The herzenbergite–teallite series

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SUMMARY. Equilibrium relations of lead–tin sulphides in the system SnS–PbSnS$_2$ were studied using a sealed silica-tube technique. A complete series of solid solutions forms in the system, and lattice parameters were found to vary lineally with composition. The melting temperature of the solid solution decreases with increasing amount of PbS from herzenbergite at 880 °C to teallite at 725 °C.

Evidences were found to indicate the existence of this series of solid solution in ore deposits.

HERZENBERGITE and teallite are two closely related sulphides of tin, but the equilibrium relationship between them has not been satisfactorily established. Gaudin and Hamlyn (1938) found 'large solubility in the solid state' and no binary compound in the system PbS–SnS. Mosburg et al. (1961), although they successfully synthesized herzenbergite and teallite from elements in sealed evacuated silica-tubes, made no attempt to study the extent of solid solution in the series.

Both sulphides were first found in the silver–tin ore deposits in Bolivia. Ramdohr (1935) gave the name herzenbergite to the mineral with the composition SnS, while teallite with the composition PbSnS$_2$ was named by Prior (1904). Herzenbergite and teallite are orthorhombic with pronounced tetragonal pseudosymmetry (Hofmann, 1935a and 1935b), and their cell dimensions are very similar in magnitude as tabulated in table I. Hofmann also pointed out that the crystal structure of the tin sulphides could be related to that of galena. The cell dimension, a (5·93 Å), of galena is about half the c of herzenbergite and teallite, and the cube face diagonal [110] (4·19 Å) in galena corresponds with a and b of the tin sulphides.

Experimental procedures. All syntheses were conducted in sealed evacuated silica tubes. Mixtures of desired compositions were prepared from elements (Fisher certified lead, 99·99 %, Fisher certified tin, 99·95 %, and USP sulphur precipitated). Heat-treatment was done in Nichrome-wound furnaces and temperatures were measured potentiometrically by chromel–alumel thermocouples. Temperature uncertainty was believed to be within ±2 °C.

X-ray diffraction was used for the identification of solid phases in the subsolidus region and for the measurement of cell dimensions of the solid solution. Six oscillations were made over the 2θ range, 35–55°, for each sample of measurement with a General Electric diffractometer. The 110 line of metallic tungsten (from Lamp Metals and Components Department, General Electric Co., Cleveland, Ohio, highly purified) at 2θ = 40·26° (a = 2·1648, Swanson and Tatge, 1953) was used as an internal standard. Ni-filtered Cu radiation was used throughout this work. Ore microscopy was used to differentiate the primary solid phases from the secondary solid phases in the determination of the solidus and liquidus of this series.

TABLE I. *Cell dimensions of herzenbergite and teallite*

	Hofmann, 1935	Mosburg *et al.*, 1961	Present study
Herzenbergite			
a	3·98	4·328	3·978
b	4·33	11·190	4·330
c	11·18	3·978	11·184
Teallite			
a	4·04	4·266	4·082
b	4·28	11·419	4·270
c	11·33	4·090	11·417

Solid solution. In the temperature range between 400 and 700 °C, treated samples of compositions SnS and $PbSnS_2$ produced sulphides whose X-ray diffraction patterns correspond well with those of natural and previously synthesized herzenbergite and teallite. Intermediate compositions in this series gave single phases showing the same structure as that of the end members. No addition or omission of diffraction lines in their X-ray diffraction patterns was observed throughout the entire series. Such evidence indicates the formation of a complete series of solid solutions between herzenbergite and teallite.

Six diffraction lines with fairly strong intensities were selected for cell dimension measurement. The *d*-spacings of lines 104, 021, 114, 200, 121, and 211 were measured to the nearest 0·01° 2θ with a metal scale. A linear relationship between cell dimension and composition is shown in fig. 1.

An attempt was made to determine the behaviour of this series at relatively low temperature. Solid solutions prepared at 700 °C and untreated mixtures made from elements were annealed at 250 °C for a period of seven months, a grinding being performed every two months. Results show no change in the solid solutions, yet reactions in the raw mixtures proceeded toward the formation of a herzenbergite–teallite phase, although none of the raw mixtures had been completely converted into a single phase.
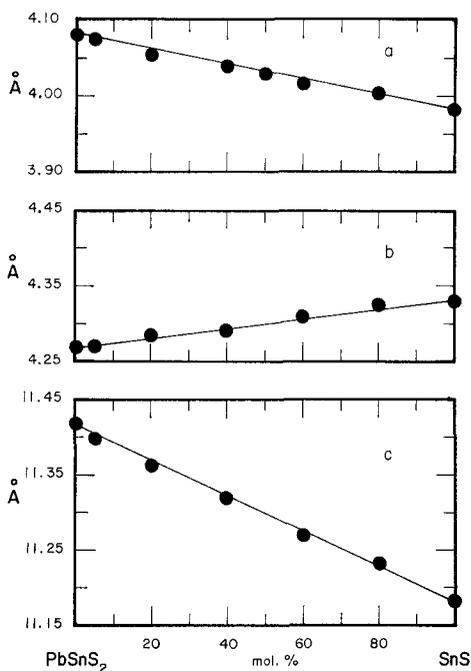
FIG. 1. Variation of cell dimensions as a function of composition in the herzenbergite–teallite series.

