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

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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 [1-10]; enhanced sintering of ceramic powder compacts, including lower sintering temperatures [11,12]; and reduced activation energies [1,2,3,11]. 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, whilst 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 (e.g. power level).

ii. Uncertainties associated with temperature measurement. Pyrometry is often used with microwave heating whilst 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. Finally, the surface temperature is usually measured. With conventional heating this will be the hottest part of the specimen, whilst 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 [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 the influence of an R.F. field [17-21]. In some cases the sample has been mixed with or surrounded by a susceptor material which provides additional thermal energy to the sample via is own intrinsic absorption of R.F. energy. 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 R.F. field 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 is detected at the expected temperature. When heated by 2.45 GHz microwave radiation the transition was detected 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. Our own studies using conventional and AC calorimetry under the influence of a microwave field (whilst initially supporting this observation) lead us to question the magnitude of temperature gradients within the apparatus which appear to adequately explain such observations without invoking non-thermal microwave effects. Measurements on other systems of interest will also be reported.

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