Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 2, 409–412

HYSTERESIS IN THE β–α PHASE TRANSITION IN SILVER IODIDE

J. G. P. Binner[1], *G. Dimitrakis*[2], *D. M. Price*[1*], *M. Reading*[3] *and B. Vaidhyanathan*[1]

[1]Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, UK
[2]Department of Electrical and Electronic Engineering, Nottingham University, Nottingham, UK
[3]Department of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, UK

The nature of the β to α phase transition in silver iodide was investigated by conventional and modulated temperature DSC and dielectric property measurements. On cooling, the high temperature phase remained stable 2.5°C below its normal transition temperature even at a very slow cooling rate 0.2°C h^{-1}. Dielectric property measurements under conventional and microwave heating suggested an anomalous effect of the latter on the β to α phase transition in this material.

Keywords: *AgI, dielectric properties, microwave effect, phase transition temperature*

Introduction

Silver iodide can exist in three crystal polymorphs at atmospheric pressure [1]. Below 147°C the β-phase is stable; this has a wurtzite structure with the iodide ions arranged in a hexagonal close packed structure and with the silver ions occupying a sublattice of interstitial tetrahedral sites. Above 147°C silver iodide undergoes a crystalline transition to the high temperature α-phase, which has a body centred cubic arrangement of iodine ions with the silver ions distributed over a sublattice of interstitial sites whose number exceeds the occupancy of silver ions. This phase is stable up to the melting temperature of 555°C. Also present below 147°C is the metastable γ-phase which differs from the β-phase in that it has a zinc blende structure with the iodide ions occupying a cubic close packed lattice. This can be viewed as a defect β-phase structure in which the iodide ions are layered ABABAB rather than ABCABC. Migration of Ag^+ though the disordered cationic lattice gives rise to exceptionally high ionic conductivity of the α-AgI phase [2]. The ordering of Ag^+ has been studied using computer simulations and it is the tendency of the cations to condense into a locally monoclinic arrangement which is unstable relative to the hexagonal (wurtzite) structure which is proposed as the driving force for the α–β phase transition [3].

Previous investigators have reported the heat capacity of silver iodide using conventional and AC calorimetry [4, 5]. These measurements have been carried out in heating only whereas Hanaya *et al.* have reported DSC studies on heating and cooling of the stabilisation of α-AgI by incorporating AgI inside porous silica [6]. In this work the nucleation of the low temperature phase is claimed to be inhibited by the reduction in AgI particle size. For bulk AgI claims have been made that the β–α phase transition can be made to occur around 100°C when the specimen is heated by microwave radiation rather than be conventional heating [7]. In this particular case, multi-phonon coupling between the electromagnetic field and vibrational motions within the AgI crystal are conjectured to stabilise the high temperature form in the same way that mechanical stress by reduction in particle size might also achieve the same effect. An alternative mechanism is the so-called 'ponderomotive effect' whereby microwave-excited ionic currents become locally rectified at interfaces (such as grain boundaries) so as to promote mass transport [8]. In the case of AgI there is no bulk diffusion of material during its structural transformation but it is not unreasonable to propose that this process might promote the formation of α-AgI.

This work reports studies on the silver iodide α–β phase transition by conventional and modulated-temperature calorimetry. We also report dielectric property measurements under conventional and microwave heating.

Experimental

The silver iodide powder (99.999%, Acros Organics) used for these studies was made into pellets with a density of 4.9±0.3 g cm^{-3}, i.e. 83% of theoretical density, by uniaxial pressing.

* Author for correspondence: d.m.price@lboro.ac.uk

1388–6150/$20.00
© 2006 Akadémiai Kiadó, Budapest
Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Differential scanning calorimetry was carried out using a TA Instruments Q1000 DSC fitted with a mechanical cooling unit. The instrument was calibrated for temperature, enthalpy and heat capacity response using indium and sapphire. All measurements were carried out using hermetically sealed pans with a cell purge of 20 mL min^{-1} of dry oxygen-free nitrogen.

