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HIGH-PRESSURE DTA APPARATUS WITH LIQUID OR GASEOUS PRESSURE MEDIUM *

OSAMU YAMAMURO, MASAHARU OGUNI, TAKASUKE MATSUO and
HIROSHI SUGA

Department of Chemistry and Chemical Thermodynamics Laboratory, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

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ABSTRACT

A novel high-pressure DTA apparatus was developed for studies on the phase behavior of crystalline materials. It operates under constant hydrostatic pressure up to 200 MPa in the temperature range between 90 and 410 K. Either liquid 3-methylpentane or gaseous helium can alternatively be used as the pressure medium. Test runs on ND_4Br crystal with liquid pressure medium proved satisfactory with respect to stability of the baseline and sensitivity of the signal. Studies on the $CH_3NH_3BF_4$ crystal, in which a new phase transition was observed, were made with two kinds of pressure media. The influence of pressure and nature of pressure medium on the peak area are described.

INTRODUCTION

Thermoanalytical techniques have been widely accepted in various fields of science. An extension of this method for studying under high-pressure conditions is worthwhile in that the phase behavior can be understood through changes in two external parameters [1]. High-pressure DTA is effective as the preliminary investigation of time-consuming, operationally complicated high-pressure calorimetry, for which the apparatus has already been constructed in our laboratory [2,3]. Incipient high-pressure DTA was carried out under several giga-Pascals pressure with solid pressure medium. The sample and reference cells were placed asymmetrically. This situation induced a large gradient in the DTA curve and investigation was limited to the phase transition accompanied with a large heat effect. Since then, effort has been made to improve baseline stability. Some features of this improvement are high sensitivity [4], microanalysis [5], indirect contact between sample and pressure medium [6].

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There is a substantial, growing interest in the low-temperature study in this field. We report here a new apparatus which works under constant pressure up to 200 MPa in the temperature range between 90 and 410 K. The sample can be pressurized by using either of two kinds of pressure media, liquid 3-methylpentane or helium gas. Pressure was controlled within 100 kPa for the former and 1 kPa for the latter. A special sample cell and a simple method of pressure sealing were devised to make sample replacement easy. Test runs on the ND_4Br crystal, whose detailed thermal properties had already been reported [9], showed a reasonable baseline stability. A heat capacity change amounting to 10 J K^{-1} mol^{-1} in the crystal was resolved as a signal a few times larger than the noise level. For the $CH_3NH_3BF_4$ crystal, a new first-order phase transition was observed at 249.8 K at atmospheric pressure. The pressure dependence of the transition line was determined. Both the effects of changing pressure and pressure medium on the peak area were examined with this transition as a probe, and were proved to be small.

APPARATUS

The apparatus consists of five parts, a DTA block, a system of pressure generation and control, a pressure-media separator (only for using liquid as pressure medium), a system of evacuation, and a system of measurement. Constant hydrostatic pressure is usually desired for the measurements. Either liquid 3-methylpentane or gaseous helium can be employed as pressure medium making direct contact with the sample, since the former is known to undergo neither crystallization nor glass transition down to about 100 K. In the case of liquid medium, 3-methylpentane and kerosene were divided by the pressure-media separator, and the latter served as the pressure medium on the side of generation and control of pressure. The present DTA apparatus aims at the clarification of phase relations in crystals. Such an apparatus should possess the following features: high sensitivity, high baseline stability, and simple operation. The DTA block was therefore designed so as to make both mounting and dismounting a sample easy, to have a symmetrical arrangement of the sample and reference cells, and to attain good thermal contact between sample and thermocouple. The control of pressure is the most important factor for definitely determining the temperature and pressure of phase transitions and for stabilizing the baseline.

The system of evacuation is based on a usual method [7] with a rotary pump, and the system of measurement also has a usual arrangement combining a digital voltmeter, a DC amplifier, and a recorder. These two systems will not be described in further detail.

