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SIMULTANEOUS DTA AND HIGH TEMPERATURE THERMOMICROSCOPY *)

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ABSTRACT

Simultaneous thermomicroscopy allows the interpretation of DTA effects and the detection of transitions too weak for usual DTA. Problems in designing high temperature microscope (HTM)-DTA combinations are presented. Modification of a horizontal HTM for simultaneous DTA is described and compared with other HTM-DTA equipments.

1. INTRODUCTION

The informations derived from a DTA or DSC diagram are: a) the fact that at a certain temperature something happened in the material under investigation (thermometric evaluation); b) the direction and amount of heat exchange (sign and area of the DTA peak: calorimetric evaluation); c) the progress of the detected phenomenon (shape of the DTA curve: kinetic evaluation). However the real nature of the process detected by DTA or DSC cannot be elucidated from the registered diagram solely. To circumvent this drawback, additional investigations are necessary for the interpretation of the DTA results.

These complementary methods of investigation should be applied, at least, under similar experimental conditions, or, better, "in situ" i.e. simultaneously with DTA on the same sample. There is still another motive to complement DTA or DSC with other experimental methods: Transformations with very small enthalpy changes or a small rate of enthalpy production or consumption can fall below the detection limit of the measuring system and their starting or end points are better recognized by other methods.

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2. COMBINATION OF DTA WITH MICROSCOPIC INVESTIGATIONS

DTA or DSC measurements are advantageously supplemented by simultaneous microscopic observations. The various extensions of the microscope e.g. polarization or interference microscopy, give additional informations. Microscopic observation can be completed by photographic or cinematographic recording. Small samples are required for microscopic investigations. Therefore the consumption of materials, energy and time are reduced in accordance with the general trend to minimize both sample and apparatus dimensions in thermal analysis.

Since DTA is a dynamic method, the state of the sample under investigation can be far from thermodynamic equilibrium. After switching from increasing or decreasing to constant temperature one can observe changes in the sample due to approaching to equilibrium in isothermal regime even at long intervals of time.

2.1 Principles of equipment

The general scheme of an apparatus for simultaneous DTA-thermomicroscopy (fig. 1) contains a) the optical system: light source (1), sample (2), microscope (3), camera (4) b) the DTA system: temperature controller (5), heater (6), sample (2) and reference (7), thermocouples (8), recorder (9). Advanced instruments are

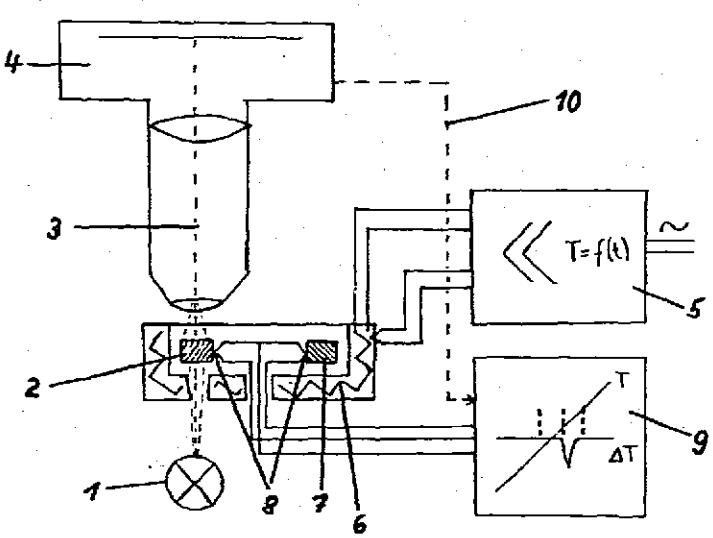

Fig. 1. General scheme of the equipment for simultaneous DTA-thermomicroscopy.

equipped with devices for atmosphere control, for temperature indication on the photographic record or for synchronization (10) to mark photographic shots on the DTA diagram.

In thermomicroscopy, contradictory demands must be considered in designing heater, sample holder and temperature sensor. To achieve a high magnification, a microscope with a short working distance should be used. To avoid any damage of the sensitive objective, one has to shield the microscope against thermal radiation/conduction, resulting in longer working distance and lower maximum magnification. Another way is to work with small samples in a small heated volume. However this results in steep temperature gradients, which, in turn, render it more difficult to achieve a stable DTA base line and good thermal resolution. Consequently, the heated volume should be not too narrow.

The chances to solve these problems by conventional means are decreased at increasing temperature. Microscope hot stages with maximum temperatures up to 400°C are in use for about 40 years, mainly to investigate phase changes in organic materials. Hot stages of this type are sold commercially, their adaption to incorporate a DTA system is obvious (ref. 1-4). It has found attractive applications e.g. in the field of liquid-crystalline mesophases (ref. 5).

