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The phase diagrams of M_2X-SiX_2 (M is Cu, Ag; X is S, Se)

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Abstract

The phase diagrams of Cu_2S-SiS_2, Ag_2S-SiS_2 and $Ag_2Se-SiSe_2$ were investigated by DTA and X-ray methods. The system Cu_2S-SiS_2 contains two compounds: Cu_2SiS_3 and Cu_8SiS_6. The compound $Cu_6Si_2S_7$ does not exist. The phase diagram of Ag_2S-SiS_2 is characterized by the presence of two ternary compounds: Ag_8SiS_6 and $Ag_{10}Si_3S_{11}$. The $Ag_2Se-SiSe_2$ system contains only Ag_8SiSe_6, which forms a eutectic on either side. The stability range and the X-ray diffraction data of the compounds are presented.

Keywords: Chalcogenide; DTA; Eutectic; Phase diagram; XRD

1. Introduction

Sulphides and selenides containing group Ib and IVb elements have been studied for a long time, but attention has been focused mainly on the crystallographic data and physical properties of these compounds as they possess interesting semiconducting properties. However, a knowledge of the phase diagram is essential in order to define the optimum conditions for preparation of the crystals and to understand the stability regions of the compounds. A survey of the literature has revealed that information on the phase equilibra of chalcogen systems containing Ib and IVb

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elements is more scarce. As part of a larger effort to synthesize new compounds for electro-optical applications we have chosen to establish the phase diagrams of the Cu–Si–S(Se) and Ag–Si–S(Se) systems and to see if any new compounds exist. Only the pseudo-binary sections along the cross sections Cu_2S–SiS_2, Ag_2S–SiS_2 and Ag_2Se–$SiSe_2$ were studied because the maximum number of compounds is to be found in these sections.

2. Experimental

The binary sulphides and selenides of Cu and Ag (Cu_2S, Ag_2S, Ag_2Se and $SiSe_2$) which were the starting components for the preparation of alloys were prepared by mixing stoichiometric amounts of pure elements (Cu, Preussag 99.999%, Ag, 99.99% Degussa; Si, H.C. Starck 99.999%; Se, Retorte 99.999% and S, Merck 99.99%) in evacuated sealed quartz ampoules. The samples were heated slowly until above the melting point of the compounds, kept at that temperature for one week, and slowly cooled. SiS_2 (99.5% purity) was obtained from ABCR.

Differential thermal analysis was carried out using a DTA apparatus constructed in this laboratory [8] and with Du Pont 900 and Perkin-Elmer DSC-2 instruments at a heating/cooling rate of 10 K min^{-1}, using silicon as a reference.

3. Results

3.1. Cu_2S–SiS_2 system

Two ternary compounds Cu_2SiS_3 [1–4] and Cu_8SiS_6 [4–7] have been well established along the pseudo-binary section Cu_2S–SiS_2. Cu_8SiS_6 belongs to the well-known argyrodite family. In addition to these two compounds, Boivin et al. [4] and Thomas and Tridot [8] have reported two additional phases, Cu_4SiS_4 (at 60 mol% Cu_2S) and $Cu_6Si_2S_7$ (at 66.6 mol% Cu_2S). Although a phase diagram of Cu_2S–SiS_2 was included, this was not entirely supported by their experimental results.

Cambi and Monselise [5] gave the earliest information on the phase diagram, only from 50 to 100 mol% Cu_2S, based on cursory thermal studies of samples with masses between 25 and 50 g. They found that Cu_8SiS_6 melted congruently at 1195°C, formed a eutectic with Cu_2S at 1062 ± 5°C and another eutectic on the SiS_2-rich side at 950°C. They did not detect the existence of Cu_2SiS_3.

We have reinvestigated the Cu_2S–SiS_2 system by DTA and X-ray methods. The phase diagram of the system is presented in Fig. 1. The existence of two ternary compounds, Cu_2SiS_3 and Cu_8SiS_6, is confirmed. Cu_8SiS_6 melts congruently at 1200 ± 5°C and Cu_2SiS_3 decomposes by a peritectic reaction into liquid and Cu_8SiS_6 at 900°C. Two eutectic reactions occur, one on the SiS_2-rich side and the other on the Cu_2S-rich side; $L \rightleftharpoons SiS_2 + Cu_2SiS_3$ at 840 ± 10°C and ≈ 40 mol% Cu_2S, and $L \rightleftharpoons Cu_8SiS_6 + Cu_2S$ at 1065 ± 5°C and ≈ 95 mol% Cu_2S.

