Canadian Mineralogist
Vol. 13, pp. 388-393 (1975)

PHASE RELATIONS IN THE PSEUDO-TERNARY SYSTEM PbS-Cu_2S-Sb_2S_3 AND THE SYNTHESIS OF MENEGHINITE

S. N. HODA* AND LUKE L. Y. CHANG
Department of Geology, Miami University, Oxford, Ohio

ABSTRACT

Two liquid fields exist in the system PbS-Cu_2S-Sb_2S_3 at 500°C; a Cu_2S-rich liquid, limited to a narrow compositional range, and a Sb_2S_3-rich liquid which occupies a larger region. Last liquids in the Cu_2S-rich liquid field solidify at 477°±5°C and in the Sb_2S_3-rich field at 461°±5°C. Besides the end members, solid phases present at 400°C in the system are boulangerite, robinsonite, zinkenite, chalcostibite, Phase B, bournonite, meneghinite, and a new phase, designated as Phase Z.

Meneghinite, whose composition has been disputed, was synthesized and found to have an elongate region of solid solution at 500°C. One end of the solid solution is close to the reported composition (in mole % PbS:Cu_2S:Sb_2S_3) 76.47 : 2.94: 20.59 (or $Pb_{26}Cu_2Sb_{14}S_{48}$), and the other has a composition of 46.00 : 11.00 : 43.00. A miscibility gap appears below 453°±5°C, separating Phase Z from the reduced field of meneghinite solid solution.

RÉSUMÉ

Il se trouve deux champs liquides dans le système PbS-Cu_2S-Sb_2S_3 à 500°C: un liquide riche en Cu_2S, limité d'une gamme de composition étroite et un liquide riche en Sb_2S_3 qui occupe une plus grande section. Les derniers liquides dans le champ liquide riche en Cu_2S se solidifient à 477°±5°C et dans le champ riche en Sb_2S_3 à 461°±5°C. A part les phases extrêmes, les phases solides présentes dans le système à 400°C sont: la boulangérite, la robinsonite, la zinkénite, la chalcostibite, la Phase B, la bournonite, la méneghinite et une nouvelle phase appelée Phase Z.

Après avoir été synthétisée, la méneghinite, dont la composition a beaucoup été discutée, présente, à 500°C, une région allongée de solution solide. Une des extrémités de la solution solide se rapproche de la composition énoncée (en molécules % PbS:Cu_2S:Sb_2S_3) 76.47 : 2.94 : 20.59 (ou $Pb_{26}Cu_2Sb_{14}S_{48}$), et l'autre extrémité a une composition de l'ordre de 46.00 : 11.00 : 43.00. Un intervalle de miscibilité apparaît au-dessous de 453°±5°C, séparant la Phase Z du champ réduit de la solution solide de méneghinite.

(Traduit par le journal

INTRODUCTION

At least twelve natural lead sulfantimonides have been reported (Chang & Bever 1973; Craig *et al.* 1973), but only three, boulangerite, robinsonite, and zinkenite, have been shown to be stable in the system PbS-Sb_2S_3 above 300°C (Craig *et al.* 1973; Garvin 1973). Under hydrothermal conditions, Robinson (1948) synthesized plagionite, semseyite, fuloppite, zinkenite, and robinsonite, but Jambor (1968), could not reproduce plagionite and fuloppite hydrothermally. Semseyite was prepared by Hoda & Chang (1975) through solid-state reactions at 300°C.

The causes of difficulty in the synthesis of lead sulfantimonide minerals are many, including the presence of additional cations in natural phases. The composition of meneghinite has been a subject of argument. Palache *et al.* (1938) proposed the formula $Pb_{13}Sb_7S_{23}$, but Berry & Moddle (1941) showed meneghinite to contain copper and suggested the formula $Pb_{26}Cu_2Sb_{14}S_{48}$. Wang (1973) reported the synthesis of a phase from $Pb_2Sb_2S_5$ which has an *x*-ray diffraction pattern corresponding to that of meneghinite, and a non-stoichiometric meneghinite of composition $Pb_{13}Sb_{8.35}S_{24.93}$ was prepared by Jambor (1975). The purpose of this nivestigation was to determine the phase relations in the system PbS-Cu_2S-Sb_2S_3 and to study the effect of copper on the formation of meneghinite.

