

An Automated High Pressure Differential Thermal Analysis System for Phase Transformation Studies

T. K. Mondal and N C Shivaprakash

Abstract—A piston cylinder based high pressure differential thermal analyzer system is developed to investigate phase transformations, melting, glass transitions, crystallization behavior of inorganic materials, glassy systems etc., at ambient to 4 GPa and at room temperature to 1073 K. The pressure is calibrated by the phase transition of bismuth and ytterbium and temperature is calibrated by using thermocouple data chart. The system developed is calibrated using benzoic acid, ammonium nitrate and it has a pressure and temperature control of $\pm 8.9 \times 10^{-4}$ GPa, ± 2 K respectively. The phase transition of $\text{As}_x\text{Te}_{100-x}$ chalcogenides, ferrous oxide and strontium boride are studied using the indigenously developed system.

Keywords—double stage crystallization, Phase transition, Quasi hydrostatic, Rigidity percolation

I. INTRODUCTION

THE Differential Thermal Analysis (DTA) technique is used in many areas of research. At higher pressure, thermal studies on chalcogenide glasses, phase transition of some inorganic and organic materials including glass transition, their kinetics of crystallization are of particular interest from fundamental and practical viewpoints [1-4].

There are several high pressure instruments described by Brunskill [5], Cohen [6], Kuballa and Schneider [7], Bousquet [8], Williams and Wendlandt [9], Locke [10] and many more researchers in this area. The instrument developed by them are very complex in their arrangement of different segments. One of the piston cylinder apparatus developed, could be used up to 5 GPa and 1473 K but the determination of pressure in this system on the sample is not a straight forward problem [5]. Around 4 GPa and 1773 K, another modified piston cylinder apparatus could be used [11-14].

Generating of higher pressure becomes more difficult with the increase of temperature in the single cylinder. Taking out thermocouples wires from the apparatus and keeping them intact under higher pressures is another problem. In order to achieve easy mounting of the sample, to reuse the sample cell, to use small amount of sample, to minimize the heat loss to

achieve accuracy, a complete automated high pressure DTA system is built.

The above features incorporated in the present study would be novelty of the system developed by us. The details of the necessary control and measurement circuitry and the related aspects are described in detail. The calibration and standardization of the complete system and analysis of the typical samples investigated are also included.

II. HIGH PRESSURE – DIFFERENTIAL THERMAL ANALYSIS SYSTEM

The system is comprised of subunits, namely piston cylinder assembly, sample cell, external heating arrangements, hydraulic system with pressure control valve unit and measurement with control electronics. The details of the subsystems are given below.

III. DETAILS OF THE SUBSYSTEMS A HYDRAULIC SYSTEM

A. Hydraulic System

Pressure is generated by a hydraulic press. It can generate pressure up to 1.81×10^4 GPa / m^2 . The pressure generation system controls the pressure with the help of a valve assembly [15]. The valve assembly consists of two directional control solenoid valves (A and B), a pressure relief valve, two flow regulators, a proportional relief valve and a pilot operated check valve in the onward oil line to prevent the rapid pressurization. The press consists of an electrically operated pump with an oil reservoir. During pressurization one solenoid valve is opened and oil enters the hydraulic cylinder to push the ram upward. The piston cylinder is mounted between the bottom ram and the fixed top plate. The applied oil pressures is read by a 8 GPa thin film pressure transducer.

B. Piston Cylinder Assembly

A cross – sectional view of a piston compound cylinder made of EN-24 steel, used for the DTA experiment, is shown in Fig. 1. The compound cylinder is made by press fitting the inner cylinder to a hollow cylinder. The main aim of this work is to design a piston cylinder, which can sustain 873K and 4 GPa pressure on the sample. When temperature goes high, the yield strength of a material goes down by 10 – 20% [16]. In the design of piston cylinder apparatus, the cylinder is subjected to maintain maximum high temperatures

T K Mondal is with the Instrumentation and Applied Physics Department, Indian Institute of Science, Bengaluru-560012, India (phone: +91-80-2293 3193; fax: 91-80-2360 0135; e-mail: tushar@isu.iisc.ernet.in, tmondal339@gmail.com).

