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Modulated temperature calorimetry of silver iodide in the presence of microwave radiation

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Abstract

Modulated temperature calorimetry has been carried out on silver iodide using a novel apparatus, which could expose the sample to conventional heating, microwave heating or any combination of the two. A 20 °C reduction in temperature for the β–α phase transition was achieved when the sample was irradiated with microwave energy. Quasi-isothermal studies also suggested that silver iodide could be transformed between states without changing its temperature when irradiated with microwaves. This study suggests a genuine ‘microwave effect’ is occurring in this material.

Keywords: AgI; Microwave effect; Modulated temperature calorimetry; Phase transition temperature

1. 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 [1–12]. It is now generally, though not unanimously, accepted that a ‘microwave effect’ exists. The primary reasons for any remaining uncertainty are the fact that the evidence is often gathered by comparing experiments performed using conventional radiant furnaces with those done in a microwave applicator of completely different specification (e.g. geometry, power level, etc.). Thus it is impossible to vary the energy source without simultaneously affecting a wide range of other variables. Furthermore, there are often associated uncertainties 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—even though the presence of the metallic shielding is known to distort the local microwave field [13]. 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 and, as a result, 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]. The variety of different theories reflect a lack of agreement about microwave/material interactions, although it is possible that there are a number of contributory factors to the microwave effect and that more than one of the above hypotheses are important.

In order to afford a direct comparison of data, a hybrid conventional/microwave heated calorimeter has been developed [17]. Although other instruments have been described which employ pure microwave power to examine specimens under the influence of an microwave field [18–22], our apparatus permits measurements to 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

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behaviour in silver iodide [23], 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) [24]. Robb et al. 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 was detected some 50 °C lower than expected. This effect was attributed to multi-phonon coupling between the microwave field and low-lying transverse optic modes of silver iodide. The current researchers have also obtained evidence for a reduction in transition temperature under the influence of microwave heating and attribute this effect to the production of defects in the β-AgI lattice which favours the formation of α-AgI [25]. In this publication studies are reported on this material using AC calorimetry under the influence of a microwave field.

2. Experimental

Polycrystalline silver iodide powder (99.999%) from Acros Organics, UK was pressed into cylindrical pellets measuring 7 mm in diameter and 5 mm high by uniaxial compression. This yielded samples of approximate density $4.9 \pm 0.3\,\mathrm{g\,cm^{-3}}$, i.e. 83% of theoretical density.

A schematic diagram of the apparatus is shown in Fig. 1. It could heat the samples using pure conventional heating, a hot gas source, pure microwave heating or in a hybrid mode with fixed amounts of microwave energy being supplied. Sample temperature was automatically controlled via the surrounding air temperature. 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 three-stub tuner in the launch section was employed to minimise reflected power. By these means the cavity could be operated in a TE_{111} mode with the maximum field intensity at the sample position.

Conventional heating of the sample was achieved by passing compressed air ($5\,\mathrm{l\,min^{-1}}$), heated by a 750 W process gas heater, around the specimen holder. The temperature of the specimen was monitored by a fluoroptic thermometer (Luxtron model 790) which was calibrated according to the manufacturer's instructions using an ice-water bath as a single reference