EXPERIMENTAL PROCEDURE

The evacuated glass-capsule technique described by Kullerud & Yoder (1959) was used in this study. Starting compositions were prepared from elemental lead (Mc/B, reagent), antimony (Baker, reagent), copper (Fisher, reagent), and sulfur (Fisher, U.S.P.). All have 99.99% or better purity.

Samples were heated in horizontal muffle furnaces in which the temperature was regulated to ±2°C. Temperatures were measured by means of calibrated chromel-alumel thermocouples and a Leeds and Northrup potentiometer. Generally, 42 days were allowed for equili-

---

*Present address: Research and Development Center, Corning Glass Works, Corning, New York.

bration at 500°C, 72 days at 400°C, and 300 days at 300°C. To check the equilibria, a number of samples were pre-heated to their melting temperature (about 800°C), quenched, ground in acetone, and annealed at the desired temperatures. In addition, some samples were prepared from synthetic sulfides (Cu_2S, PbS, and Sb_2S_3) as starting materials. Regardless of procedure, the final phase assemblages showed identical *x*-ray powder diffraction patterns.

At the end of the heat treatment, samples were quenched in air. Identification of phases was mainly by *x*-ray powder diffraction using Ni-filtered copper radiation, but polished sections proved very valuable for distinguishing primary and secondary phases. Cell dimensions were calculated to ±0.02Å using a least-squares refinement program. The (110) reflection of metallic tungsten ($a = 2.1648$Å) was used as an internal standard.

Previous Studies

Phase relations in the related binary systems are known. Craig *et al.* (1973) and Garvin (1973) discussed the system $PbS-Sb_2S_3$ in detail, and a summary was made by Chang & Bever (1973). The composition of robinsonite in the form of $6PbS \cdot 5Sb_2S_3$ used in the present study is taken from Craig *et al.* (1973), and Hoda & Chang (1975). In the system $PbS-Cu_2S$, a simple eutectic relationship exists (Craig & Kullerud 1968).

In the system $Cu_2S-Sb_2S_3$, Gaudin & Dicke (1939) prepared two phases, Cu_3SbS_3 and $CuSbS_2$. Cambi & Elli (1965) confirmed Gaudin & Dicke's findings and proposed a phase diagram showing three eutectics at 583.2°C and 83.28 mole % Cu_2S, 541.8°C and 58.73 mole% Cu_2S, and 496.0°C and 20.12 mole% Cu_2S. They also observed the formation of two cubic phases in Cu_3SbS_3, α with $a = 10.41$Å and β with $a = 10.31$Å, and related them by a phase transition. Godovikov & Il'yasheva (1970) reported on orthorhombic, wittichenite-equivalent phase of Cu_3SbS_3 at 480°C. This phase melts at 618°C, and on cooling it yields an assemblage of α- and β-phases.

Skinner *et al.* (1972) found a Phase B of composition Cu_3SbS_3, stable above 359°C; below 359°C phase B decomposes to chalcostibite