N C Shivaprakash is with the Instrumentation and Applied Physics Department, Indian Institute of Science, Bengaluru-560012, India.

(873 K) and maximum internal pressure on the sample (4 GPa) that transmits to the internal surface of the cylinder. Assuming that the axial pressure on the sample holder transmits nearly equal in all direction but not exactly or equal to the applied pressure. That is why the sample cell is not exactly in hydrostatic condition but near to it. That is called the quasi hydrostatic condition. Under high pressures, the thickness of the wall of the pressure vessel will be relatively large and so the usual assumption regarding the uniform stress distribution in the wall of the pressure vessel is not valid and the theory of thin cylinders cannot be applied. The thickness of the cylinder is calculated by the Clavirono's equation [17,18]. To analyze the apparatus under high temperatures and high pressures effectively, the Finite Element Analysis (FEA) is used with the help of ANSYS software [19]. Using the shape functions the strain and stress are determined. The dimensions of the piston and compound cylinder and the operating conditions (maximum temperature and pressure) are estimated and compared with the experimental results.

The entire assembly is heated by two heaters. The internal heater heats the sample. The heat loss to the surroundings is arrested by a guard heater fitted around the cylinder. The cylinder is fitted on a cylindrical bottom flange used to hold the sample cell. The bottom flange has five through holes and step with five grooves for heater and three pair of thermocouple wires. Ceramic beads are used to insulate the wires from the cylinder wall.

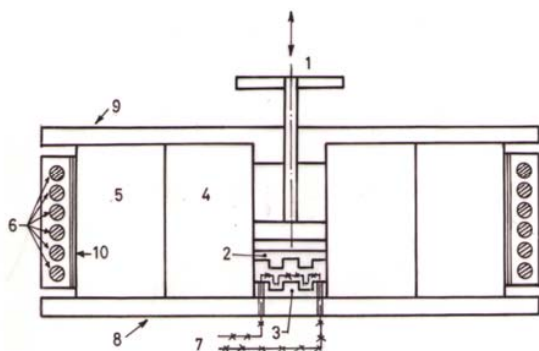


Fig. 1 A cross – sectional view of a piston compound cylinder made of EN-24 steel, used for the DTA experiment.

1. Piston 2. Cap for the sample cell 3. Sample cell 4. Inner cylinder
5. Outer cylinder 6. Coils of the guard heater 7. Internal heater wire
8. Bottom flange 9. Top flange

C. Sample Cell

The sample cell consists of two cylindrical grooves of 3 mm depth on 6 mm thick pyrophyllite disk. These two cylindrical grooves are used for sample and reference material holder and each can accommodate 10 to 15 mg of material. Thermocouples and heater wires are taken out of the cell by the bottom holes matching with the flange holes. Teflon is also used as sample holder for low temperatures. Being a compressible material, it can act as a closed container under pressure.

D. Measurement of Pressure

The excitation voltage for the pressure transducer is maintained at 10 V DC \pm 5 mV and the full scale output is 70.0mV \pm 1mV. The transducer has sensitivity of 2 ± 0.1 mV, stability ± 0.25 % FSO and hysteresis better than 0.3 % FS. The output of the transducer is connected to an instrumentation amplifier. The digital input output timer (DIOT) card has got two 8255 for data input and output and a timer circuit. The conversion of the conditioned pressure transducer output to corresponding system pressure and its comparison with set pressure are undertaken using the software. A commercial pressure measurement and display system is attached with the hydraulic line to get more accuracy.

