Thermochimica Acta, 237 (1994) 133-141
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01598-W

A differential thermal analysis (DTA) apparatus for the investigation of liquid crystalline compounds at high pressures

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(Received 14 June 1993; accepted 9 September 1993)

Abstract

A DTA apparatus is presented for the temperature range 300-600 K, and up to 1 GPa pressure. It was designed for the investigation of liquid crystals but can also be used for other substances. The heater is wound directly on the DTA measuring head within the high-pressure gas chamber. The sample is hermetically encapsulated in an upside-down small glass bulb which is completely submerged in a metallic liquid. This new kind of sample encapsulation enables a completely hysteresis-free pressure transmission and an absolute protection of the substance from contamination by the pressure medium in a DTA measuring head.

INTRODUCTION

The phase diagram of a substance shows basic and general relationships of its high pressure behaviour. Thermal methods provide a suitable means to determine the transition lines under pressure [1, 2]. In this paper, we present a DTA apparatus for the investigation of liquid crystalline substances under elevated pressure. In the design of the measuring head we took care to provide an absolute gas-tight separation between the substance and the pressure-transmitting medium (argon), a hydrostatic transmission from the pressure gas on the probe, and a sufficiently exact and sensitive measurement of pressure and temperature (for details, see ref. 3).

THE HIGH-PRESSURE DTA EQUIPMENT

The experimental set-up is outlined in Fig. 1. For generating high pressure we used the high-pressure gas compressor IF 012 A (Unipress, Warsaw) working up to 1.5 GPa. The pressure was measured in the third stage of the intensifier of the compressor, which was hydrostatically con-

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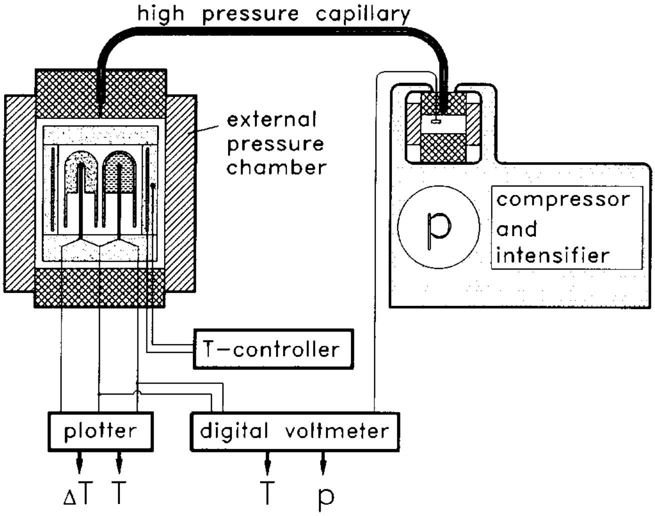

Fig. 1. The experimental set-up of the high-pressure DTA apparatus.

nected with the external working chamber (internal diameter 20 mm) by a beryllium–bronze capillary. The working chamber contained the DTA measuring head. The temperature could be changed linearly using a simple electronic device (workshop made), which worked with regulation steps of 0.025 K and allowed heating rates between 0.01 and 10 K min^{-1}. The voltages from the DTA thermocouples were sent to a plotter to draw the DTA curves ($\Delta T - T$, $\Delta T - t$) and to a digital voltmeter (resolution 1 μV). In addition to the temperature measurement, the digital voltmeter was used for the determination of the pressure.

Determination and calibration of pressure and temperature

For the pressure measurement, we used a commercial Manganin® resistor coil (Unipress, Warsaw) in the four-wire mode. During all calibrations and ordinary measurements, the high-pressure vessel of the compressor (third stage) and the pressure sensor were kept at a constant temperature of 299.7 ± 0.1 K. The pressure dependence of the electrical resistance R of the Manganin® coil was calibrated (for details, see ref. 3) with reference to the exactly known melting line of mercury [4]. Using a quadratic equation [5]

$$R = R_0(1 + \gamma_1 p + \gamma_2 p^2) \qquad (1)$$

to represent the weak non-linearity of the $R-p$ relation, we obtained from the fit of the calibration data the coefficients $\gamma_1 = 2.373 \times 10^{-5}\ \mathrm{MPa}^{-1}$ and $\gamma_2 = -1.9 \times 10^{-10}\ \mathrm{MPa}^{-2}$, with $R_0 = 88.197\ \Omega$ (0.1 MPa, 299.7 K).