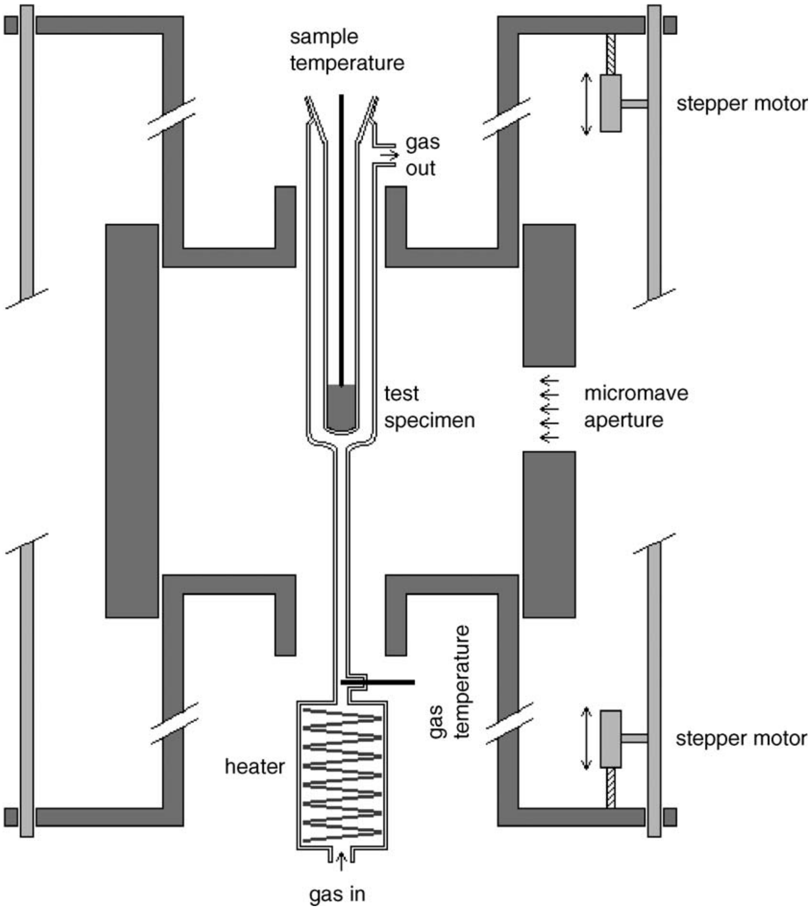

Fig. 1. Schematic diagram of test cavity showing arrangement for heating sample and positions of temperature sensors.

point. 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.

In the present work, the equipment was operated as a modulated temperature calorimeter in which the sample temperature was programmed to oscillate between two limits using the heated air supply. From the amplitude of the air temperature oscillation, $\langle T_{\mathrm{A}}\rangle$, required to achieve the desired sample temperature oscillation, $\langle T_{\mathrm{S}}\rangle$, it was possible to estimate the specific heat capacity, C_p, of the specimen according to the relation [26]:

$$C_p = k\langle T_{\mathrm{A}}\rangle/\langle T_{\mathrm{S}}\rangle$$

where k is a correction for the thermal mass of the sample holder, specimen and heat losses in the system (i.e. the baseline). Over a narrow temperature range, k was assumed to be constant and so the data was simply normalised to the published specific heat capacity of silver iodide [27,28] as the interest was not in establishing precise measurements of this parameter but to use the changes in C_p that accompany the phase transition to locate the temperature at which it occurred under different heating conditions.

3. Results and discussion

Fig. 2 shows raw data obtained from an experiment in which the specimen temperature was alternated by ±2 °C about a mean value every 2 min. These temperature steps were repeated for 1 h and then the mean value incremented by 2 °C in order to perform a step-wise temperature sweep. The derived heat capacity data are shown in Fig. 3. Here 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 as expected.

Fig. 4 shows raw data obtained using the exactly same temperature program, but with the specimen irradiated with 50 W of microwave power and correspondingly less conventional energy. There is a noticeable drop in the average air temperature required to maintain the specimen at the set point between 128 and 130 °C indicating that coupling between the sample and the microwave field has increased due to the formation of α-AgI. The derived heat capacity data shown in Fig. 5 does not show a peak in heat capacity at the phase transition as in Fig. 3, a feature that is discussed below, but there is a characteristic decrease in the baseline heat capacity that indicates that the phase transition has occurred over the temperature range 128–130 °C. When the microwave power level was increased to 75 W, and the conventional energy reduced further to enable the same temperature