E. Measurement of temperature and differential temperature

In the sample cell, canthal wire is used as heating element. In order to electrically isolate the heating element from the thermocouple junctions, ceramic wool is used. One thermocouple placed in the reference sample and another thermocouple in the sample, form the differential amplifier. The third thermocouple placed in the reference sample gives the temperature of the cell. The fourth thermocouple, reads the temperature of the guard heater. Chromel – Alumel thermocouples are used to measure the temperature and the temperature difference. The out put of the thermocouple placed inside of the sample cell is amplified, cold junction compensated and filtered for noise. An instrumentation amplifier is used to amplify the differential output. The out put of instrumentation amplifier is filtered for noise. This output is fed to a computer after analog to digital conversion (channel 2 of 0809 A/D) through the DIOT card.

F. Temperature control

A pulse width modulation circuit maintains the temperature at the set value. To compensate the heat loss and to make the sample cell near adiabatic, a guard heater is introduced outside the piston cylinder. The power input to the internal heater is controlled by a computer. All these controls are achieved by the second 8255 in the DIOT card.

G. Pressure control unit

The ON/OFF control is used for solenoid valve and the current control is used the proportional relief valve. The set pressure and the incoming pressure are compared by the software. In the case of incoming pressure is less than the set pressure, the directional control solenoid valve is activated and the oil is allowed to enter the hydraulic cylinder. When it reaches the set pressure the directional control valve is deactivated. The excess pressure due to inertia is fine tuned by the proportional control valve.

IV. EXPERIMENTATION

Samples characteristics curves are obtained without applying pressure at the beginning. Here the samples are heated at different heating rates and corresponding curves are recorded. Subsequently by maintaining the heating rate

constant, pressure is applied. The developed software takes the sample temperature, differential temperature and the pressure. It also controls the temperature, pressure and the external heater temperature for various inputs.

A. Calibration of the system Temperature calibration

Chromel – alumel thermocouples produces 40 μV per degree Kelvin. The analog to digital converter (ADC 0809) is a 8 bit and the maximum input voltage to it is 5 volts. The minimum voltage required for reading one digit of hexadecimal character is 20 mV. In the present setup, temperature is measured from 304 to 873 K.

B. Pressure calibration

The pressure is calibrated by the phase transitions of bismuth (Bi) metal and ytterbium at ambient temperature. The calibration at high temperatures is done by the ytterbium (Yb) phase transition.

C. Calibration of differential thermal analysis system

The determination of the heat of transition of the reactive sample from the area under the peak of differential temperature versus temperature is a widely used procedure in DTA [4]. Following is the relation commonly used in differential thermal analysis.

$$\Delta H \text{ m C} = k A \Delta T_s \quad (1)$$

where ΔH is the heat of transition in Joules / Kg, m is the mass of reactive sample in Kg, k is the calibration coefficient and A is the curve peak area in m^2 , ΔT_s is the differential temperature sensitivity in $\text{deg (K)} / \text{m}$, C is the chart speed respectively. Benzoic acid and ammonium nitrate samples are used to find the calibration coefficient. Taking $\Delta H = 0.0527$ Joules / Kg at 398 K for ammonium nitrate and $\Delta H = 0.1473$ Joules / Kg at 122.3 K for benzoic acid, the mass of each has been taken as $m = 10^{-5}$ Kg. Considering ΔT_s and C values constant and measuring the peak area in each run with the help of equation no 1, the value of k is calculated. The calculated k values coincide with each other for benzoic acid [4] and ammonium nitrate [4].

