# INVESTIGATIONS OF NON-THERMAL MICROWAVE EFFECTS USING HYBRID CONVENTIONAL/MICROWAVE HEATING CALORIMETRY

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## ABSTRACT

A hybrid calorimeter is described whereby the test specimen may be heated using either hot air and/or microwave radiation. Thus it is possible to study phase transitions of materials under conditions ranging from purely conventional heating to pure microwave heating or mixtures thereof. Measurements using silver iodide showed that its phase change from the low temperature β-phase to the high temperature α-phase (which normally occurs at 147°C) was shifted to a progressively lower temperature with increasing microwave power. Furthermore, quasi-isothermal studies suggested that silver iodide could be transformed between states without changing its temperature by irradiating it with microwave energy. Examination of specimens heated purely by microwave energy using a thermal imaging camera indicated that large temperature gradients occurred in the sample after it had partially transformed to the α-phase. It is therefore possible that any microwave effect could be a consequence of these temperature gradients.

## INTRODUCTION

Microwave heating is an attractive form of alternative energy source for the processing of materials. In addition to the benefits of rapid and more specific heating, many studies have shown enhancements in the rates of a range of processes in ceramic, polymeric and organic systems [1-10], enhanced sintering of ceramic powder compacts (including lower sintering temperatures) [11,12], and reduced activation energies [1,2,3,11] above and beyond any purely thermal effect due to the specimen's temperature. Such behaviour has been termed 'the microwave effect' although doubts have been raised about its true nature. The primary reasons for any remaining uncertainty are:

*i.* The inability to vary the energy source between conventional and microwave heating in the same apparatus. Microwave heating experiments are performed in a microwave applicator (waveguide or cavity), whereas conventional experiments are typically carried out in a separate, radiant furnace of totally different specification (e.g. power level).

*ii.* Uncertainties associated with temperature measurement due to differences in measurement technique. Thermocouples are commonly employed in conventional experiments whereas pyrometry is often used with microwave heating. Furthermore, the surface temperature is commonly measured at one or more discrete locations without acknowledgment of the possibility that the temperature distribution within the specimen might be different between the two heating methods. This leads to difficulties in making a direct comparison of data.

The precise nature, origins and magnitude of the microwave effect are far less well established. A number of theories have been postulated [1,8-12]. These include: lowered activation energies [11]; enhanced diffusion due to increased vibrational frequency of the ions caused by the electric field of the microwave radiation [8,9]; the excitation of a non-thermal phonon distribution in the polycrystalline lattice [10,14]; quasi-static polarisation of the lattice near point defects [15]; and the ponderomotive action of the high frequency electric field on charged vacancies in the ionic crystal lattice [16]. 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 a differential scanning calorimetry. Instruments have been described which employ pure microwave power to examine specimens under its influence [17-21]. In some cases, the sample was mixed with, or surrounded by, a susceptor material which provided additional thermal energy to the sample via is own intrinsic absorption of microwave radiation. Thus there is little ability to control the ratio of conventional to microwave induced heating of the sample. In this work, we describe a novel 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 microwaves and thus measurements can be made with a combination of energy inputs from 100% conventional to 100% microwave power.

This apparatus has been used to investigate reports of anomalous behaviour in silver iodide which undergoes a solid state phase transition at 147°C from the low temperature β-phase (wurtzite structure) to the high temperature ionically conducting α-phase (body centred cubic iodide containing a disordered silver ion sublattice) [22]. Robb *et al* have studied this transition using temperature resolved *in situ* powder X-ray diffraction [23]. Under the influence of conventional heating the structural transition was detected at the expected temperature. When heated by 2.45 GHz microwave radiation the transition occurred some 50°C lower than expected. This effect was attributed to multi-phonon coupling between the RF field and low-lying transverse optic modes of silver iodide. This work reports studies on this material using conventional and AC calorimetry under the influence of a microwave field complemented by measurements of the temperature gradients within the sample obtained from IR thermography.

## EXPERMENTAL

A schematic diagram of the apparatus is shown in figure 1. A rectangular waveguide (not shown) was used to launch microwave radiation from a continuously variable 500 W magnetron operating at 2.45 GHz into a cylindrical cavity containing the specimen holder at its axis. Motorised chokes at the top and bottom of the cavity were adjusted so that the E-field within the cavity (measured by loop antennas orthogonal to the specimen) was maximised. Ancillary tuning by a manual 3-stub tuner in the launch section was employed so as to minimise reflected power. By these means the cavity could be operated in a $TE_{111}$ mode with the maximum field intensity at the locus of the sample position.

