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High phase-transition temperature for β-AgI to α-AgI and an explanation of the memory effect

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The AgI thermal transition of the β phase (wurtzite structure) to the α phase (body-centered-cubic structure) occurred at a higher temperature (162 °C) than that previously reported (~147 °C). It is believed that this higher temperature is the result of these gelatin-grown β-phase microcrystals being unusually free of included γ phase and other crystal defects that would serve as α-phase nucleation sites. Introducing defects into these grains catalyzed this transition at the lower temperature. Having two distinct phase-transition temperatures explains the memory effect that has been reported in some AgI microcrystalline samples.

INTRODUCTION

Silver iodide can have three fundamental phases at atmospheric pressure: the β or hexagonal structure of the wurtzite type, the γ or face-centered cubic structure of the zinc blend type, and the α or body-centered cubic structure occurring at high temperature. It is generally accepted that the β phase is the stable phase at all temperatures below 147 °C and the γ phase is metastable.

The β and γ phases almost always occur as mixtures, and their ratio is not easily determined.[1,2] X-ray powder diffraction has been the technique used to analyze microcrystalline samples but the predominant reflections of the γ phase overlap with reflections of the β phase, requiring a relative intensity analysis. Even this analysis can be difficult since relative intensity changes can also be caused by preferential orientation of the microcrystalline particles. Sometimes helpful is the unique γ-phase reflection at 1.6236 Å (56.695° for Cu $K\alpha$), but this (400) reflection has a low relative intensity ($I/I_{\max}=0.06$), which limits its usefulness. Also, particular care must be taken in handling β-phase samples because moderate grinding or compression can result in the formation of γ phase.[3,4]

Probably because of these difficulties, samples believed to be pure β phase have turned out to be mixtures. For example, the x-ray diffraction line intensities of pure β phase reported by the National Bureau of Standards[5] were shown by Berry[2] to be due to a mixture containing 30% γ phase. Similarly, an x-ray powder diffraction pattern published for a "pure β-phase" sample[6] is more consistent with a sample containing ~33% γ phase.

Not only do these two phases readily coexist, but even a number of polytypes consisting of regular stacking of the cubic and hexagonal layers have been reported.[7–10]

It is generally accepted that the β phase or mixtures of (β,γ) phases transform to the α phase when heated to ~147 °C, and the change is not usually reversible upon cooling because of a possible change in the β:γ ratio.[10–13] A memory effect has been reported for the β:γ ratio of microcrystalline samples heated above the 147 °C transition temperature and then recooled; the original ratio is regenerated. This memory effect is irreversibly erased if the sample is heated above ~170 °C.[4,13]

It has been proposed by Burley that this effect is an intrinsic property of AgI brought about by preferential occupation of certain silver ion sites when heated near the transition temperature.[13] However, the preferential occupancy of the silver ions within the temperature range of interest (147 °C to ~170 °C) is of questionable importance since it does not appear to be affecting the ionic conductivity of the α phase, which is a superionic conductor. After the abrupt, 4-orders-of-magnetic change in conductivity at the transition temperature (147 °C), only a very small and relatively constant increase in conductivity occurs at higher temperatures.[14]

This paper describes unusual thermal data obtained from a β-phase AgI microcrystalline sample that is believed to be unusually free of crystal defects such as γ-phase inclusion, fractures, and lattice strain.

EXPERIMENT

General

All operations (except x-ray diffraction) were conducted under red safelights.

Low gelatin freeze-dried β-phase AgI microcrystals: β-phase powder

An AgI suspension was prepared by the controlled addition of $AgNO_3$ and NaI solutions to a stirred vessel containing a bone gelatin solution. The gelatin solution was maintained at 35 °C and pI of 3.0 throughout the 266-min precipitation.[15]

The suspension had a very pale yellow color like dairy cream. The resulting microcrystals were monodisperse 0.26-μm truncated hexagonal bipyramids (measured across the basal plane). X-ray diffraction analysis showed the microcrystals were pure β-phase AgI.

A portion of the suspension (1 mol) was centrifuged free of bulk gelatin, then resuspended in distilled water (1 L). A solution containing 50 mg of active proteolytic enzyme[16] was added and the mixture was stirred for 30 min at 40 °C. It was then centrifuged (sufficiently to settle the microcrystals but still leave them resuspendable without scraping or grinding the sludge) and resuspended in distilled water twice, and finally freeze-dried to yield a free-flowing powder. Combustion analysis of this powder showed that only a small amount of gelatin remained (0.7% C, <0.3% N, and H). X-ray powder diffraction pattern showed this material to still be pure β-phase AgI.