Microscopes for higher temperatures ($\geq$700°C) have to withstand a high thermal load. Uncommon ways must be gone in their construction (ref. 6) to prevent the microscope from thermal damage. Non-conventional microscopes with long working distance, arranged horizontally or reversely, can be combined with conventional heater systems, the latter eventually enclosed in a water-cooled case. On the other hand, non-conventional systems of heater, sample holder and temperature sensor with minimized power consumption can be coupled with conventional microscopes without cooling arrangements.

2.2 Non-conventional microscopes with "classical" heater systems

An inverted microscope with high-temperature stage has been modified to investigate metallic samples by DTA (ref. 7). As a reference a nickel rod is inserted in a hole of the test sample. The difference in temperatures of the observed metallic surface and the interior of the reference is measured by thermocouples. The reference rod can be omitted to measure ΔT between the

surface and the interior of the sample. The temperature front advancing through the sample causes a DTA curve deviating from the usual view but suitable to recognize transformations. Differences in the behavior of sample surface and bulk are readily detected. Since the sample is observed from below, melting and crystallization of molten material cannot be studied.

For a horizontal high temperature microscope a DTA specimen holder assembly was tested (ref. 8). A pressed disk of the sample material is placed on a platinum sheet. Together with two Pt10Rh wires this forms the ΔT thermocouple. This arrangement did not prove successfully due to problems of thermal conductivity between the shrinking sample and the Pt sheet. It was substituted by another one with two-wire thermocouples of the usual type. Here sample and reference for DTA are contained in small platinum crucibles. A pressed disk of the sample material is placed close to them for microscopic observation. Since two separate samples are used for DTA and microscopy, respectively, this technique is not a truly simultaneous one. Melting samples form a thin film, hardly visible by the horizontal optical path of the microscope. They cannot be investigated.

This drawback is avoided in an arrangement developed from our sample holder system (ref. 9) to observe melting samples in a commercial high temperature microscope (ref. 10). This equipment (fig. 2) contains a small, horizontally-arranged, air-cooled, tube furnace (1) with noble metal winding (2) and a horizontally arranged optical system with a relay lens (3) between the microscope objective and the furnace to achieve a high working distance. The powdered sample is pressed in a thin platinum tube (4), lying with its axis parallel to the optical axis of the microscope. For DTA the platinum tube is placed on a thermocouple previously bended as a hook to admit the tube (5). A second thermocouple (6) is holding analogously another platinum tube (empty or filled with alumina), acting as the reference body (7). The sample temperature is monitored on a galvanometer readable through the microscope ocular. A third thermocouple is the sensor of the temperature control system (not shown). To minimize temperature gradients, the measuring head is surrounded by a platinum tube (8). A platinum baffle (9) with a hole to permit observation is placed in the furnace near the sample holder.

If the sample melts (fig. 2c,d), it is held in the sample tube

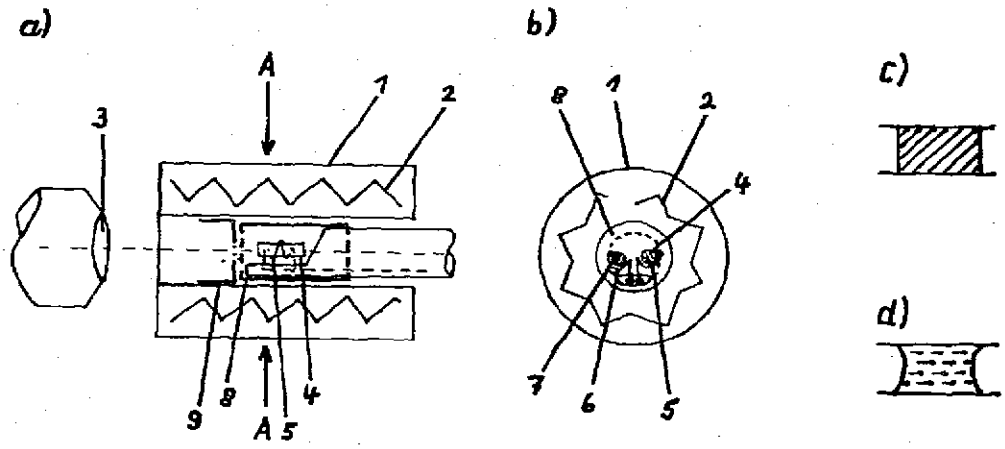

Fig. 2. DTA in a horizontal high temperature microscope
a) longitudinal section b) cross section A-A c) tube with sample before melting d) after melting.

by capillarity. Here it forms a surface perpendicular to the optical axis, readily observable in reflected light. The sample is illuminated by a high pressure mercury vapour lamp via a ring diaphragm. Thermal radiation of the incandescent sample and furnace is discriminated by a green filter. Sample volumes are $< 10\ mm^3$; the low thermal capacity results in a good sensitivity of the measuring system.

