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CONSTITUTION OF THE $AgSbS_2$-PbS, $AgBiS_2$-PbS, AND $AgBiS_2$-$AgBiSe_2$ SYSTEMS

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ABSTRACT

Complete series of solid solutions with the disordered NaCl-type structure exist in the pseudo-binary $AgSbS_2$-PbS and $AgBiS_2$-PbS systems. Thus, synthetic compositions corresponding to the minerals freieslebenite and diaphorite in the $AgSbS_2$-PbS system have high temperature forms with the disordered NaCl structure. Only this cubic form was obtained for the composition corresponding to the mineral schermirite in the $AgBiS_2$-PbS system. Lattice constants as a function of composition for the cubic phase are presented. Negative departures from Vegard's law occur, similar to those observed in the $AgSbSe_2$-$AgSbTe_2$-$AgBiSe_2$-PbTe-PbSe system. The locus of temperatures and compositions for the order-disorder transition in these systems has been determined. The form of the phase diagram for the $AgSbS_2$-PbS system and published structure data for $AgSbS_2$, diaphorite, and freieslebenite indicate that all of the ordered solutions are related.

The high and low temperature modifications of $AgBiS_2$ and $AgBiSe_2$ form a complete series of solid solutions. The phase diagram for this system has been determined. Lattice constants as a function of composition for the cubic phase follow Vegard's law, and this is presumed to be the case for the low temperature form.

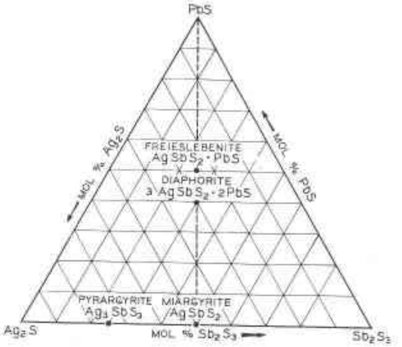
INTRODUCTION

It has been shown that the ternary compounds $AgSbSe_2$ and $AgSbTe_2$, and the high temperature forms of $AgBiSe_2$ and $AgBiTe_2$ have a disordered NaCl structure (1) and form a complete series of solid solutions (2). In addition, the first three compounds form a complete series of solid solutions with the cubic (NaCl) compounds, PbTe and PbSe (3). No new phases were found to exist in these ternary-binary systems, as in the case of the $AgSbS_2$-PbS system.

The high temperature forms of $AgSbS_2$ and $AgBiS_2$ also have the disordered NaCl structure (1, 4). Se and Te stabilize the high temperature form of $AgSbS_2$ at room temperature. The low temperature form of $AgBiS_2$ is hexagonal and isostructural with $AgBiSe_2$ (1). The low temperature form of $AgSbS_2$ has been determined to be monoclinic (5, 4). This study, which is a part of a broad program concerned with the semiconducting behavior of compounds containing three or more elements (6, 7), was undertaken to determine the phase relationships in the $AgSbS_2$-PbS, $AgBiS_2$-PbS (Figs. 1 and 2) and $AgBiS_2$-$AgBiSe_2$ systems.

PROCEDURE

Except for the $AgSbS_2$-PbS alloys, each specimen was prepared by mixing the stoichiometric amounts of the constituent elements, placing the mixture in fused silica or vycor tubes, evacuating, sealing off, heating to



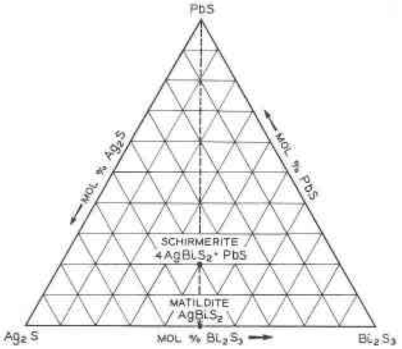


FIG. 1. (left) The $AgSbS_2$-PbS pseudo-binary cut in the PbS-Ag_2S-Sb_2S_3 system.
FIG. 2. (right) The $AgBiS_2$-PbS pseudo-binary cut in the PbS-Ag_2S-Bi_2S_3 system.