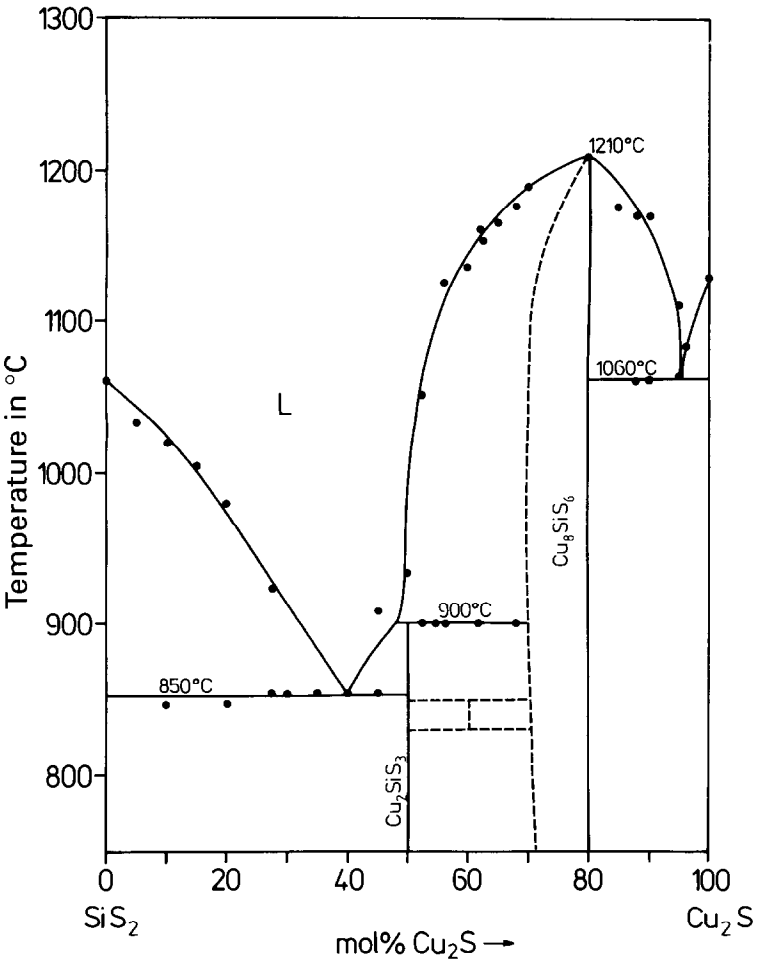

Fig. 1. Phase diagram of the Cu_2S–SiS_2 system.

The region between 50 and 80 mol% Cu_2S is complex as it reportedly contains many compounds and several invariant reactions. To clarify this, we made additional DTA and X-ray studies in this region using mixtures of pure Cu_2SiS_3 and Cu_8SiS_6. The stability range of the compounds and the invariant reaction temperatures could be determined. Room temperature X-ray patterns of mixtures of Cu_2SiS_3 and Cu_8SiS_6 annealed at 500, 600 and 700°C in the composition range 50–68 mol% Cu_2S showed two-phase mixtures of Cu_2SiS_3 and Cu_8SiS_6, but between 68 and 80 mol% Cu_2S, revealed only a single compound, Cu_8SiS_6. Furthermore, samples between 68 and 80 mol% Cu_2S did not exhibit any thermal effect until the liquidus, except due to the phase transition of argyrodite at lower temperatures. We therefore concluded that Cu_8SiS_6 has a homogeneity range from 68 to 80 mol% Cu_2S between about 500 and 900°C. Samples from 50–68 mol%

Cu_2S, however, showed two clear thermal effects, one at 900°C and another at 770°C. The thermal effect at 900°C could be explained from the peritectic decomposition of Cu_2SiS_3, but the reason for the effect at 700°C is not clear.