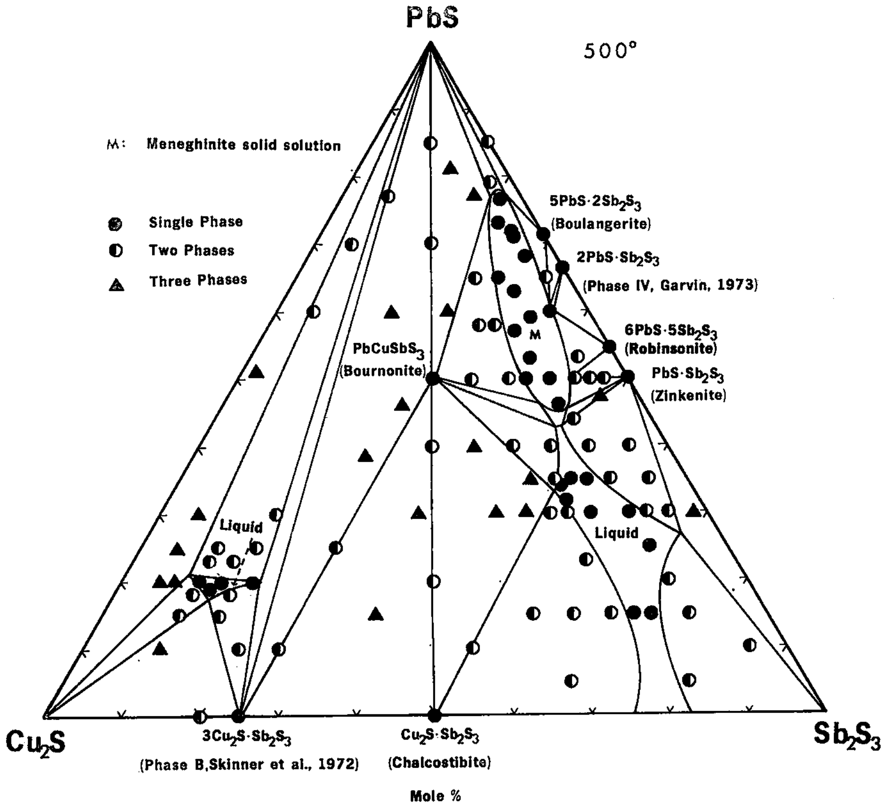

FIG. 1. Phase relations in the system $PbS-Cu_2S-Sb_2S_3$ at 500°C.

+ tetrahedrite + antimony. This decomposition is complicated by a metastable phase transition of phase B to phase B′ at 122±3°C. Tatsuka & Morimoto (1973) showed that the composition Cu_3SbS_3, prepared either by slow cooling from a melt or by annealing the cooled melt at 300°C, produced tetrahedrite + antimony; *i.e.* phase B was not obtained. This tetrahedrite has a superstructure with $a = 20.84$Å, twice that of normal tetrahedrite, which disappears at 350°C. Above 361°C the assemblage tetrahedrite + antimony reacts to form phase B.

EXPERIMENTAL RESULTS

Phase relations

Phase relations in the system at 500°C are shown in Figure 1, based on experimental data indicated. A Cu_2S-rich liquid forms in the system, occupying a small region approximately between 63-70 mole% Cu_2S, 18-20 mole% PbS and 10-17 mole% Sb_2S_3. It is characterized by a rapid crystallization of bluish-gray dendrites of chalcocite during quenching. In the three-phase region of Cu_2S, PbS, and liquid, quenched samples show the liquid to have crystallized in the interstitial space as minute eutectic intergrowths of chalcocite and galena, the phenocrysts being either galena or chalcocite. Quenched samples of liquid compositions close to the PbS-Cu_3SbS_3 join contain large crystals of galena, Cu_3SbS_3, or tetrahedrite and metallic antimony. Tetrahedrite and Cu_3SbS_3 are very similar in optical characteristics. They were distinguished by etch tests made with KCN which attacks tetrahedrite rapidly but shows negative results with Cu_3SbS_3. The Cu_2S-rich lqiuid completely crystallizes at 477°±5°C.

The liquid on the Sb_2S_3 side of the system covers a region limited to 0-47 mole% PbS, 5-25 mole% Cu_2S, and 45-82 mole% Sb_2S_3. A liquid of composition 34 mole% PbS, 17 mole% Cu_2S, and 49 mole% Sb_2S_3 formed a homogeneous glassy mass with high reflectivity. However, more commonly, the liquid in this region tends to crystallize rapidly with the formation of needles of stibnite or dendrites of chalcostibite, depending on composition. The Sb_2S_3-rich liquid completely crystallizes at 461°±5°C.