Structure of DTA block

Figure 1 is the sectional drawing of a cyclindrical DTA block. The block (A) was constructed from copper–beryllium allow. Two wells C1 and C2 (6

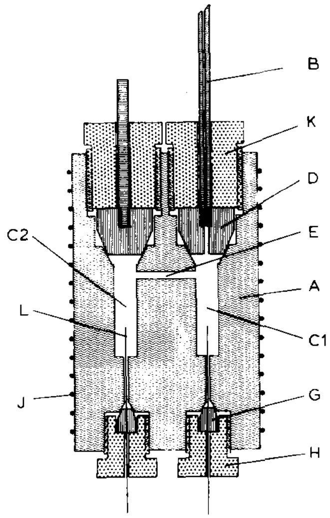

Fig. 1. Sectional drawing of a DTA block. (A) Body; (B) high-pressure tubing; (C1, C2) sample chambers; (D, G) plugs; (E) hole for transmitting pressure; (H, K) nuts; (J) heater wire; (L) thermocouple.

mm in diameter and 25 mm in depth) were drilled symmetrically in the block. One for the reference was occupied by an empty cell, and the other by a sample cell. The use of copper–beryllium alloy was based on its high thermal conductivity and strong mechanical property. A stainless-steel-sheathed thermocouple (L) was fixed at plug G with silver solder. This fixing method made repair of the thermocouple easy. Pressure was applied through strainless-steel tube B, and E is a hole for transmitting the same pressure to C2. Exchanging the sample cell in C2 is a rather complicated operation for such an apparatus. Therefore, the metallic cone connection between a stainless-steel plug (D) and a taper of the block was applied for simplicity to seal pressure in the block instead of Bridgeman's method which is usually adopted. The diameter of the contact circle was about 9 mm. The desired pressure (200–300 MPa) was considered to be within the safety region. Plug D was forced to push up under the influence of inner pressure. Therefore, a saw-toothed type of screw was devised for bolt K to withstand this force. The stainless-steel rod on the sample side, whose diameter is the same as the high-pressure tube B, was used to draw up the plug D. Heater wire J was wound around the outside of the block and the whole block was placed inside the glass jacket in the same way as for an apparatus for DTA under atmospheric pressure [7].

Figure 2 shows the sample cell embedded snugly in the block. Its outer tube and bottom plate were made of stainless steel, and the re-entrant inner tube was made of copper. The amount of sample in terms of depth was almost the same as the length of the copper tube.

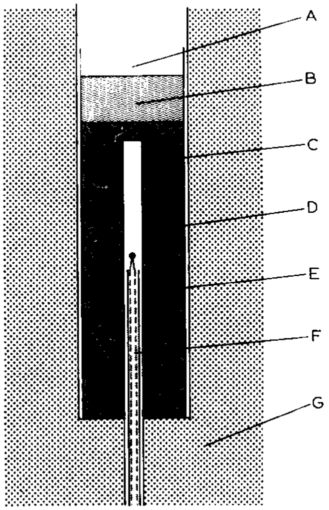

Fig. 2. Schematic drawing of a sample cell. (A) Pressure medium; (B) sheets of polyethylene packing; (C) stainless-steel cell; (D) sample; (E) re-entrant well of copper; (F) sheathed copper–constantan thermocouple; (G) body of the DTA block.

Polyethylene foil was packed tightly over the sample in the cell to prevent it from flowing out of the cell. The inner tube was in the center of the cell, and a thermocouple junction was adjusted in height to the middle of the tube.

The sample cell was devised and used for easiness of exchanging the sample and for potential application to various kinds of samples. Substitution of sample was fulfilled only by replacement of the cell. The inner copper tube had the purpose of protecting the thermocouple from making direct contact with the crystal sample resulting in its breakage. Its length could be made longer or shorter.

