Sci. Annals, Fac. Sciences, Univ. Thessaloniki, **23**, 31 (1983)

THE EXISTENCE OF A NEW HIGH TEMPERATURE PHASE OF HgI_2 AND THE PREPARATION OF α - HgI_2 SINGLE CRYSTALS (GROUP THEORY ARGUMENTS)

By

S.N. TOUBEKTSIS, E.K. POLYCHRONIADIS and N.A. ECONOMOU

(University of Thessaloniki)

and A. TOUSIMIS *(Biodynamics Laboratory)*

Abstract: *The main principles concerning the transition of the yellow phase β-HgI_2 to the red phase α-HgI_2 are analyzed. This establishes that no genealogical relation exists between the two phases and a new phase was sought that would lead to a parental compound. This was confirmed by DTA measurements which indicated that the yellow phase transform to a new phase at the temperature 259°C leading to a red phase presumably of tetragonal symmetry. Single crystals of this high temperature phase quenched in ice water lead to single crystals of the α-HgI_2, without passing through the β-phase transition.*

HgI_2 apart from its technological importance imposes a real problem concerning its physical behaviour. It is well known that HgI_2 undergoes a phase transition, which depending on the purity of the material, lies in the vicinity of 127 °C. The low temperature phase is tetragonal with a space group D_{4h}^{15} and the high temperature phase is orthorhombic with a space group C_{2v}^{12}. Apart from that, two other phases have been reported, a tetragonal phase of space group D_{4h}^{19} and a superstructure of the α - HgI_2 phase which is considered metastable[1]. In seeking the genealogical relation among these structures we applied Landau and Lifshits criterion[2] which states that for group G_0 to transform into G_1 through a second order transition, $G_1 \subset G_0$. This criterion is a necessary condition as proved by Birman[3]. He also

1. S. Gauthier, I.F. Nicolau, J. Appl. Cryst 15, 461 (1982)
2. G. La Lynbarskii. The application of Group Theory in Physics, Pergamon Press, 1960.
3. J.L. Birman, J. Physique (Coll. Intern. sur le composes IV-VI, $C_4$29 (Suppl.) 151 (1968).

introduced a subduction criterion. Applying Seitz's symbolism the operators for the four space groups are

yellow phase β - HgI_2 (C_{2v}^{12}) $\{\sigma_x/00\frac{1}{2}\}$ $\{\sigma_y/000\}$

red phase α - HgI_2 (D_{4h}^{15}) $\{C_{4z}^{+}/00\frac{1}{2}\}$ $\{C_{2x}/\frac{1}{2}\,\frac{1}{2}\,0\}$ $\{1/\frac{1}{2}\,\frac{1}{2}\,0\}$

tetragonal metastable phase (D_{4h}^{9}) $\{C_{4z}^{+}/0\frac{1}{2}0\}$ $\{C_{2x}/\frac{1}{2}\,\frac{1}{2}0\}$ $\{1/\frac{1}{2}\,\frac{1}{2}\,0\}$

which can hardly fulfill the Landau-Lifshits criterion while the superstructure phase obviously is directly related to the α phase. Therefore a real problem is imposed, what is the parental structure of this compound. Of course the β - HgI_2 to α - HgI_2 transition due to the abrupt volume change was proposed to be a first order transition[4] and presumably the metastable phase occurs through a transition of similar order. Nevertheless the stability of the α - phase, the possible existence of a superstructure of the α - HgI_2 phase, and the stability enhancement with increased purity leads to thoughts that the tetragonal phase is a starting point in seeking for a parental structure.

We proceeded in a carefull study of the thermal behaviour of HgI_2 up to the melting point. For this a DTA (DSC-2 Perkin-Elmer) instrument was used and slow scanning measurements were taken. We used Merck proanalysis material. The measurements showed three deviations from the base line (fig. 1). The first one at a temperature 133°C, which coincided to the previous established critical temperature for the α - HgI_2 to β - HgI_2 transition. The second one occured 4 degrees before the last one which was due to the melting transformation. Therefore a new phase occured just prior to the melting.

