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A DIFFERENTIAL SCANNING CALORIMETRIC STUDY ON PHASE TRANSFORMATIONS OF HgI_2
II. The dependence of stoichiometry on the α to β transformation temperature

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The influence of stoichiometry on the mercuric iodide α to β transformation temperature was studied in a limited region around the exact stoichiometry. It is concluded that although this influence is small, the transformation temperature has its highest value at the exact stoichiometry composition.

α - HgI_2 is a wide band-gap semiconductor, which is used as nuclear detector at room temperature. As it is known mercuric iodide transforms at about 130° from its red α - HgI_2 phase to its yellow β - HgI_2 one and the melting appears at about 259°. Although the transformation and the melting points are known, there is little information in the literature about the phase diagram of the material. All the work done referring to the dependence of stoichiometry on the transformation temperature is limited to a narrow band on both sides of the exact stoichiometry [1, 2].

The aim of the present work is to contribute in this direction adding some experimental results to the dependence of the stoichiometry on the α - β transformation temperature.

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Experimental

Crystal Growth

In order to study the stoichiometry dependence on the α - β transformation temperature we have to choose a crystal growth method that has the possibility of growing crystals in different stoichiometry. So the method used was the vertical and moving vapor method [3] that has this possibility due to the fact that the crystals were grown from the melt. According to this method adding or not I_2 in several proportions into the charge, we can grow from the melt β - HgI_2 single crystals, deviated from the exact stoichiometry, few degrees below the melting point. By quenching them to room temperature we obtained α - HgI_2 polycrystalline ingots. The absence of single crystallinity is not a disadvantage for this study as the specimens used are finally powdered. Moreover the method has an advantage. As the growth mechanism in this is the Vapor-Melt-Solid (VMS mechanism), the impurities distribution is constant in all the length of the growing crystal except for the two ends [3]. For this reason the small pieces used to prepare the specimens are taken from the inner part and from the middle of the solid ingot. So we can have different specimens with the same stoichiometry and the same impurities concentration. This is essential for the precise determination of the stoichiometric proportion of the constituents.

The specimens used have a molar ratio I_2/Hg variation from 1.890 to 2.047. The starting material was a) Merck pro analysis HgI_2 and I_2 or b) High purity, 6N, HgI_2 and I_2.

All the measurements were done using four specimens taken from the same ingot. The results were spreaded always within the accuracy of the measurements.

Chemical analysis

In order to find the deviation from the exact stoichiometry composition two methods were applied [4].

1. The determination of the excess mercury e.g. Hg^+, Hg^o is based on oxidation of Hg by I_2, and titration of the excess unreacted iodine with standard $Na_2S_2O_3$. The sensitivity of the method was $y = 0.003$ ($Hg_{1+y}I_2$).

2. The determination of the excess iodine is based on the spectrophotometric determination of the iodine complex with o-toluidine in the presence of I^- ions. This sensitivity was $x = 0.007$ (HgI_{2+x}).

Transformation temperature determination

For the $\alpha - \beta$ transformation temperature determination a differential scanning calorimeter (DSC-2 Perkin Elmer) was used. Although this is a dynamical method, an accuracy of $\pm$ 0.3° in the temperature determination was achieved, which is agreeable in the present study. This means that the deviations between the measurements of the different specimens are detec-Table. The accuracy of $\pm$ 0.3° is an experimental result. As it is known, the impurities concentration also influences the transformation temperature. The last varies between 2000 ppm and 3500 ppm in the commercial material and between 150 ppm and 300 ppm in the purified one and could be expected to give an uncertainty in the temperature determination. However the spreading of the experimental values of the temperature are always within the $\pm$0.3° limits. This happens due to the fact that, as we have already written, the four specimens that were taken from the same ingot have the same impurities concentration.

The temperature determination has been done at the 0 % of the transformation [5]. This must be defined as this transformation concerns a non isothermal procedure.

The capsules used in the DSC measurements were the commercially available stainless steel capsules (LVC, Perkin Elmer), after careful cleaning. These do not react with mercuric iodide at low temperatures and do not introduce new impurities to the material.

As it is known [5], five factors affect the transformation temperature: heating rate, grain size, purity, heating pretreatment and stoichiometry. In order now to find the dependence of stoichiometry on the mercuric iodide α to β transformation temperature, the other four factors must be kept constant. So the values of these have been chosen as follow: Heating rate: 1.25 deg/min, Grain size: 150 $\pm$50 μm, Purity: a. Merck pro analysis, b. 99.9999 % (by Tousimis R. C.). Heating pretreatment: All specimens are heated for the first time.

