

## Differential thermal analysis under high hydrostatic pressures. Application to determination of phase diagram of semiconductors<sup>1</sup>

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### Abstract

In order to determine the melting curve of different materials under high gas pressures, a system for differential thermal analysis has been developed. A gas compressor with three stages of compression allows us to obtain pressures up to 1.5 GPa. The furnace in which the test material and the reference (boron nitride) are placed can operate up to 1000°C. This equipment was used at first to determine the melting curve of mercury telluride: the melting point decreases with pressure, and the slope of the melting curve is close to that reported in the literature, but the phase transition from zinc blende to cinnabar ( $B_3 \rightarrow B_9$ ) was not observed in our pressure range. This equipment was later used to study the influence of iron doping on the liquidus. The melting point, which was slightly lower in this case, also decreased with pressure.

### INTRODUCTION

We were interested in the phase diagram of mercury telluride (HgTe) in order to characterize this material under high hydrostatic pressures. This phase diagram had already been plotted by Jayaraman et al. [1], but working conditions were different from ours: non-hydrostatic pressures, large uncertainties of measurement ( $\pm 0.1$  GPa for pressures,  $\pm 3^\circ\text{C}$  for temperatures). In order to resume this study, realization of a differential thermal analysis procedure under high gas pressures was necessary.

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## EXPERIMENTAL

Our initial equipment for material growth consisted of the following parts.

(a) The gas compressor with three stages of compression connected in series. The first stage allowed us to obtain a gas pressure of 76 MPa, the second a gas pressure of 375 MPa and the third one a gas pressure of 1.5 GPa. By regulation of compression rate, experiments could be made between 0.1 and 1.5 GPa. Gas pressures were measured by a manganin coil (sensitivity  $\pm 1\%$ ).

(b) The gas pressure chamber (inside diameter 30 mm) incorporated three metal jackets. At its ends two plugs were fitted; one for the gas capillary (inside diameter 0.3 mm) and the other for electrical connections.

(c) The furnace, in which the heater was a graphite spiral divided into three zones by four graphite electrodes. Each was regulated separately by a Eurotherm 818 unit, so that a uniform temperature could be obtained over the whole crucible. The temperature profile was evaluated by three thermocouples (Pt/Rh 6%–Pt/Rh 30%). The distance between the first and the third thermocouple was 40 mm. Thermal fluctuations did not exceed 1°C under steady-state conditions; when the temperature was changed with a high cooling or heating rate (i.e. 100°C min<sup>-1</sup>), they reached 2°C.

With this equipment, only the addition of a fourth thermocouple was necessary to obtain a differential thermal analysis system. This new thermocouple allowed us to measure the difference in temperature between the material and the reference (boron nitride), both of them placed in the crucible, during the heating and cooling runs. The furnace is shown schematically in Fig. 1.

The DTA signals were checked for heating and cooling runs in the temperature region close to the expected melting/freezing point. The heating/cooling rate did not much affect the melting point, so a rate of 50°C min<sup>-1</sup> was chosen. This rate appeared to be the best for subsequent data analysis. The difference between the melting and freezing points did not exceed 5°C.

For DTA measurement, polycrystalline ingots of materials were prepared by a standard procedure in a quartz ampoule; pure HgTe single crystals, provided by R. Triboulet (C.N.R.S. Meudon, France) were also used. In our experiments the gaseous pressure medium was argon.

## RESULTS

We were interested first in the diagram for HgTe. In Fig. 2, as an example, we show the DTA signal for the HgTe melting/freezing process at 0.7 GPa. Our results, compared with those of Jayaraman et al., are plotted in Fig. 3. The melting point decreases with pressure. The slope of

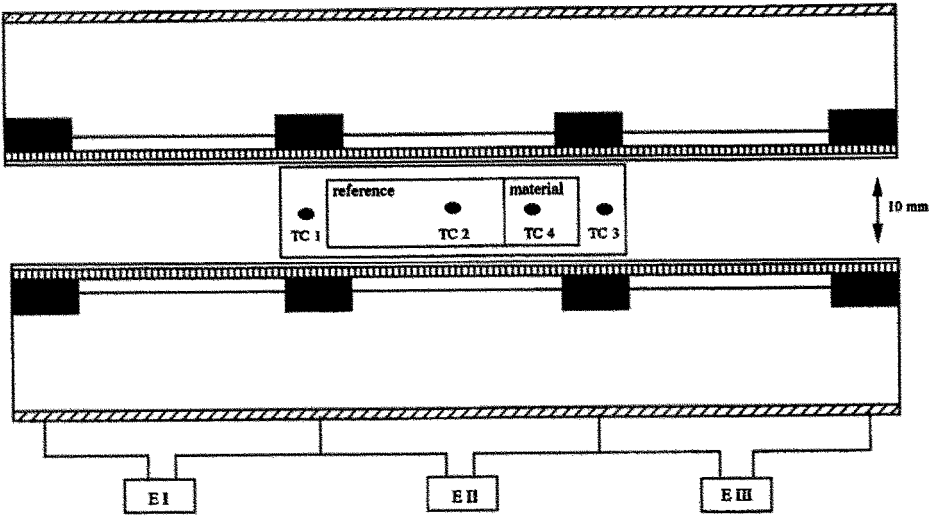


Fig. 1. Scheme of the furnace.