Visual inspection of the sample during heating, showed that the material at 133 °C changed from red to yellow as expected for the α - HgI_2 to β - HgI_2 transition. At the temperature 259°C the yellow β - HgI_2 phase turned to a red solid material and at the temperature 263°C the material melted to a high viscous liquid which immediately lost its high viscosity.

We attempted an X ray powder analysis of the high temperature

4. A. Gaumann, Chimia (Aarau) 20, 82 (1966).

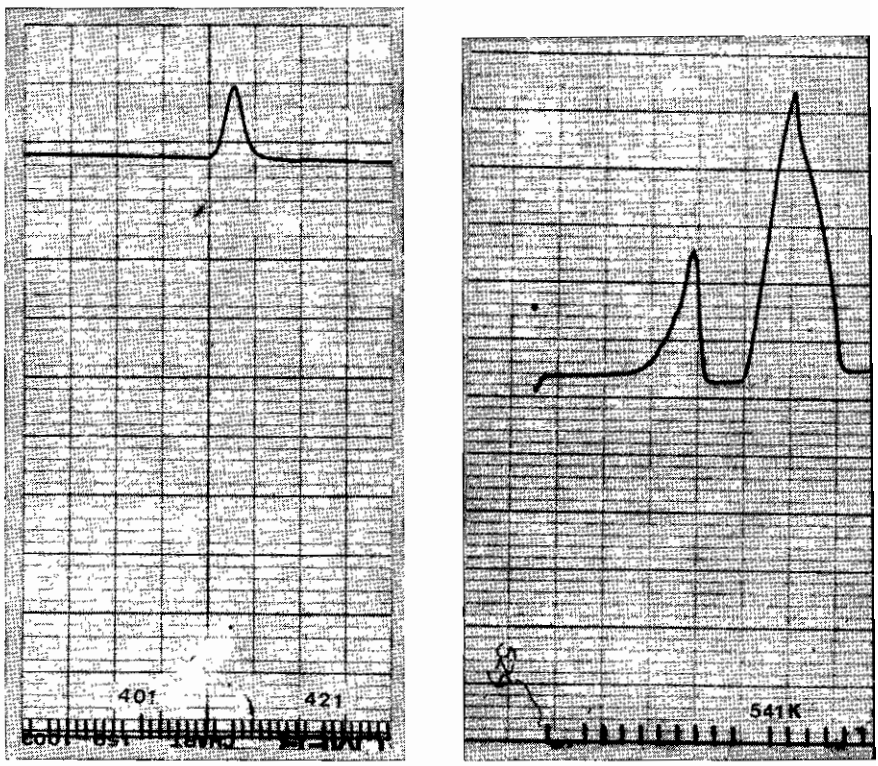
solid phase but due to the high volatility of the compound and the small temperature range of stability we obtained only evidence that this high temperature red phase was tetragonal.

Quenching the material from the temperature 259° C were the high temperature phase is stable to room temperature the phase obtained was the red α-phase of HgI_2, without passing through the β-phase, as proved by ×-ray powder analysis (fig. 2).

After establishing these facts the procedure of growing single crystals of α - HgI_2 was confined into growing single crystals at the temperature range of the stability of tne high temperature red phase and quenching them to ice temperature.

By using a quartz ampoule with a tapered end and the charge material under vacuum 10^{-5} mmHg we were able to grow single crystals ot a conical shape of 0,6cm length and 0,6cm base diameter (fig. 3).

