# EVIDENCE FOR NON-THERMAL MICROWAVE EFFECTS USING HYBRID CONVENTIONAL/MICROWAVE HEATING

**J Binner\*, D Price\*, J Wang\*, B Vaidhyanathan\* & M Reading\*\***
**\* IPTME, Loughborough University, Loughborough, UK**
**\*\* Dept of Chemical Sciences, University of East Anglia, Norwich, UK**

ABSTRACT

Clear evidence for the microwave effect has been observed during experiments in which a variety of materials have been heated using both conventional and hybrid heating, but in each case using the same experimental system. A hybrid single mode cavity has been used to investigate the microwave effect during phase changes in silver iodide, barium titanate and benzyl, whilst a hybrid multimode cavity has been used to investigate the microwave effect during sintering and grain growth in a range of ceramic materials with different dielectric properties. Although evidence for the microwave effect was not found in every case, where it was found the results could not be explained purely in terms of temperature gradients within the materials.

INTRODUCTION

Many investigators have reported unexpected effects resulting from the use of microwave radiation as an alternative energy source during the processing of materials. However, uncertainty remains since microwave heating experiments are often performed in a microwave applicator whilst the corresponding conventional experiments are typically carried out in a separate, radiant furnace of totally different specification (e.g. power level). Research has now been performed on a number of materials systems using two different hybrid conventional/microwave applicators in which the energy source can be varied without affecting a wide range of other variables. In the first series of experiments, a hybrid single mode cavity has been used to investigate the microwave effect during phase changes in silver iodide, barium titanate and the organic compound benzil via examination of the thermal properties, including the specific heat capacity. In the second series, a hybrid multimode cavity has been used to investigate the microwave effect during sintering and grain growth in a range of ceramic materials with different dielectric properties, viz. alumina, zirconia and zinc oxide. In both cases, it was possible to heat the samples using exactly the same heating profile but with varying amounts of microwave energy.

EXPERIMENTAL
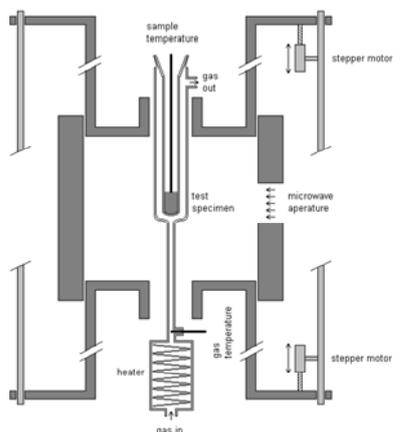


A schematic diagram of the hybrid single mode cavity is shown in figure 1, it has been described in detail elsewhere [1]. It was used to examine phase changes in three different materials, viz. silver iodide (AgI), barium titanate ($BaTiO_3$) and benzil, via examination of the thermal properties of these materials. In each case, the samples were heated using both pure conventional (a hot gas stream) and hybrid (microwave plus conventional) heating.

**Figure 1:** Schematic diagram of the hybrid single mode cavity.

Zinc oxide (ZnO), 3 mol% doped yttria partially stabilised zirconia (3-YSZ) and alumina ($Al_2O_3$) pellets were pressed from different grades of each powder, micron and submicron sized in the case of the ZnO, submicron and nano for the 3-YSZ and three different nanopowders for the $Al_2O_3$. Each series of pellets were sintered at two different temperatures for one hour using <u>exactly</u> the same time/temperature profile whilst varying the fraction of microwave and conventional power used.

RESULTS

***Single mode cavity:*** No effect on the phase transformation was observed with the use of microwave energy for either benzil or $BaTiO_3$. However, fig. 2 shows results obtained on heating AgI at 1°C min$^{-1}$ using increasing levels of a constant background of microwave power. The difference between the air and sample temperature ($\Delta T$) is
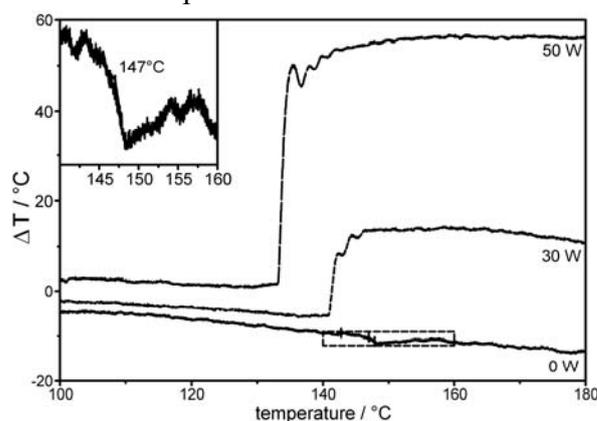


