THE PRODUCTION OF SINGLE CRYSTALS OF AgI

D. R. MILLS, C. M. PERROTT and N. H. FLETCHER

Department of Physics, The University of New England, Armidale, N.S.W. Australia

A method is described for growing crystals of hexagonal silver iodide from a solution of AgI in concentrated aqueous KI solution. This method relies on convective circulation of the growth solution between two chambers held at different temperatures and produces large single crystals much more rapidly than previous methods. A successful method of transforming these crystals to the high temperature cubic phase is also described.

1. Production of β-AgI single crystals

Single crystals of the wurtzite phase of silver iodide (β-AgI) have been grown by three methods[1–3], the most satisfactory of which was described by Cochrane[2]. In this method, a concentrated aqueous solution of KI saturated with AgI is held at constant temperature and slowly diluted by downward diffusion of distilled water into the growth solution. Dilution causes supersaturation with AgI and good quality crystals are produced. These crystals are transparent and pale yellow in colour, they take several months to grow, and are of two habits: either hexagonal prisms up to 20 mm in length and 2 mm diameter, or pyramids up to 5 mm high and 2 mm basal diameter. Cochrane[4] observed, however, that if the temperature of the solution was allowed to fall, crystals which had grown actually dissolved.

This observation indicates that the solubility of AgI in aqueous KI solution decreases with increasing temperature and, since published data[5] are available for dilute KI solutions only, one of us (D.R.M.) measured the temperature dependence of the solubility of AgI in concentrated KI solutions. The results (fig. 1) show that, if an aqueous solution of KI is prepared and saturated with AgI at 23 °C, heating of the solution to 40 °C (say) causes a significant amount of AgI to precipitate. The greatest amount of silver iodide is deposited when the original KI solution has a concentration of about 4 mole/litre and this is therefore the optimum concentration to use in any method of crystal growth based on the temperature dependence of AgI solubility in KI solutions.

On this basis, we have developed a new method for growing β-AgI single crystals. The apparatus is depicted in fig. 2. It is wholly constructed from pyrex, in order to avoid contamination of the solution, and completely sealed, to prevent evaporation of water and the subsequent shift from the optimum concentration to higher and less favourable KI concentrations. The use
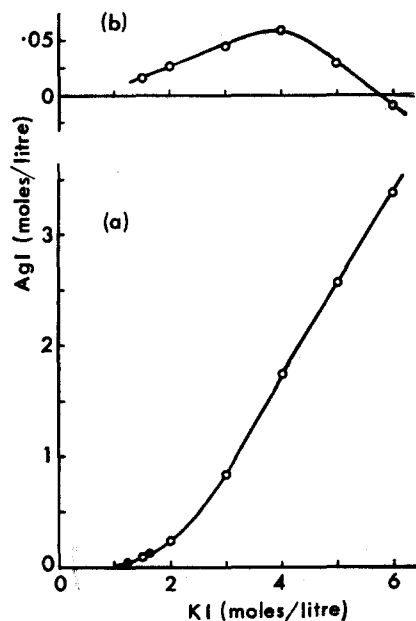

Fig. 1. (a) Solubility of AgI in KI solution at 23 °C shown as a function of the concentration of the initial KI solution (solid circles represent published data[5]). (b) Number of moles of AgI precipitated when a litre of solution saturated with AgI at 23 °C is heated to 40 °C.
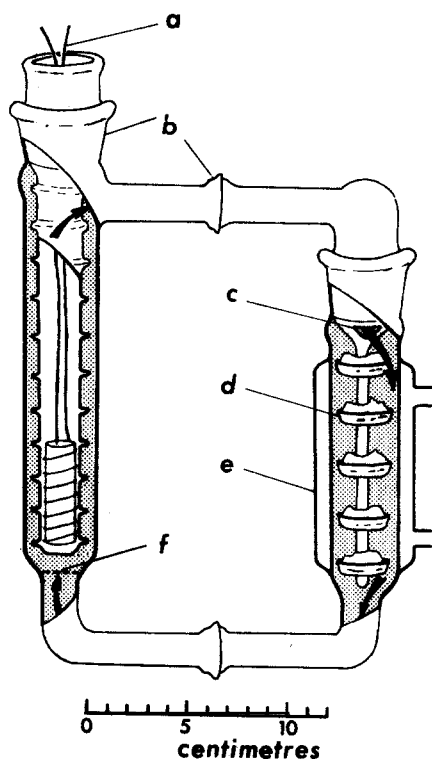
Fig. 2. Schematic drawing of crystal growing apparatus. The apparatus is constructed from pyrex and the growth solution circulates by convection in the direction shown by the arrows. (a) Electrical leads to heater within central tube. (b) De-mountable ground joints. (c) Re-entrant hole for growth solution. (d) Cup containing undissolved AgI. (e) Cooling jacket. (f) Porcelain filter.

of tapered and spherical joints allows the apparatus to be dismantled for cleaning, removal of crystals or replenishing the solution. No insulation need be wrapped on the surfaces, but the apparatus must be kept in a dark-room so as to prevent photodecomposition of the chemicals used.

