

## POLYMORPHISM OF SILVER IODIDE

G. BURLEY, *National Bureau of Standards, Washington 25, D. C.*

## ABSTRACT

The polymorphic relationship of silver iodide at atmospheric pressure has been re-investigated using high temperature *x*-ray diffraction and differential thermal analysis techniques. A hexagonal (wurtzite type) and a face-centered cubic (zincblende or sphalerite type) phase can exist between liquid helium temperature and 147° C. The latter is metastable over this entire range. From 147° C. to the melting point at 555° C. a disordered body-centered cubic phase is the stable modification. The methods of preparation and transformation are summarized and a qualitative explanation of phase stabilization is presented.

## INTRODUCTION

As part of a project studying the crystallographic properties of silver iodide, the phase relationships of the mineral iodyrite and its polymorphs have been reinvestigated and major changes in the existing concepts have been found necessary.

The literature reports silver iodide to be trimorphic at atmospheric pressure. A face-centered cubic (low-cubic) structure, of the zincblende-type, was reported as the result of powder *x*-ray diffraction studies of the silver halides by Wilsey (1921) and confirmed by Davey (1922). However, Aminoff (1922) pointed out that iodyrite was known to have hexagonal symmetry from optical data. Laue diffraction patterns from a cleavage sheet showed a hexagonal structure of the wurtzite-type. Wilsey (1923) studied the crystal structures of silver iodide prepared from silver nitrate and potassium iodide in considerably greater detail. He concluded from the variation of the intensity of diffraction lines common to both proposed structures, and from the presence of lines which could be assigned to only one of these, that varying proportions of both structures existed in all his preparations. Bloch and Möller (1931) reported that the low-cubic form was obtained by powdering any coarse crystalline preparation. They prepared the pure hexagonal form by dissolving silver iodide in concentrated potassium iodide and precipitating the silver iodide by dilution of the solution. The stability regions of the two low-temperature modifications were determined by heating low-cubic and hexagonal samples at 125° C. and 135° C. for six weeks. The samples held at 125° C. did not change, while at 135° C. the low-cubic form changed into the hexagonal. On this basis these authors concluded that the hexagonal phase is the stable form between 135° C. and 147° C. and the low-cubic phase is stable below 135° C. Kolkmeijer and van Hengel (1934) found that silver iodide was precipitated from solution in the cubic form if  $\text{Ag}^+$  ions were in excess, and in hexagonal form if  $\text{I}^-$  ions were in excess.

Strock (1934) showed that silver iodide converts to a body-centered cubic (high-cubic) structure above 147° C. He concluded that in this phase the iodine atoms are in regular lattice sites, while the two silver atoms in the unit cell are randomly distributed among thirty possible sites, not all of which have the same coordination number.

A paper on the polymorphism of silver iodide by Majumdar and Roy (1959) appeared recently, in which the existence of the low-cubic phase of AgI was discounted entirely.

For silver iodide the high-cubic phase stable above 147° C. is often designated  $\alpha$ , the hexagonal phase as  $\beta$ , and the low-cubic phase as  $\gamma$ . In addition to these, a cubic phase with the sodium chloride-type structure has been found at pressures above 3000 bars by Bridgman (1915) and by Jacobs (1938).

The present study was designed to establish the stability limits of the phases of silver iodide existing at atmospheric pressure, and to clarify the reasons for the possible coexistence of two phases at room temperature.

#### SAMPLE PREPARATION

The silver iodide used initially was prepared by precipitation from solution. Solutions of varying concentration of silver nitrate and sodium iodide were mixed in different proportions and in different order. In addition, concentrated aqueous solutions of silver iodide in silver nitrate and of silver iodide in sodium iodide were prepared and precipitation induced by pouring these into an excess of water. A large excess of iodide ion invariably produced the hexagonal phase. Increased amounts of silver ion increased the percentage of the low-cubic phase coprecipitated. This is essentially in agreement with the literature.

Commercially available silver iodide consists primarily of the hexagonal phase. From this, the low-cubic phase could be prepared (1) by heating to near the melting point and quenching the high-cubic phase thus produced in air or water, (2) by lengthy grinding in a mortar and pestle, or (3) by the application of hydrostatic pressure. Complete conversion to the low-cubic form appeared to be impossible.