Conventional heating of the sample was achieved by passing compressed air, heated by a 750 W process gas heater, around the specimen holder. The temperature of the specimen is monitored either by a fluoroptic thermometer (Luxtron model 790) or by a thermal imaging camera (FLIR Systems Thermovision® A40). The fluoroptic thermometer was calibrated according to manufacturer's instructions using an ice-water bath as a single reference point. The thermal imaging camera was calibrated for temperature by measuring the emissivity of the sample held at known temperatures in a conventional furnace. The power supplied to the heater and magnetron, input air temperature and sample temperature were recorded by A/D converters (PicoLog ADC-16 and TC-08). A temperature controller (Eurotherm 2408) was used to control the power to the heating system which could either be operated with pure conventional heating, pure microwave heating or a hybrid fashion with fixed

amounts of microwave energy being supplied in addition to automatic control of sample temperature via the surrounding air temperature.

Silver iodide powder (99.999%, Acros Organics), was made into solid pellets (approximate density 4.9±0.3 g $cm^{-1}$ ; 83% of theoretical density) by uniaxial pressing and used for these studies.

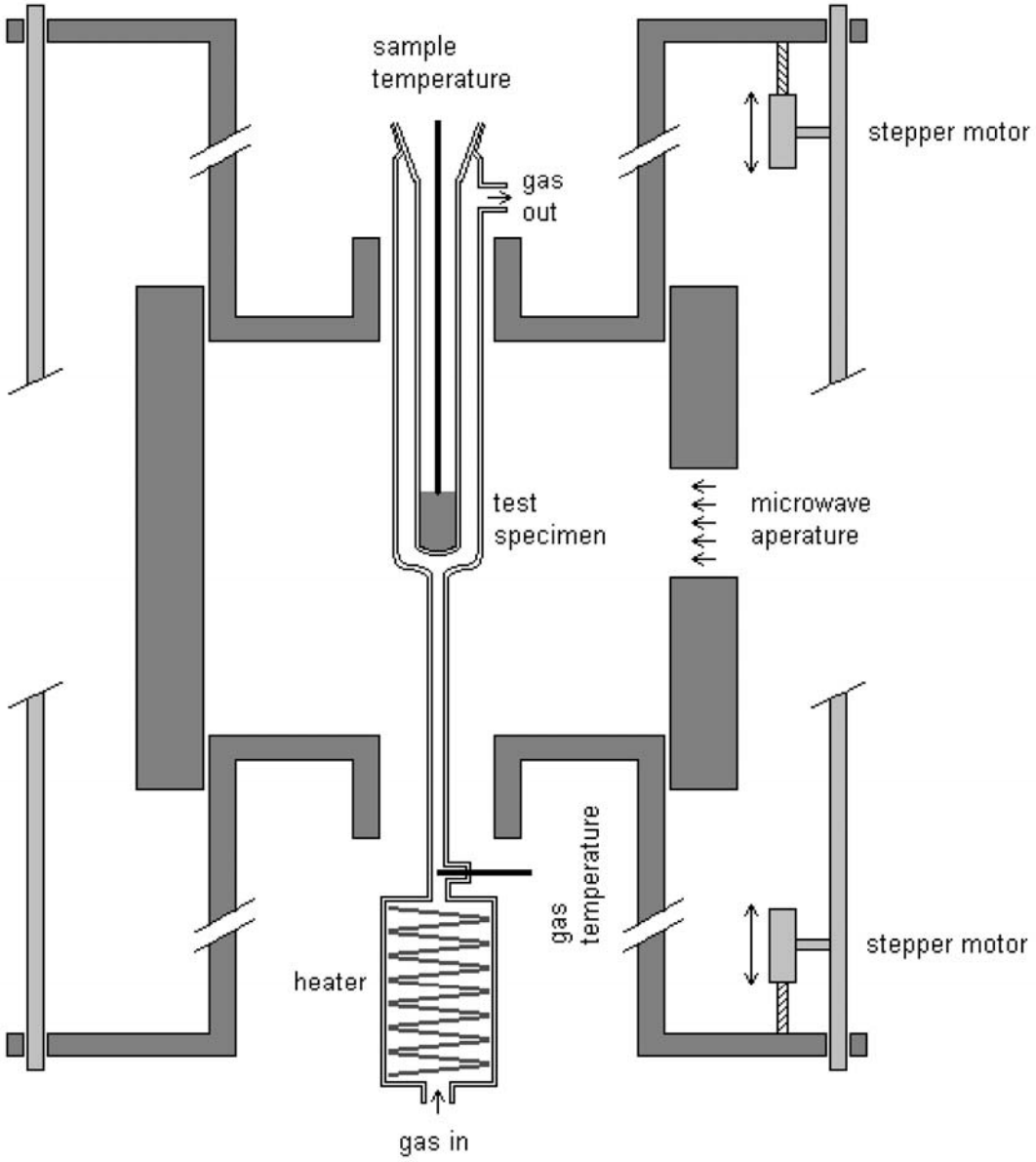


Figure 1. Schematic diagram of test cavity showing arrangement for heating sample and positions of temperature sensors.