The maximum deviation of eqn. (1) from a straight line between the first (0.1 MPa) and the last data point (756.9 MPa; i.e. the melting pressure of mercury at 273.15 K), described by

$$R = R_0(1 + \gamma p) \quad (2)$$

with $\gamma = 2.36 \times 10^{-5}\ \mathrm{MPa}^{-1}$, amounts to only 2.5 mΩ and 1.1 MPa, respectively, in the middle part of the parabola. Reported data lie between 1.0 MPa and 2.1 MPa [6]. The results of our calibration agree with reported data (2.2×10^{-5}–$2.5 \times 10^{-5}\ \mathrm{MPa}^{-1}$ [5, 6]).

For temperature measurement, we used type K thermocouples (diameter of the thermoelectric wires 0.1 mm; glass fibre isolated), calibrated against standard thermometers. The pressure dependence of the thermoelectric response of the thermocouples was taken into consideration, according to Getting and Kennedy [7].

The estimated maximum error for the determination of the pressure amounts to ± 0.6 MPa ($p \leq 150$ MPa), and ± 1.1 MPa ($p > 150$ MPa), respectively, and for the determination of the temperature ± 0.5 K ($T \leq 473$ K) and ± 0.9 K ($T > 473$ K), respectively. By test measurements we were able to determine the melting temperature of highly purified indium (429.6 K [8]) and tin (505.0 K [8]) within a deviation of 0.1 K at lower temperatures. In addition, comparative pressure measurements with officially calibrated Bourdon manometers yielded maximum deviations of 0.2 MPa at 160 MPa.

The DTA measuring head

The DTA measuring head was placed in the external high-pressure chamber (see Fig. 1). The central part of the DTA measuring head (see Fig. 2) consists of a tantalum cylinder A (outer diameter 13 mm) with two titanium tubes B within a 7 mm × 12 mm (inner diameter) hole in A. The heating wire C is wound meander-like around the cylinder A. For the thermal and electrical isolation, we used asbestos paper and vitro ceramic material D. The sample E is inside a small glass bulb F (inner diameter 4 mm, outer diameter 6 mm). The sample capsule F and the reference capsule H are entirely immersed in liquid gallium G (for temperatures <300 K, mercury can be used), within the DTA oven. Because of the buoyancy, sample E remains within the upper part of the little glass bulb F, which is open at the bottom. The reference capsule is made of vitro ceramic. The use of a second glass bulb F, filled with a substance such as paraffin or silicon oil, as a reference capsule did not prove to be advantageous compared to the vitro ceramic capsule. The sample and reference capsules are fixed by a clip I.

An adapter part of the piston of the external chamber contains the thermocouples for measurement and control, as well as the sockets for the heating current supply. The thermocouple for the power control is within a metal tube ($\phi_0 = 0.8$ mm) and the DTA thermocouples are in two glass tubes ($\phi_0 = 1.3$ mm) with the hot junctions on the top. If the measuring

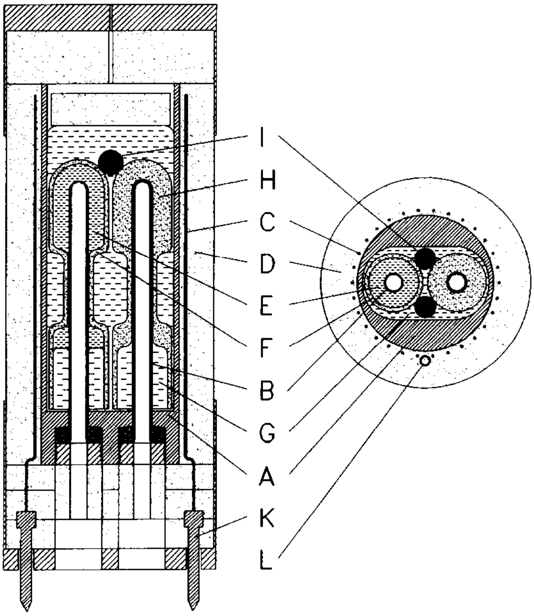

Fig. 2. The oven of the DTA measuring head; for key, see text.