800° C., holding at this temperature for four hours, and furnace cooling. For the $AgSbS_2$-PbS alloys, Ag_2S and Sb_2S_3 were used for the $AgSbS_2$ component because of the miscibility gaps existing in this ternary system. If the elements are used, very high temperatures are required to pass over the miscibility gaps, and this results in excessive sulfur pressures. Differential thermal analyses were made to determine liquidus,

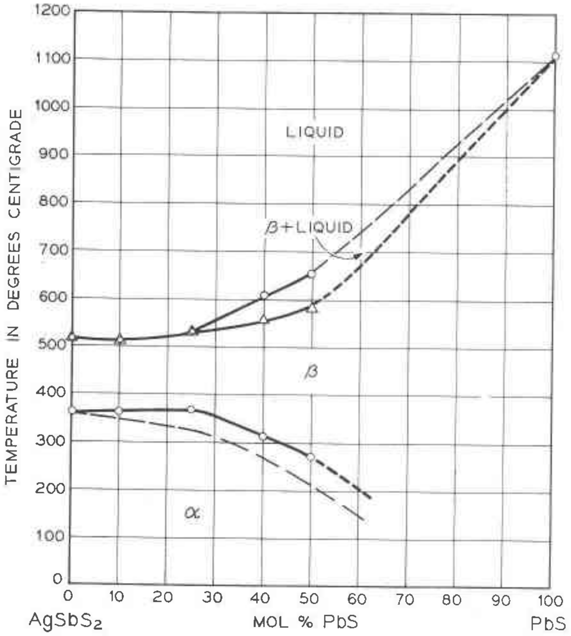


FIG. 3. The $AgSbS_2$-PbS system.

solidus, and solid state transformation temperatures. $AgSbS_2$ and $AgBiS_2$ appear to have low dissociation pressures.

X-ray powder photographs (CuK_α radiation, Norelco Straumanis type cameras of 114.6 mm. diameter) were taken of all samples. In the tables of *x*-ray data, unless otherwise noted, the data refer to as-cast samples.

Samples that were water quenched from high temperatures were sealed in evacuated pyrex tubes. A quench was considered sufficiently rapid when the tube shattered. Annealing experiments were also carried out on samples sealed in evacuated pyrex tubes. All annealed samples were furnace cooled.

THE $AGSBS_2$-PBS SYSTEM

The phase diagram for this system (Fig. 3) was determined up to 50 mol % Pbs.* Lattice constants for the disordered NaCl phase (β) as a function of composition are shown in Fig. 4 and Table 1;* presumably the β phase extends to 100% PbS. Negative departures from Vegard's law occur in this system, as well as in the $AgBiS_2$-PbS system discussed below. This behavior is similar to that observed in the $AgSbSe_2$-$AgSbTe_2$-$AgBiSe_2$-PbSe-PbTe system (3). These departures were explained as pos-

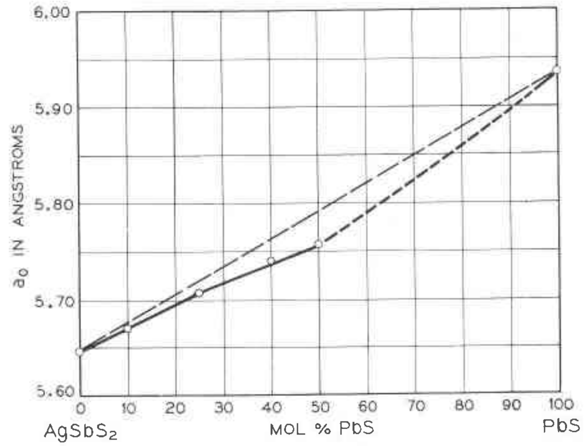


FIG. 4. Lattice constants at 25° C. for the cubic β-phase in the $AgSbS_2$-PbS system.