the melting curve is close to that reported in the literature, but the phase transition from zinc blende to cinnabar ( $B_3 \rightarrow B_9$ ) has not been observed. Complementary experiments made in the same conditions but with pressures up to 2 GPa (at the High Pressure Research Centre of the Polish Academy of Sciences, Warsaw) led us to anticipate a triple point near 1.7 GPa.

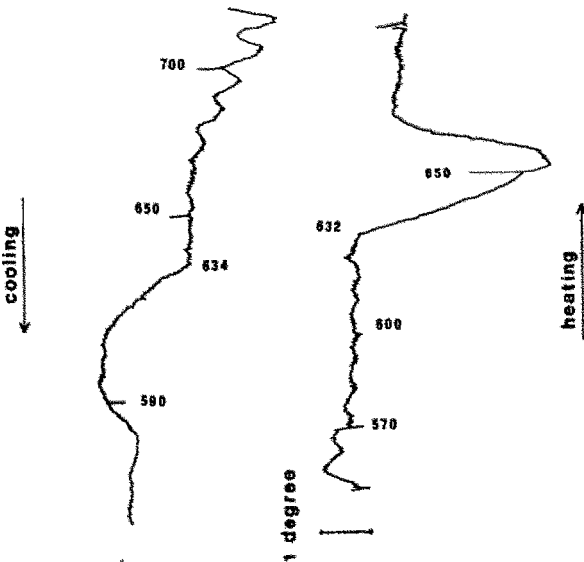


Fig. 2. DTA signal for the HgTe melting/freezing process at 0.7 GPa.

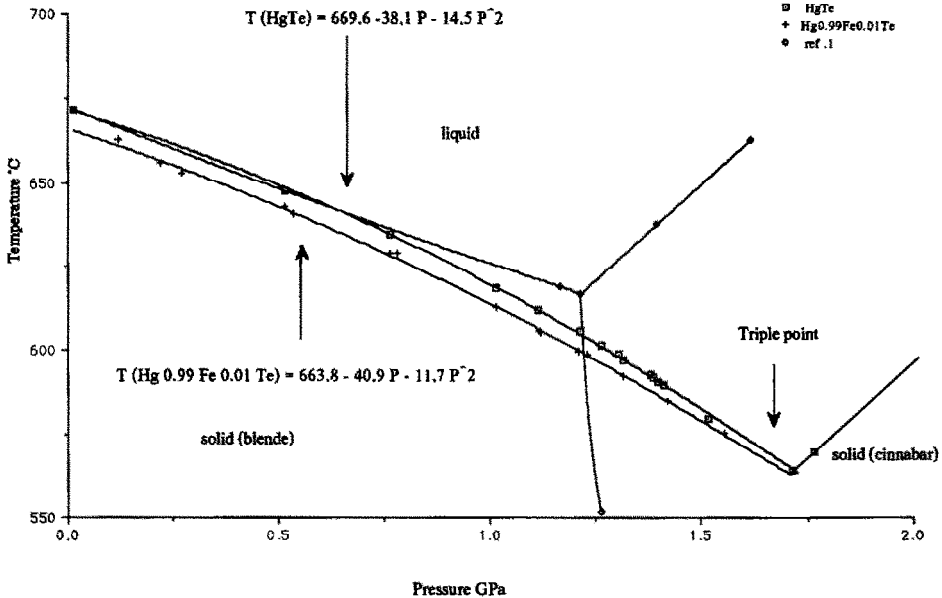


Fig. 3. Diagram  $(T, P)$  of HgTe. Influence of iron doping on the liquidus.

We later studied the influence of iron doping on the liquidus. The melting point, which is slightly lower in this case, also decreases with pressure (Fig. 3). This slight difference results from the low solubility of iron in HgTe. X-ray diffraction, metallographic examinations and EDX measurement permit us to state that the limit of solubility is 1 at%. It will be interesting here also to make complementary experiments under higher pressures to see if iron in HgTe stabilizes the zinc blende structure, as is the case in HgSe or with manganese in HgTe [3].

## CONCLUSION

Differential thermal analysis under high gas pressures, with close regulation of temperature and good precision for pressure measurement, has been performed. The new equipment allowed us to determine the  $(T, P)$  diagram for HgTe in our pressure range, and to observe a weak influence of iron doping on the liquidus.

Similar work has been carried out with HgSe; the main advantage of this compound is that its phase transition occurs at a lower pressure. The melting curves (B3 → liq) and (B9 → liq) are well determined, but the triple point is not yet known with precision. This work is in progress.

## REFERENCES

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