Solid state and solution techniques with metallic silver and mercuric iodide were also used in the preparation of silver iodide. Additional samples were prepared by dissolving silver iodide in aqueous ammonia and evaporating the solutions to dryness at 100° C. The various methods used are outlined in Table I.

Single crystals were prepared by slow evaporation of a saturated solution of silver iodide in 30% aqueous hydriodic acid at room temperature. Always the pure hexagonal phase, they formed either as hexagonal plates or hexagonal pyramids. In the latter case spiral hexagonal steps could

TABLE I. SUMMARY OF PREPARATIVE METHODS FOR AgI

Number	Method of Preparation	Phase
1	50 ml 1N NaI+50 ml 1N AgNO <sub>3</sub>	mixture
2	50 ml 1N AgNO <sub>3</sub> +50 ml 1N NaI	mixture
3	200 ml 3N AgNO <sub>3</sub> +50 ml 1N NaI	fcc
4	200 ml 3N AgNO <sub>3</sub> +50 ml 0.1 N NaI	fcc
5	100 ml 1N AgNO <sub>3</sub> satd. with AgI in 1000 ml H <sub>2</sub> O	fcc
6	100 ml 3N NaI satd. with AgI in 1500 ml H <sub>2</sub> O	hex
7	Ag metal (powder)+I <sub>2</sub> vapor (200° C.-sealed tube)	hex
8	Ag metal (powder)+50% aq. HI (25° C)	hex
9	AgI heated to 550° C.-quenched in water	fcc
10	AgI heated to 550° C.-cooled slowly	hex
11	#3 added slowly to 1000 ml H <sub>2</sub> O	fcc
12	5g HgI <sub>2</sub> (solid)+200 ml 1N AgNO <sub>3</sub> (95° C.)	fcc
13	1g Ag metal diss. in 500 ml 3N KI+3g I <sub>2</sub>	hex
14	80% hex AgI ground in mortar	fcc
15	80% hex AgI pressed at 10,000 atm.	fcc
16	1g AgI (#6)+200 ml 15 N NH <sub>4</sub> OH (100° C.)	hex
17	1g AgI (#6)+200 ml 3N NH <sub>4</sub> OH (100° C.)	hex
18	1g fcc AgI (#14)+200 ml 15 N NH <sub>4</sub> OH (100° C.)	mixture

sometimes be observed, indicating growth by a screw dislocation mechanism normal to the basal plane. All attempts to grow single crystals of the low-cubic phase of silver iodide were unsuccessful.

#### PROCEDURES AND RESULTS

The phase relationships in the silver iodide system were investigated by static and dynamic heating and differential thermal analysis techniques.

Samples of both the hexagonal and low-cubic forms were maintained at a constant temperature for two to five weeks. The temperature in successive experiments was varied from 90° to 150° C. at ten degree intervals, except that an additional run was made at 135° C. X-ray analysis was performed both before and after heating. The hexagonal form showed no phase change at any temperature, only a sharpening of the x-ray reflections due to annealing. The low-cubic form, however, was progressively more completely converted to the hexagonal form as the temperature was increased above 135° C.

As opposed to the static method above, both the differential thermal analysis and high temperature x-ray diffraction methods offer a dynamic method of establishing equilibrium conditions. Differential thermal analysis, at a speed of 1°/minute, was carried out from room temperature to above the transition to the high temperature form at 147° C. No change of slope was observed in the curve for either phase until the

strongly endothermic peak at  $147^{\circ}$  was reached. The transition point was identical for both phases, within the limits of error, and represents the conversion to the high-cubic phase.

In heating experiments designed to follow both the rate and actual temperature range of transformations, approximately thirty different samples were studied by high-temperature  $x$ -ray diffraction. The apparatus has been previously described (Mauer, 1955). The range studied through repeated heating cycles was from room temperature to above the melting, or decomposition, temperature at  $555^{\circ}$  C. In the interval between  $50^{\circ}$  to  $150^{\circ}$  C. the temperature was varied in increments of ten degrees to  $100^{\circ}$  C., and of five degrees above this. The angular region between  $22^{\circ}$  and  $26^{\circ}$  in  $2\theta$  was scanned continuously, at a rate of  $0.5^{\circ}$  per minute. All phases show at least one strong characteristic reflection in this range and identification is unambiguous.