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* The melting point and solid state transformation temperature of $AgSbS_2$ (514° C. and 360° C. respectively) are in agreement with the values obtained by Jensen (8). The melting point of PbS was taken from reference 9. The solidus temperatures were determined by comparing the differential analyses data with those of the ternary compounds which freeze isothermally.

* Lattice constants for $AgSbS_2$, $AgBiS_2$, and $AgBiSe_2$ were taken from reference 1. The lattice constant for PbS was taken from reference 10.

TABLE 1. LATTICE CONSTANTS AT 25°C. FOR THE CUBIC β PHASE IN THE $AgSbS_2$-PbS SYSTEM

Composition (Mol per cent)	Lattice constant (Å)
$AgSbS_2$	5.647 ± 0.003
90 $AgSbS_2$–10 PbS*	5.670 ± 0.003
75 $AgSbS_2$–25 PbS*	5.708 ± 0.003
60 $AgSbS_2$–40 PbS*	5.74 ± 0.01
50 $AgSbS_2$–50 PbS*	5.758 ± 0.004
PbS	5.936

* Held 3 hours at 500° C., quenched in H_2O.

sibly due to the formation of vacancies, because the valence electron to atom ratio changes in this system, and/or to distortions arising from clustering of atoms of the β solution for eventual transformation.

The low temperature form (α phase) of the mineral miargyrite, as well as of synthetic $AgSbS_2$, has been determined to be monoclinic (space group $A2/m$) (4, 5). An ingot of synthetic $AgSbS_2$, cooled from 800° C. to room temperature in 24 hours, and samples of $(AgSbS_2)_{0.9}(PbS)_{0.1}$ and $(AgSbS_2)_{0.75}(PbS)_{0.25}$ annealed one week at 330° C., gave identical x-ray powder patterns and were not isostructural with the α phase reported by Graham.** However, a zone refined sample of $AgSbS_2$, annealed one week at 330° C., gave a powder pattern which did match Graham's powder data.

The structure of diaphorite (ideal formula $(AgSbS_2)_{0.6}(PbS)_{0.4}$, α phase, Figs. 1 and 3) has been determined by Hellner (11) and is monoclinic (space group $P2_1/a$). The structure of freieslebenite (ideal formula $(AgSbS_2)_{0.5}(PbS)_{0.5}$, α phase) has been determined by Palache, et al (12) to be monoclinic (space group $P2_1/n$). Hellner (11, 13) has shown that the structures of diaphorite and freieslebenite can be deduced from the PbS structure. Indeed, this research shows* that synthetic compositions corresponding to these minerals have a high temperature form with a disordered NaCl structure. Synthetic samples of $(AgSbS_2)_{0.6}(PbS)_{0.4}$ and $(AgSbS_2)_{0.5}(PbS)_{0.5}$, as well as samples annealed 17 days at 150° C., were identical but different from the published powder data for the minerals (9). In addition, the x-ray patterns were different from photographs of synthetic $AgSbS_2$, $(AgSbS_2)_{0.9}(PbS)_{0.1}$ and $(AgSbS_2)_{0.75}(PbS)_{0.25}$ dis-

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** The high angle lines on the photographs of all the ordered samples were extremely broad and in nearly all cases not discernible. On the other hand, the cubic form, which was quenched to room temperature, gave sharp high angle reflections in all cases, with $K\alpha_1$ and $K\alpha_2$ resolved. This indicates that the ordered structures were in a high degree of strain.

* As predicted jointly by the author and S. Geller.