The dielectric properties of silver iodide were measured during conventional heating using the cavity perturbation technique [9–11]. The apparatus consisted of a cylindrical brass cavity (245 mm diameter and 24.5 mm high) with two internal loops, constructed from semi-rigid coaxial cable, used probe the electromagnetic response of the system at its resonant frequencies. A silica glass tube packed with silver iodide was introduced along the axis of the cavity. This surrounded by an outer silica glass tube through which hot air could be passed so as to heat the sample. The temperature of the specimen was measured using a fluoroptic thermometer (Luxtron model 790) in order to avoid affecting the electromagnetic field within the cavity. The transmission peak frequency (f_S) and quality factor ($f/\Delta f_{3dB}$) of the cavity were measured periodically during heating using network analyser (Hewlett Packard, HP8714ET) centered on the TM_{010} and TM_{020} modes at 615 and 1413 MHz respectively.

Using measurements on the unperturbed transmission peak frequency and quality factor and the corresponding measurements with the cavity containing the test specimen allows the dielectric constant (ε') and dielectric loss factor (ε'') to be calculated using the following equations;

$$\varepsilon' = 1 + \frac{(f_0 - f_S)V_0}{2f_0V_S} \quad (1)$$

$$\varepsilon'' = \frac{1}{4}\left(\left|\frac{1}{Q_0} - \frac{1}{Q_S}\right|\right)\frac{V_0}{V_S} \quad (2)$$

where: V_0 and V_S are the volumes of the cavity and sample, respectively; f_0 and f_S are the unperturbed and perturbed peak frequencies, respectively; Q_0 and Q_S are the unperturbed and perturbed quality factors, respectively.

Microwave heating of the sample was achieved using a smaller cavity (radius 58 mm; height 77 mm) increasing the power supplied to the cavity in between measurements using an amplifier driven by the output from the network analyser so as to achieve the required temperature program [12]. The sample holder was modified so that conventional heating could be applied using a hot air jacket around the specimen. Thus measurements could be made under pure conventional and pure microwave heating in the same assembly without disturbing the specimen.

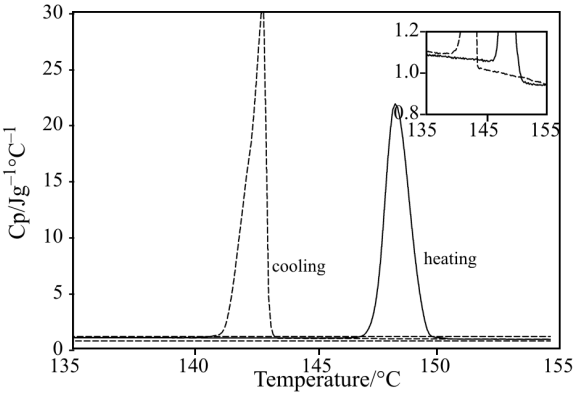

Fig. 1 Heat capacity of AgI measured at 1°C min^{-1} on cooling and reheating. Inset shows baseline heat capacity either side of the transition

Results and discussion

Figure 1 shows the heat capacity of silver iodide on cooling from 180 to 120°C at 1°C min^{-1} and then re-heated to 180°C at the same rate. The extrapolated onset of the β–α phase transition on heating occurs at 147°C as expected however the formation of the low temperature phase occurs some 3°C lower. An expansion of the baseline heat capacity of the specimen shows a reversible 0.2 J g^{-1} $°C^{-1}$ change in heat capacity between the crystalline forms in agreement with earlier studies [4]. Hysteresis in the transition between crystal structures is not unusual and has been observed in other systems [13, 14]. One approach to establishing the absolute limit of this discrepancy between the transition point on cooling and that seen on heating is to observe the transition at progressively slower rates of temperature change and extrapolating the measurements to zero heating and cooling rates [15].