High-pressure system for liquid pressure medium

Figure 3 shows a schematic drawing of the pressure control system for liquid pressure medium that applies hydrostatic pressure to the sample and keeps it constant. Pressure generated at A was read from the scale of a Heise pressure gauge (C). The role of kerosene as pressure medium was replaced by 3-methylpentane at separator F. Pressure control was carried out by regulating the temperature of the kerosene reservoir (D). A minor change in pressure brought a corresponding change in resistance of a strain-free Manganin coil in a thermostatted oil bath (E). The resistance constitutes one arm of a Wheatstone bridge, and an electric signal was produced by the bridge in response to the deviation of the resistance from a preset value. This signal was used to regulate the temperature of the reservoir. The inner volume of the kerosene reservoir was about forty times larger than the

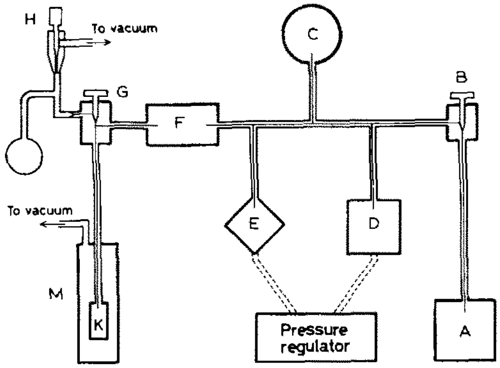

Fig. 3. Scheme of high-pressure system for liquid pressure medium. (A) Pressure generator; (B, G) valves; (C) Heise pressure gauge; (D) kerosene reservoir; (E) Manganin resistance manometer; (F) pressure-media separator; (H) polytetrafluoroethylene cock; (J) glass casing.

volume of chambers in the block (K). Assume, for example, a temperature change of 100 K in the block during measurement. This induces a pressure change due to thermal expansion of pressure medium and the other parts of the apparatus. With the present system it could be compensated by changing the temperature of the kerosene reservoir by about 3 K. The method made it possible to control the pressure automatically within 0.1 MPa over the whole temperature and pressure ranges [2]. This stable control of pressure contributed to a large extent to baseline stability as described later.

Glass bulb J and polytetrafluoroethylene (PTFE) cock H were used to introduce 3-methylpentane into the high-pressure system after mounting a sample cell in the block (K). First, 3-methylpentane in J was outgassed by freeze–thaw cycles repeated with cock H opened and valve G closed. Next, valve G was opened and the high-pressure system on the left-hand side of the separator (F) was evacuated. Finally, cock H was closed and the liquid in J was introduced into the high-pressure system by vacuum distillation. The extent the system had been filled with liquid could be followed by a signal from the separator (F).

Pressure media separator

A pressure-media separator (Fig. 4) was used for separating liquid pressure media and checking the tightness of the high-pressure seal of the DTA block. The separator was composed of a high-pressure system containing a core (F), a cathetometer (H), and a differential transformer (G). Plugs (E1) and (E2) were fixed at both ends of a cylinder (D) by Bridgeman's method of sealing. Soldered onto E1 was the open end of a phosphorus–copper bellows (B) which could expand or contract by a very small difference in pressure (< 0.02 MPa). A core (F) was made of Permalloy, possessing high magnetic permeability, and connected to the closed end of the bellows with a

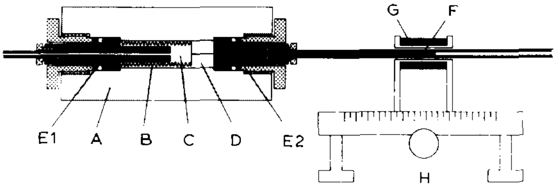

Fig. 4. Sectional drawing of a pressure-media separator. (A) Body; (B) bellows; (C) chamber for liquid 3-methylpentane; (D) chamber for liquid kerosene; (E1, E2) plugs; (F) Permalloy core; (G) differential transformer; (H) cathetometer.

thin stainless-steel rod. If volume change occurred on the block side filled with 3-methylpentane for some reason, the bellows expanded or contracted so as to keep the pressure constant resulting in a change in position of the core. This change was monitored by the output signal of the secondary coil of the differential transformer (G) annexed onto a cathetometer, and followed by a shift in position of the transformer to keep the output signal equal to zero. Therefore, if there was a pressure leak in the block, it could be detected as a stationary shift of the position of the core (F).

