Bulletin of Electrochemistry 2 (2) Mar.-Apr. 1986 pp. 197-200

DIFFERENTIAL THERMAL ANALYSIS: ITS ROLE IN MATERIALS STUDY

J KUPPUSAMI, V SUNDARAM AND A SUNDARA RAJ
Central Electrochemical Research Institute, Karaikudi – 623 006

ABSTRACT

Differential Thermal Analysis (DTA) is one of the thermoanalytical techniques developed for the study of solid materials and is being extensively used in metallurgy. This provides a sensitive and reliable method of resolving the fine details of the heating and cooling curves.

New solid materials, particularly superionic solids, are formed by solid solutions between two or more compounds and undergo phase transitions. These two aspects can be studied from the phase-diagram with a knowledge of the transition temperatures at various compositions of the components which can be studied by DTA.

This paper describes the construction of a small, compact laboratory model DTA set up, the working of which is tested with a few known systems.

Results are also presented and discussed for a new system AgI – TlI which is being studied to understand its superion characteristics.

Key words: DTA, Solid Electrolytes, Super-ion conductors, Phase Transitions

INTRODUCTION

Differential Thermal Analysis, popularly known as DTA, has been extensively applied for qualitative and quantitative analysis of chemical compounds in raw materials and in products of industrial processes [1]. Among a number of techniques employed in the study of materials, DTA finds an important place in constructing phase diagram which in turn is very essential in the study of the two important aspects of materials viz. formation of solid solutions and existence of various phases [2].

Phase diagrams represent geometrically the heterogeneous equilibria existing in a system and have pressure, composition and temperature as the coordinates. The various regions on these diagrams are separated by phase boundaries at which stable phase assemblage must change, by appearance of a new phase or both and for a system of constant mass, such a process constitutes a phase change. Phase diagram indicates the possibilities of formation of chemical compounds, optimisation of processes for the development of materials for electronic industry [3] and gives information on the conditions (temperature, composition, etc) at which these phases exist. Such information is very essential for development of new materials.

The objectives of phase analysis consists of: (a) Characterisation of individual compound and assessment of its purity (b) Identification of individual compounds in a mixture and assessment of their proportions (c) Observation of the sequence of reactions occurring in a mixture of raw materials (d) Characterisation of a specific type of reaction and (e) Establishment of the eutectic compositions in alloys.

The applicability of DTA to phase studies arises from the fact that the energy changes occurring at phase boundaries can be detected and correlated with appropriate equilibrium reactions. DTA is a thermo-analytical technique for recording the difference in temperature between a substance and a reference when they are subjected to identical heating or cooling process at a controlled rate. The record obtained is known as DTA curve and if the substance is thermally active, this shows a series of peaks whose positions are determined by the composition and crystal structure of the substance. DTA originated as a development of cooling curves widely used in metallurgical investigations [4] and later was extended to non-metallic systems. In recent years, it has been widely employed in the determination of phase diagrams of multicomponents. It is now employed in a variety of situations along with other direct methods like x-ray and electron diffraction, spectroscopy and thermogravimetry. The DSC (Differential Scanning Calorimetry), which is closely related to DTA, is a technique of recording the energy required to establish zero temperature difference between the substance and a reference against either time or temperature when both are subjected to identical temperature regimes in an environment of controlled heating or cooling.

The merit of DTA is that all energy changes occurring in the sample during heating are clearly observable. DTA can sometimes reveal minor structural distinctions not so clearly indicated by other means and can be applied to check the identity of two samples. This is very useful in distinguishing natural materials from different sources. DTA reveals the range of stability of any material or the temperature to which the material is to be heated for a specific change to occur. Another advantage of DTA is the rapidity with which data are obtained.

The important applications of DTA include: (a) Identification – Qualitative and quantitative (b) Phase diagrams (c) Hydration – dehydration (d) Thermal and oxidative stabilities (e) Polymerisation (f) Purity (g) Reactivity and catalytic activity.

It has applications in the areas of metals, minerals, fuels, paints, pharmaceuticals, ceramics, explosives, forensic chemistry, plastics, soils, textiles, etc. Its application in the Solid State Materials Science is very vital, as explained earlier, in the synthesis of newer materials.

In this background, this paper gives details of construction of a simple laboratory type DTA unit and its performance characteristics.