This equipment is used to study phase diagrams (ref. 11,12) for crystal growth. We have investigated molybdate and phosphate systems especially to detect congruent or incongruent melting behavior. The DTA diagram of melting of crystalline $LiBi(PO_3)_4$, (fig. 3a), and the photos taken simultaneously (fig. 3c-e) indicate congruent melting at 800^oC. An undistorted ring-shaped reflected image of the ring diaphragm is typical for a completely molten sample (fig. 3e). This melt, rapidly cooled, forms a glass. When heating again, the typical DTA curve with glass transformation, recrystallization and melting (fig. 3b) is recorded. This interpretation is supported by the photos (fig. 3f-o). The glass transformation (near 400^oC) is made evident by smoothing of the distorted image of the ring diaphragm. The reflectivity of the sample increases drastically during crystallization and, in turn,

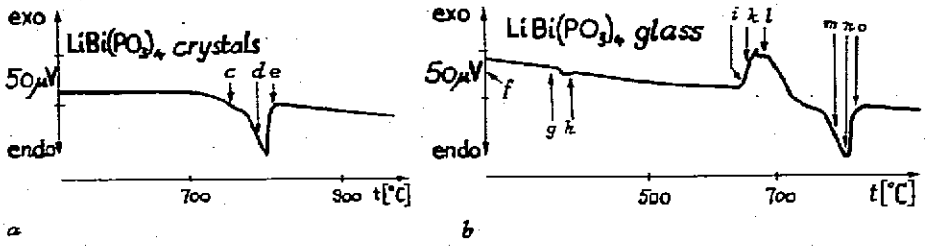

Fig. 3 a) and b). For legend, see page 239

decreases during the melting of the recrystallized sample.

The compound $PbZr(PO_4)_2$ is melting incongruently. It can be crystallized from a molten solution in an excess of lead phosphate. HTM-DTA is applied to determine liquidus temperatures in the system $PbO-ZrO_2-P_2O_5$. Melting in the system starts at the eutectic near 960°C, clearly detectable by the DTA peak (fig. 4a) and shrinking of the pressed sample (fig. 4b,c). Progress of melting is observed by the microscope (fig. 4d-g). Dissolution of the last crystals (fig. 4g) in the melt upon heating can be observed in the microscope even in those cases where no DTA effect is detectable due to the steep increase of the liquidus line.

Very small samples $< 1\ mm^3$ can also be observed in a horizontal high temperature microscope when hanging as a small grain or molten droplet on the thermocouple (ref. 13). An empty thermocouple near to the first one acts as the reference for simultaneous DTA.

2.3 Non-conventional sample holder assembly with "classical" microscope

An original conception of a fine thermocouple loop, acting simultaneously as a heater and a sample holder ("tri-function thermocouple") was developed (ref. 14) to record heating and cooling curves of a microscopically observed sample. Heating is achieved by a controlled current through the thermocouple. A solid state rectifier allows one half-wave of the current (50 or 60 sec^{-1}) to pass. In the time of the second half-wave a synchronized periodic switch connects the thermocouple to the temperature measuring system.