V. SYSTEM PERFORMANCE

A. Demonstration study of samples at ambient pressure

i. Benzoic acid

The benzoic acid is heated at 10 deg / min and the DTA curve obtained shows two peaks, one at 395 K and another at 533 K. These two peaks correspond to melting and boiling point of benzoic acid respectively.

ii. Ammonium nitrate (AN)

During the use of AN as an oxidizer, the temperature automatically raises because of burning of the fuel. In the present study three transitions of AN and the melting of the same are observed. On heating from room temperature at 2 K/min, humid ammonium nitrate transformed from phase IV into phase III (313K), then phase III into phase II (355K) and phase II –I (401K) [20]. The DTA curves for this are shown in Figure 2 (a).

iii. $\text{As}_{50}\text{Te}_{50}$

The semi-conducting $\text{As}_{50}\text{Te}_{50}$ glasses are prepared by melt quenching method. First $\text{As}_{50}\text{Te}_{50}$ sample is heated at 2K / min in the DTA cell at ambient pressure. Two exothermic peaks are recorded at two different temperatures 455 K and 485 K respectively. These two peaks show the double stage thermal crystallization [21]. This establishes the system developed by us.

B. Demonstration study of samples at higher pressures

i. Benzoic acid

Benzoic acid is pressurized and heated. It is found that the first peak (the melting point) remains at same temperature. The boiling point of benzoic acid is shifted to higher temperature because of increase in pressure. These values match with the available reported data [4].

ii. Ammonium nitrate

When pressure is applied all the phase transition III, II and I corresponding to 315 K, 355 K and 424 K shift to higher temperatures 333.69 K, 393 K and 465 K respectively (Fig 2(a)) [22 -23]. Phase transition of AN from one polymorphic stage to another is very important as an oxidizer even at higher pressures.

iii. $\text{As}_{50}\text{Te}_{50}$

The composition dependence of crystallization of $\text{As}_x\text{Te}_{100-x}$ glasses is very interesting. It has been found that $\text{As}_x\text{Te}_{100-x}$ glasses with $x < 40$ exhibit a single stage crystallization on heating. On the other hand, glasses with $x \geq 40$ show a double stage crystallization. The composition $x = 40$ show at which the crystallization behavior of these glasses is found to change can be associated with two structural effects known as rigidity percolation and chemical ordering overriding each other at this composition [21]. When pressure is applied this crystallization behavior of these glasses would change further as it has demonstrated for 0.08 GPa pressure. The sample is kept at constant pressure for some time and heated. The DTA curve of differential temperature versus temperature is shown in Fig 2(b) for $\text{As}_{50}\text{Te}_{50}$ system. The first exothermic peak has become endothermic and shifted from 455 K to 453 K. The second exothermic peak remains exothermic but shifts to 553 K from 485 K.

C. The DTA curve of iron

Iron (Ferric oxide) is heated to 873 K and pressurized, the temperature drops to 773.8 K. This corresponds to the $\alpha \rightarrow \gamma$ phase transition [24] in it. This is shown in Fig 3(a). The experiment is repeated keeping the temperature of the sample at 800 K and pressurized to 0.15 GPa. The transition comes at 873 K.

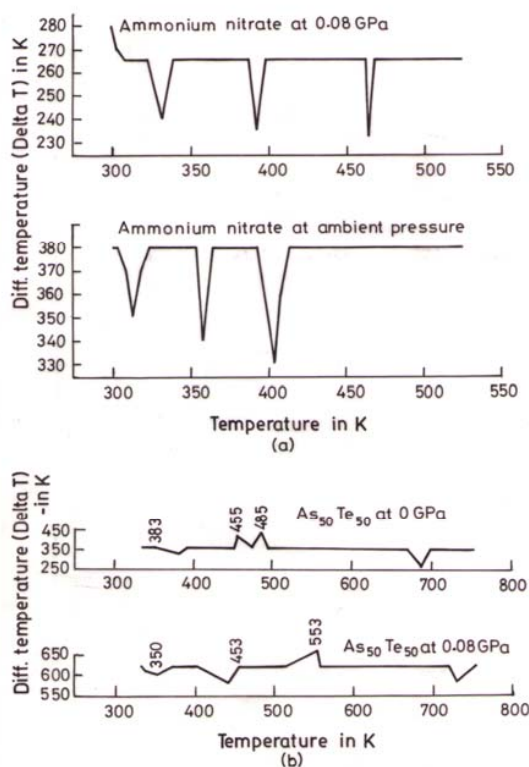


Fig. 2 (a) Phase transition of ammonium nitrate at ambient and at 0.08 GPa. Fig. 2(b) The DTA curve of differential temperature versus temperature for $\text{As}_{50}\text{Te}_{50}$ system at ambient and at 0.08 GPa