EXPERIMENTAL

In normal thermal analysis, when a sample heated at a constant rate undergoes a phase transition at a particular temperature involving an endothermic reaction (energy is absorbed), most heat energy is needed for the corresponding rise in temperature and a plateau is observed in the temperature–time diagram. If the reaction is exothermic (energy is released), there will be a rapid change of slope of the above diagram. This is not very accurate and reliable because of external causes. A more refined technique is the DTA, in which the temperature is recorded in a differential manner. The sample and a reference like alumina which will not undergo any phase change over a wide range of temperature, are heated at a constant rate in the same furnace. The difference in temperature, ΔT, will be zero till the heat content of the sample is constant. When it changes abruptly due to a

phase change, a peak is observed in the DTA trace (T vs Δ T) and the start of the peak marks the transition temperature.

CONSTRUCTION OF THE DTA

The essential parts of a DTA unit are: (i) A furnace (ii) A cell to hold the sample and reference (iii) Thermocouples and (iv) A recorder.

Furnace

A small furnace operating at 220 V, having a dimension of 25 x 18 x 24 cm and going up to 800°C was constructed. The heating zone for inserting the cell has an aperture of 4.5 cm dia and a depth of 11 cm so that the sample and reference will be at the centre of the hot zone.

The performance of the furnace is illustrated as a heating-cooling curve in fig. 1. It is seen that heating and cooling are uniform and the rate of heating can be controlled by the input to the furnace.

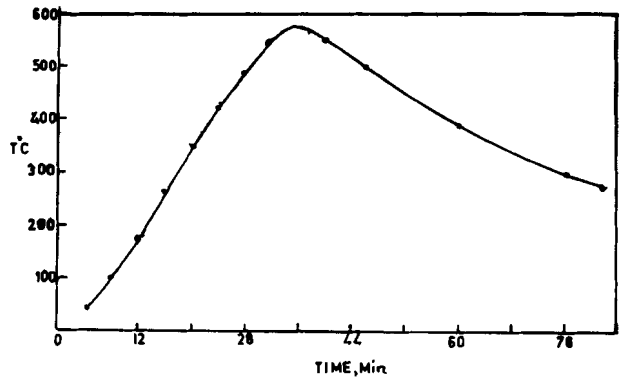

Fig. 1 Heating and cooling curve of the furnace

Cell design

The cell design is shown in fig. 2. This consists of a solid alumina (or ceramic) cylinder of diameter 4 cm and length 10 cm so that it can just be inserted

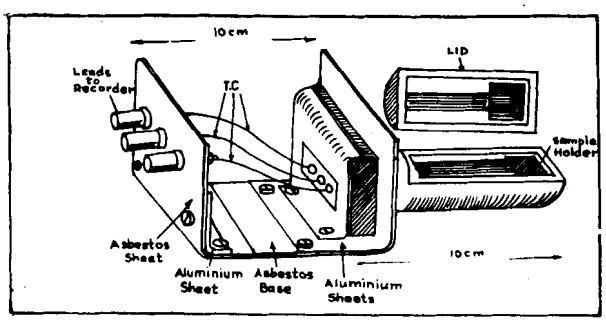

Fig. 2 Cell design

into the furnace. A portion of the cylinder is split into two parts, the upper one with a volume less than half of the cylinder serving as the lid. There are two corresponding rectangular hollow regions in these two parts so that the sample and the reference kept in a 2-compartment cubical alumina crucible or two separate crucibles can be inserted almost air-tight into the cylinder and closed. The other end of the cylinder is attached to a thick asbestos base by means of a small Z-shaped aluminium bracket and screwed at the bottom. At the other end of the asbestos base is attached another small asbestos sheet in a vertical manner by means of a small-L-shaped aluminium bracket. Binding posts are provided at the top of this vertical sheet for connecting the thermocouples and taking output leads to the recorder. This sheet is separated by sufficient distance from the cylinder and connected through the asbestos base only. Thus the binding terminals (servicing as cold junctions) are sufficiently prevented from heating during the course of the experiment.

Thermocouples

Two chromel-alumel thermocouples are employed to detect the temperature of the sample and reference. They are separated by inserting through capillary like silica tubes and taken to the respective compartments through small holes on the front surface of the cylinder and narrow grooves inside the closed cylinder.

Recorder

The DTA peaks were recorded using Philips PM 8132 Xt - Y_1 - Y_2 Recorder. The temperature was recorded as X mode with a sensitivity of 1 mV / cm (~ 24° C / cm) and Δ T as Y_1 with a sensitivity of 0.074 mV/cm (~ 2° C / cm). The heating rate was about 6 to 7° C per minute.

RESULTS

The DTA curves for different samples studied are given in fig. 3 to fig. 9.