Connecting two circuits of this type allows the recording of a

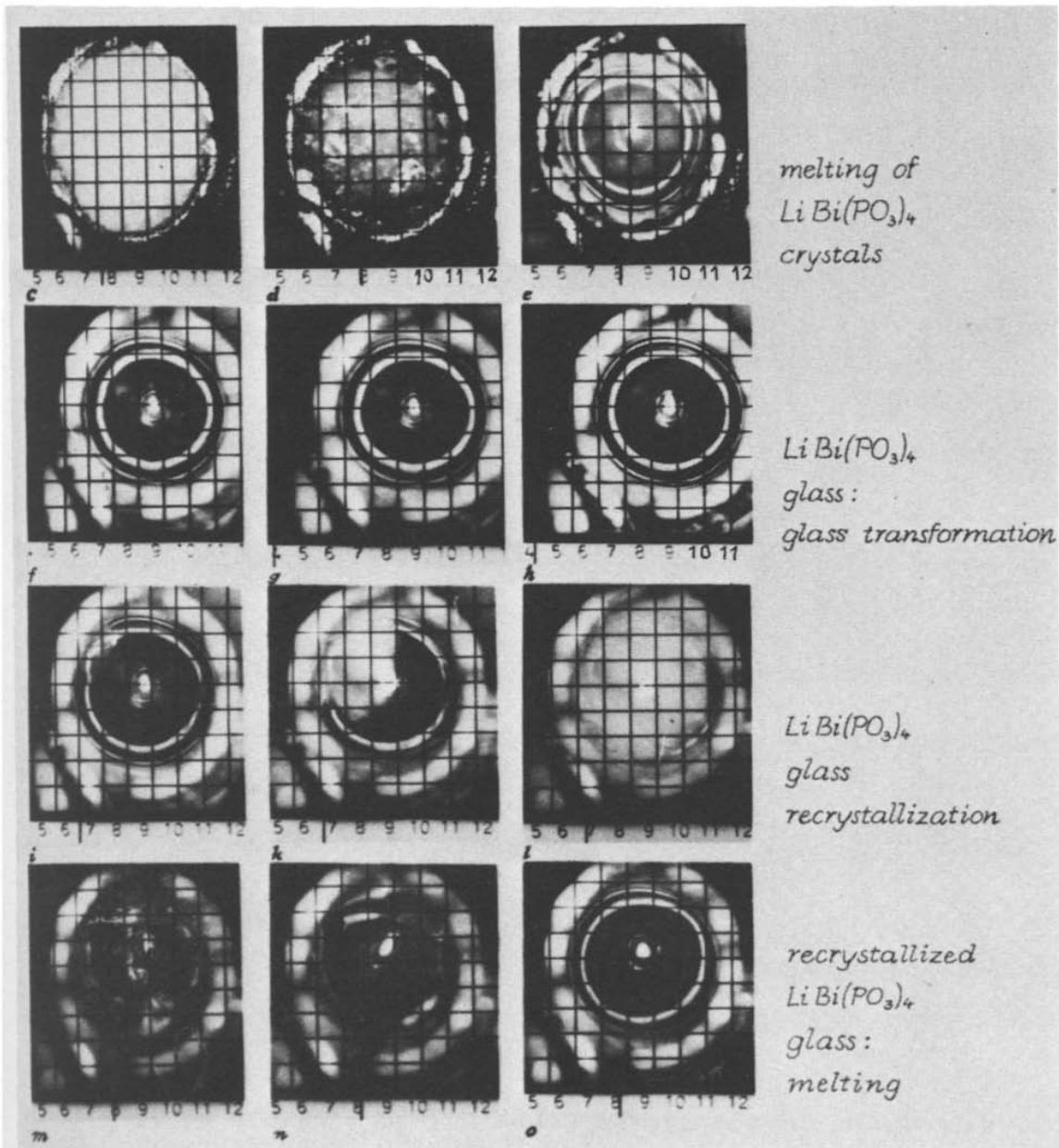

Fig. 3. Melting and crystallization of $LiBi(PO_3)_4$: a) DTA of $LiBi(PO_3)_4$ crystals b) DTA of $LiBi(PO_3)_4$ glass c) to o) microscopic photos, taken at the temperatures indicated on the DTA curves: c) 760° d) 780° e) 810°C f) quenched glass, 25° g) 390° h) 420° i) 660° k) 675° l) 685° m) 795° n) 810° o) 820°C.