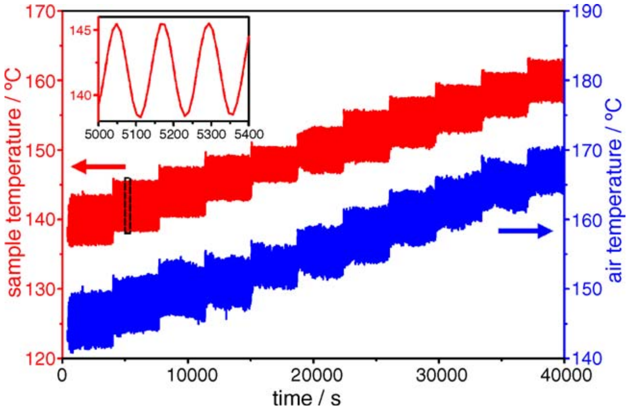

Fig. 2. Raw data for a stepwise isothermal modulated temperature calorimetry experiment on AgI in the absence of microwave energy. Inset shows expansion of sample temperature response over several modulations.

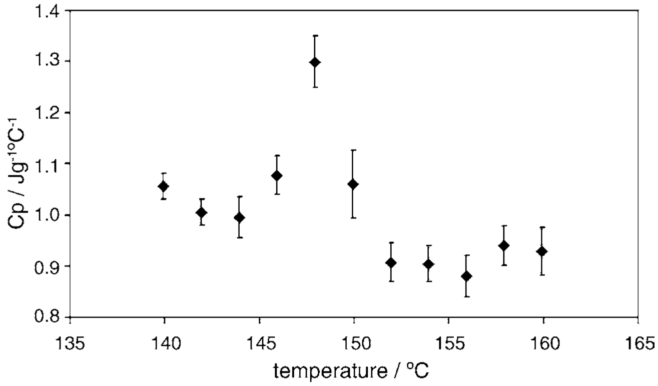

Fig. 3. Heat capacity of AgI derived from the raw data in Fig. 2.

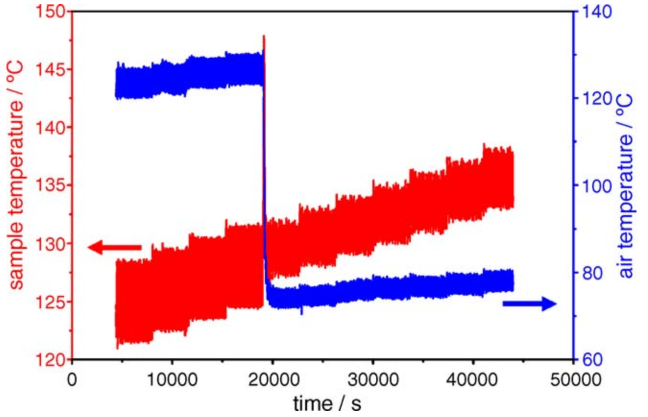

Fig. 4. Raw data for a stepwise isothermal modulated temperature calorimetry experiment on AgI in the presence of 50 W of microwave energy.

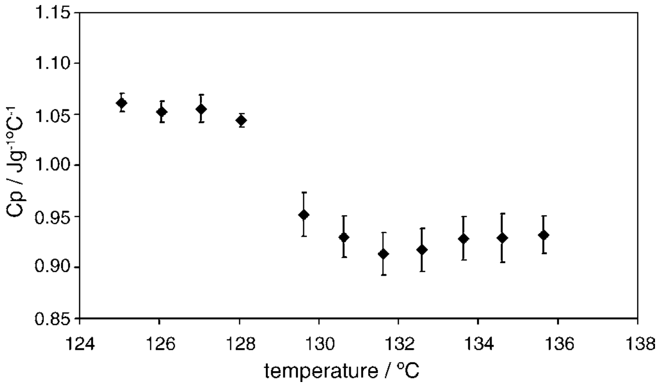

Fig. 5. Heat capacity of AgI derived from the raw data in Fig. 4.