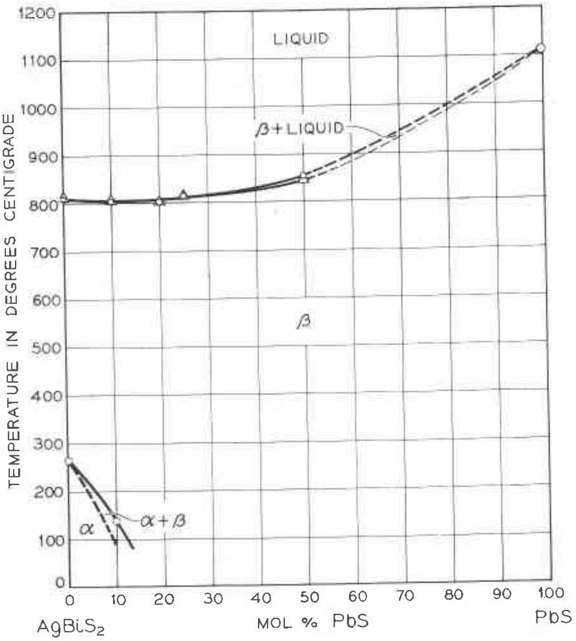

FIG. 5. The AgBiS$_2$-PbS system.

cussed above. The differences here showed up in a splitting of the low angle lines for the PbS rich compositions.

The form of the phase diagram (Fig. 3) and the published structure data for miargyrite, diaphorite and freieslebenite indicate that all of the ordered solid solutions (denoted by α phase) are related. The fact that the powder patterns of AgSbS$_2$ and the ordered solid solutions are not identical may be due to the presence of metastable phases, and equilibrium was not attained during the time of annealing.

The AgBiS$_2$-PbS System

As pointed out above, the high temperature form of AgBiS$_2$ is disordered NaCl (β phase) and the low temperature form (α phase) is hexagonal (space group P$\bar{3}m1$). The high and low temperature forms of AgBiSe$_2$ are isostructural with AgBiS$_2$ (1). On heating, hexagonal AgBiSe$_2$ transforms at 120° C. to a rhombohedral form (space group $R\bar{3}m$) and on further heating, transforms to the NaCl structure at 287° C. (1, 2). The transformation from the hexagonal to the rhombohedral form of AgBiSe$_2$, which involves slight atomic displacements, was shown to exist by high temperature x-ray photography (1). No heat effect

TABLE 2. LATTICE CONSTANTS AT 25° C. FOR THE CUBIC β PHASE IN THE $AgBiS_2$-PbS SYSTEM

Composition (Mol per cent)	Lattice constant (Å)
$AgBiS_2$	5.648±0.003
90 $AgBiS_2$–10 PbS*	5.660±0.003
80 $AgBiS_2$–20 PbS	5.684±0.003
75 $AgBiS_2$–25 PbS	5.690±0.003
75 $AgBiS_2$–25 PbS*	5.690±0.003
50 $AgBiS_2$–50 PbS	5.752±0.003
50 $AgBiS_2$–50 PbS*	5.751±0.003
PbS	5.936

* Held 3 hours at 500° C., quenched in H_2O.

is observed for this transition, and it is concluded to be higher than first order (1, 2). No similar attempt was made to establish the existence of this transition in $AgBiS_2$, but it is presumed that this intermediate form of $AgBiS_2$ exists* (1).

The phase diagram for this system (Fig. 5) was determined up to 50 mol % PbS, and presumably a complete series of solid solutions (β) having the disordered NaCl structure exists in this system. Lattice constants for the β phase as a function of composition are shown in Fig. 6 and Table 2.

A sample of $(AgBiS_2)_{0.8}(PbS)_{0.2}$ (ideal composition of the mineral schirmerite) annealed five weeks at 100° C. was still cubic and did not

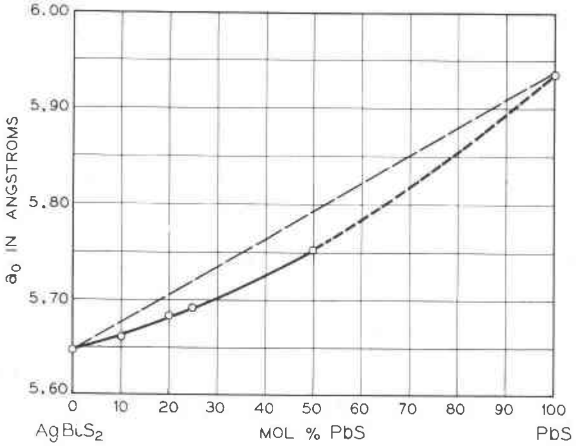

FIG. 6. Lattice constants at 25° C. for the cubic β-phase in the $AgBiS_2$-PbS system.