The hexagonal phase remained unchanged to the transition temperature at  $147^{\circ}$  C., where it converted to the high-cubic phase. As this transition was quite sharp and easily reversible, and the high-cubic phase then persisted essentially unchanged to the melting temperature of  $555^{\circ}$  C., only the region below  $147^{\circ}$  C. was further investigated in detail.

The changes which occurred when a low-cubic sample was heated from room temperature are shown in Fig. 1. Since some conversion to the hexagonal modification occurred above  $120^{\circ}$ , but apparently very little of the reverse, most heating experiments with the  $x$ -ray diffractometer furnace were made using the silver iodide quenched from near the melting point as starting material. This consisted primarily of the low-cubic phase.

For samples which had a very high initial fraction of the low-cubic phase, or had been ground to an extremely small size, the transition to the hexagonal phase seemed to begin between  $90^{\circ}$  and  $100^{\circ}$  C. Those which had been quenched and ground vigorously generally showed the lowest initial transition temperature, indicating that the previous history of the sample was of some importance. All samples, except those consisting primarily of the hexagonal phase, showed some conversion at  $120^{\circ}$  or below. In this range, the conversion was quite slow and was accompanied by some annealing of the low-cubic phase, indicated by a decrease in the breadth of the diffraction peaks.

Between  $120^{\circ}$  and  $135^{\circ}$  C. the transformation rate increased markedly. Even at the lower end of this temperature range, significant changes could be observed after heating a sample for a number of hours.

Above  $135^{\circ}$  C. the rate of conversion to the hexagonal phase became more rapid and proceeded further to completion. It was always irreversible even after prolonged heating at constant temperature. The easily re-

versible transition to the high-cubic phase always occurred at  $147^{\circ}\text{C}$ ., regardless of the ratio of the two phases present.

Bloch and Möller (1931) reported the persistence of mixtures of phases in heating a specimen slightly above the  $147^{\circ}\text{C}$ . transformation temperature and then cooling to about  $135\text{--}140^{\circ}\text{C}$ . This was also noted in the

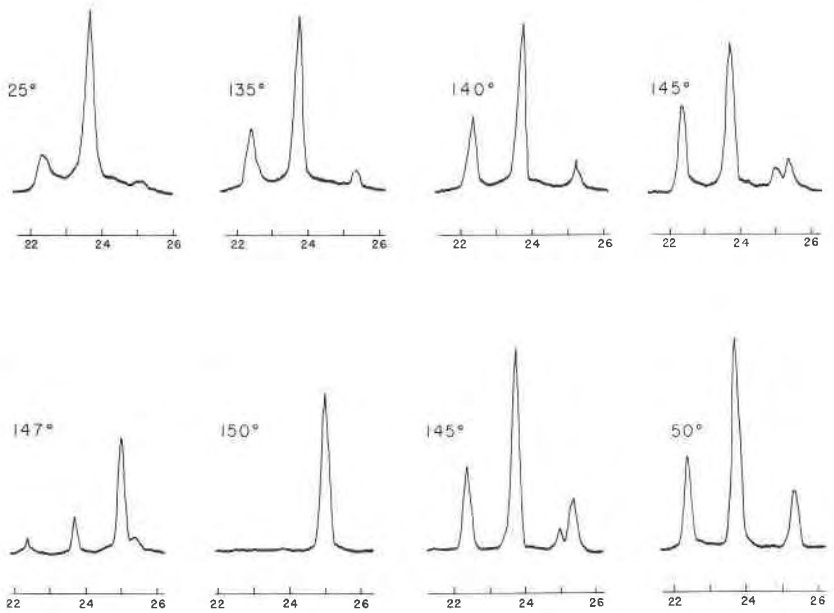


FIG. 1. Diffractometer tracings illustrating the phase changes of silver iodide as a function of temperature (CuK $\alpha$  radiation)

low-cubic: (111) =  $23.70^{\circ}$

hexagonal: (100) =  $22.30^{\circ}$ ; (002) =  $23.70^{\circ}$ ; (101) =  $25.34^{\circ}$

high-cubic: (110) =  $25.00^{\circ}$

course of this work. An apparent memory effect seemed to be shown by all samples consisting of a mixture of the low-cubic and hexagonal forms. There was a tendency to convert at least a fraction of the low-cubic to the hexagonal phase during this temperature cycling, increased by repeated transitions through this region. A typical heating curve is shown in Fig. 2 and the increase in the hexagonal phase for a sample held at  $145^{\circ}\text{C}$ . for a considerable length of time in Fig. 3.