As shown in fig. 2, the apparatus comprises two chambers connected at top and bottom by horizontal tubes. The right-hand chamber is held at 23 °C by the attached cooling jacket and the growth solution (4 mole/litre KI) is saturated with AgI by virtue of the large amount of undissolved AgI in the chamber. The left-hand chamber is heated by an electrical heater (10 W) situated within the central tube. This heats the solution in the chamber to about 40 °C and causes continuous circulation of the solution from one chamber to the other by convection. Thus, the cold solution moves from right to left along the bottom tube and

enters the left-hand chamber through a porcelain filter which restricts the flow rate. The solution is heated in the lower part of this chamber and rises in the chamber, contributing to crystal growth on the surface of the inner tube, before moving across the top tube and re-entering the right-hand chamber where it is cooled and re-saturated with AgI.

The quality of the crystals produced by this method is very dependent on the speed and uniformity of flow of the supersaturated solution past the irregular surface of the heater tube. It has been found that good quality crystals are produced in the left-hand chamber if the speed of flow is restricted to about 2 mm/sec. Faster flow rates result in the formation of inferior quality crystals, both in this chamber and in the upper cross-arm of the apparatus.

The crystals produced are of one habit only, regular hexagonal prisms, and may be up to 6 mm long and 8 mm across. They are transparent and identical in appearance to those grown by Cochrane's method but grow much more quickly, being produced in 3 weeks. Since they are produced very rapidly, there is a chance that more potassium impurity might be contained in these crystals than in those grown by Cochrane's method. Accordingly, we grew crystals by both methods, washed them in distilled water for two days and determined the potassium content by a flame photometer test. The results showed an order of magnitude difference, crystals grown by our method containing 340 ppm potassium and those grown by Cochrane's method containing 35 ppm potassium. These impurity levels are not very high and are quite acceptable for most physical studies. Some crystals have to be rejected because of the occurrence of small axial holes which extend right through the crystals, but these holes do not include the parent solution.

Neutron diffraction data to be published shortly have shown that the crystals have the wurtzite structure. There is absolutely no evidence to suggest the formation of the other low temperature (cubic zinc-blende) polymorph of silver iodide.

2. Production of α-AgI single crystals

The high temperature (α) phase of silver iodide has a very unusual structure with the cations distributed statistically throughout the spaces of a regular bcc lattice of anions, but it has been subjected to limited study

because of the unavailability of single crystals. We have produced single crystals of α-AgI quite reliably by the following method, which involves the transformation of single crystals from the β to the α form at 150 °C. Hexagonal crystals are cleaved at room temperature in order to produce perfectly flat basal surfaces and then placed on a small flat metal disc which has been preheated to about 250 °C. In this way, the transformation of the crystal is propagated uniformly along the hexagonal c-axis direction and very few crystals have been observed to fault on transformation. The largest crystal transformed by this method measured 8 mm across and 3 mm in the c-axis direction.

If, however, an attempt is made to use less severe heating rates or to propagate the transformation in a direction normal to the c-axis, marked crazing of the crystal always results. This is evidently a result of the fact that the transformation of β to α-AgI is martensitic with habit plane (0001). The mechanism of the transformation was proposed by Burley[6]), on the basis of structural details, as occurring through opposing shifts of alternate (0001) planes of iodide ions through $\pm\frac{1}{8}a$ [01$\bar{1}$0], followed by a small distortion of the iodine lattice from a(hex) = 4.59 Å to a(bcc) = 5.05 Å and subsequent rearrangement of the mobile silver ions. The validity of this proposal has been established by the very success of our method of producing α-AgI

crystals and the fact that we have used comparative Laue photographs of the crystals being transformed to establish the crystallographic correspondences

$$\text{hex } [0001] \equiv \text{bcc } [011],$$
$$\text{hex } [\bar{2}110] \equiv \text{bcc } [100],$$
$$\text{hex } [01\bar{1}0] \equiv \text{bcc } [0\bar{1}1],$$

which are those predicted by the Burley mechanism.

References

1) E. Lakatos and K. H. Lieser, Z. Physik. Chem. NF **48** (1966) 228.
2) G. Cochrane, Brit. J. Appl. Phys. **18** (1967) 687.
3) E. S. Halberstadt, Nature **216** (1967) 574.
4) G. Cochrane, Ph.D. Thesis, University of New England, Australia (1968).
5) W. F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds*, 4th ed., Vol. 1 (Van Nostrand, New York, 1958) p. 95.
6) G. Burley, Acta Cryst. **23** (1967) 1.