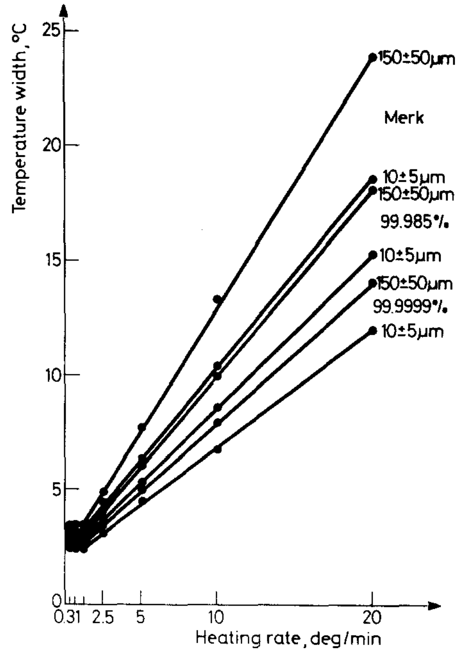

Fig. 3 Diagrammatical representation of the influence of heating rate, grain size and purity on the peak width. The three zones correspond to specimens of purity 99.9999%, 99.985% and commercial powder. The two frontier lines of each zone correspond to 10 ± 5 μm and 150 ± 50 μm respectively

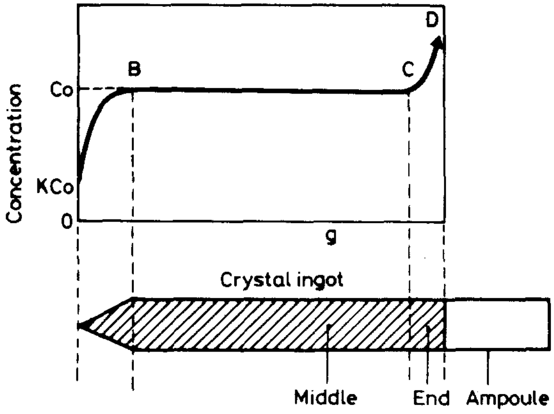

Fig. 4 Impurities distribution *vs.* the portion of solidified material (g)

Table 4 Transformation temperature and peak width of different specimens taken from beginning, middle and end of crystal ingot

Specimen	Heating rate, deg/min	Grain size, μm	Purity	Transform. temp., peak width, °C Specimen location in crystal ingot beginning	 middle	 end
Al–1	2.5	150 ± 50	99.9999%	133.2/3.4	133.0/3.3	134.1/3.9
Al–2	2.5	150 ± 50	99.985 %	133.0/4.1	133.4/4.2	134.2/4.9
Al–3	2.5	150 ± 50	Merck	133.6/5.0	133.8/5.0	134.6/5.8

Table 5 Influence of heating pretreatment on peak width. Specimens were heated at 1.25 deg/min, cooled to 110 °C at 1.25 deg/min and immediately reheated at same rate

Specimen	Heating rate, deg/min	Grain size, μm	Purity	Peak width, °C Heating pretreatment 1st heating	 2nd heating
Al–1	1.25	150 ± 50	99.9999%	3.2	4.2
Al–2	1.25	150 ± 50	99.985 %	4.0	4.6
Al–3	1.25	150 ± 50	Merck	5.0	5.2

B4 Heating pretreatment

Specimens that are heated a second and a third time show broader peaks during the transformation. This indicates a strongly non-isothermal procedure. It may be due to the fact that there are parts of the specimens which, due to hysteresis, are not transformed (from the β to the α-phase) during cooling. If the specimens remain for 5 days at room temperature, they then show the same behaviour as in the first heating. As the broadness of the peak determines the peak width, the latter is affected by the heating pretreatment. Table 5 shows the peak width variation for different specimens heated at a rate of 1.25 deg/min, cooled to 110° at a rate of 1.25 deg/min and reheated immediately at the same rate.

B5 Stoichiometry

The influence of stoichiometry on the peak width was found to be insignificant.

Discussion and conclusions

The factors that affect the α to β-phase transformation of mercuric iodide were found to be the heating rate, grain size, purity, heating pretreatment and stoichiometry. An experimental study of their influence on the transformation temperature and the peak width permits the following findings:

1. Mercuric iodide is transformed within a range of temperatures (peak width), which is increased on increase of the heating rate above 1.25 deg/min, while the peak width is constant below this rate. This increase seems to be due to the ability of the material to transform at its own rate, which can not be forced by the heating rate. Accordingly, the rate of the transformation resists, leading to an increase in the peak width.
2. Decrease of the grain size of the specimen affects the peak width by making the peak shape more sharp. This indicates that the transformation becomes less non-isothermal.
3. Specimens heated a second time immediately after cooling, and independently of the cooling rate, exhibit different behaviour during the transformation relative to that the during first heating. This second heating shows the same behaviour when, after cooling the specimens remain, for 5 days at room temperature. As appears from the DSC diagrams, the difference is due to the hysteresis that exists in the transformation mechanism during cooling, and on the second heating some parts of the specimen are found to be untransformed (at the β phase). This does not mean that the transformation from the β to the α-phase lasts for 5 days, but that the material needs a long time to equilibrate itself, something it finds difficult during thermal treatment.

The experimental study relating to the influence of different factors on the $\alpha-\beta$ transformation has so far involved the heating of the material. During cooling, the $\beta-\alpha$ transition seems to be affected by the same factors very slightly. The hysteresis is now the dominant phenomenon, which is affected drastically by the initial and final temperatures. The transformation time increases greatly and in specific cases it becomes very long, i.e. grains of the material remain in the yellow β-phase for a prolonged time at room temperature. The quantitative expression of the influence of the different factors on the $\beta-\alpha$ transformation during cooling is now under investigation.

The present study of the $\alpha-\beta$ transformation by means of DSC must be complemented with other methods. A detailed study of the transformations will increase our knowledge of the physics of the material. This is essential for the further improvement of its detecting properties, a feature that has made it a very interesting technological material.

References

1 J. B. Newkirk, Acta Metallurg., 4 (1956) 316.
2 G. Dishon, M. Schieber, L. Ben-Dor and L. Halitz, Mat. Res. Bull., 16 (1981) 565.
3 I. F. Nicolau and G. Rolland, Mat. Res. Bull., 16 (1981) 759.
4 S. N. Toubektsis, E. K. Polychroniadis and N. A. Economou, J. Crystal Growth, 79 (1986) 427.
5 S. N. Toubektsis, Ph.D. Thesis, University of Thessaloniki, Thessaloniki 1988.
6 As has been proved by the transformation curves, S. N. Toubektsis and E. K. Polychroniadis, J. Thermal Anal. to be submitted.
7 S. N. Toubektsis and E. K. Polychroniadis, J. Mat. Sci. Lett., 6 (1987) 1270.
8 V. G. Smith, W. A. Tiller and J. W. Rutter, Can. J. Phys., 33 (1955) 723.

Zusammenfassung — Mittels Differential-Scanning-Kalorimetrie wurde der Einfluss verschiedener Faktoren auf die $\alpha-\beta$ Umwandlung von Quecksilberjodid quantitativ untersucht. Dabei wurde die Umwandlungstemperatur und die Signalbreite beim Erhitzen der Substanz beobachtet. Es wurde ein Versuch unternommen, die experimentellen Ergebnisse zu erklären.

Резюме — С помощью дифференциальной сканирующей калориметрии проведено количественное изучение различных факторов, затрагивающих $\alpha-\beta$ превращение иодида ртути. Прослежены температура этого перехода и ширина пика во время нагрева. Представлена попытка объяснения экспериментальных результатов.