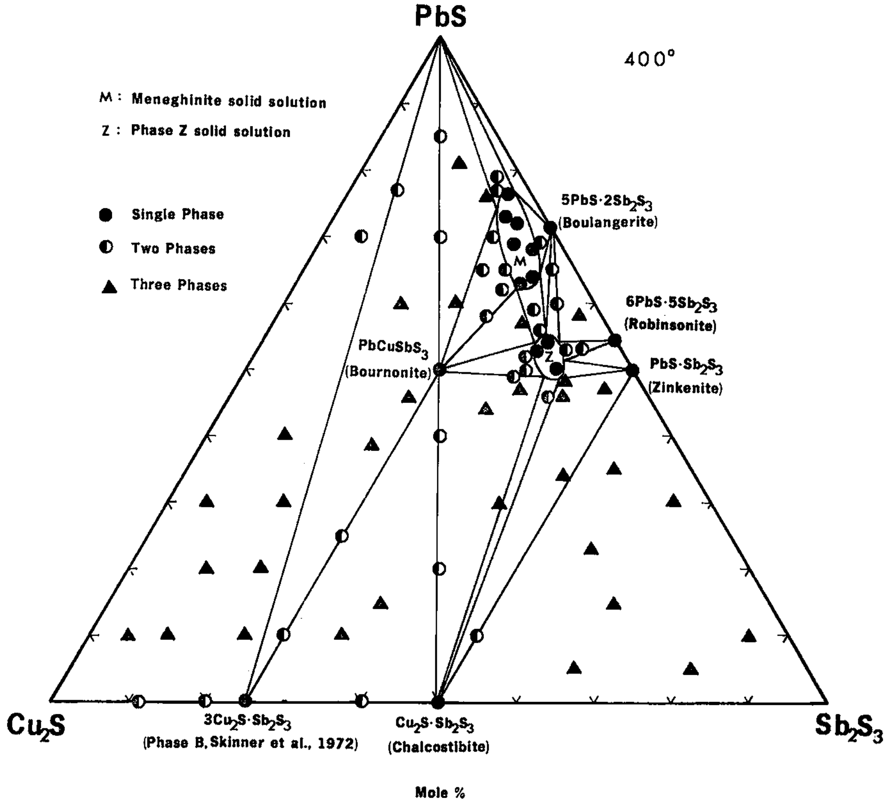

FIG. 2. Phase relations in the system PbS-Cu_2S-Sb_2S_3 at 400°C.

Both chalcostibite ($CuSbS_2$) and bournonite ($PbCuSbS_3$) form readily in the system, and show no shift in *d*-spacings in the binary and ternary phase assemblages. Therefore, they are considered to be strictly stoichiometric. At 500°C, meneghinite has an elongate region of solid solution, and is in equilibrium with all lead sulfantimonides, galena, and bournonite. *X*-ray diffraction data for meneghinite in the binary and ternary phase assemblages match those of meneghinite in the solid solution. No meneghinite was produced from compositions along the $PbS\text{-}Sb_2S_3$ join as had been reported by Wang (1973).

Phase relations in the region containing Cu_3SbS_3 are complicated by the presence of non-quenchable phase transitions as shown by Skinner *et al.* (1972) and Tatsuka & Morimoto (1973). The three reported phases, α, β (Cambi & Elli 1965; Skinner *et al.* 1972) and phase B (Godovikov & Il'yasheva 1970; Skinner *et al.* 1972; Tatsuka & Morimoto 1973) were all observed in the quenched samples. In addition, finely disseminated antimony was present in all phase assemblages in the region. Because of the non-quenchable nature of phase transitions in Cu_3SbS_3, stable phase assemblages observed at room temperature in the present study were extrapolated to 500°C using Skinner *et al.*'s data.

At 400°C, the system is represented entirely by solid phases as shown in Figure 2. A miscibility gap appears in the meneghinite solid-solution region between 54 and 63 mole% PbS. The lead-poor portion shows *x*-ray diffraction patterns quite different from those of meneghinite, and is designated as a new phase Z. Other solid phases present at 400°C are boulangerite, robinsonite, zinkenite, chalcostibite, phase B, bournonite, and the end members.

