

Interdiffusion of S and Se in tiemannite

NABIL Z. BOCTOR AND JOHN B. BRADY

*Geophysical Laboratory, Carnegie Institution of Washington
Washington, D.C. 20008*

Abstract

Diffusion coefficients for S-Se interdiffusion in tiemannite (HgSe) single crystals have been determined in the temperature range 500°–700°C. The measured diffusivities may be fit by the equation

$$D = (5.7 \times 10^{-12}) \exp \frac{-105,000}{8.314T} \text{ cm}^2/\text{sec}$$

An activation energy for S-Se interdiffusion of 105 kJ/mole is derived from the diffusion data. The S-Se interdiffusion coefficients are larger than sulfur self-diffusion coefficients in sulfides that have the same crystal structure as tiemannite.

Introduction

To date most studies of sulfur diffusion have been concerned with the self-diffusion of this element in sulfide minerals such as pyrrhotite, Fe_{1-x}S (Condit *et al.*, 1974), sphalerite, ZnS (Gobrecht *et al.*, 1967) wurtzite, ZnS (Blount *et al.*, 1967) and hawleyite, CdS (Kumar and Kroger, 1971; Sysoev *et al.*, 1969). No data on sulfur diffusion in selenide-type minerals are known. Tiemannite, HgSe , commonly contains minor amounts of sulfur substituting for Se in its structure. In some localities, however, the isomorphous substitution of S for Se is very extensive. Almost the entire range of HgSe – HgS compositions has been observed in nature, as at the Lucky Boy Mine, Marysvale District, Utah (Bethke, 1957; Boctor, 1976). Tiemannite was selected for investigation of sulfur diffusion in selenide-type minerals because (1) equilibrium relations in the Hg – S – Se system are well known (Boctor, 1976) and (2) high-purity single crystals of HgSe were available.

Experimental methods

Tiemannite is typically a nonstoichiometric compound. It may contain an excess of mercury over selenium of 1.1–1.8 atom percent or an excess of selenium over mercury of 0.2–0.9 atom percent in the temperature range 230°–700°C (Boctor and Kullerud, 1979). The tiemannite crystals used were all rec-

tangular slabs ($\approx 5 \times 3$ mm) cut from a large single crystal grown by the vapor-transport method in the presence of excess mercury (Laboratory for Crystal Growth, Purdue University). The crystals were compositionally homogeneous and contained 1.3 atom percent excess Hg. The tiemannite crystals were polished and completely surrounded by tightly packed, powdered synthetic cinnabar, HgS ($< 0.063 \mu\text{m}$ in diameter), in silica tubes with closely fitting silica rods to reduce the vapor volume. The silica tubes were evacuated, sealed under vacuum, and annealed at 700°, 600°, and 500°C, respectively, for periods of 168, 288, and 408 hr. The vapor pressure over the charges was that of the system, and no attempts were made to control the sulfur or selenium fugacities. In each experiment, the tiemannite crystal retained its form and polished surfaces and was easily separated from the HgS powder after the run. Compositional profiles were determined with the electron microprobe from polished cross sections of each tiemannite crystal. For Hg analyses, $M\alpha$ radiation was used; for S and Se analyses, $K\alpha$ radiation was used. Synthetic HgSe was used as a standard for Se and Hg. The HgS , provided by Materials Research Company, was used as a standard for S. Atomic number, absorption and fluorescence corrections of raw electron microprobe data were performed with the MAGIC IV computer program of Colby (1971).

Experimental results

Members of the HgSe–HgS solid-solution series are cubic (sphalerite structure) above 345°C. Diffusion rates should therefore be independent of diffusion direction in tiemannite, a prediction confirmed by the results. Typical sulfur compositional profiles are shown in Figure 1 along with curves previously fitted to the data on probability paper (*cf.* de Silva and Mehl, 1951, p. 161). Within the limits of accuracy of the electron microprobe (± 2 percent of the measured concentration), the tiemannite crystals have remained binary [(S + Se):Hg constant] during the diffusion experiments. Therefore, the boundary conditions of the experiment are suitable for the Boltzmann-Matano solution (Matano, 1933). The preserved polished surface of each tiemannite crystal marks a surface across which there has been an equal and opposite net flux of sulfur and selenium; thus the polished surfaces are by definition Boltzmann-Matano interfaces for these experiments. Although data were not obtained for the selenium distribution in the HgS powder, knowledge of the location of the Boltzmann-Matano interface permits the determination of diffusivities from the tiemannite single-crystal profiles alone. A discontinuity in physical properties at the interface between the tiemannite single crystal and the HgS powder does not preclude the use of the Boltzmann-Matano solution (Jost, 1950; Appel, 1968).