## RESULTS AND DISCUSSION

Figure 2 shows results obtained on heating silver iodide at 1°C $min^{-1}$ exposed to increasing levels of a constant background of microwave power. The difference between the air temperature and sample temperature (ΔT) is plotted against the sample temperature and is analogous to a Differential Thermal Analysis (DTA) measurement [24]. With no microwave power, the curve shows the characteristic endothermic peak accompanying the normal phase transition at 147°C. In the presence of microwave energy the shape of the curve changes due to the increased coupling of the α-phase with microwaves compared to the β-phase, resulting in a sharp drop in conventional heating power required to maintain the programme temperature. It appears that the phase transition is shifted to lower temperatures under the influence of increasing levels of microwave energy.

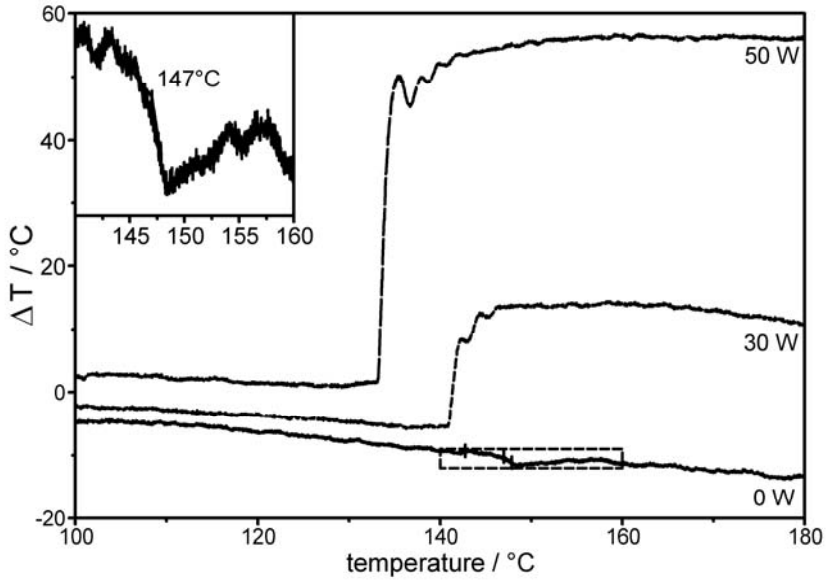


Figure 2. DTA data for silver iodide heated at 1°C $min^{-1}$ under increasing levels of microwave power (inset shows expansion of 0 W curve in transition region).

Rather than use a linear rising temperature profile, the sample temperature can be programmed to oscillate between two temperatures. The ratio of the amplitudes of the specimen and air temperatures is proportional to the heat capacity of the test specimen. This is the basis of AC calorimetry [25] and data for silver iodide obtained in the absence of any microwave field using the present apparatus is shown in figure 3. In this particular measurement, the specimen temperature was alternated by ±2°C about a mean value over a cycle time of 2 minutes for a period of 10 minutes and then the mean value incremented by 2°C so as to perform a step-wise temperature sweep. The phase transition of silver iodide is accompanied by a peak in heat capacity at the normal transition temperature and there is a reduction in heat capacity from the β-phase to the α-phase.