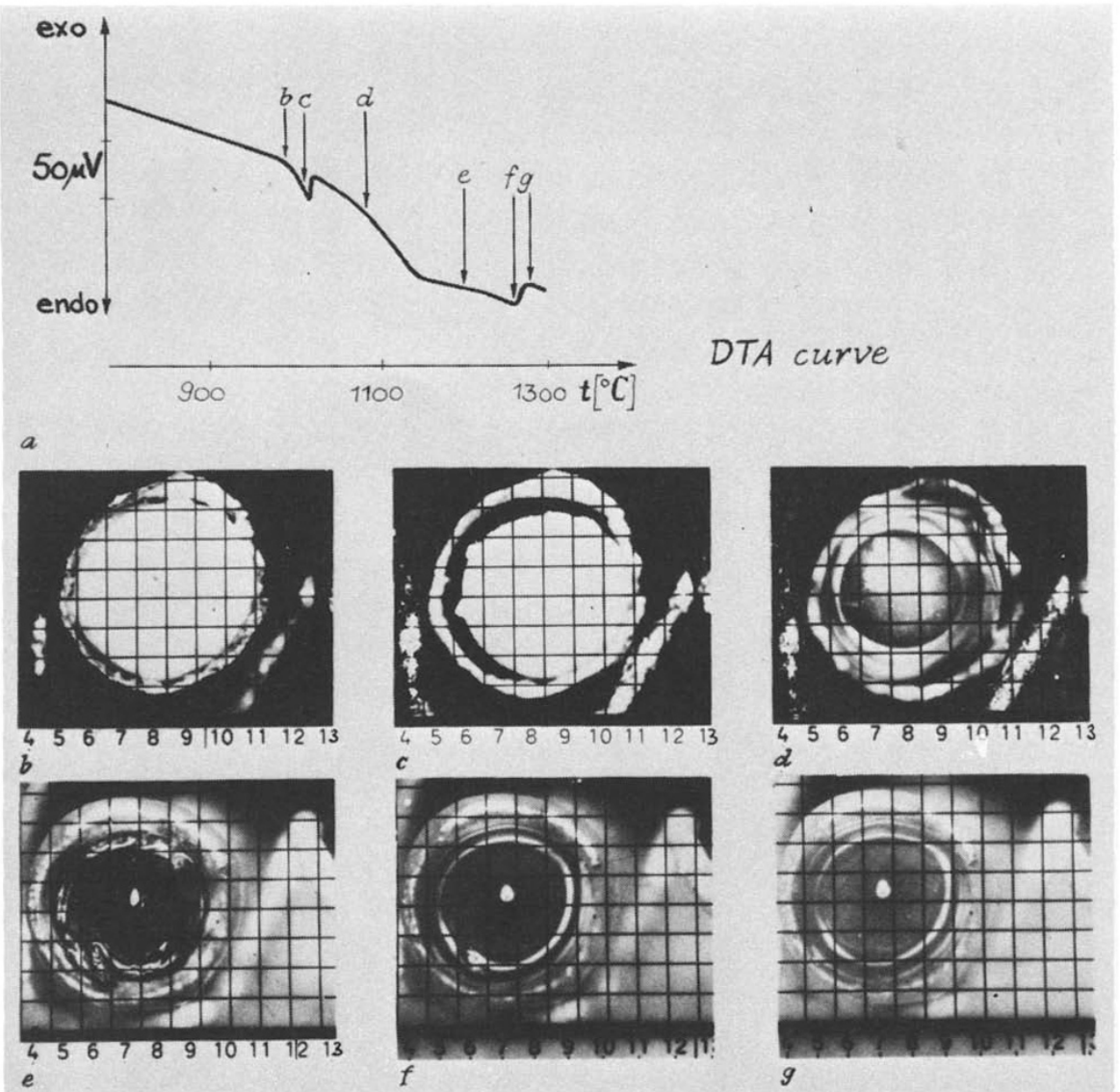

Fig. 4. Melting in the system $PbO-ZrO_2-P_2O_5$: a) DTA b) to g) microscopic photos, taken at the indicated temperatures: b) 960° c) 995° d) 1060° e) 1200° f) 1260° g) 1280°C.

DTA curve (ref. 15). A motor-driven variac is used to realize an approximately linear temperature program. Again, the thermocouples are heated by one half-wave of the alternating current. In the interval between the heating pulses the thermocouples are electro-

magnetically switched as to measure T and ΔT. This instrument is characterized by its very low heating power (a few Watts only), absence of cooling devices, small mass ($\lesssim 1$ mg), the possibility to achieve high heating and cooling rates (in excess of 100^{0}/sec) and high optical magnification. This combined instrument has been applied to study crystallization in the sodium borate-niobate system (ref. 16), glasses (ref. 17) and Mg-Ca-titanate system (ref. 18). Further developments were concerned with the separation of sample and reference thermocouple to halve the heat generated near the microscope objective (ref. 19), temperature regulation by a feedback system using thyristors (ref. 20) and quantitative measurements of enthalpies by a modified DSC principle (ref. 21).

3. CONCLUSIONS

Among the various combinations of DTA and thermomicroscopy, the best perspectives in the field of high temperature research can be predicted for those instruments using the tri-function thermocouple. The first, using a conventional tube furnace with a bigger heated volume and larger samples approaches conventional DTA. Temperature gradients can be controlled. This conception is easily realized starting with a commercial high temperature microscope and conventional DTA components.

The latter variant approaches the ideas of microscopists, using a normal microscope for transmitted light and specially developed electronics. Since the samples are very small, surface effects (evaporation, oxidation) play a more important role. Extremely rapid temperature changes are possible and offer additional possibilities for investigation.

Both conceptions add a new dimension to combined thermal analysis, they make the operator see what happens with his sample when thermal effects occur. They are worth more attention by thermoanalysts.

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