

# Hybrid microwave/conventionally heated calorimeter

Jon G. P. Binner and Duncan M. Price<sup>a)</sup>

*Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, LE11 3TU United Kingdom*

Mike Reading

*Department of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, NR4 7TJ United Kingdom*

Bala Vaidhyanathan

*Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, LE11 3TU United Kingdom*

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The design and construction of a calorimeter in which the specimen may be heated by microwave radiation and/or hot air is described. The apparatus was used to examine the effect of microwave radiation on the melting of benzil (89 °C) and the solid-state phase transition of silver iodide (147 °C). Reproducibility of transition temperature determinations were within  $\pm 1$  °C. No changes were observed for benzil but silver iodide exhibited an apparent reduction in transition temperature to around 120 °C in the presence of microwaves, which increased with the level of microwave irradiation. © 2005 American Institute of Physics. [DOI: 10.1063/1.1938787]

## I. INTRODUCTION

Many investigators have reported unexpected effects resulting from the use of microwave radiation as an alternative energy source during the processing of materials. This has included apparent evidence for accelerated kinetics for a range of processes in ceramic, polymeric and organic systems;<sup>1–10</sup> enhanced sintering of ceramic powder compacts, including lower sintering temperatures;<sup>11,12</sup> and reduced activation energies.<sup>1–3,11</sup> It is now generally, though not unanimously, accepted that a “microwave effect” exists. The primary reasons for any remaining uncertainty are:

- i. The inability to vary the energy source without simultaneously affecting a wide range of other variables. For example, while microwave heating experiments are performed in a microwave applicator, the corresponding conventional experiments are typically carried out in a separate, radiant furnace of totally different specification.
- ii. Uncertainties associated with temperature measurement. Pyrometry is often used with microwave heating while thermocouples are used in the conventional experiments. When a single technique is used, it is usually a shielded thermocouple—although the presence of the metallic shielding is known to distort the local microwave field.<sup>13</sup> Finally, the surface temperature is usually measured. With conventional heating this will be the hottest part of the specimen, while with microwave heating it will be the coolest. This leads to difficulties in making a direct comparison of data.

The precise nature, origins and magnitude of the effect are far less well established. A number of theories have been postulated.<sup>1,8–12</sup> These include: lowered activation energies;<sup>11</sup> enhanced diffusion due to increased vibrational frequency of the ions caused by the electric field of the microwave radiation;<sup>8,9</sup> the excitation of a nonthermal phonon distribution in the polycrystalline lattice;<sup>10,14</sup> quasistatic polarization of the lattice near point defects;<sup>15</sup> and the ponderomotive action of the high frequency electric field on charged vacancies in the ionic crystal lattice.<sup>16</sup> One of the reasons for the development of so many different theories is a basic lack of knowledge about microwave/material interactions.

The effect of heat on materials is often studied using thermoanalytical techniques such as differential scanning calorimetry.<sup>17</sup> Instruments have been described which employ pure microwave power to examine specimens under the influence of an electromagnetic field.<sup>18–24</sup> In some cases the sample has been mixed with or surrounded by a susceptor material which provides additional thermal energy to the sample via its own intrinsic absorption of microwave energy. Although this affords a means to heat materials which may have little interaction with the microwave radiation, there is little ability to control the ratio of conventional to microwave heating that results in the sample. In this work we describe a design of calorimeter which combines conventional and microwave heating in a single device. The temperature and heat flow monitoring system does not interact with the microwave field and thus measurements can be made with a combination of energy inputs from 100% conventional to 100% microwave power.

## II. INSTRUMENT

A schematic diagram of the apparatus is shown in Fig. 1. A rectangular waveguide (not shown) is used to launch mi-