High-pressure system for gaseous pressure medium

A gaseous high-pressure system is, in principle, the same as a liquid one but without the separator nor the arrangements for introducing 3-methylpentane into the system. The details of the system will be reported elsewhere [3], and only its outline is described here. A double-head model helium–gas compressor (Nova Swiss 554, 3330-2) served to generate pressure. The pressure was directly transmitted through tubing to the sample in the DTA block. Pressure regulation was performed within 1 kPa (instead of 100 kPa in the case of liquid medium) during measurement by using a high sensitivity PID control circuit because compressibility and heat of compression of a gas were much larger than those of a liquid.

EXPERIMENT ON ND_4Br CRYSTAL

ND_4Br crystal has the CsCl structure in the β-phase at room temperature and atmospheric pressure. ND_4^+ ions are known to be disordering between the two different orientations. When cooled, the crystal transforms into the tetragonal phase in which adjacent ND_4^+ ions take a parallel orientation along the *c*-axis and an antiparallel one within the *ab*-plane and Br^- ions shift their position a little along the *c*-axis with the accompanying shortening of the $N-D \cdots Br$ hydrogen bond. Further cooling brings the crystal back into the same cubic structure as the β-phase. All the ND_4^+ ions in this phase

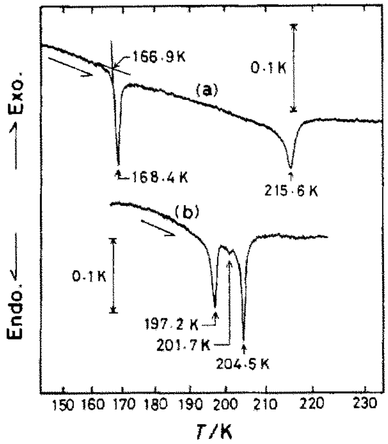

Fig. 5. DTA curves of ND_4Br crystal in the heating direction using liquid medium; (a) 0.101 MPa; (b) 55.8 MPa.

have parallel orientations. The two ($\delta \rightarrow \gamma$ and $\gamma \rightarrow \beta$) phase transitions approach each other in temperature with increasing pressure. There is a triple point near 66 MPa and only the two phases δ and β are found above this pressure [8]. Watanabe et al. [9] reported complicated behavior in the neighborhood of the triple point including the appearance of a new peak in the heat capacity curve. The total entropy of phase transitions from the δ to β phases is almost equal to $R \ln 2$. This is the typical value of the phase transitions due to disordering in the positions and orientations of molecules and ions. The results of DTA on ND_4Br crystals under certain constant pressures are shown in the following so as to exemplify the performance of this apparatus.

The sample used was taken from the same batch as that prepared for high-pressure calorimetry [9]. The deuteration level was 99.5%. The heating rate was 1–2 K min^{-1} in all the measurements.

Figure 5 compares two heating curves of DTA obtained at different pressures. The upper curve is at 0.1 MPa (atmospheric pressure), and the lower is at 55.8 MPa, which is a pressure in the neighborhood of the triple point. Two phase transitions are clearly recognized, and the shape of DTA curves is very similar to the temperature dependence of heat capacity reported previously. The $\gamma \rightarrow \beta$ phase transition which appears in the higher temperature region gradually changed its characteristic shape from λ-type to first-order type with increasing pressure. A new small peak appeared at 201.7 K in the curve at 55.8 MPa. This corresponds to the unique property of this substance observed in the high-pressure calorimetric measurement.

Figure 6 shows results on heating at 101.3 and 205.2 MPa. It is clear that the $\delta \rightarrow \beta$ phase transition has a first-order characteristic at 101.3 MPa but no longer has the characteristic at 205.2 MPa which is close to the tricritical point pressure ($\sim$ 230 MPa).

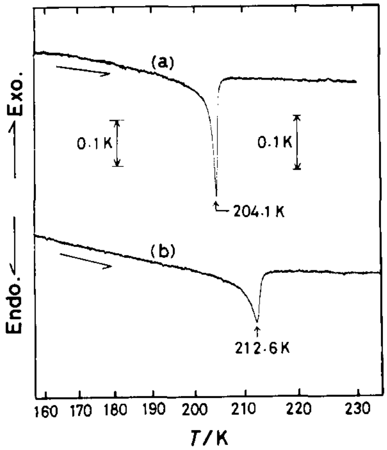

Fig. 6. High-pressure DTA curves of ND_4Br crystal on heating using liquid as the pressure medium: (a) 101.3 MPa; (b) 205.2 MPa.