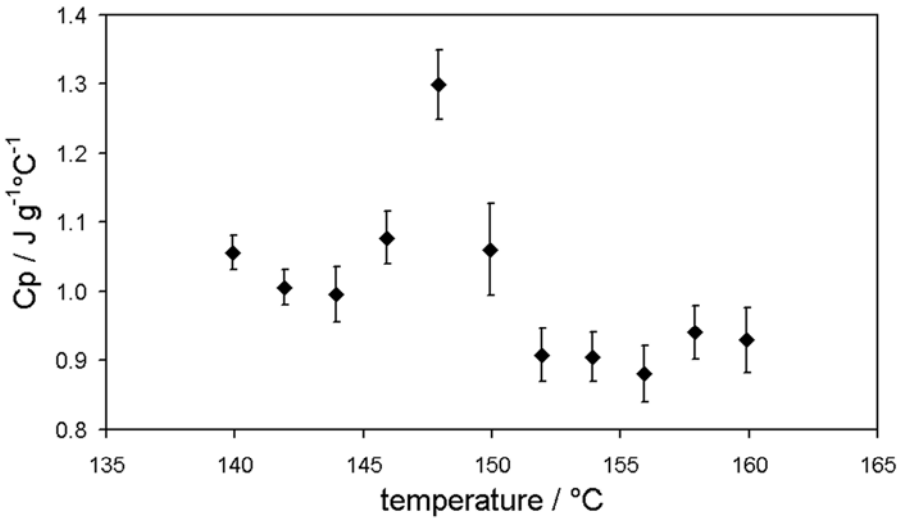


Figure 3. Heat capacity of silver iodide measured by AC calorimetry.

Figure 4 shows similar data for silver iodide measured with a background of 50 W microwave power. The peak in heat capacity at the phase transition was not detected due to difficulties in temperature control during the actual phase transition itself but the occurrence of the phase change can be detected by the characteristic drop in baseline heat capacity between 128 and 130°C which agrees with the transition temperature obtained under the same microwave power by DTA in figure 2.

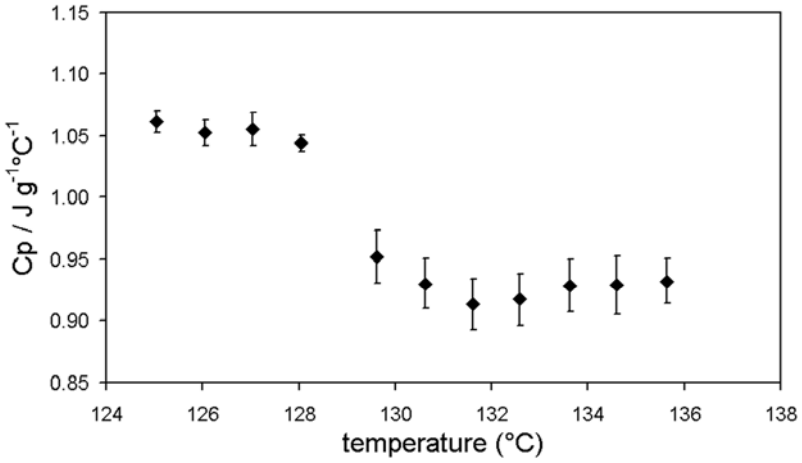


Figure 4. AC calorimetry data for silver iodide with a 50 W microwave power background.

Rather than change the average temperature of sample, an experiment was carried out whereby the specimen temperature was alternated between 132 and 128°C over a period of two minutes as the microwave power was cycled in a stepwise fashion between 0 W and 70 W. Figure 5 shows a plot of the specimen's apparent heat capacity as a function of microwave power and it appears that silver iodide can be transformed reversibly between β-AgI and α-AgI under quasi-isothermal conditions by the influence of microwave radiation. Again, these data are consistent with those shown in figures 2 and 4.