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: d.m.price@lboro.ac.uk

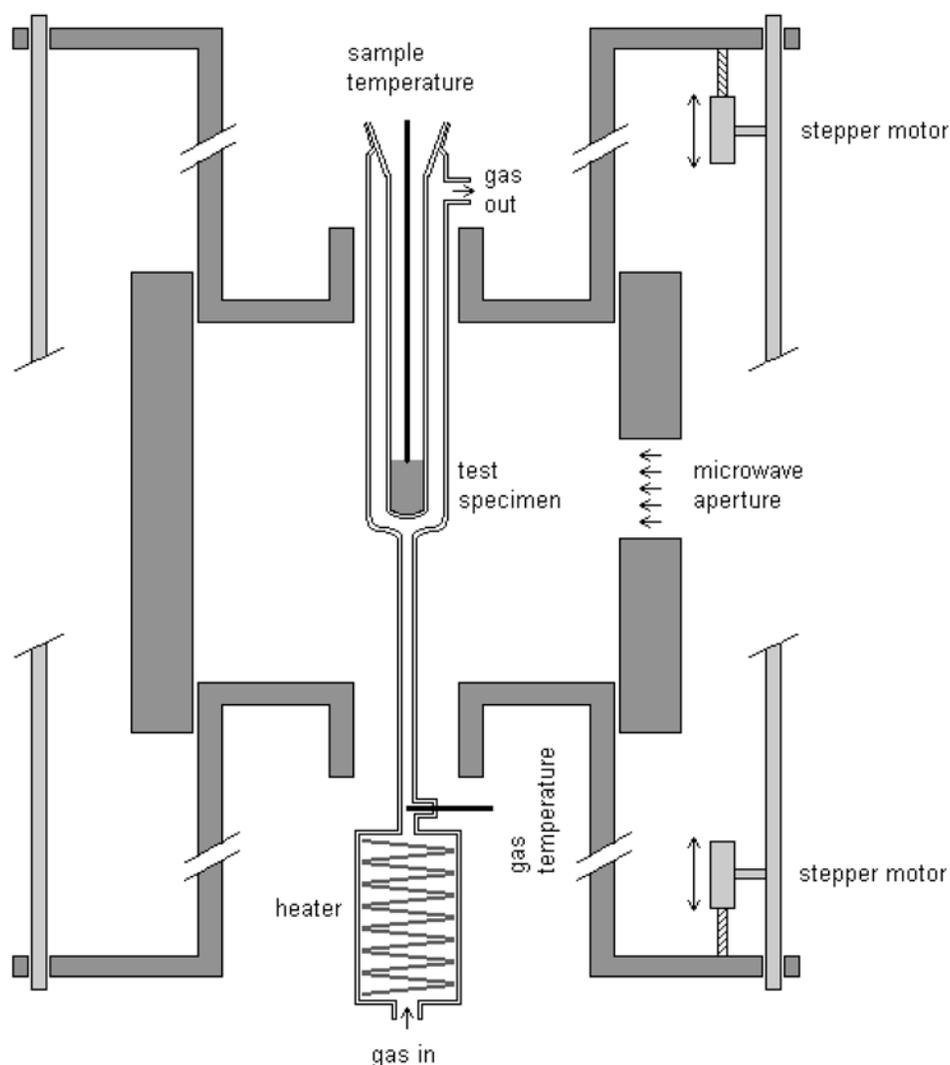


FIG. 1. Schematic diagram of apparatus showing the arrangement of the test specimen and positions of temperature sensors.

microwave radiation from a continuously variable 500 W magnetron operating at 2.45 GHz through an aperture plate measuring 24 mm  $\times$  34 mm into a cylindrical cavity of internal diameter 100 mm containing the specimen holder at its axis. Motorized chokes at the top and bottom of the cavity can be adjusted so that the  $E$  field within the cavity, measured by loop antennas orthogonal to the specimen, is maximized. The distance from the top of choke plate to internal surface of plunger is 220 mm. A marked scale is mounted besides the plungers to aid in the centering of the chokes relative to the specimen. Ancillary tuning by a manual three-stub tuner in the launch section can be employed in order to minimize reflected power. By these means the cavity is operated in a  $TE_{111}$  mode with the maximum field intensity at the sample position.

The specimen holder is fashioned from concentric Pyrex glass tubes of 17 and 10 mm outside diameter with wall thicknesses of 1 mm. The inner tube is rounded into a bulb and inserted into the outer tube which reduces in diameter at the base of the bulb. Conical ground-glass joints are used to ensure that there is a uniform gap between the walls of the tubes. The material under investigation is then placed in the open bulb, a sample size of approximately 500 mg being used for each experiment.

Conventional heating of the sample is achieved by passing compressed air, heated by a 750 W process gas heater (RS Components) around the specimen holder. The specimen itself is not directly exposed to the air supply and can be blanketed with an inert gas (or under vacuum) if required. The temperature of the specimen is monitored by a fluoroptic thermometer (Luxtron model 790) calibrated according to the manufacturer's instructions using an ice-water bath as a single reference point. The power supplied to the heater and magnetron, input air temperature and sample temperature are recorded by analog-to digital (A/D) converters (PicoLog ADC-16 and TC-08). A proportional integral differential temperature controller (Eurotherm 2408) is used to control the power to the heating system, which can either be operated with pure conventional heating, pure microwave heating or in a hybrid mode with fixed amounts of microwave energy being supplied in addition to automatic control of sample temperature via the surrounding air temperature.

