Phase Transitions in Silver Gold Chalcogenides

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The phase transitions of the compounds Ag_3AuX_2 (X = S, Se, Te) and the compound AgAuS were investigated by X-ray diffraction methods and differential thermal analysis. Ag_3AuSe_2 and Ag_3AuTe_2 are cubic body-centered ($a \approx 5$ Å, $Z = 1$) above 270 and 320°C, respectively. Ag_3AuS_2 and AgAuS are cubic primitive ($a \approx 5$ Å) above 185 and 307°C, respectively.

The heats of transition are: Ag_3AuTe_2 2.9 kcal/mole, Ag_3AuSe_2 6.7 kcal/mole, Ag_3AuS_2 4.0 kcal/mole, and AgAuS 3.5 kcal/mole.

The low-temperature modification of AgAuS (stable below 307°C) is monoclinic: $a = 8.38$, $b = 13.42$, $c = 9.09$ Å; $\beta = 111.4°$; the possible space groups are $I2$, Im, and $I2/m$. There are 16 units AgAuS in the cell.

Introduction

The silver chalcogenides $Ag_2X(X = S, Se, Te)$ have been the subject of a large number of investigations. The interest stems from the remarkable electrical properties and from the fact that the compounds (except Ag_2Se) possesses two high-temperature phases, characterized by either a body-centered or a face-centered packing of anions. In both kinds of anion packings the cations are statistically distributed over several types of interstitial sites (*1*). The body-centered cubic cell ($a \approx 5$ Å) contains 2 Ag_2X; the face-centered cubic cell ($a \approx 6.3$ Å) 4 Ag_2X. In Table I the allotropic forms and the temperatures of the phase transitions are summarized. For the description of polymorphs the nomenclature utilized by Kracek (*2*) will be followed. The crystalline phase that can exist in equilibrium with the liquid or disproportion products will be assigned the roman numeral I; those phases stable at successively lower temperatures will be assigned numerals of increasing value.

There is confusion in the literature about the transitions of Ag_2Se. Tavernier et al. (*3*) found an endothermic heat effect at 425°C which was ascribed to a bcc → fcc transition. Other investigations do not confirm this. We studied the thermal behaviour of Ag_2Se by high-temperature X-ray methods and differential thermal analysis; no bcc → fcc transition was observed.

The transition temperatures, in particular those of the II → I transitions depend on the stoichiometry; Ag_2S in equilibrium with Ag transforms from bcc to fcc at 622°C, in equilibrium with S at 586°C. For Ag_2Te the II-I transition occurs (*4*) at 689°C in the presence of Ag and 802°C in the presence of Te.

As far as we are aware, the only known crystalline compound Au_2X is Au_2S. It has been claimed (*5*) to have a Cu_2O-type structure.

Several silver gold chalcogenides (Ag, $Au)_2X$ are

TABLE I

CRYSTAL SYMMETRY AND TRANSITION TEMPERATURES OF SILVER CHALCOGENIDES Ag_2X

	III	III → II	II	II → I	I
Ag_2S	Monoclinic	176.3°C	bcc	586°C	fcc
Ag_2Se			Orthorhombic	139°C	bcc
Ag_2Te		145°C	fcc	802°C	bcc

known: Ag_3AuS_2, $AgAuS$, Ag_3AuSe_2, Ag_3AuTe_2, and $Ag_{11}AuTe_6$. The compounds Ag_3AuX_2 are formed (6) by interaction between Ag_2X precipitates and thiogold (I) complexes, for instance dithiosulfatoaurate (I) ions. Only Ag_3AuS_2 reacts with an excess of the thiogold (I) complex yielding successively crystalline $AgAuS$ and amorphous Au_2S. Ag_3AuS_2 (7) and Ag_3AuTe_2 (8) could also be synthesized from the elements. Ag_3AuTe_2 is known as the mineral petzite.

The ternary system Ag-Au-Te was investigated by Cabri (9). He found three polymorphs of Ag_3AuTe_2. Ag_3AuTe_2 III is cubic, $a = 10.65$ Å; the powder pattern of Ag_3AuTe_2 II (stable between 210 and 319°C) was not indexed. Ag_3AuTe_2 I is cubic body-centered, $a = 5.20$ Å at 363°C. The phase diagram indicates a continuous solid solution between Ag_3AuTe_2 I and Ag_2Te I. A compound with a lower gold content, $Ag_{11}AuTe_6$, is formed at about 50°C from Ag_3AuTe_2 III and Ag_2Te III. At 415°C this compound disproportionates.