We are proceeding now further to develop a suitable metbod in order to grow crystals at any desired volume.



a *b*

Fig. 1. Thermogram of HgI_2 showing the three phase transition temperatures at 133 °C (a), 259 °C and the melting at 263 °C (b)

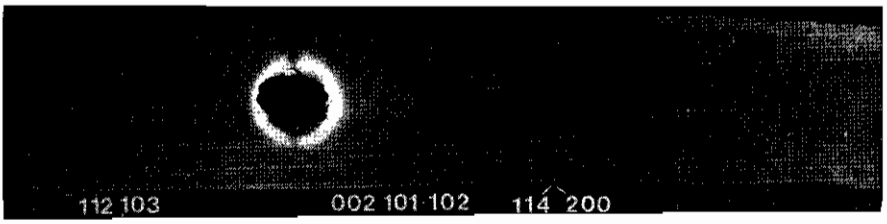


Fig. 2. X-ray powder diagram of the quenched material identifying the red a-phase of HgI_2

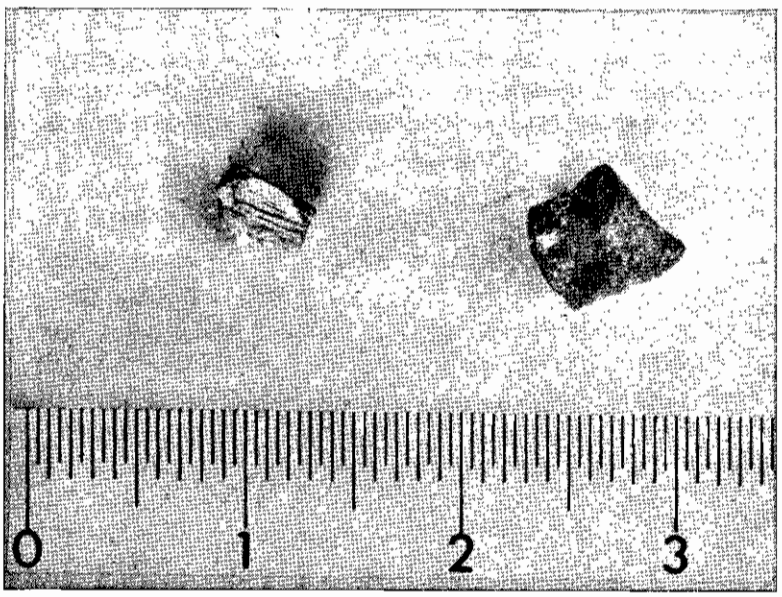


Fig. 3. Single crystals of a-HgI_2.

Η ΥΠΑΡΞΗ ΚΑΙΝΟΥΡΓΙΑΣ ΦΑΣΗΣ ΥΨΗΛΗΣ ΘΕΡΜΟΚΡΑΣΙΑΣ ΤΟΥ HgI_2 ΚΑΙ Η ΠΑΡΑΣΚΕΥΗ ΜΟΝΟΚΡΥΣΤΑΛΛΩΝ α - HgI_2 (ΣΥΖΗΤΗΣΗ ΜΕ ΔΕΔΟΜΕΝΑ ΤΗΣ ΘΕΩΡΙΑΣ ΟΜΑΔΩΝ

Σ.Ν. ΤΟΥΜΠΕΚΤΣΗΣ, Ε.Κ. ΠΟΛΥΧΡΟΝΙΑΔΗΣ, Ν.Α. ΟΙΚΟΝΟΜΟΥ

(Πανεπιστήμιο Θεσσαλονίκης)

Α. ΤΟΥΣΙΜΗΣ *(Biodynamics Laboratory)*

Οι αρχές που αφορούν τη μετατροπή της κίτρινης φάσης β - HgI_2 στην κόκκινη φάση α - HgI_2 αναλύονται. Από την ανάλυση αυτή προκύπτει ότι γενεαλογική σχέση μεταξύ των δύο δομών δε δύναται να υπάρξει και γι'αυτό αναζητείται η μητρική δομή. Βρέθηκε από μετρήσεις διαφορικής θερμικής ανάλυσης ότι η κίτρινη φάση μετατρέπεται σε μια νέα φάση στη θερμοκρασία 259 ^{0}C που οδηγεί σε μια κόκκινη φάση με τετραγωνική δομή. Μονοκρύσταλλοι αυτής της υψηλής φάσης με πάγωμα στο μίγμα πάγου και νερού οδηγούν σε μονοκρυστάλλους της α - HgI_2 φάσης, χωρίς να διέλθουν από τη β - HgI_2 φάση.