The ratio of the hexagonal to low-cubic phases never decreased, regardless of its initial value. Powder samples of the pure hexagonal phase heated in air for times ranging from two weeks to several months at tem-

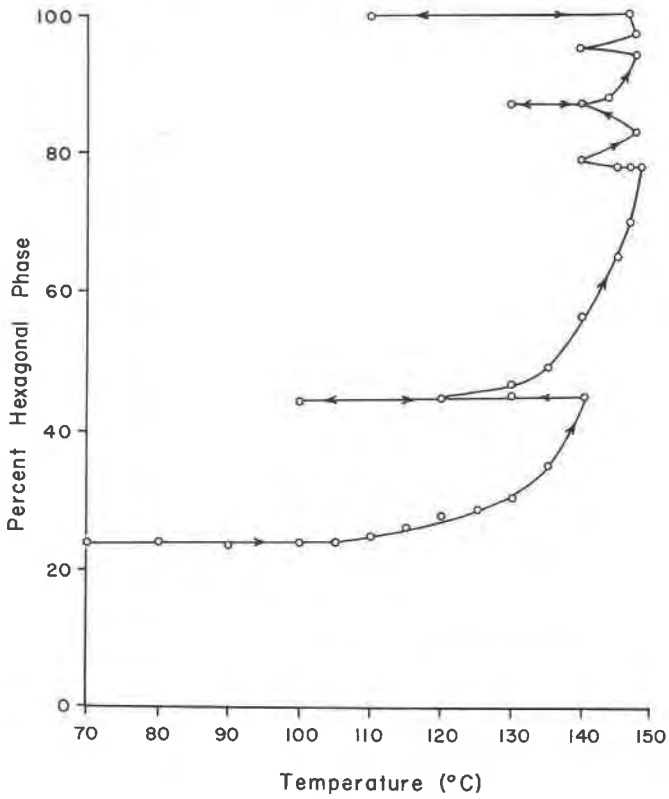


FIG. 2. Changes of phase composition of a representative sample through several heating cycles.

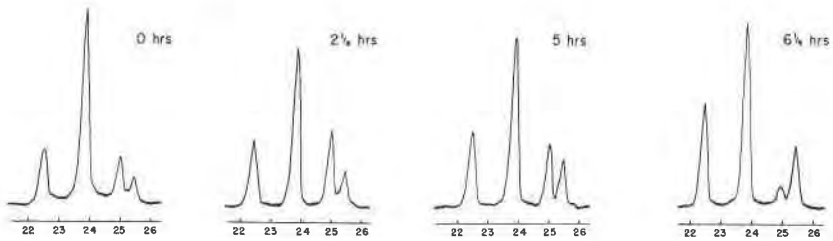


FIG. 3. Powder x-ray diffractometer tracings illustrating the rate of transformation at 146° C.

peratures from 120–140° C. did not show any low-cubic phase. Conversely, samples containing from 50% to over 80% of the low-cubic phase showed a rapidly increasing rate of conversion to the hexagonal phase above 135° C. It has thus been shown fairly conclusively that the low-cubic to hexagonal conversion is irreversible under all ordinary conditions.

The Clausius-Clapeyron equation indicated that the NaCl-type high pressure form might be stable at low temperatures, if the heat of transformation is small. A powder sample of silver iodide was cooled slowly to liquid helium temperature while a continuous record of the  $x$ -ray diffraction pattern was made. No phase transformation was observed in this region.

An increase in pressure was found to increase the amount of the low-cubic phase, and essentially complete conversion occurred at pressures below 100 bars. This was the most reproducible method of preparing this form of silver iodide. The powder was compressed into pellet shape, which was then broken up and ground in a mortar. The process may be analogous to the mechanics of grinding, where a large local pressure is also applied.