Tavernier et al. (3) determined the temperatures of the transitions of silver gold chalcogenides Ag_3AuX_2 by means of differential thermal analysis. The temperatures reported for Ag_3AuTe_2 agree with those given by Cabri.

The crystal structures of the room-temperature modifications of Ag_3AuX_2 have been reported (10–12). The anion packing is approximately body-centered; gold is coordinated by two, silver by four chalcogen atoms. Ag_3AuS_2 was described to be cubic, $a = 9.72$ Å space group $P4_13$ by Messien et al. (12). We confirmed, however, the tetragonal cell given by Graf (7).

We report the results of an X-ray study of the phase transitions of Ag_3AuX_2 and of $AgAuS$. The results of Cabri (9) for Ag_3AuTe_2 were confirmed. The high-temperature forms of Ag_3AuTe_2 and Ag_3AuSe_2 are closely similar to the cubic body-centered modifications of Ag_2Se and Ag_2Te. The high-temperature modifications of $AgAuS$ and Ag_3AuS_2 are cubic primitive with two units of $AgAuS$ and one unit of Ag_3AuS_2 per cell. A structure determination of these phases is in progress. Table II summarizes data for all phases Ag_3AuX_2 and $AgAuS$.

In addition, we determined the heats of transition of these compounds by means of differential thermal analysis. The transition temperatures agreed well with those reported by Tavernier et al. (3).

Experimental

Ag_3AuTe_2, Ag_3AuSe_2, Ag_3AuS_2, and $AgAuS$ were prepared by heating mixtures of the elements in evacuated quartz tubes; the samples were heated at 500°C for four days and slowly cooled to room temperature.

The samples were studied by differential thermal analysis with an apparatus constructed by Drs. J. C. Wildervanck and Drs. J. Koopstra. The ΔT signal (from a Pallador I thermocouple) was amplified about 10^4 times and plotted versus T (from a chromel-alumel thermocouple) by an X-Y recorder (Hewlett–Packard, 7001 AM). The sensitivity is about 0.16°C/cm. The heating rate was 10°C/min. The samples were sealed in evacuated glass (pyrex) holders with a kick in the thin-walled bottom in which the thermocouple joint is placed. The heat effect was determined by comparing the area of the DTA peaks with those of transitions with known heat effect. On calibrating with metals (melting of Sn and Bi) an effect of 0.71 mcal was found to correspond to 1 mm² on the X-Y recorder. The heat of transition of Ag_2S (177°C) was found to be 1.2 kcal/mole, that of Ag_2Se (133°C) 2.1 kcal/mole.

TABLE II

CRYSTAL DATA AND TRANSITION TEMPERATURES OF Ag_3AuX_2 AND $AgAuS$

Compound	Room Temperature Modification	Transition Temp. (°C)[a]	High-Temp. Modification	References[b]
Ag_3AuTe_2	Cubic, $a = 10.38$ Å, $Z = 8$	220(189), 320(290)	bcc, $a = 5.26$ Å(385°C)	(9, 10)
Ag_3AuSe_2	Cubic, $a = 9.95$ Å, $Z = 8$	270(251)	bcc, $a = 5.06$ Å(290°C)	(11)
Ag_3AuS_2	Tetragonal, $a = 9.75$, $c = 9.85$Å, $Z = 8$	185(158)	cubic, $a = 4.94$ Å(190°C)	(7, 12)
$AgAuS$	Monoclinic, $a = 8.38$, $b = 13.42$ $c = 9.09$ Å, $\beta = 111.4°$, $Z = 16$	307(300)	cubic, $a = 5.10$ Å(310°C)	

[a] Transition temperatures (except AgAuS) taken from Tavernier et al. (3). In parentheses the temperatures observed on cooling.

[b] The references refer to the crystal structures of the room-temperature modifications.

The literature (13) values are 1.4 ± 0.4 kcal/mole and 1.6 ± 0.4 kcal/mole, respectively. For Ag_2Se a somewhat larger value, 2.2 kcal/mole, has been found by Banus (14). The accuracy of our values is estimated to be about 20%.

X-Ray diagrams at room temperature were taken with a Philips diffractometer and a Nonius Guinier–de Wolff camera. High-temperature powder patterns were taken with a Guinier–Lenné camera (Nonius). The temperature was varied continuously with heating and cooling rates of 10°C/hr. In most cases, the samples were sealed in very thin quartz capillaries to prevent oxidation and loss of chalcogen vapour.