head is plugged onto the adapter, the DTA thermocouples are introduced into the titanium tubes B, the thermocouple for the power control is positioned in a small tube L between a loop of the heating wire C, and the electrical contacts K for the heating current are put into the corresponding sockets. Because the glass tubes for the DTA thermocouples are elastically mounted, the hot junctions press against the closed ends of the tubes B and thus guarantee good thermal contact. An electrical contact at these points is prevented by a thin layer of varnish and corundum powder on the hot junctions.

The usable temperature range of the DTA measuring head is limited at the low temperature end by the freezing temperature of the liquid metal used (Ga, ≈303 K; Hg, ≈234 K), and at the high temperature end by the mechanical stability of the steel chamber ($T < 430$ K at the inner radius of the pressure chamber), which permits temperatures within the thermally isolated interior of the DTA head of 600 K. The very low vapour pressure of gallium would allow even higher temperatures to be applied, but its strong tendency to form alloys has to be considered and was the main reason for using titanium and tantalum in the central parts of the DTA oven.

During all measurements the external chamber was kept at a constant temperature (293 K).

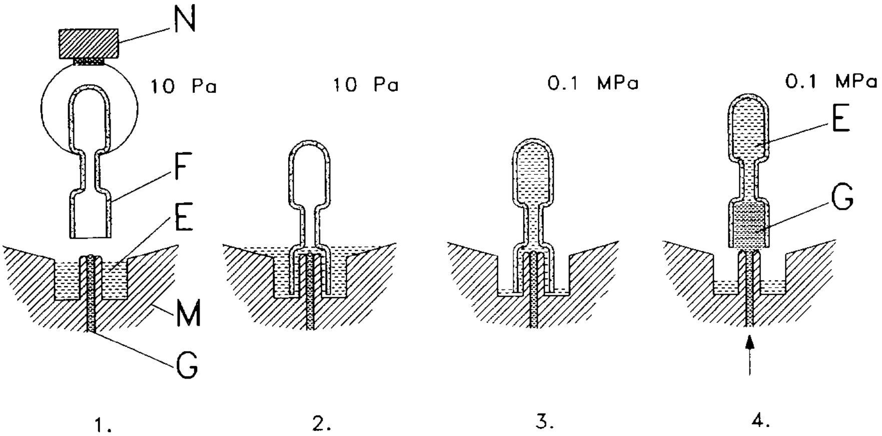

Fig. 3. The "encapsulation" of the sample. For a complete description, see text.

Sample preparation

To fill the sample capsule, we used the device sketched in Fig. 3. In the first step, the substance E has to be melted several times in the small heatable crucible M under vacuum. When bubble formation in the melt stops, the glass bulb F can be lowered into the melt using a manipulator N. Increasing the pressure (argon) to normal pressure values presses the liquid sample into the sample capsule (a small surplus substance is necessary to have no bubbles in the sample capsule). In the last step, liquid gallium G has to be pressed through the central hole in the crucible. The sample capsule is lifted and the sample is sealed (step 4 in Fig. 3). Afterwards the sample container can be taken from the crucible (slowly and carefully to prevent loss of gallium), slid over tube B in the pre-heated DTA oven (which already contains some gallium), and, as for the reference capsule, fastened by the clip I and covered with liquid gallium G (see Fig. 2). Finally, after crystallization of the sample in the sample capsule, it is useful to evacuate the whole measuring head to remove all gas from the interior of the DTA oven.