Differential scanning calorimetry

The DSC data were obtained using a Du Pont 910 DSC. For coolant control a Du Pont LNCA-II was used. The calorimeter was calibrated using 99.999 99% indium metal for temperature and energy calibration. The samples were placed, without compression, into aluminum pans that were then hermetically sealed. Both heating and cooling curves were run at 5 °C/min under a nitrogen purge.

RESULTS AND DISCUSSION

An x-ray diffraction powder pattern of an almost completely randomly oriented sample of the β-phase powder was obtained using the Rigaku θ-θ diffractometer and Cu $K\beta$ radiation. The powder was loaded into the horizontal sample holder without compression. The pattern ($2\theta = 15-55°$) had a nearly perfect match, both in peak position and intensity, for that calculated for β-phase AgI. The integrated diffraction intensities for the $(10\bar{1}0)$, (0002), and $(10\bar{1}1)$ reflections were 1.65:1.12:1, which is in excellent agreement with Despotovic and Popovic calculated ratios of 1.72:1.13:1.[17] No contamination by the cubic γ phase was detected (estimated purity >98%).

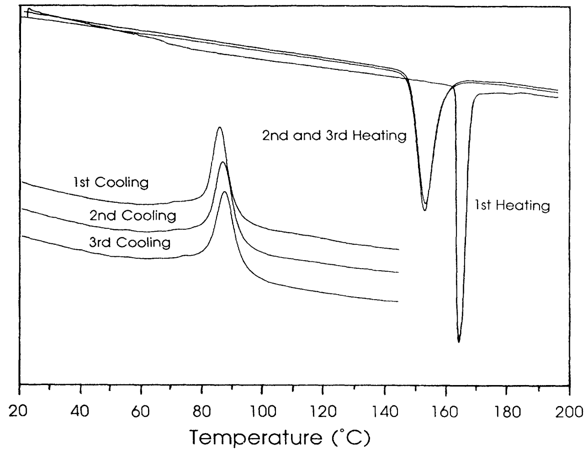

FIG. 1. Differential scanning calorimetry curves showing the three heating (to 200 °C) and cooling curves for the β-phase powder. Note the change in the α-phase transition temperature due to crystal defects formed during the first cooling. (For clarity, the curves have been displaced along the vertical axis.) These data were obtained at a heating/cooling rate of 5 °C/min. The onset and peak temperatures for the first heating were 162.4 and 163.9 °C. Using 1 °C/min, they were 161.5 and 162.2 °C and using 10 °C/min, they were 162.7 and 165.3 °C. This good consistency indicates a relatively small thermal lag at 5 °C/min.

DSC measurements on the β-phase powder showed that the transition of β to α phase occurred at a higher temperature (162.4 °C onset, 163.9 °C peak, $\Delta H = 1.29$ kcal/mol) than has previously been reported for this transition (~147 °C).[18] Upon cooling, a large thermal hysteresis of ~72 °C was observed ($\Delta H = 1.27$ kcal/mol). Heating this same sample a second and third time resulted in a shifted and broadened endothermic peak that was now consistent with the usually cited lower phase-transition temperature (second heating: 147.7 °C onset, 152.7 °C peak, $\Delta H = 1.29$ kcal/mol). For all three coolings, the exotherm peaks obtained upon cooling were essentially the same (~92 °C onset) (Fig. 1).

Since AgI undergoes an abrupt ~6% lattice expansion when transitioning to the lower temperature phases,[19,20] numerous crystal defects could form. Crystal defects, which in the context of this study include cubic stacking faults (i.e., γ phase), were found in thermally cycled β-phase powder. A sample of the β-phase powder was heated to 190 °C, then allowed to air cool rapidly (<2 min). X-ray diffraction analysis showed that the ratios of peak intensities had dramatically changed and there were broad new peaks at 3.62, ~2.184, ~2.054, and ~1.582 Å. This sample did not contain α-phase AgI since this phase is reported to have its main peaks at 3.58, 2.53, and 2.066 Å (Ref. 21) and the sample lacked the long-wavelength absorption characteristic of α phase. The diffractometer tracing of this sample (Fig. 2) was nearly identical with that published by Davis and Johnson for a sample containing approximately equal amounts of β-phase and $7H$ polytype AgI.[9] The broadness of the peaks in $7H$ polytype-containing samples may indicate an admixture with other polytypes, or a high degree of structural disorder in the $7H$ polytype. [A sample cooled much more slowly in a vacuum oven (~8 h) contained mostly γ phase with ~10% $7H$ polytype material present.]