Ag_3AuTe_2

Our samples of Ag_3AuTe_2 always contained some unreacted gold and Ag_2Te. A high-temperature Guinier photograph, made with the sample in air of 10^{-2} Torr pressure, showed phase transitions at about 200 and 320°C. The Guinier pattern of the intermediate-temperature phase (stable between 200 and 320°C) is complicated and could not be indexed. Above 320°C Ag_3AuTe_2 is cubic body-centered, with $a = 5.26$ Å at 385°C. The reflections observed are given in Table III. The results of Cabri (9) were also completely confirmed.

The heat of transition at 220°C is 2.9 kcal/mole; a small heat effect was observed at 320°C.

Ag_3AuSe_2

The transition temperature (DTA) is 267°C [Tavernier et al. (3) 270°C]. At that temperature Ag_3AuSe_2 becomes cubic body-centered, $a = 5.06$ Å at 290°C. In Table III the Guinier pattern at 290°C is given. The high-temperature X-ray photograph

did not show further phase transitions; at about 730°C the compound melts.

The heat of transition at 267°C is 6.7 kcal/mole.

Ag_3AuS_2

Above 183°C (Tavernier et al. 185°C) Ag_3AuS_2 is cubic primitive with $a = 4.94$ Å at 190°C (and not cubic body-centered such as Ag_2S II). The Guinier pattern is given in Table IV.

The heat of transition at 183°C is 4.0 kcal/mole. In sealed vessels (DTA ampoules) the phase transition is reversible; on cooling from about 450°C the phase transition occurred at 155°C; no peaks from Ag_2S were observed. A high-temperature X-ray photograph made with the sample mounted on teflon tape, the camera being kept at a pressure of 10^{-2} Torr. showed rapid decomposition above the transition temperature:

$$2Ag_3AuS_2 \rightarrow 3Ag_2S + 2Au + \tfrac{1}{2}S_2^{\uparrow}.$$
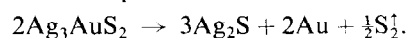
At 280°C only Ag_2S II and Au were present.

AgAuS

The powder pattern of AgAuS, synthesized from the elements agreed with that published by Tavernier (6). The cell dimensions of the room-temperature modification were found by single-crystal methods. AgAuS II is monoclinic; at 20°C $a = 8.38$, $b = 13.42$, $c = 9.09$ Å, $\beta = 111.4°$. The cell is body-centered. The possible space groups are $I2$, Im, and $I2/m$. The cell volume is 963 Å^3; that of Ag_2S III ($a = 4.229$, $b = 6.931$, $c = 7.862$, $\beta = 99.61°$, space group $P2_1/n$, $Z = 4$) (15) is 227.2 Å^3. We may assume that there are 16 units AgAuS in the cell.

Above 307°C AgAuS is cubic primitive, $a = 5.01$ Å at 310°C. The powder pattern is given in Table IV. At about 730°C the compound melts. AgAuS has, just like Ag_3AuS_2, a high-sulfur vapour pressure at elevated temperatures. It decomposes readily

TABLE III

GUINIER PATTERNS OF Ag_3AuTe_2 (385°), Ag_3AuSe_2 (290°C), AND Ag_2Se II (140°C)

hkl	Ag_3AuTe_2 d(Å)	Int	Ag_3AuSe_2 d(Å)	Int	Ag_2Se d(Å)	Int
110	3.72	st	3.57	m^-	3.53	vw
200	2.63	st	2.53	vw	2.50	vst
211	2.15	vst	2.06	st	2.04	vst
220	1.86	m	1.78	m	1.77	m
310	1.66	mw	1.60	vw	1.58	vw
222	—	—	1.46	vw	—	—
321	1.41	mw	1.35	w	1.34	m^+
400	1.32	w	1.26	w	1.25	m

TABLE IV

GUINIER PATTERNS OF Ag_3AuS_2 (190°)C AND AgAuS (310°C)

hkl	AgAuS d(Å)	Int	Ag_3AuS_2 d(Å)	Int
110	—	—	3.50	vw
111	2.90	st	2.86	vst
200	2.51	m	2.49	w
211	2.04^5	w	2.01^5	st
220	1.77	m	1.75	st
311	1.51	w	1.49	m
222	1.45	w	1.42	m^-

according to $2\ AgAuS \rightarrow Ag_2S + 2Au + \frac{1}{2}S_2^{\uparrow}$. In sealed vessels (DTA ampoules) the phase transition is reversible; on cooling from about 450°C the phase transition occurred at 298°C; no peak from Ag_2S was observed. The heat of transition was estimated to be 3.5 kcal/mole.

Acknowledgments

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