Results and conclusions

Table 1 shows all the experimental results for both pro analysis (MPA) and high purity (HP) specimens. Also the stoichiometry dependence on the transformation temperature is shown in Fig. 1. This in fact is a part of the phase diagram of the material near the exact stoichiometry (I_2/Hg = 2.000).

Table 1 Dependence of stoichiometry on the mercuric iodide α to β transformation temperature (Purity HP: High Purity, MPA: Merk pro analysis)

No	Purity	I_2/Hg	Temperature, °C
1	HP	1.971	133.7
2	HP	1.965	133.6
3	HP	1.953	133.6
4	HP	1.947	133.5
5	HP	1.936	133.5
6	HP	1.921	133.3
7	HP	1.915	133.2
8	HP	1.903	133.0
9	HP	1.890	133.0
10	MPA	2.007	134.9
11	MPA	2.008	134.9
12	MPA	2.009	134.8
13	MPA	2.010	134.6
14	MPA	2.013	134.7
15	MPA	2.015	134.7
16	MPA	2.018	134.6
17	MPA	2.021	134.6
18	MPA	2.022	134.6
19	MPA	2.026	134.3
20	MPA	2.028	134.2
21	MPA	2.030	134.1
22	MPA	2.033	134.1
23	MPA	2.034	134.1
24	MPA	2.036	134.0
25	MPA	2.039	134.0
26	MPA	2.040	133.9
27	MPA	2.047	133.8

From the diagram it is concluded that the influence of stoichiometry on the transformation temperature is small at least in the region that we have studied. Also the temperature takes its highest value at the exact stoichiometry. Finally with the combination of the results of the present study with previous ones that have already been presented elsewhere [4], it can be concluded that specimens of higher purity present generally lower transformation temperatures.

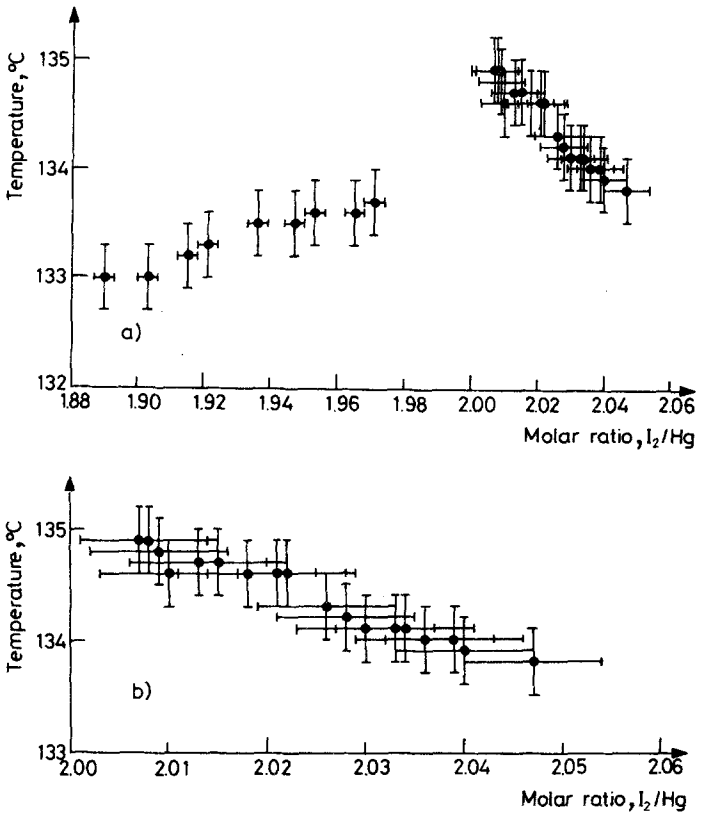

Fig. 1 (a) Dependence of stoichiometry on the transformation temperature. Every horizontal bar represents the spreading of the analysis results for all the four specimens taken from the same ingot. Every vertical bar represents the corresponding spreading of the temperature measurements of the same specimens.
(b) An enlargement of the I-rich region

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Zusammenfassung — In einem begrenzten Intervall in der Nähe der exakten Stöchiometrie von Quecksilberjodid wurde der Einfluß der Stöchiometrie auf die α/β Umwandlungstemperatur untersucht. Es konnte festgestellt werden, daß dieser Einfluß zwar gering ist, die Umwandlungstemperatur ihren größten Wert jedoch bei der exakten Stöchiometrie erreicht.