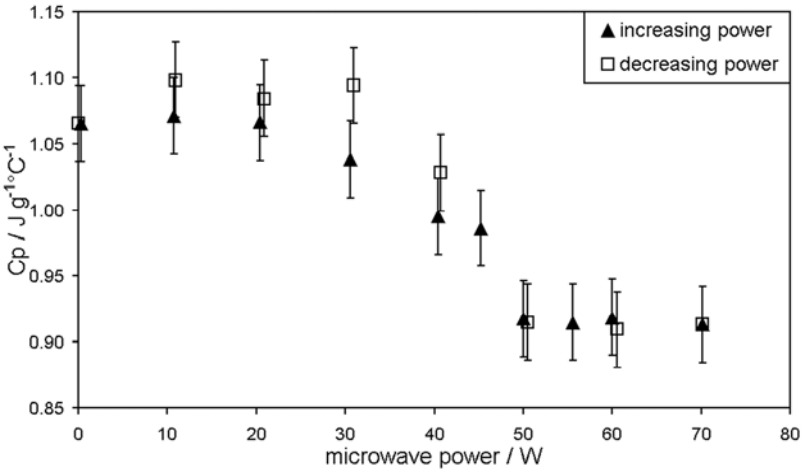


Figure 5. AC calorimetry data for silver iodide at 130°C under different levels of microwave power.

Whilst the DTA and AC calorimetry data provide evidence for a non-thermal microwave effect in silver iodide, the presence of temperature gradients within the specimen cannot be discounted. A thermal imaging camera was therefore used in place of the fluoroptic thermometer to monitor the specimen's temperature during pure microwave heating. Example data are shown in figure 6 for 150 and 75 W microwave power. Changes in heating rate occurred around 90°C due to increased coupling of the specimen with the microwave field suggesting the formation of some of the α-phase. Accompanying this phenomenon was a dramatic increase in thermal gradient (determined by the difference between the minimum and maximum temperatures of the specimen) across the specimen. Thus hot spots appeared in the sample concurrent with the formation of α-AgI. Below 90°C, the sample

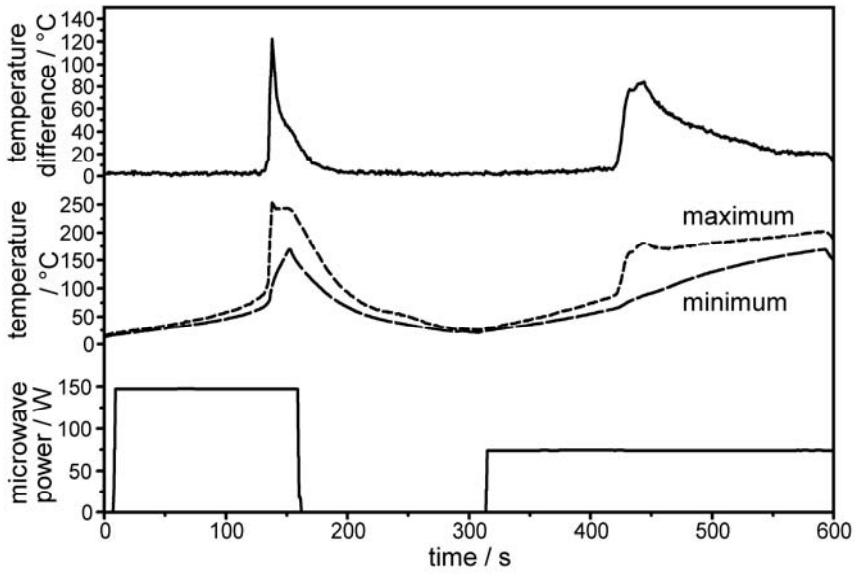


Figure 6. Temperature *vs* time profiles of silver iodide heated by 150 and 75 W microwave power.

was fairly uniform in temperature. Above this temperature, inhomogeneities in the sample and/or microwave field could have caused hot spots to appear and thus form α-AgI locally. Alternatively, a genuine non-thermal microwave effect would cause nuclei of α-AgI to be generated at a lower temperature than normal and these then lead to localised superheating. In order to decide between these possibilities, it would be necessary to improve the spatial resolution of the thermal imaging camera and/or devise a means of 3-dimensional mapping of the temperature distribution within the sample.

## CONCLUSIONS

These studies demonstrate the utility of a novel form of thermal analysis whereby conventional heating can be augmented by microwave radiation. Both conventional DTA and AC calorimetry can be carried out using the same instrument. Studies on silver iodide showed that there is an apparent reduction in the β-α phase transition from 147°C to the vicinity of 90°C under the influence of increasing levels of 2.45 GHz radiation. IR thermography indicated that this effect is accompanied by the appearance of large temperature gradients within the specimen although it is uncertain whether this microwave effect is a cause or consequence of these inhomogeneities in sample temperature.

## ACKNOWLEGEMENT

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