A comparison of phase relations at 400°C (Fig. 2) and at 300°C (Fig. 3) shows an increase in size of the miscibility gap between phase Z and meneghinite solid solution with decreasing temperature. The shrinkage is largely toward the meneghinite composition $Pb_{26}Cu_8Sb_{14}S_{48}$. Phase relations in the $Cu_2S\text{-}PbS\text{-}CuSbS_2$ portion can only be established by studying the larger system Cu-Pb-Sb-S.

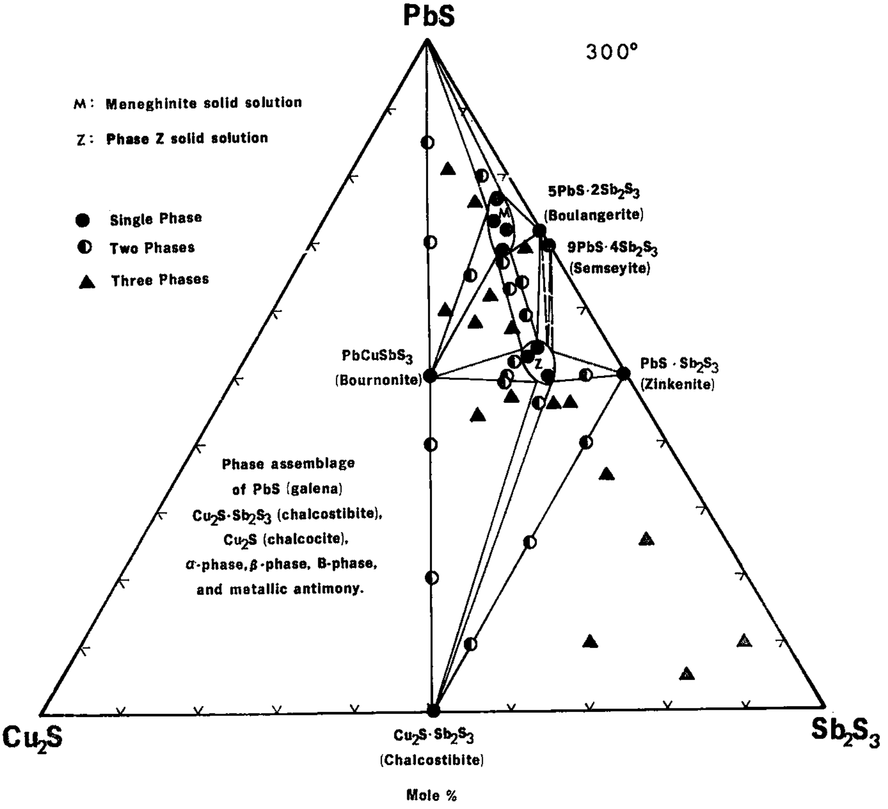

FIG. 3. Phase relations in the $Cu_2S{\bullet}Sb_2S_3\text{-}Sb_2S_3\text{-}PbS$ portion of the system $PbS\text{-}Cu_2S\text{-}Sb_2S_3$ at 300°C.

Pseudo-ternary phases

Meneghinite was synthesized in the temperature range 500°-300°C. It was found that a minimum of 2.94 mole% Cu_2S is essential for the formation of stoichiometric meneghinite in the system PbS-Cu_2S-Sb_2S_3. At 500°C, meneghinite shows an elongate region of solid solution, one end of which coincides with the composition (in mole% PbS:Cu_2S:Sb_2S_3) 76.47:2.94:20.59 ($Pb_{26}Cu_2Sb_{14}S_{48}$), reported by Berry & Moddle (1941) and the other has an approximate composition of 46.00:11.00:43.00. *X*-ray powder diffraction data of synthetic meneghinite, ($Pb_{26}Cu_2Sb_{14}S_{48}$), match well with those given by Berry & Moddle (1941) for a natural sample from Tuscany, Italy. There is no omission or addition of reflections in *x*-ray diffraction patterns throughout the solid solution. The crystallinity of meneghinite solid solution decreases with decreasing PbS-content as revealed by poor diffraction patterns. The cause of this poor crystallinity is not known. Samples with compositions in this region have fine grain size after heat treatment, but so do samples with compositions in other regions, which produced well-crystallized phases. The use of pelletized samples for a prolonged period (142 days at 500°C) did not improve the crystallinity. Using indices given by Berry & Moddle (1941), cell dimensions were calculated for two meneghinites, 76.47:2.94:20.59 and 72.00:4.00:24.00. They are, respectively, $a=11.34$, $b=24.62$, $c=8.26$Å and $a = 11.28$, $b = 24.77$, $c = 8.24$Å. A decrease in *a* and *c* and an increase in *b* with decreasing PbS-content were illustrated.