Regarding the existence of two other compounds in this region, namely Cu_4SiS_4 at 66.6 mol% Cu_2S and $Cu_6Si_2S_7$ at 60 mol% Cu_2S, we found no evidence that the latter exists. From the X-ray data given in the literature, it can be concluded that the composition of this compound is $Cu_5Si_2S_7$; the structure was determined by Dogguy et al. [9]. However, X-ray patterns of alloys at 60 mol% Cu_2S (corresponding to Cu_4SiS_4) annealed at temperatures between 830 and 850°C always contained lines in addition to the lines due to Cu_2SiS_3 and Cu_8SiS_6. In samples which were annealed below 830°C, these extra lines vanished and only Cu_2SiS_3 and Cu_8SiS_6 lines were present. High temperature X-ray experiments on samples in the composition range 58–66 mol% Cu_2S did not reveal the existence of a compound at 66 mol% Cu_2S. Therefore Cu_4SiS_4 might exist over a very narrow temperature range of about 20°C around 850°C. Careful single-crystal studies at elevated temperatures are needed to establish its presence conclusively.

3.2. Crystal structures

Contrary to Hahn et al. [2] and Rivet et al. [1], we observed that Cu_2SiS_3 does not undergo any structural transformation. Neither high nor room temperature X-ray studies of annealed and quenched samples showed any evidence to that effect. Hahn and co-workers did not report the powder diffraction data, but analysis of Rivet's X-ray data revealed that his high temperature modification is in fact a mixture of Cu_2SiS_3 and argyrodite. Our powder diffraction data of Cu_2SiS_3 are in agreement with those of Rivet et al. for the low temperature phase, but yielded different lattice parameters. According to our results, Cu_2SiS_3 is monoclinic with the lattice constants $a = 633.3$, $b = 1122.5$ and $c = 627.5$ pm, and $\beta = 107.32°$. The X-ray data are given in Table 1. The lattice parameters of Cu_2SiS_3 at room

Table 1
X-ray powder data of Cu_2SiS_3

d_{cal}/ pm	d_{obs}/ pm	hkl	d_{cal}/ pm	d_{obs}/ pm	hkl
560.4	559.9	020	231.5	231.6	222
531.7	530.5	110	222.1	222.2	221
463.0	462.3	111	207.8	207.9	241
409.1	409.4	021	193.7	193.8	312
353.8	354.0	111	188.0	187.9	023
299.4	299.2	002	186.4	186.3	202
296.6	296.7	112	184.8	184.9	223
271.0	271.2	221	164.1	164.2	152
265.8	265.8	220	154.3	154.3	333
235.5	235.3	112			

temperature reported in the literature are: $a = 529.0$, $c = 507.8$ pm, tetragonal symmetry [1], and $a = 1151$, $b = 534$, $c = 816$ pm and $\beta = 98.95°$, monoclinic [2]. The lattice constants $a = 699.8$, $b = 690.35$, $c = 976.82$ pm were obtained for orthorhombic Cu_8SiS_6, compared with the parameters $a = 699.3$, $b = 690.0$, $c = 977.2$ pm, $Pmn2_1$ [7], based on single-crystal studies.

3.3. Ag_2S-SiS_2 system

The partial phase diagram of Ag_2S-SiS_2 has been determined by Cambi and Elli [10] and Gorochov and Flahaut [11]. The existence of a ternary compound, Ag_8SiS_6, in this cross section has been clearly established [4,6,10–13]. Gorochov [13] reported that this compound melted congruently at 940°C and formed a eutectic with Ag_2S at 735°C and 90 mol% Ag_2S, whereas Cambi and Elli [10] found a value of 959°C for the melting point and 759°C for the eutectic between Ag_2S and Ag_8SiS_6. Besides Ag_8SiS_6, Mandt and Krebs [14] reported the existence of a second ternary compound, $Ag_{10}Si_3S_{11}$. They prepared single crystals of this compound by reacting $Ag_2S + Si + S$ in evacuated quartz ampoules and made a detailed crystal structure analysis. The compound is triclinic ($P\bar{1}$) with the lattice constants: $a = 1241.4$, $b = 1347.6$, $c = 645.9$ pm, $\alpha = 78.92°$, $\beta = 77.61°$, $\gamma = 68.71°$.