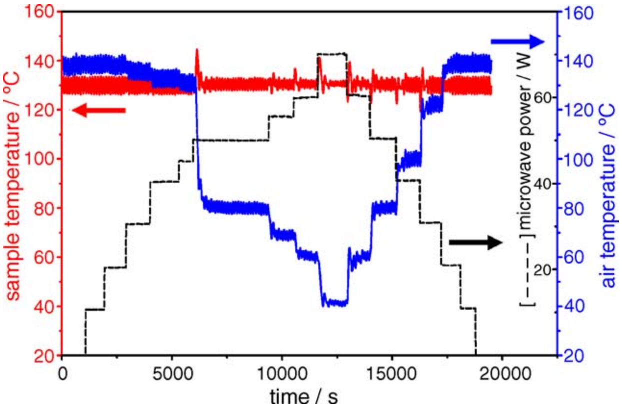

Fig. 6. Raw data for a quasi-isothermal modulated temperature calorimetry experiment on AgI with increasing and decreasing levels of microwave energy.

programme to be followed, the apparent transition temperature was reduced to around 120 °C. Use of higher microwave powers was not possible due to difficulties in controlling the specimen temperature immediately after it had transformed to α-AgI, making clear identification of the transition temperature impossible.

A further experiment using modulated temperature calorimetry in combination with microwave heating is illustrated in Fig. 6. Unlike earlier measurements, the average specimen temperature was set to 130 °C and modulated by ±2 °C about a mean value every 2 min for the whole experiment. The background microwave power was then cycled in small steps between 0 W (no power) and 70 W, the amount of conventional heat being reduced to maintain the average set temperature. The resultant derived heat capacity data are shown in Fig. 7. It will be observed that there was a reversible transformation between β-AgI and α-AgI with the change in the microwave energy level, the incident power at the transition point, ~50 W, being consistent with the same change seen under the stepwise heating data in Fig. 5. Again, there was no peak in heat capacity seen during the transition, c.f. Fig. 3. In earlier studies by modulated-temperature DSC it was postulated that this excess heat capacity seen under conventional heating was a consequence of the formation of defects in the β-AgI lattice which precede the formation α-AgI [25]. The absence of an excess heat capacity in the presence of microwaves prior to the phase change suggests that microwave irradiation (rather than the background thermal field) provides a mechanism for defect formation (perhaps by concentrating existing defects or by an interaction which creates new ones) and thus “catalyses” the transition to the α-phase.

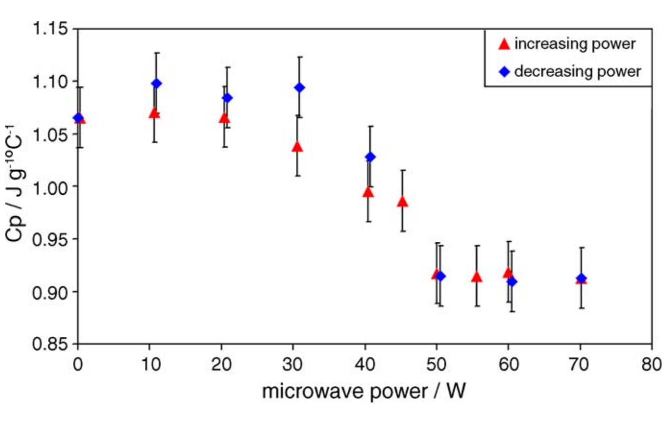

Fig. 7. Heat capacity of AgI derived from the raw data in Fig. 6.

4. Conclusions

Modulated temperature calorimetry of silver iodide using hybrid microwave/conventional heating showed that the β–α phase transition temperature of silver iodide was reduced from 147 °C to at least 120 °C when the specimen was exposed to microwave irradiation. No excess heat capacity (attributed to defect formation) was observed under conditions where the specimen was irradiated by microwaves. This indicated a potential mechanism for this effect by which the electromagnetic field promotes the formation of defects in the low temperature lattice via an athermal process. These defects then initiated transformation to the high temperature form under conditions when it would be metastable. By cycling the microwave power while the average specimen temperature was not changed it was shown that this effect is reversible.