Incongruent melting of meneghinite solid solution was observed. Meneghinite of lower PbS-content melts to meneghinite of higher PbS-content and liquid. Two meneghinites, with compositions of 76.47:2.94:20.59 and 81.11:5.56, 13.33, having the highest PbS-contents among all determined, melt to galena and liquid. Melting points determined are, in order of increasing PbS-content, 510°±5°C for 50.00:10.00:40.00 and 50.00:13.00:37.00, 521°±5°C for 59.00:8.00:33.00, 531°±5°C for 63.00:8.00:29.00, 592°±5° for 68.00:4.00:28.00, and 605°±5°C for 76.47:2.94:20.59 and 81.11:5.56:13.33.

The three compositions, which produced Phase Z, are 50.00:10.00:40.00, 53.00:11.00:36.00, and 54.00:9.00:37.00. They all gave diffuse *x*-ray powder diffraction patterns. Relative intensities and *d*-spacings measured are: 3.58(4), 3.53(10), 3.42(10), 3.28(5), 3.12(7), 3.09(3), 2.99(5), 2.90(5), 2.87(7), 2.83(4), 2.71(4), 2.30(3), 2.16(5), 2.12(3), 2.02(8), 1.926(1), 1.903(1), 1.799(2).

Bournonite ($PbCuSbS_3$) synthesized in the present study has cell dimensions of $a = 8.17$, $b = 8.69$, $c = 7.82$Å, which agree well with those given by Leineweber (1956): $a = 8.16$, $b = 8.71$, $c = 7.81$Å.

DISCUSSION

The system PbS-Cu_2S-Sb_2S_3 contains three ternary phases, bournonite, meneghinite, and a new phase Z. Bournonite with a composition of $PbCuSbS_3$ has no range of solid solution in the system as judged from its constancy of *d*-spacings in the binary and ternary phase assemblages. There is no observable substitution between Cu and Pb.

Meneghinite solid solution covers a region starting from the generally reported composition, $Pb_{26}Cu_2Sb_{14}S_{48}$, and extending toward the PbS-poor and Sb_2S_3-rich compositions. The few analyses of natural meneghinite available thus far show an absence of compositions having PbS-content poorer than $Pb_{26}Cu_2Sb_{14}S_{48}$ (Fredriksson & Anderson 1964; Burnol *et al.* 1965; Aicard *et al.* 1968). Fredricksson & Anderson (1964) reported that the bulk composition of meneghinite from its type locality (Tuscany, Italy) agrees fairly well with the formula, $Pb_{26}Cu_2Sb_{14}S_{48}$, proposed by Berry & Moddle (1941). However, electron beam scanning photographs revealed micron-sized particles of exsolved galena which cannot be separated from meneghinite according to Fredriksson & Anderson. The chemical analyses, therefore, would tend to show bias toward lead concentration. The presence of a miscibility gap and the shrinkage in the range of meneghinite solid solution with decreasing temperature indicate that the lead-poor variety is unlikely to occur in nature.

No equivalent natural phase has been reported for the new phase Z. If it does not break down at lower temperatures, a mineral of the composition, $Pb_5Cu_2Sb_8S_{18}$ or close to it, may be found in the future. The B′-phase of Skinner *et al.* (1972) was recently identified in the Ilimaussaq alkaline intrusion, southern Greenland (Karup-Møller & Makovicky 1974).

REFERENCES

AICARD, P., PICOT, P., PIERROT, R. & POULAIN, P. A. (1968): Sur la présence de meneghinite dans deux gites français. *Bull. Soc. franc. Miner. Crist.* **91**, 497-499.