Even though no region of thermodynamic stability can apparently be assigned the low-cubic phase at atmospheric pressure, it can persist once it is obtained. The powder  $x$ -ray diffraction patterns in this case showed several lines which could be indexed neither on the basis of the hexagonal unit cell, nor on the assumption of lattice stacking faults. This is in direct contradiction to the conclusions of Majumdar and Roy (1959) but in agreement with most of the previous work on the phase relations of

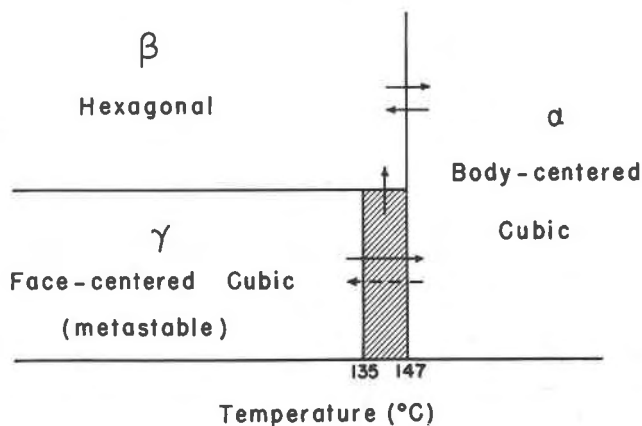


FIG. 4. Schematic diagram showing the phase relationships of silver iodide at atmospheric pressure in the pertinent temperature range.

silver iodide. The conversion under pressure to a metastable phase is characteristic of a monotropic system. The stability curve of the metastable form in this case intersects that of the stable form above the conversion temperature of the latter to either the third phase or the liquidus.

The general relationship of the three phases of silver iodide which can exist at atmospheric pressures is shown in Fig. 4. The temperature range between 135° and 147° C. represents the region where conversion of the low-cubic to the hexagonal form occurs at rapid rates.

The observed behavior of silver iodide suggests that: (1) At atmospheric pressure, the low-cubic phase is metastable with respect to the hexagonal phase at all temperatures below 147° C. (2) Above 147° C., only the high-cubic phase can exist. (3) A hypothetical transition from the hexagonal to the low-cubic phase would occur at a temperature above the actual stability region of both, and within the stability region of the high-cubic phase.

#### LATTICE ENERGY AND BONDING

The observed stability relation of the two phases of silver iodide is in accord with that predicted from theoretical considerations. The lattice energy for each phase is proportional to the negative of the Madelung constant for that structure, and the phase of lowest energy has the greatest expected stability. The most precise available values of the Madelung constant, based on the shortest cation-anion distance, are 1.64073 for the wurtzite (hexagonal) and 1.63806 for the zincblende (low-cubic) structure (Johnson, 1961). The effective charge,  $z$ , on each atom was derived from the expected covalent bond character (Pauling, 1948), and the value of the Born exponent,  $n$ , was chosen as applicable to atoms with a xenon core.

The difference in lattice energies for the two phases can be calculated by means of the formula:

$$\Delta U = \frac{(N) \cdot (\Delta\alpha) \cdot (z)^2 \cdot (e)^2}{r} \left(1 - \frac{1}{n}\right),$$

where

- $N$  = Avogadro's number =  $6.023 \times 10^{23}$  molec/mole,
- $\Delta\alpha$  = diff. of Madelung constants =  $2.67 \times 10^{-3}$ ,
- $z$  = ionic charge = 0.72,
- $e$  = electron charge =  $4.8 \times 10^{-10}$  esu,
- $r$  = interatomic distance =  $2.81 \times 10^{-8}$  cm, and
- $n$  = repulsion coefficient = 11.

Then,

$$\begin{aligned} \Delta U &= 63 \times 10^8 \text{ ergs/mole} \\ &= 149 \text{ cal/mole} \end{aligned}$$



Even though the magnitude of this calculated energy difference is small, it clearly indicates the theoretically greater stability of the hexagonal phase.

The calculated values of the silver-iodine covalent and ionic bond lengths are 2.74 Å and 3.18, respectively. The silver-iodine distance in the hexagonal structure has been determined as 2.814 Å (Burley, 1963). The corresponding value for the low-cubic structure is 2.808 Å, calculated from the lattice constant of the unit cell. The slightly smaller interatomic distance for the low-cubic structure appears to be significant and indicates a very slightly larger amount of covalent bonding. This can, however, be readily neglected in the lattice energy calculation.