References

[1] M.A. Janney, H.D. Kimrey, Mater. Res. Soc. Proc. 189 (1991) 215.
[2] M.A. Janney, H.D. Kimrey, M.A. Schmidt, J.O. Kiggans, J. Am. Ceram. Soc. 74 (1991) 1675.
[3] D.A. Lewis, Mater. Res. Soc. Proc. 269 (1992) 21.
[4] R.J. Giguere, Mater. Res. Soc. Proc. 269 (1992) 387.
[5] J.D. Katz, R.D. Blake, V.M. Kenkre, Ceram. Trans. 21 (1991) 95.
[6] M. Willert-Porada, T. Krummel, B. Rohde, D. Moormann, Mater. Res. Soc. Proc. 269 (1992) 199.
[7] P. Boch, N. Lequeux, P. Piluso, Mater. Res. Soc. Proc. 269 (1992) 211.
[8] Z. Fathi, I. Ahmed, J.H. Simmons, D.E. Clark, A.R. Lodding, Ceram. Trans. 21 (1991) 623.
[9] J.G.P. Binner, N.A. Hassine, T.E. Cross, J. Mater. Sci. 30 (1995) 5389.
[10] J.H. Booske, R.F. Cooper, I. Dobson, L. McCaughan, Ceram. Trans. 21 (1991) 185.
[11] M.A. Janney, H.D. Kimrey, Ceramic Powder Science II, American Ceramics Society, 1988, p. 919.
[12] M.A. Janney, C.L. Calhoun, H.D. Kimrey, Ceram. Trans. 21 (1991) 311.
[13] J.G.P. Binner, B. Vaidhyanathan, J. Wang, Proceedings of the Ninth International Conference on Microwave and High Frequency Heating, Loughborough, UK, 2003, pp. 477–480.
[14] J.H. Booske, R.F. Cooper, L. McCaughan, S. Freeman, M. Binshen, Mater. Res. Soc. Proc. 269 (1992) 137.
[15] S.A. Freeman, J.H. Booske, R.F. Cooper, B. Meng, J. Kieffer, B.J. Reardon, Proceedings of the Microwave Absorbing Materials for Accelerators Conference, Newport News, VA, 1993.
[16] K.I. Rybakov, V.E. Semenov, Phys. Rev. B 49 (1994) 64.
[17] J.G.P. Binner, D.M. Price, M. Reading, B. Vaidhyanathan, Rev. Sci. Instrum. 76 (2005) 064902.
[18] G.M.B. Parkes, P.A. Barnes, E.L. Charsley, G. Bond, Anal. Chem. 71 (1999) 5026.
[19] G.M.B. Parkes, P.A. Barnes, E.L. Charsley, G. Bond, J. Thermal Anal. 56 (1999) 723.
[20] G.M.B. Parkes, G. Bond, P.A. Barnes, E.L. Charsley, Rev. Sci. Instrum. 71 (2000) 168.
[21] G.M.B. Parkes, P.A. Barnes, G. Bond, E.L. Charsley, Thermochim. Acta 356 (2000) 85.

[22] A. Nesbitt, P. Navabpour, C. Nightingale, T. Mann, G. Fernando, R.J. Day, Meas. Sci. Technol. 15 (2004) 2313.
[23] G.R. Robb, A. Harrison, A.G. Whittaker, Phys. Chem. Commun. 5 (2002) 135.
[24] M. Parrinello, A. Rahman, P. Vashishta, Phys. Rev. Lett. 50 (1983) 1073.
[25] J.G.P. Binner, G. Dimitrakis, D.M. Price, M. Reading, B. Vaidhyanathan, J. Thermal. Anal. Calorim., in press.
[26] Y. Kraftmakher, Phys. Rep. 356 (2002) 1.
[27] R. Shaviv, E.F. Westrum Jr., F. Grønvold, S. Stølen, A. Inaba, H. Fuji, H. Chihara, J. Chem. Thermodyn. 21 (1989) 631.
[28] R.A. Vargas, M.E. Pacheo, Solid State Ionics 37 (1990) 209.