Parameters of the DTA equipment

The measured sensitivity of the equipment

$$E = \frac{\text{peak area } [\mu\text{V} \times \text{s}]}{\text{supplied energy}} \qquad (3)$$

was determined as about 0.3 μV mW^{-1}. For the equalization of the temperature difference ΔT between the sample and the reference capsule

TABLE 1

Clearing line data (T/K) for the compounds 7CB and 8OCB from different sources (interpolated values)

p/MPa	7CB			8OCB		
	Ref. 9	Ref. 10	This work	Ref. 11	This work [a]	This work [b]
0	314.7	315.2	315.6	353.2	353.2	353.2
50	338.5	332.0	333.6	369.7	369.9	370.0
100	362.1	348.7	350.9	385.4	385.5	385.8
150	385.3	365.2	367.4	400.5	400.4	400.6

[a] First measuring series to 826.5 MPa. [b] Second measuring series to 200.7 MPa.

$$\frac{\Delta T}{\Delta T_0} = \mathrm{e}^{-t/k} \qquad (4)$$

where ΔT_0 is the theoretical value of ΔT at $t = 0$ s, we found a time constant k of 1.6 s.

Usually, the volume of the sample was about 30 mm^3. A transition energy of 60 mJ per 30 mg of substance yields a maximum ΔT of 0.1 K between the two thermocouples in the case of a heating rate of 1.5 K min^{-1}. To realize a heating rate of 2 K min^{-1} at a temperature of 600 K we needed a heating power of about 200 W at a pressure of 1 GPa. Because of the nearly isochoric conditions in the pressure chamber, the pressure changes during the heating or cooling processes. These changes are 0.02 MPa K^{-1} at 100 MPa, 0.1 MPa K^{-1} at 300 MPa and 0.2 MPa K^{-1} at 600 MPa.

To produce a complete phase diagram, including repetitions of some transition points, long measuring periods (days, weeks) can occur. In all cases, the sample should not undergo decomposition. The transitions were repeatable, with no evidence that the pressure gas contaminated the sample or that the sample container was broken.

RESULTS

To estimate the reliability of the complete high-pressure DTA equipment, test measurements of the compounds 4-*n*-heptyl-4′-cyano-biphenyl (7CB) and 4-*n*-octyloxy-4′-cyano-biphenyl (8OCB) were performed. The comparison of the temperatures of the nematic–isotropic transition (clearing points) in Table 1 for 8OCB shows a satisfactory agreement with literature data. The small differences in the middle-pressure range lie within the error limits. In the case of 7CB even at normal pressure the clearing temperatures clearly differ. The divergences are too great to be interpreted without assuming an impurity or a decomposition. The latter is not relevant to our measurements, because we determined a depression of the clearing point of only

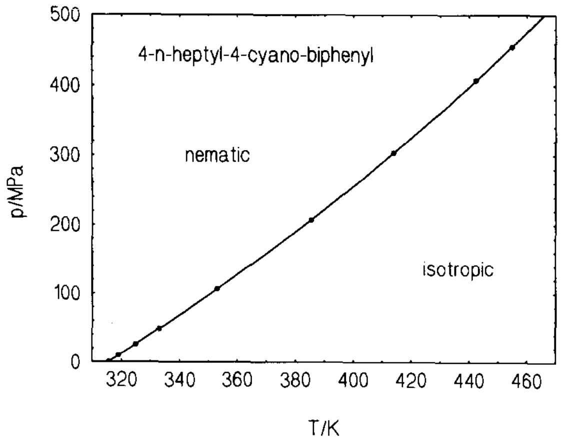

Fig. 4. Phase diagram of 7CB.

0.1 K after the measurements at 455 MPa. The clearing temperature of our 7CB was higher than that cited in the references which suggests a higher purity for our material. Therefore, we believe that our values are correct.

For pressures higher than 150 MPa, no sufficiently accurate data are available for comparison.