Figure 2 shows stepwise isothermal modulated temperature DSC measurements on silver iodide. The average sample temperature was decreased in 0.2°C steps and held quasi-isothermally at this temperature for one hour. The complex heat capacity was obtained

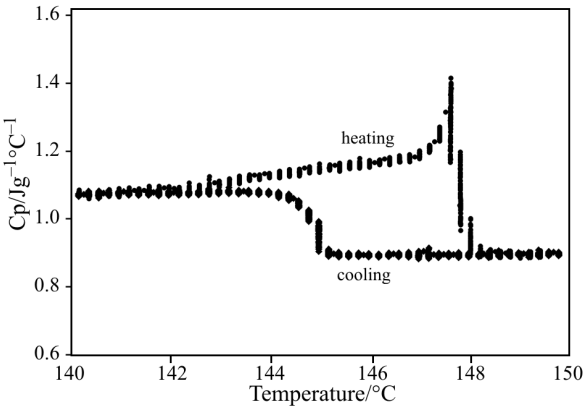

Fig. 2 Complex heat capacity of AgI measured on very slow stepwise cooling (0.2°C h^{-1}) and re-heating

from the ratio of the amplitude of the heat flow divided by amplitude of the heating rate using a temperature modulation of 0.1°C amplitude and period of 100 s. The heat capacity data for both cooling and heating agree well outside the transition region but it is apparent that the α-AgI phase does not begin to convert to the low temperature β-form until around 145°C. On re-heating the specimen the heat capacity data diverges from that obtained on cooling around 143.5°C and the transition can be seen to proceed to α-AgI form 147.6°C. Burley reports that under similar conditions of slow cooling through the phase transition the hexagonal β-phase is formed in preference to the metastable γ-phase [16]. The excess heat capacity between 143.5 and 147.6°C represents contributions from Frenkel defects forming in the hexagonal lattice which precede the structural change to the α-phase [17].

Figure 3 shows measurements of the dielectric permittivity (ε′) and loss factor (ε′′) for silver iodide at 615 and 1413 MHz. Again there is a similar degree of hysteresis in the transformation on cooling and heating commensurate with that observed by conventional DSC under the same cooling and heating rates. There does not appear to be any dependence of transition temperature on the frequency used for the measurements.

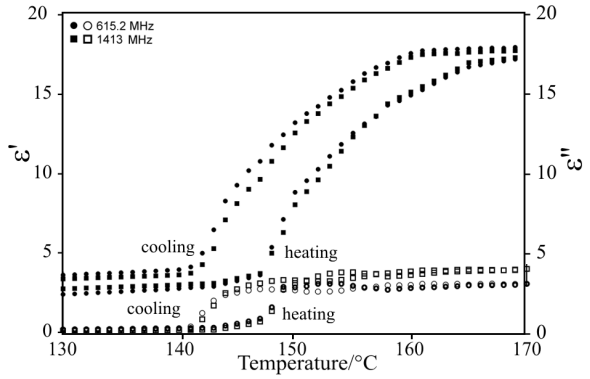

Fig. 3 ●,■ – Permittivity and ○, □ – loss factor of silver iodide on cooling and reheating at 1°C min^{-1} for two different frequencies

Figure 4 shows measurements of the dielectric permittivity (ε′) of silver iodide measured at 2.45 GHz using conventional and microwave heating. The transition temperature observed under conventional heating is in good agreement with the studies reported above but the change in dielectric properties under microwave heating is shifted to around 120°C. This observation lends support the findings of Robb *et al.* who used X-ray powder diffraction measurements under conventional and microwave heating to show that the β–α phase transition occurred around 100°C when the specimen was irradiated with microwaves [7]. These workers propose that multi-phonon