#### ROLE OF INTERSTITIAL ATOMS

Certain of the observed stability relations of silver iodide may be explained with simple crystal chemical arguments. In stoichiometric silver

TABLE II. COORDINATION SPHERES OF INTERSTITIAL SITES

Type Site	Hexagonal Phase		Low-Cubic Phase	
Tetrahedral	(1) 4I	(2) 4Ag	(1) 4I	(2) 6Ag
Octahedral	(1) 6I	(2) 6Ag	(1) 6I	(2) 4Ag

Note: (1) = first coordination sphere.  
(2) = second coordination sphere.

iodide both ions have four nearest neighbors of the other kind in both the hexagonal and low-cubic structures. The bonding is partly covalent; therefore, coordination rules based on ionic radius ratios do not strictly apply. The two structures consist of sheets of iodine atoms, with the silver atoms in the interstices. Both the hexagonal and low-cubic phases have tetrahedral and octahedral holes in the iodine framework, of which only half the tetrahedral sites and no octahedral sites are occupied by silver. Excess cations introduced will enter available interstitial sites, either tetrahedral or octahedral, depending on the ionic radius. For an interstitial cation in either type of site, the number of nearest neighbors (iodine atoms) and next nearest neighbors (silver atoms) is given in Table II.

The number of nearest neighbor iodine atoms is always four in the tetrahedral and six in the octahedral sites. The difference occurs for the second nearest silver neighbors. On the basis of the applicable Coulombic forces, the lower silver coordination for the interstitial cation is favored

TABLE III. THE EFFECT OF INTERSTITIAL CATIONS

Cation	Ionic Radius	Phase
Fe <sup>3+</sup>	0.64	hex
Li <sup>+</sup>	0.68	hex
Cu <sup>2+</sup>	0.72	hex
Na <sup>+</sup>	0.94	hex
Ca <sup>2+</sup>	0.99	hex + fcc
Ag <sup>+</sup>	1.26	fcc
K <sup>+</sup>	1.33	fcc
Ba <sup>2+</sup>	1.34	fcc
NH <sub>4</sub> <sup>+</sup>	1.43	fcc
Cs <sup>+</sup>	1.67	fcc

since each silver ion contributes to the repulsive energy and increases the instability.

An excess of cations in the tetrahedral sites should stabilize the hexagonal phase, while an excess in the octahedral sites should stabilize the low-cubic phase. In each case the lower second-nearest neighbor silver coordination applies. If additional cations are introduced into the stoichiometric silver iodide lattice, the resultant phase should then be determined by the ionic size of these atoms. The radius ratio,  $R_{M^+}/R_{I^-}$ , for tetrahedral coordination varies between 0.225 and 0.414 and for octahedral coordination between 0.414 and 0.732 (Pauling, 1948). The radius of the iodide ion, corrected for a fifteen per cent deviation from close-packing, is 2.34 Å. This corresponds to a cation radius between 0.53 and 0.97 Å for the tetrahedral sites and between 0.97 and 1.71 Å for the octahedral sites.

When silver iodide is quenched from a temperature near its melting point it forms primarily the low-cubic phase. When various cations in amounts varying from five to ten mole per cent are added and the mixture quenched, the resultant phase distribution follows the above hypothesis closely. This is illustrated in Table III.

The hypothesis can be extended to explain both the formation of the low-cubic phase by quenching alone and the predominant precipitation of this phase from solutions containing an excess of the silver cation. At high temperatures a small amount of decomposition often occurs with the consequent loss of some iodine vapor. Upon quenching, local supersaturation of silver is then likely, and this may be expected to lead to a predominance of the low-cubic modification.

The extremely rapid precipitation of silver iodide by dilution of a solution of silver iodide in silver nitrate again results in a local excess of silver

ions. Under these circumstances almost the pure low-cubic form is obtained. In the case of rapid precipitation by dilution of a solution of silver iodide in sodium iodide the opposite occurs. In this case a local deficiency of silver ions is produced. The crystallization rate is then controlled by the diffusion velocity of the silver ions and predominantly the hexagonal phase is formed.

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