**Figure 2:** DTA data for AgI heated at 1°C min$^{-1}$ under increasing levels of microwave power.

plotted against the sample temperature, analogous to a DTA measurement. With no microwaves, the curve shows a characteristic endothermic peak accompanying the normal phase transition at 147°C. With microwaves 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 the level of conventional heat required to maintain the programme temperature. The phase transition is clearly shifted to lower temperatures with increasing microwave power.
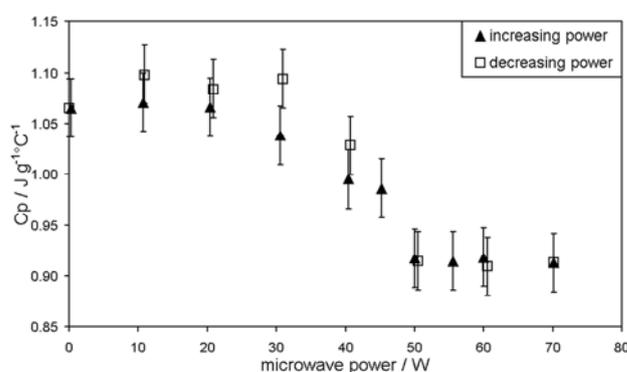


**Figure 3:** AC calorimetry data for silver iodide at 130°C under different levels of microwave power.

The sample temperature could also be programmed to oscillate between two values. The ratio of the amplitudes of the specimen and air temperatures was proportional to the heat capacity of the test specimen; this is the basis of AC calorimetry. Data for AgI in which the specimen temperature was varied between 128 and 132°C over a two minute period as the microwave power was cycled in a stepwise fashion between 0 and 70 W is shown in fig. 3. It may be observed that the AgI transformed reversibly between the α and β forms as a result of varying microwave power under quasi-isothermal conditions.

Whilst the DTA and AC calorimetry data provide evidence for a non-thermal microwave effect in AgI [2], 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. Changes in heating rate at ~90°C suggested increased coupling and hence the formation of some α-phase. Below 90°C, the sample was fairly uniform in temperature whilst above this temperature hot spots appeared,

suggesting that nuclei of α-AgI were generated well below the normal transformation temperature. An alternative explanation could be that the microwave field or the sample itself were not homogeneous, leading to the hot spots. To decide between these possibilities, it would be necessary to improve the spatial resolution of the thermal imaging camera.

*Multimode cavity:* The final density of the ZnO ceramics after sintering are shown in figure 4; the low final densities achieved were deliberate since it ensured that any differences in densification were visible. It can be clearly seen that densification was enhanced by the presence of a microwave field, with the enhancement becoming more significant the greater the level of microwave power used. Similar results were obtained for the 3-YSZ powders, although the magnitude of the effect was smaller, whilst the $Al_2O_3$ powders showed only an extremely small difference. The greatest effect occurred at low sintering temperatures, i.e. in the early stages of sintering, with up to a 24% density enhancement at 680$^{o}$C for the submicron ZnO powder, figure 5a. The final average grain size of the samples also followed a similar trend, figure 5b.
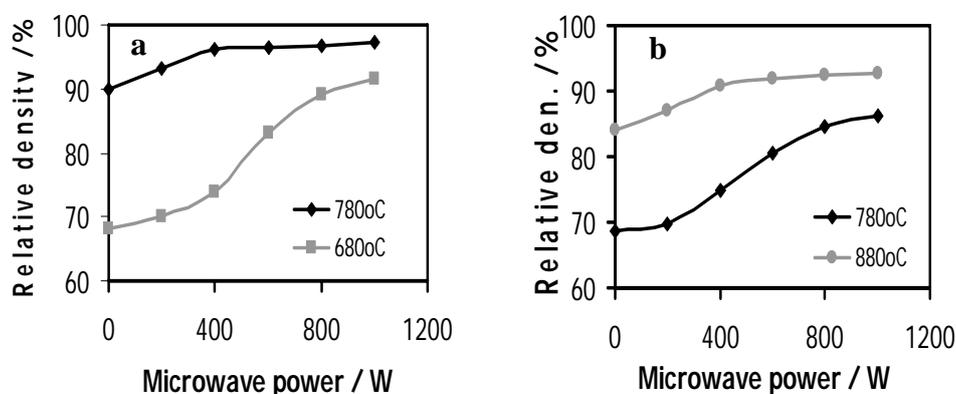