Alternatively crystal defects were introduced into a sample of the β-phase powder by grinding briefly in a mortar and pestle.[3,4] This sample had only the usually cited lower phase-transition temperature on the first heating (149 °C onset, 154 °C peak). A mixture of ground and nonground samples resulted in both DSC peaks.

Some differently precipitated samples of AgI micro-

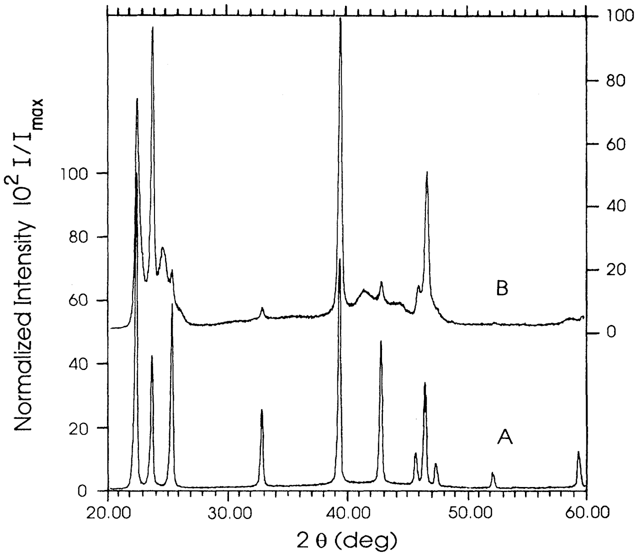

FIG. 2. Powder diffraction patterns using Cu$K\alpha$ radiation (a) of the β-phase powder (having some preferential orientation) and (b) of the β-phase powder that had been heated to 190 °C and rapidly air cooled (~30 s). The pattern of the heat-treated sample is nearly identical to that prepared by Davis and Johnson, which contains approximately equal amounts of 7*H* polytype and β-phase AgI (Ref. 9).

crystals that were found to contain mixed phases were also examined by DSC. They had a low phase-transition temperature upon the first heating (147±1 °C).

An observed increase in the phase transition temperature of very small AgI particles in pores (~0.02 μm) has been attributed to the effect of surface tension on homogeneous nucleation.[22] This effect should be relatively insignificant for these larger microcrystals and also could not explain the differences in the phase transition temperatures observed for similarly sized particles reported above. It appears that the higher than expected phase-transition temperature of the β-phase powder is due to its lack of crystal defects. The formation of crystal defects during the first cooling results in a lower phase-transition temperature for the second and third heatings that is near the value which is widely cited. The lack of two distinct endo- thermic peaks for previously heated samples shows that every microcrystal now contains crystal defects (including mixed phases). If this higher phase-transition temperature results from superheating, as suspected, then each microcrystal would need only a single nucleation site to lower its transition temperature.

Based on these results, the reported memory effect can be explained. Samples which show this effect must consist of a mixture of defect-free β-phase AgI microcrystals and other microcrystals containing mixed β and γ phases. Upon heating between 147–162 °C, only the mixed phase microcrystals would undergo the transition to α phase while the rest would remain β phase. Upon cooling, these α-phase microcrystals would change back to mixed phase microcrystals. The abundance of these microcrystals and the difference in their compositional change caused by the heat/cool cycle would determine the extent that the sample's overall composition changes.

CONCLUSIONS

Relatively pure β-phase AgI microcrystals were found to have a higher α-phase transition temperature (162 °C) than previously reported for AgI. Upon cooling, the phase transition was not reversible. A rapidly cooled (<2 min) sample of AgI contained a mixture of about equal amounts of the 2*H* (β phase) and 7*H* polytypes. Samples which contain some γ phase or 7*H* polytype have a lower phase-transition temperature (~147 °C). The general lack of two DSC peaks suggests that mixed AgI phases usually occur within the same microcrystals.

The ~147 °C phase transition temperature reported in the literature for β-phase AgI may indicate the presence of crystal defects such as the inclusion of γ-phase AgI. The extent of defects needed to produce a lowering in the phase-transition temperature was not determined but if this higher phase-transition temperature is a result of superheating, then a small amount in each crystal would be sufficient. The reported memory effect is readily explained by assuming that the samples which show this effect consist of a mixture of pure β-phase microcrystals and mixed phase microcrystals.

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