### III. EXPERIMENT AND RESULTS

Measurements were carried out on benzil (Acros Organics 99%+) and silver iodide (99.999% overall purity, Acros Organics). The benzil was pre-melted by heating the tube in

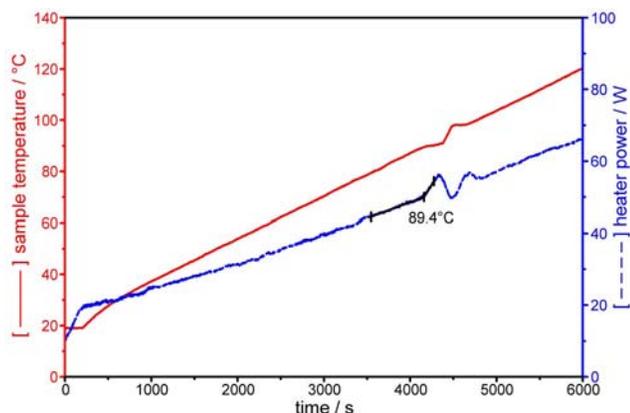


FIG. 2. (Color online) Plot of sample temperature and heater power for benzil heated at 1 °C/min using conventional means.

air so that the thermometer was in good contact with the specimen. The silver iodide powder was made into cylindrical pellets with a density of  $4.9 \pm 0.3 \text{ g cm}^{-3}$  (i.e., 83% of theoretical density) by uniaxial pressing. All measurements were carried out on heating from room temperature at 1 °C/min. A low heating rate was chosen due to the relatively large specimen size compared to conventional thermal analysis which employs samples an order of magnitude smaller.

Figure 2 shows the sample temperature and heater power versus time curves for benzil heated purely by conventional means. As the melting temperature, 89 °C, is reached the amount of power required to heat the specimen increases due to the latent heat of fusion of the material. During fusion, the specimen temperature remains constant until the sample is completely molten at which point there is a temporary overshoot in the temperature program. The onset of the rise in heater power corresponding to the plateau in sample temperature is indicated in Fig. 2 and agrees well with the expected melting point for benzil.

Figure 3 shows similar data for benzil heated by microwave irradiation only. Again, there is a similar plateau in specimen temperature as the material fuses. This occurs close to the expected transition temperature and within the error of measurement ( $\pm 1 \text{ }^\circ\text{C}$ ) of the temperature measure-

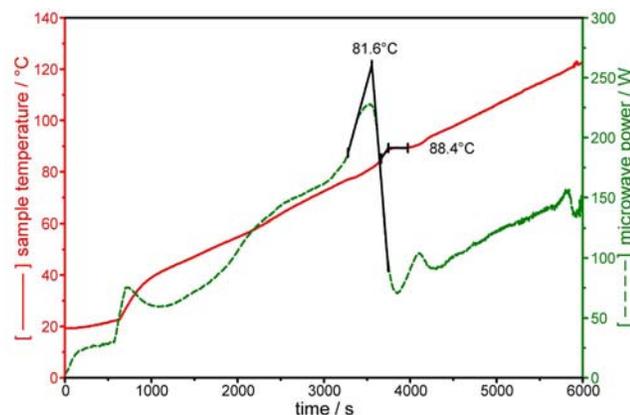


FIG. 3. (Color online) Plot of sample temperature and microwave power for benzil heated at 1 °C/min using microwave heating.

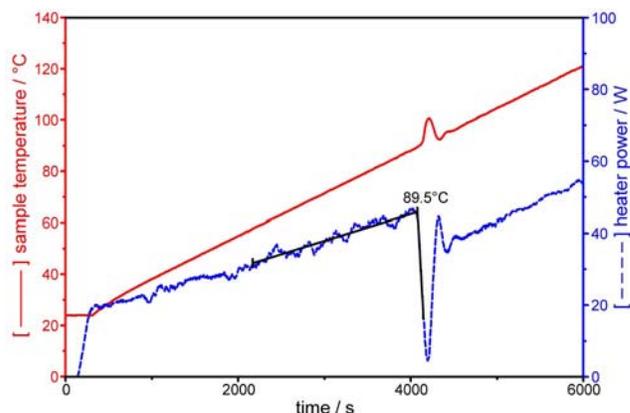


FIG. 4. (Color online) Plot of sample temperature and heater power for benzil heated at 1 °C/min using with 200 W microwave irradiation.

ment system. Unlike conventional heating, there is also an increase in microwave power required to heat the specimen which occurs below the melting temperature which could be evidence of a pre-melting phenomenon. As molten benzil is formed this couples more strongly with the microwave field and consequently the power required to heat the specimen decreases.

Figure 4 shows the sample temperature and heater power required to heat benzil under a constant microwave background of 200 W. The effects of microwave and conventional heating were not additive owing to the flow of air around the outside of the sample reducing the heating that resulted from the application of microwaves. As the sample melted the coupling between the sample and the microwave field increased and the amount of conventional power required to maintain the temperature program decreased accordingly. The presence of microwaves appeared not to influence the temperature at which the fusion of benzil occurred.