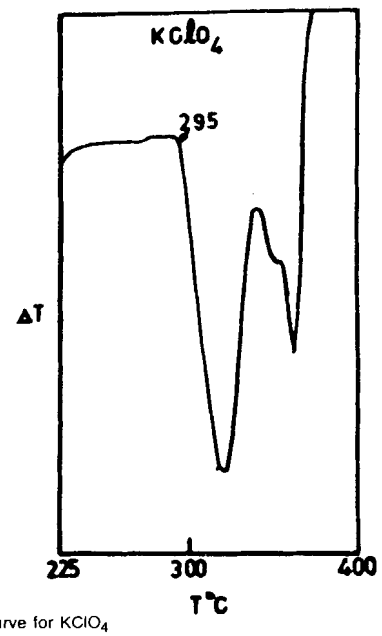

Fig. 3: DTA curve for $KClO_4$

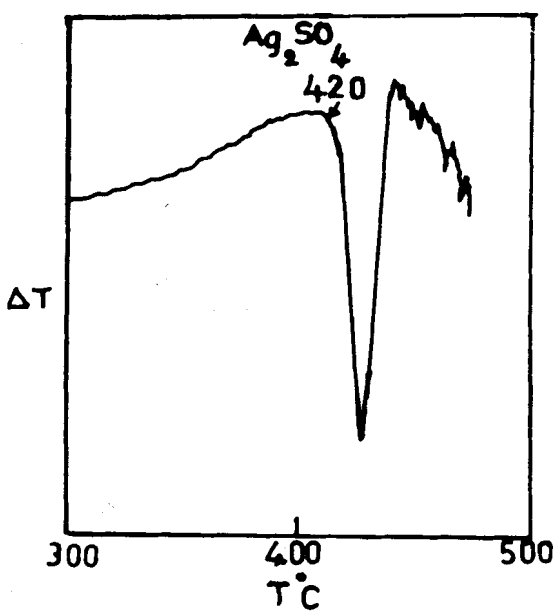

Fig. 4: DTA curve for Ag_2SO_4

Figs. 3 and 4 represent the DTA curves for $KClO_4$ and Ag_2SO_4 which are normally used as standards authorised by NBS-ICTA for temperature calibration. The onset of the peaks occurs at 295°C and 420°C respectively while their reported values are 299 ± 6°C and 424 ± 7°C.

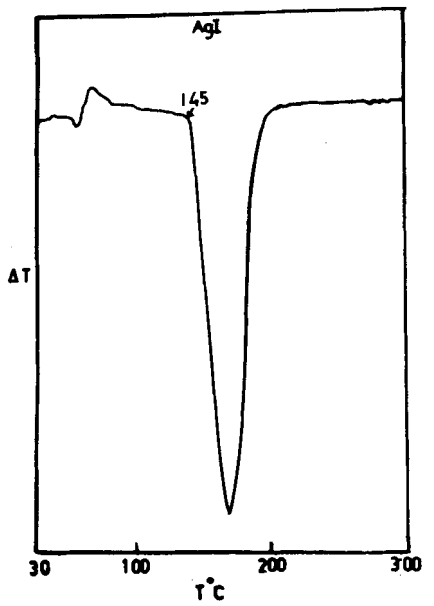

Fig. 5: DTA curve for AgI

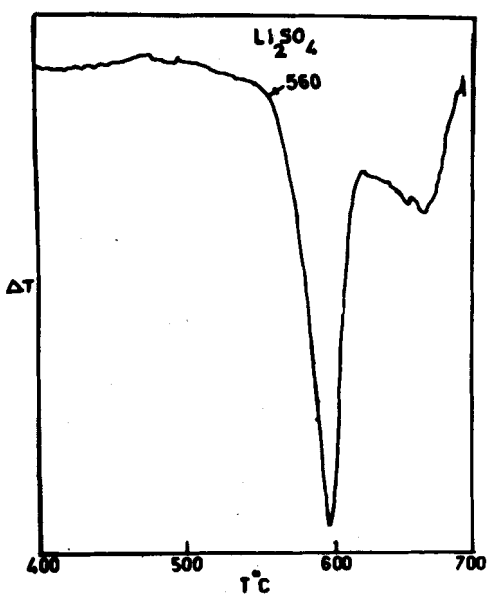

Fig. 6: DTA curve for Li_2SO_4

Figs. 5 to 8 are the records of the DTA curves for AgI, Li_2SO_4, Na_2SO_4 and TlI. These systems are being investigated for application in ambient temperature solid electrolyte batteries and galvanic sensors. AgI shows a peak at 145°C, Li_2SO_4 at 560°C. Na_2SO_4 at 242°C and TlI at 180°C while the reported values are 147°C for AgI, 570°C for Li_2SO_4, 242°C for Na_2SO_4 and 168°C for TlI. A compound prepared by heating at 200°C a mixture of 50 m/o each of AgI and TlI for 24 hrs in vacuum showed peaks at 143°C, 197°C and 222°C (fig. 9). This shows the possibility of a compound formation when the constituents are mixed in a proper ratio and heated at the appropriate temperature.