Berry, L. G. & Moddle, D. A. (1941): Studies of mineral sulpho-salts: V. Meneghinite from Ontario and Tuscany. *Univ. Toronto Studies, Geol. Ser.* **46**, 5-17.

Burnol, L., Picot, P. & Pierrot, R. (1965): La meneghinite des gisements de Saki et de Gouskhalat, Iran. *Bull. Soc. franc. Miner. Crist.* **88**, 290-293.

Cambi, L. & Elli, M. (1965): Processi idrotermali. Sintesi di solfosali da ossidi di metalli e metalloidi. Nota II—Cuprosolfoantimoniti. *Chimica Industria.* 47, 136-147.

Chang, L. L. Y. & Bever, J. E. (1973): Lead sulfosalt minerals: Crystal structures, stability relations, and paragenesis. *Minerals Sci. Engng.* **5**, 181-191.

Craig, J. R., Chang, L. L. Y. & Lees, W. R. (1973): Investigations in the system Pb-Sb-S. *Can. Mineral.* **12**, 199-206.

——— & Kullerud, G. (1968): Phase relations and mineral assemblages in the copper-lead-sulfur system. *Amer. Mineral.* **53**, 145-161.

Fredriksson, K. & Anderson, C. A. (1964): Electron probe analyses of copper in meneghinite. *Amer. Mineral.* **49**, 1467-1469.

Garvin, P. L. (1973): Phase relations in the Pb-Sb-S system. *N. Jb. Min. Abh.* **118**, 235-267.

Gaudin, A. M. & Dicke, G. (1939): The pyrosynthesis, microcopic study and irridescent filming of sulfide compounds of copper with arsenic, antimony, and bismuth. *Econ. Geol.* **34**, 214-232.

Godovikov, A. A. & Ilyasheva, N. A. (1970): The antimony analog of wittichenite, a new phase in the system $Cu_2S-Sb_2S_3$. *Acad. Sci. USSR, Earth Sci. Sect.* **190**, 133-135.

Hoda, S. N. & Chang, L. L. Y. (1975): Phase relations in the systems $Ag_2S-PbS-Sb_2S_3$ and $Ag_2S-PbS-Bi_2S_3$. *Amer. Mineral.*, **60**, 621-633.

Jambor, J. L. (1968): New lead sulfantimonides from Madoc, Ontario—Part 3. Syntheses, paragenesis, origin. *Can. Mineral.* **9**, 505-521.

——— (1975): Synthetic copper-free meneghinite. *Geol. Surv. Can. Paper* **75-1**, Pt. B, 71-72.

Karup-Møller, S. & Makovicky, E. (1974): Skinnerite, Cu_3SbS_3, a new sulfosalt from the Ilimaussaq alkaline intrusion, South Greenland. *Amer. Mineral.* **59**, 889-895.

Kullerud, G. & Yoder, H. S. (1959): Pyrite stability relations in the Fe-S system. *Econ. Geol.* **54**, 533-572.

Leineweber, G. (1956): Struktur-Analyse des Bournonite und Seligmannits mit Hilfe der Superposition-Methoden. *Zeits Krist.* **108**, 161-184.

Palache, C., Richmond, W. E. & Winchell, H. (1939): Crystallographic studies of sulfo-salts: baumhauerite, meneghinite, jordanite, diaphorite, freieslebenite. *Amer. Mineral.* **23**, 821-836.

Robinson, S. C. (1948): Synthesis of lead sulphantimonides. *Econ. Geol.* **43**, 293-312.

Skinner, B. J., Luce, F. D. & Makovicky, E. (1972): Studies of the sulfo-salts of copper. III. Phases and phase relations in the system Cu-Sb-S. *Econ. Geol.* **67**, 924-938.

Tatsuka, K. & Morimoto, N. (1973): Composition variation and polymorphism of tetrahedrite in the Cu-Sb-S system. *Econ. Geol.* **67**, 425-434.

Wang, N. (1973): A study of phases on the pseudobinary join $PbS-Sb_2S_3$. *N. Jb. Min. Mh.*, 79-81.

Manuscript received April 1975, emended July 1975.