Compounds with lower Ag_2S content claimed by other investigators, such as $Ag_6Si_2S_7$ [4,10,12] and Ag_2SiS_3 [4], were not found by Mandt and Krebs [14]. At the corresponding compositions they observed that the samples were heterogeneous mixtures of Ag_8SiS_6, $Ag_{10}Si_3S_{11}$, SiS_2 and small amounts of an unidentified phase. Gorochov [13] also studied this system in somewhat more detail, but found no evidence for Ag_2SiS_3 or $Ag_6Si_2S_7$ phases either. We constructed the phase diagram based on high and low temperature X-ray and DTA results. The diagram is shown in Fig. 2. The Ag_2S-rich side of the diagram between Ag_8SiS_6 and Ag_2S is in agreement with the literature data. The phase Ag_8SiS_6 melts congruently at 970°C and forms a eutectic with Ag_2S at 770°C and $\approx$93 mol% Ag_2S. The liquidus on the SiS_2-rich side was difficult to determine owing to the high vapour pressure of SiS_2.

In agreement with Mandt and Krebs [14], we could not detect Ag_2SiS_3 or Ag_2SiS_7. Comparison of our powder diffraction data of samples quenched from 400 and 600°C at the stoichiometric compositions corresponding to these compounds, revealed that they were a mixture of Ag_8SiS_6, $Ag_{10}Si_3S_{11}$ and an unidentified phase. The lines from the unidentified phase, however, were present in all the samples between 5 and 60 mol% Ag_2S. Samples between 55 and 80 mol% Ag_2S exhibited a clear thermal arrest at 710°C. This could be interpreted from the peritectic decomposition of $Ag_{10}Si_3S_{11}$ into liquid and Ag_8SiS_6.

3.4. $Ag_2Se-SiSe_2$ system

Gorochov [13] determined the pseudo-binary $Ag_2Se-SiSe_2$ system on the Ag_2Se-rich side only. He found the existence of the compound Ag_8SiSe_6, which melted congruently at 930°C and formed a eutectic with Ag_2Se at 850°C and 94 mol% Ag_2Se. Ag_8SiSe_6 belongs to the family of argyrodites [13,15]. The stable form of

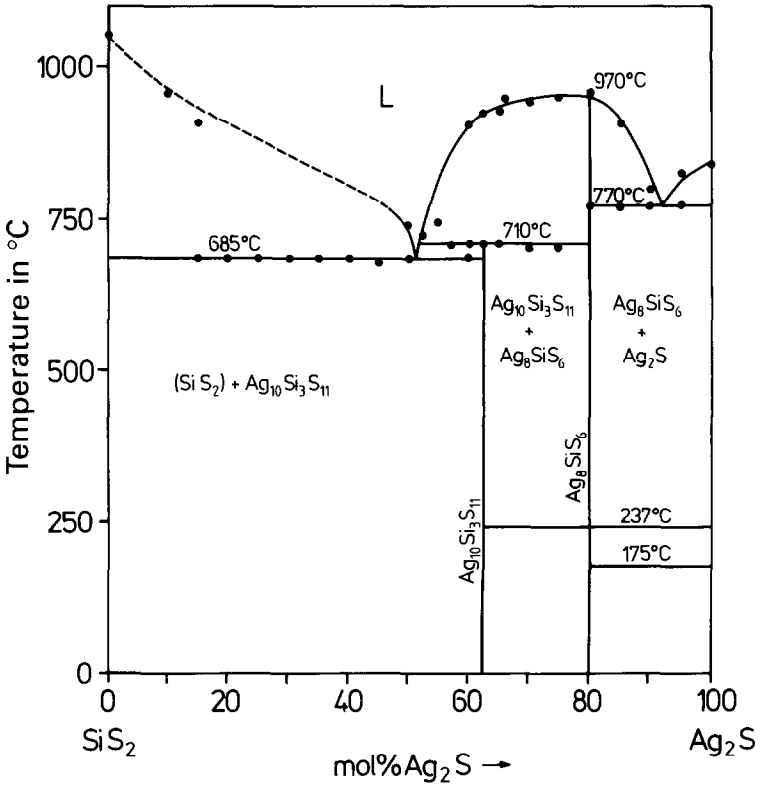

Fig. 2. Phase diagram of the Ag_2S–SiS_2 system.