All the absolute values of transition temperatures which were taken as the peak temperature agreed with the results from the high-pressure calorimetric measurement within ± 0.5 K. There was slight noise, independent of pressure. The magnitude of about 0.05 μV corresponding to ± 2 mK is principally attributed to the noise level of the DC amplifier and other electric equipment. The magnitude of signal, namely the sensitivity, was about one third compared with those in the usual measurements under atmospheric pressure. In the case of this substance, ND_4Br, a heat capacity change of 10 J K^{-1} mol^{-1} was recorded as about 0.2 μV (which corresponds to 8 mK) using a heating rate of 1.5 K min^{-1}. These would indicate the high baseline stability and the high sensitivity of the present apparatus in view of various adversities encountered in high-pressure DTA.

EXPERIMENT ON $CH_3NH_3BF_4$ CRYSTALS

$CH_3NH_3BF_4$ crystals were prepared from an aqueous solution of methylamine by adding hydrotetrafluoroboric acid, purified by repeated recrystallization from methanol solution, and finally dried in vacuo at room temperature for more than 12 h. Elemental analysis gave the following results: C, 10.20 (10.10); H, 5.11 (5.09); N, 11.76 (11.78) wt%. The values in parentheses are calculated values. DTA of the crystal was carried out by using both gaseous and liquid pressure media in the temperature range 100–410 K and the pressure range up to 200 MPa. The heating rate was 1–2 K min^{-1} in all the measurements. The transition temperature was determined as the rising temperature of the peak.

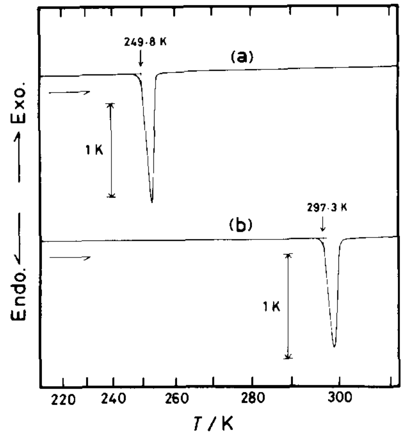

Fig. 7. DTA curves of $CH_3NH_3BF_4$ crystal in the heating direction using helium gas as the pressure medium: (a) 0.101 MPa; (b) 195.0 MPa.

Figure 7 shows the heating curves of DTA taken at 0.1 MPa (a) and 195.0 MPa (b) with helium gas as pressure medium. Large and sharp endothermic peaks appeared at 249.8 K in (a) and 297.3 K in (b). The peak in (b) is a little broader than that in (a) because the heating rate at transition temperature in the former (1.0 K min^{-1}) was slower than that in the latter (1.7 K min^{-1}). The corresponding peaks on cooling appeared at 243.7 K for 0.1 MPa and at 291.3 K for 195.0 MPa. These large hysteresis phenomena (about 6 K) indicate that this phase transition is of first order. The enthalpy of transition at 0.1 MPa was determined to be 5.17 kJ mol^{-1} from a separate DSC measurement by using a Perkin-Elmer DSC-2, corresponding to an entropy of transition of 20.7 J K^{-1} mol^{-1}. This large entropy change would indicate that this phase transition is associated with the orientational disorder of both the $CH_3NH_3^+$ cation and the BF_4^- anion. The P–T phase diagram of $CH_3NH_3BF_4$ is shown in Fig. 8. The pressure dependence of the transition temperature was determined to be 0.242 K MPa^{-1}. The volume change at the transition point is thus calculated to be 5.01 cm^3 mol^{-1} with the help of the Clausius–Clapeyron equation. This volume change is fairly large compared with those of the ordinary transitions in ionic crystals. Almost the same results as described above were obtained by using the liquid 3-methylpentane as pressure medium.