Robb, Harrison, and Whittaker have carried out measurements of the x-ray powder diffraction patterns of silver iodide under conventional and microwave heating.<sup>25</sup> Silver iodide undergoes a solid-state transformation from the low temperature  $\beta$  phase (wurtzite structure) to the high temperature ionically conducting  $\alpha$  phase (body centred cubic iodide containing a disordered silver ion sublattice) at 147 °C.<sup>26</sup> They reported that silver iodide transformed to the  $\alpha$  phase around 110 °C under microwave heating, a decrease of over 30 °C from that obtained using conventional heating. This was attributed to multi-phonon coupling between the microwave field and the crystal lattice which promotes the formation of interstitial sites and/or displacement of iodide atoms which stabilize the high temperature structure under conditions in which it would normally exist.

Figure 5 shows the difference in specimen and air temperature ( $\Delta T$ ) as a function of sample temperature for silver iodide heated under different levels of background microwave irradiation. This method of data presentation is equivalent to a differential thermal analysis measurement on the sample using the ambient temperature as the reference point rather than an inert sample.<sup>27</sup> In the absence of microwave energy the sample showed an endothermic peak in  $\Delta T$  com-

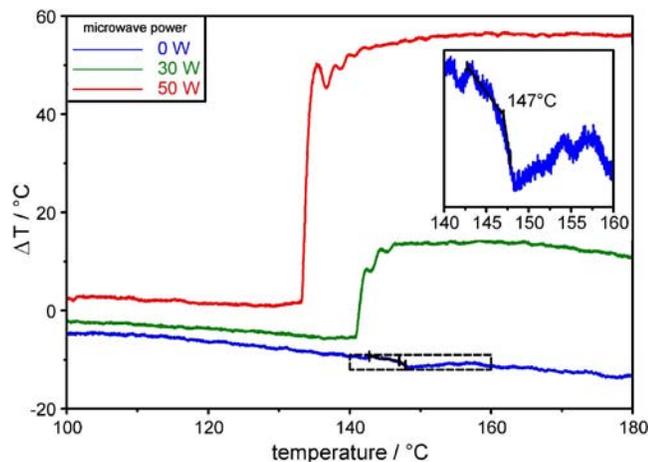


FIG. 5. (Color online) Plot of temperature difference  $\Delta T (=T_{\text{air}} - T_{\text{sample}})$  for silver iodide heated at  $1\text{ }^{\circ}\text{C}/\text{min}$  using different levels of background microwave irradiation (indicated). Inset shows expansion of curve for pure conventional heating ( $0\text{ W}$  microwave power).

mencing at  $147\text{ }^{\circ}\text{C}$ , which is the expected transition temperature. As the background level of microwave power was increased the curves exhibited stepwise changes in  $\Delta T$  and occurred at lower temperatures. The change in shape of the transition can be attributed to the increased coupling of the  $\alpha$  phase with the microwave field, thus less conventional heating was required to follow the temperature program. The decrease in onset temperature supports the finding of Robb and co-workers that microwave irradiation lowers the phase transition temperature of silver iodide. When the specimen was heated using microwave irradiation alone (Fig. 6) the decrease in power required to heat the sample occurred at around  $120\text{ }^{\circ}\text{C}$ , although the step change was appreciably broadened. This might indicate that the transition was less sharp under these conditions and that both phases coexisted

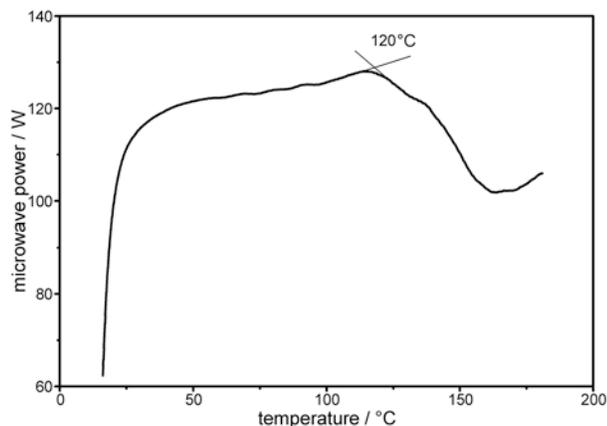


FIG. 6. Plot of microwave power vs sample temperature for silver iodide heated at  $1\text{ }^{\circ}\text{C}/\text{min}$  using microwave heating.

until around  $150\text{ }^{\circ}\text{C}$ . This could be due to temperature gradients within the specimen and further work is required to investigate this.

Measurements were also made during controlled cooling. However, studies on the structural transition in silver iodide by conventional thermal analysis techniques showed that the phase change exhibited hysteresis in that transformation is not perfectly reversible.<sup>28</sup> Furthermore, because  $\alpha$ -silver iodide couples very strongly with a the microwave field, it proved very difficult to cool specimens from this state using the compressed air supply in the presence of microwaves. Again, this leads to the danger of creating large thermal gradients across the specimen.

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