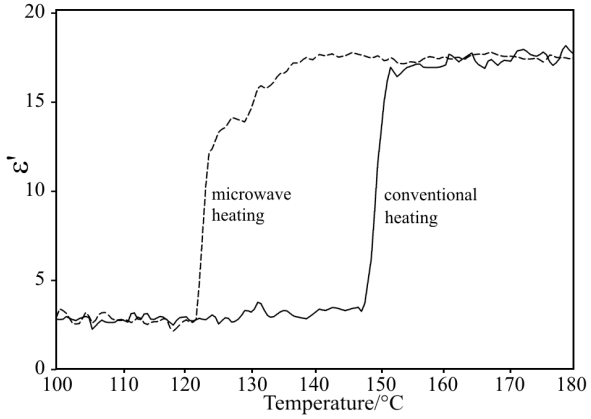

Fig. 4 Permittivity of AgI at 2.45 GHz measured under conventional heating and microwave heating at 1°C min^{-1}

coupling between the microwave field and low-lying transverse optic modes within the β-AgI lattice promote the formation of the α-AgI phase. Our studies by modulated-temperature calorimetry however support the hypothesis that defect formation might be an alternative mechanism by which the formation of the high temperature phase can be catalysed.

Conclusions

Calorimetric and dielectric property measurements on silver iodide indicate that the high temperature α-phase remains stable for several degrees below the normally accepted transition temperature (147°C) for this material. While this effect is too small to account for stablisation of α-AgI at much lower temperatures under the influence of mechanical strain or microwave irradiation as reported elsewhere, the formation of defects by these external influences may be a mechanism by which the β–α phase transition temperature can be reduced. Dielectric property measurements on silver iodide under conventional and microwave heating indicated that use of the latter can reduce the β–α phase transition temperature to around 120°C.

Acknowledgements

Dielectric property measurements under microwave heating were performed at the University of Manchester Institute of Science and Technology with the assistance of Dr. Richard Day and his group.

References

1 M. Parrinello, A. Rahman and P. Vashishta, Phys. Rev. Lett., 50 (1983) 1073.

2 D. A. Keen, J. Phys.: Condens. Matter, 14 (2002) R819.
3 P. A. Madden, K. F. O'Sullivan and G. Chiarotti, Phys. Rev. B, 45 (1992) 45.
4 R. Shaviv, E. F. Westrum Jr., F. Grønvold, S. Stølen, A. Inaba, H. Fuji and H. Chihara, J. Chem. Thermodyn., 21 (1989) 631.
5 R. A. Vargas and M. E. Pacheo, Solid State Ionics, 37 (1990) 209.
6 M. Hanaya, I. Osawa and K. Watanabe, J. Therm. Anal. Cal., 76 (2004) 529.
7 G. R. Robb, A. Harrison and A. G. Whittaker, Phys. Chem. Comm., 5 (2002) 135.
8 S. A. Freeman, J. H. Booske and R. F. Cooper, J. Appl. Phys., 83 (1998) 5761.
9 F. Horner, T. A. Taylor, R. Dunsmuir, J. Lamb and W. Jackson, J. Inst. Electr. Eng., 93 (1946) 53.
10 N. J. Damaskos and B. J. Kelsall, Microwave Journal 38 (1995) 140.
11 S. Li, C. Akyel and R. G. Bosisio, IEEE Transactions on Microwave Theory and Techniques MTT-30, (1) (1982) 100.
12 A. Nesbitt, P. Navabpour, C. Nightingale, T. Mann, G. Fernando and R. J. Day, Meas. Sci. Technol., 15 (2004) 2313.
13 C. C. Stephenson and A. C. Zettlemeyer, J. Am. Chem. Soc., 66 (1944) 1405.
14 D. G. Thomas and L. A. K. Staveley, J. Chem. Soc., (1951) 2572.
15 D. M. Price, J. Thermal Anal., 45 (1995) 1285.
16 G. Burley, J. Phys. Chem., 68 (1964) 1111.
17 K. Shai and J. B. Wanger Jr., Phys. Rev. B, 23 (1981) 6417.

Received: July 6, 2005
Accepted: February 3, 2006

DOI: 10.1007/s10973-005-7154-1