With this transition as a probe, we investigated the effect of changing pressure on the area of the DTA peak in both experiments with gaseous helium and liquid 3-methylpentane as pressure media. Figure 9 shows the ratio of the peak area at each pressure to that at 0.1 MPa after correcting for the difference in thermoelectric power of the thermocouple at each transition temperature. Open circles represent the data obtained by using gaseous medium and triangles by using liquid medium. The absolute areas of DTA peaks at 0.1 MPa with different pressure media were almost the same. This is

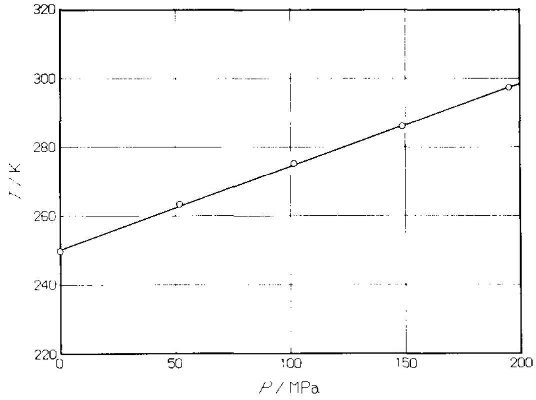

Fig. 8. Phase diagram of $CH_3NH_3BF_4$ crystal. Pressure dependence of the transition temperature is calculated to be 0.242 K MPa^{-1}.

expected from the fact that thermal conductivities of gaseous helium and liquid 3-methylpentane are almost the same at 250 K and 0.1 MPa: 0.150 W m^{-1} K^{-1} for the former and 0.135 W m^{-1} K^{-1} for the latter, respectively. A glance at the figure shows that the area decreases with increasing pressure and that this tendency is remarkable in the case of a gaseous medium. Generally, the area of a DTA peak is inversely proportional to thermal conductivity between the sample and the DTA block. Such heat conduction occurs in the present apparatus through the pressure medium. Therefore, the decrease in area is considered to be due to the increase in thermal conductivity of the pressure medium, which is salient in a gaseous medium.

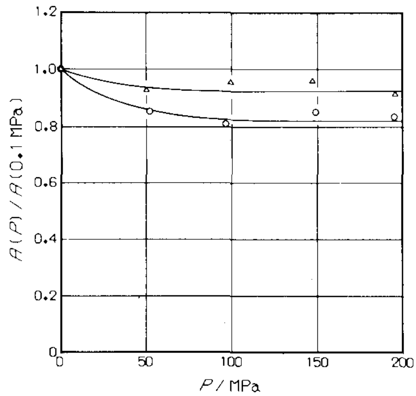

Fig. 9. Pressure effect on the DTA peak area relative to that at 0.1 MPa after correction for the temperature dependence of thermoelectric power of the thermocouple. (○) Data using gaseous medium, (△) using liquid medium.

CONCLUDING REMARKS

It was found that the position of the thermocouple junction inside the re-entrant tube is an important factor in baseline stability and sensitivity of the DTA curve. Exothermic or endothermic effects of the sample were transmitted inwards more sensitively than outwards because the thermal conductivity of copper is more than ten times higher than that of stainless steel. No significant difference was expected in the effects transmitted from the sample between upper and lower portions of the inner tube, because the depth of sample and the length of copper tube were the same. Thus, the thermocouple might detect the thermal anomaly of the sample sensitively and efficiently. Heat conduction, however, also occurs upwards through the pressure medium, especially when using helium gas at high pressure, so that it was difficult to obtain the same sensitivity as that of an ordinary DTA apparatus using about 10 kPa of gas as heat exchanger. Results on the test samples of ND_4Br and $CH_3NH_3BF_4$ showed satisfactory sensitivity and baseline stability. It is now possible to clarify the phase relation of a substance with respect to temperature and pressure. If the sample cell is revised so as to avoid direct contact between sample and pressure medium by using bellows, the application of the present apparatus could be extended to studies on fluid systems including melting phenomena.

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