The phase diagrams of the compounds 7CB (Fig. 4) and 8OCB (Fig. 5) clearly demonstrate the stabilizing effect of pressure on the liquid-crystalline phase [12]. The supercooling effect of the liquid-crystalline/solid-crystalline phase transition was amplified by increasing pressure. In the case of 7CB, no crystallization occurred, either at normal pressure or at high pressure. The series of the DTA traces shown in Fig. 6 shows a clear increase in the

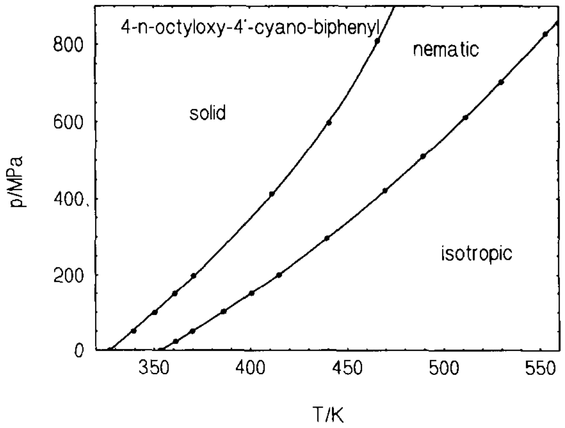

Fig. 5. Phase diagram of 8OCB the known smectic A–nematic transition was not taken into account.

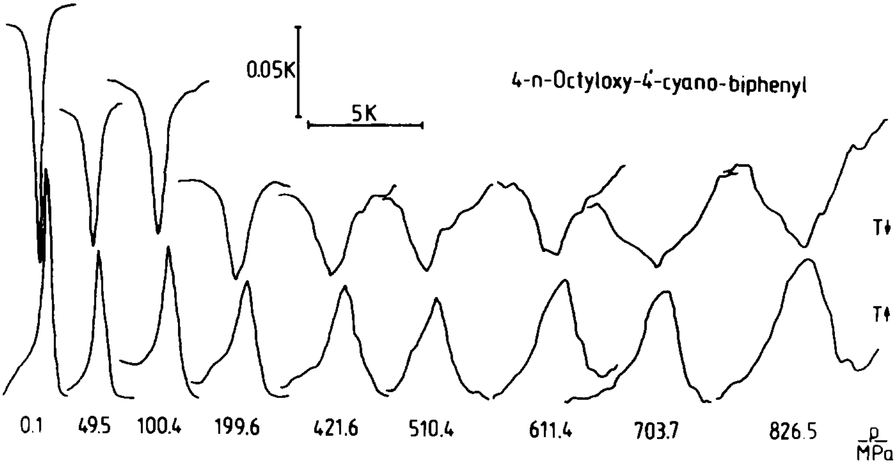

Fig. 6. $\Delta T-T$ DTA traces of the compound 8OCB at different pressures. $T\downarrow$ indicates a decreasing temperature run (cooling rate 1.5 K min^{-1}) and $T\uparrow$ an increasing temperature run (heating rate 1.5 K min^{-1}).

peak area, which indicates an increase in the nematic isotropic transition enthalpies. This behaviour agrees with the result of Kleinhans [11].

CONCLUSIONS

This high-pressure DTA equipment is a new type of construction which uses a heater inside the high-pressure vessel. It has been shown that the described encapsulation method provides reliable measurements without any danger of sample contamination by the pressure gas or resistance to the transfer of hydrostatic pressure to the sample (no hysteresis). Because the pressure and the temperature can be determined exactly, the phase transition lines are highly reliable.

In this regard, we remark that liquid crystals (especially their nematic–isotropic transitions) could be a useful pressure and/or temperature standard in the moderate pressure and temperature range (to about 600 K and 1.5 GPa). Some liquid crystalline compounds are quite thermally stable, e.g. 8OCB. The nematic–isotropic transition takes place without any hysteresis at precisely determinable $p-T$ values and the transition is easy to observe, e.g. by DTA or optically. Unfortunately there are too few exact (order of magnitude 1 MPa, 0.1 K) determinations of the clearing lines of the liquid crystalline compounds available at lower pressures and none available above 1 GPa.

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