CONCLUSION

It is clear from the above results that the set-up works satisfactorily and by a control of the sensitivity of the recorder and the heating rate, better resolution of very closely spaced peaks can be obtained.

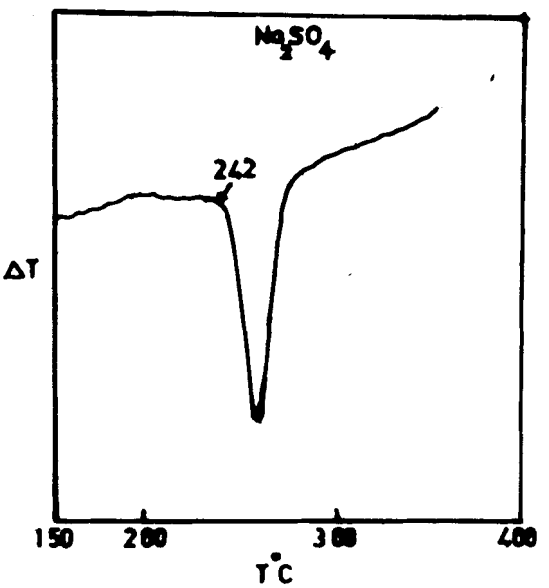

Fig. 7: DTA curve for Na_2SO_4

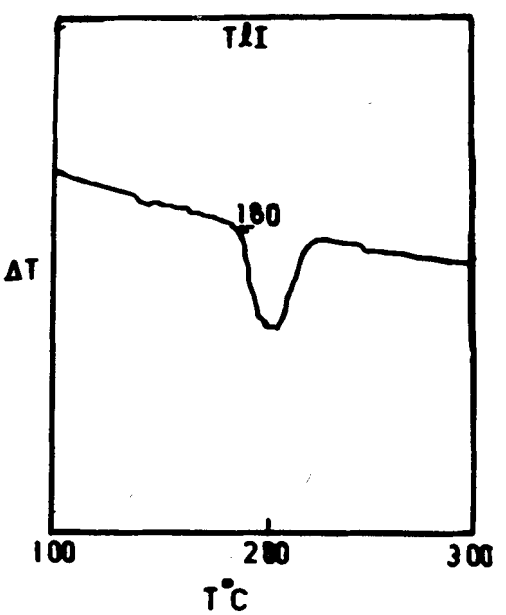

Fig. 8: DTA curve for TlI

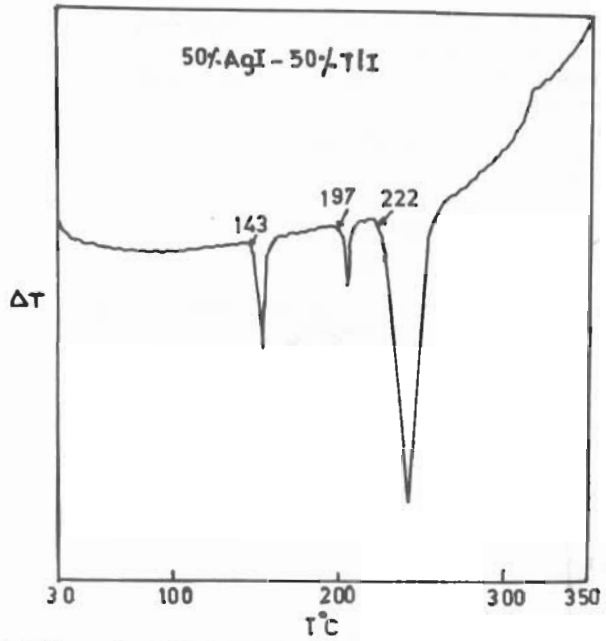

Fig. 9: DTA curve for 50% AgI – 50% TlI

Acknowledgement: The authors wish to express their sincere thanks to Dr V K Venkatesan, Head, Division of Electrochemical Materials Science for keen interest and encouragement in the present investigation.

REFERENCES

1. R C Mackenzie, *Differential Thermal Analysis,* Academic Press, London, Vol I, Fundamental Aspects (1970) and Vol 2, Applications (1972)

2. S Chandra, *Superionic solids,* North-Holland (1981)

3. G F Voronin, *Mat Elektron Tekh,* 1983 (2) Cmp. 4-15

4. S H Avner, *Introduction to Physical Metallurgy,* 2nd Edn, McGraw-Hill, Kogakusha