The extension of this solid solution series beyond the composition of teallite into the PbS-rich portion of the system PbS–SnS was found to be very limited, even at temperatures near the melting point around 700 °C. Phase transition, such as to the galena-type structure, was not found in the herzenbergite–teallite series. Orthorhombic symmetry persists all the way to the melting points.
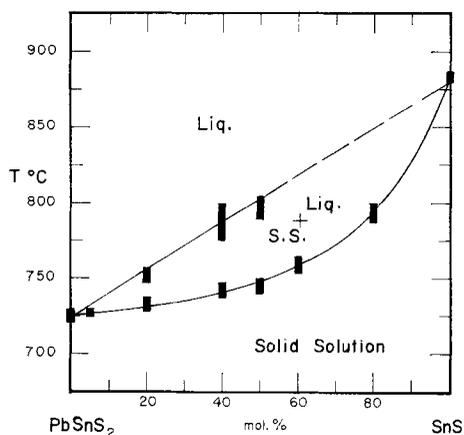
FIG. 2. Melting relation in the herzenbergite–teallite series.

Melting relation. The melting point of herzenbergite was reported to be 881·5 °C (Moh, 1963), while no information has been found for teallite. On the basis of microscopic examination of polished sections, melting points of herzenbergite and teallite were recorded at 880±3 and 725±3 °C, respectively, and a melting relation is shown in fig. 2. To differentiate primary from secondary phases is not an easy task in samples quenched from temperatures near the solidus or liquidus. Thus a range of temperatures, instead of a sharp point of melting, is illustrated in fig. 2. The best melting curve that can be constructed from data obtained is a continuous curve with no inflection in its slope.

Natural occurrences of herzenbergite–teallite minerals have been reported from several places; the most important and best studied is no doubt from the ores in Bolivia, whose geology has been described in detail by Campbell (1942)[1] and recently by Turneaure (1960). Herzenberg (1949) reported a series of herzenbergite–teallite minerals from Bolivia district to have chemical compositions varying from S 18·15 %, Pb 42·8 %, Sn 34·0 % to S 19·9 %, Pb 20·8 %, Sn 30·4 % with zinc content increasing with decreasing lead up to 14·0 %. Eleven chemical analyses made by Berndt (1954) of Bolivian tin ores gave a range of lead from 19·7 to 40·8 %, a range of tin from 23·3 to 44·2 %, and a range of sulphur from 14·1 to 20·9 % with small amounts of Zn, Fe, Cu, etc. Such variation in chemical composition clearly demonstrates the natural occurrence of the herzenbergite–teallite series.

REFERENCES

BERNDT (F.), 1954. *Neues Jahrb. Min., Monatsh.* 200–4.
CAMPBELL (D. F.), 1942. *Econ. Geol.* 37, 87–115.
GAUDIN (A. M.) and HAMLYN (W. T.), 1938. Ibid. 33, 868–88.
HERZENBERG (R.), 1949. *Publ. Tecn. Inst. Boliviano Ingen. Minas y Geol.* 4 pp.

[1] The teallite and herzenbergite used in the present study are parts of Campbell's original samples now a part of Cornell's ore collection.

HOFMANN (W.), 1935a. *Fortschr. Min. Krist. Petr.* **19**, 30–1.
—— 1935b. *Zeits. Krist.* **92**, 161–85.
MOH (G.), 1963. *Carnegie Inst. Washington, Yearbook* **62**, 197–8.
MOSBURG (S.), ROSS (D. R.), BETHKE (P. M.), and TOULMAN (P.), 1961. *U.S.G.S. Prof. Paper*, **424–C**, C347–8.
PRIOR (G. T.), 1904. *Min. Mag.* **14**, 21–7.
RAMDOHR (P.), 1935. *Zeits. Krist.* **92**, 186–9.
SWANSON (H. E.) and TATGE (E.), 1953. *Nat. Bur. Standards (U.S.), Circ.* **539–I**, 28.
TURNEAURE (F. S.), 1960. *Econ. Geol.* **55**, 217–54, 574–606.