Ag_8SiSe_6 at room temperature is face-centred cubic with the lattice constant $a = 1086$ pm and space group $P4_232$ [6].

The complete quasi-binary section of Ag_2Se–$SiSe_2$ determined from XRD and DTA is given in Fig. 3. Ag_8SiSe_6 melts congruently at 985 ± 5°C and forms a eutectic on either side with $SiSe_2$ and Ag_2Se at 685 ± 10°C and ≈ 45 mol% Ag_2Se, and 800 ± 5°C and ≈ 95 mol% Ag_2Se, respectively. The high-temperature X-ray pattern of 50 mol% Ag_2Se annealed at 600°C, and room temperature X-ray results of samples between 0 and 80 mol% Ag_2Se, showed only lines due to Ag_8SiSe_6 and $SiSe_2$. No evidence for the existence of compounds besides Ag_8SiSe_6 was found. This was further confirmed by DSC measurements.

Ag_8SiSe_6 undergoes several crystallographic transformations at 132, 70, 40 and 10°C [12]. We could obtain well-defined thermal arrests for alloys between 80 and 100 mol% Ag_2–Se at 132°C. The other phase transition temperatures shown in the phase diagram are taken from the literature.

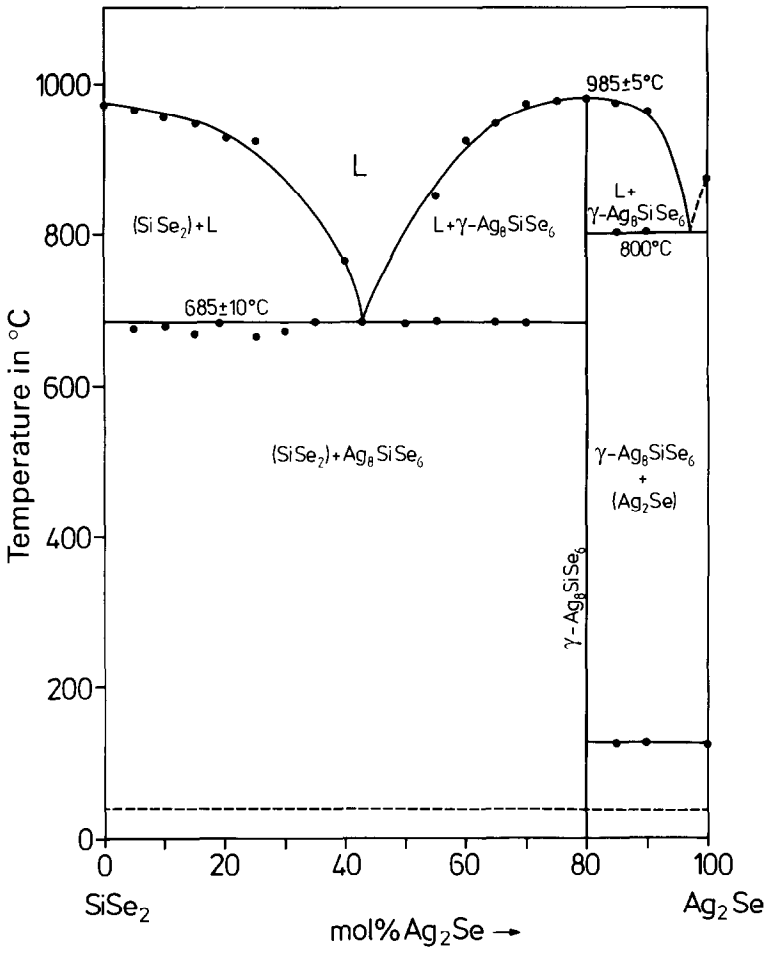

Fig. 3. Phase diagram of the Ag_2Se–$SiSe_2$ system.

Acknowledgements

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