**Figure 4:** Density curves for ZnO for a) submicron at 680 and 780$^{o}$C and b) micron powders and at 780 and 880$^{o}$C.
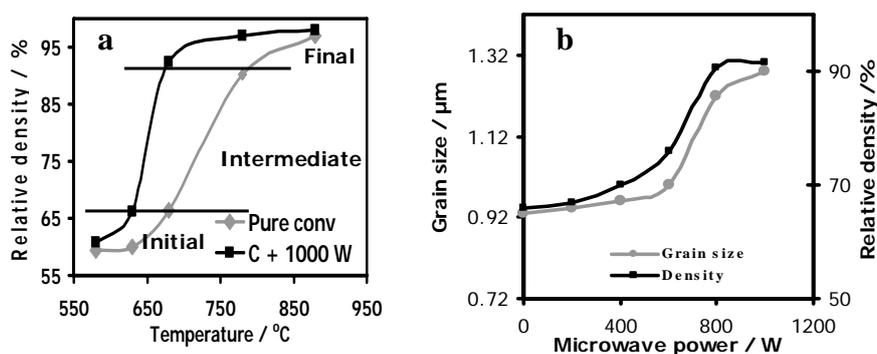


**Figure 5:** a) The greatest effect occurred at low sintering temperatures, i.e. in the early stages of sintering. b) The final average grain size of the samples also followed a similar trend.

As far as the authors are aware, these results can only be explained by two possibilities. The first is that the so-called 'microwave effect' is genuine. However, the second is that the different levels of microwave and conventional power used have resulted in significantly different thermal gradients within the samples since it is known that microwave heating leads to an 'inverse temperature gradient', i.e. the centre of the body is hotter than the surface. Based on the results in figures 4a and b, these gradients would have to be at least 100$^{o}$C in the ZnO pellets during sintering since in both cases the density achieved with conventional plus 1 kW of microwave

power is actually higher than that for achieved with pure conventional heating using a 100°C higher sintering temperature. When the differences in temperature between the edge and centre of the pellets, as measured by two optical thermometers, were considered it could be seen that they were generally smaller the greater the microwave power used and that, in every case, the measured temperature gradients were <20°C. This is significantly smaller than would be required to explain the densification effects observed above. In a further attempt to eliminate the temperature gradient possibility, a high resolution thermal imaging camera was used to monitor the temperature profile across the face of the samples during the sintering schedule. The results for the ZnO pellets sintered at 680°C are shown in figure 6, they show that, whilst the temperature gradients were larger in the case of the hybrid heated samples, even the largest were ≤10°C. Even though these are surface gradients and they will be larger at the centre of the compacts, they cannot explain the variation in sintered densities observed as a function of microwave power. Very similar results were obtained when using the 3-YSZ samples [3]. This therefore appears to be firm proof of the existence of the so-called 'microwave effect during sintering.
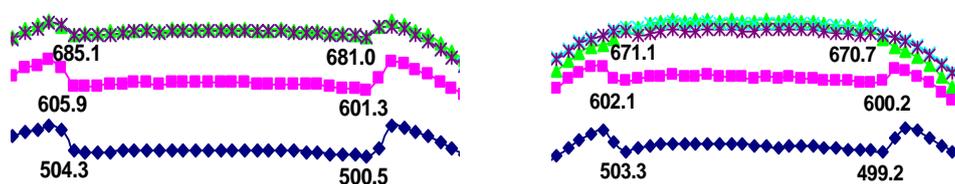


**Figure 6:** Temperature profiles during heating and at the hold temperature for ZnO samples heated using a) conventional heating and b) conventional plus 1 kW of microwave power.

CONCLUSIONS
Two completely different investigations have been pursued into the so-called 'microwave effect', one based on the measurement of thermal properties associated with phase changes using a single mode cavity and the other the determination of sintering characteristics of ceramic materials using a multimode cavity. However, in both cases the equipment allowed heating to be accomplished, in the same cavity and using exactly the same experimental configuration, with either pure microwave, pure conventional or any combination of hybrid heating. Whilst only a subset of the total results obtained have been presented here due to space restrictions, the results show clearly that a microwave effect can be observed. The sintering investigation clearly showed a relationship between the magnitude of the effect and the dielectric characteristics of the material; the higher the dielectric loss the greater the effect. A possible explanation of the effect in terms of temperature gradients was discounted in both cases. Although temperature gradients were present, as expected, they were substantially too small to account for the results observed.

REFERENCES
1. J Binner, DM Price, B Vaidhyanathan & M Reading, *Rev. of Sci. Instrum.* In press.
2. J Binner, DM Price, M Reading & B Vaidhyanathan, *Thermochimica Acta*. To be submitted.
3. J Wang, B Vaidhyanathan and J Binner, *J. Am. Ceram. Soc.* To be submitted.

ACKNOWLEDGEMENTS