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* No notation for this transition is made on the $AgBiS_2$-$AgBiSe_2$ diagram, Fig. 7.

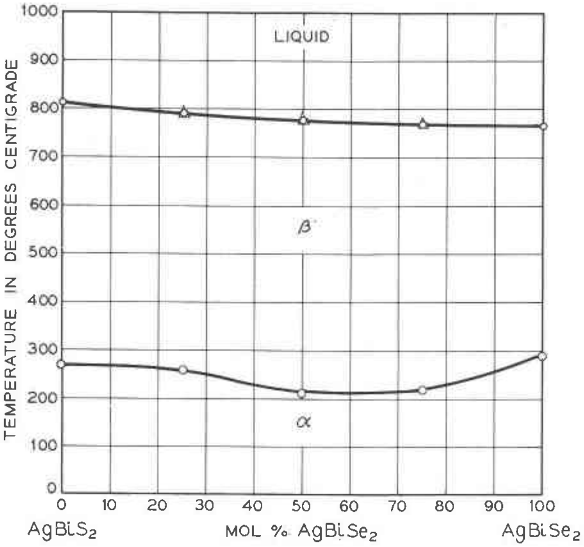

FIG. 7. The $AgBiS_2$-$AgBiSe_2$ system.

show any evidence of ordering. Crystallographic data for the mineral are not available. Wichman (14) has pointed out that the specimen used by Harcourt (15) for his table for identification of ore minerals probably was a member of the tetrahedrite group and not schirmerite.

THE $AgBiS_2$-$AgBiSe_2$ SYSTEM

The phase diagram (Fig. 7) shows complete series of α and β solid solutions. Lattice constants as a function of composition (Table 3, Fig. 8) for the β phase follow Vegard's law, similar to that observed in the $AgBiSe_2$-$AgBiTe_2$ system (2). Presumably, similar behavior should occur for the α solid solutions.

TABLE 3. LATTICE CONSTANTS AT 25° C. FOR THE CUBIC β PHASE IN THE $AgBiS_2$-$AgBiSe_2$ SYSTEM

Composition (Mol per cent)	Lattice constant (Å)
$AgBiS_2$	5.648±0.003
75 $AgBiS_2$–25 $AgBiSe_2$*	5.701±0.003
50 $AgBiS_2$–50 $AgBiSe_2$*	5.734±0.003
25 $AgBiS_2$–75 $AgBiSe_2$*	5.783±0.003
$AgBiSe_2$	5.832±0.003

* Held at 500° C. for 3 hours, quenched in H_2O.

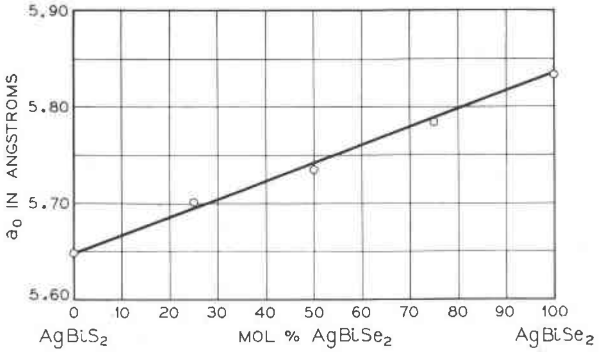

FIG. 8. Lattice constants at 25° C. for the cubic β-phase in the $AgBiS_2$-$AgBiSe_2$ system.

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