D. The DTA curve of Strontium boride

The purpose of using Strontium (Sr) is to convert the radio isotopic decay energy into a useful source of electrical power. An apparatus is required to carry out such experiments. Thus the construction of the model of the apparatus, investigation of possible compound forms of Strontium cladding requirements, selection of energy conversion, and biological shielding are to be investigated. Compound forms of Sr are being studied as pure ceramics, ceramics with non-metallic additives, and cermets. Cladding requirements such as element insertion and lid welding are under test. The problem of heat transfer, including a method employing helium gas under 12 atmospheric pressure, is being analyzed. So thermal conductivity and stress measurements are important for strontium and strontium boride [25]. The strontium boride is heated to 1050 K and pressurized to 3 GPa. The temperature falls to 583 K. To achieve the same at 4 GPa, the strontium boride is heated to 683 K (Fig 3(b)). The temperature of the sample is raised first and pressurized.

VI. CONCLUSIONS

A simple piston cylinder is used for the high pressure DTA experiment. Teflon and pyrophyllite are used as the pressure

transmitting medium. Pressure in the sample cell is in the quasi

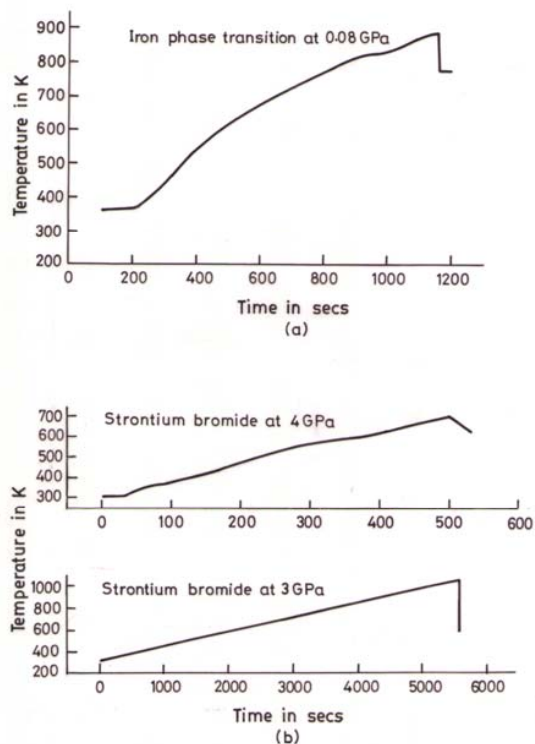


Fig. 3 (a) The $\alpha \rightarrow \gamma$ phase transition of Iron (ferric oxide) at 873 K at 0.08 GPa. Fig. 3(b) Pressure induced transition at 683 K of strontium boride at 4 GPa and at 1050 K at 3 GPa

hydrostatic range. The pressure is calibrated by the observation of bismuth and ytterbium phase transition at ambient and at high temperatures. The calibration undertaken at ambient temperature usually holds good at high temperatures. The benzoic acid and the ammonium nitrate are heated separately without pressure. These results exactly match with the standard values from the literature. From this, the calibration coefficient values are obtained and these values comes closer in both the cases. The same samples are repeated with pressure. The DTA curve of benzoic acid under pressure also matches with the reported results. The double stage crystallization of $\text{As}_{50}\text{Te}_{50}$ at ambient pressure and shifting of the peaks at high pressures prove the accuracy of the instrument. The study of phase transitions of ferric oxide and strontium boride compound in the present study establishes the performance of the developed DTA system.

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