Table 1. Interdiffusion coefficients for S and Se in tiemannite

T , °C	$S/(S + Se)$	D , cm^2/sec
700	0.5	$3.5 (\pm 1.0) \times 10^{-11}$
700	0.2	$2.7 (\pm 1.0) \times 10^{-11}$
600	0.5	$0.9 (\pm 0.8) \times 10^{-11}$
600	0.2	$1.1 (\pm 1.0) \times 10^{-11}$
500	0.5	$1.2 (\pm 0.5) \times 10^{-12}$
500	0.2	$1.1 (\pm 0.5) \times 10^{-12}$

Slopes and areas were obtained graphically from the compositional profiles and used to compute the diffusion coefficients listed in Table 1. Uncertainties are based on the reproducibility of electron microprobe and graphical determinations. No concentration dependence of the interdiffusion coefficients can be verified within the limits of precision, although it appears that more sulfur-rich compositions yield slightly higher diffusivities. Because the variation of molar volume with composition is not known, the diffusion coefficients could not be corrected for possible volume effects. The measured diffusivities can be expressed by the equation

$$D = (5.7 \times 10^{-12}) \exp \frac{-105,000}{8.314T} \text{ cm}^2/\text{sec}$$

An activation energy for S–Se interdiffusion of 105 kJ/mole is derived from the data.

Discussion

The interdiffusion coefficients determined for tiemannite are larger than sulfur self-diffusion coefficients in sulfides with the same structure, such as sphalerite (Gobrecht *et al.*, 1967). This result is consistent with the suggestion of Stevenson (1973, p. 435) that interdiffusion coefficients for the chalcogenides, because of thermodynamic nonideality, are expected to be much larger than the self-diffusion coefficients. The activation energy for S–Se interdiffusion determined in this study is also within the range reported by Stevenson (1973, Table 7.1) for similar minerals.

Mercury ores are believed to form in the temperature range 100°–250°C (Dickson, 1964). Members of the tiemannite–metacinnabar series occasionally show compositional zoning (Bethke, 1957). The fast diffusion rates at high temperatures we obtained support a low-temperature origin for these ores. If the mercury ores had experienced high temperatures, compositional zoning might not be preserved. A study of S–Se interdiffusion under hydrothermal

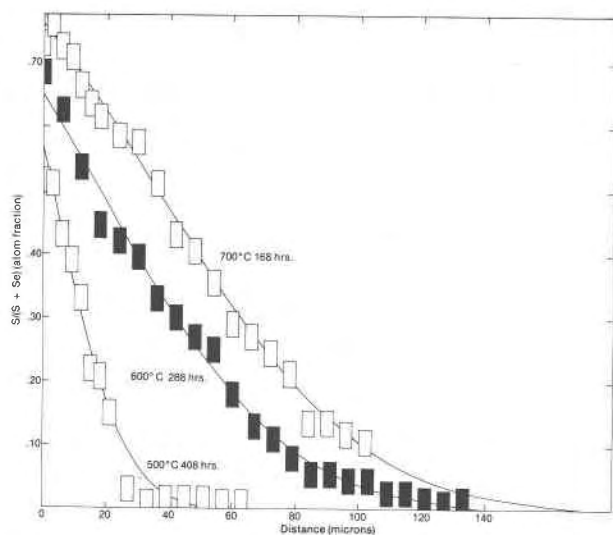


Fig. 1. Compositional profiles measured with the electron microprobe of the sulfur content of the tiemannite crystals with respect to distance from the crystal surface. The curves are a best fit of the data obtained using probability graph paper.

conditions and an evaluation of the effect of variations in $f(S_2)$ and $f(Se)$ on the diffusion coefficients are needed, however, before the data can be applied quantitatively to mercury ores.

Acknowledgments

The authors are grateful to Drs. A. W. Hofmann, H. K. Mao, and H. S. Yoder, Jr., for critical comments on the manuscript.

References

- Appel, M. (1968) Solution for Fick's 2nd law with variable diffusivity in a multi-phase system. *Scripta Metallurgica*, 2, 217-222.
- Bethke, P. M. (1957) *The Sulfoselenides of Mercury and Their Occurrence at Marysvale, Utah*. Ph.D. Thesis, Columbia University, New York.
- Blount, H. G., G. A. Marlora and H. B. Richard (1967) Self diffusion of S in ZnS. *J. Appl. Phys.*, 38, 3995.
- Boctor, N. Z. (1976) *The Mercury-Selenium-Sulfur System and Its Geological Implications*. Ph.D. Thesis, Purdue University, West Lafayette, Indiana.
- and G. Kullerud (1979) Phase relations in the mercury-selenium system. In V. A. Zharikov, V. I. Fonarev and V. A. Karikovshii, Eds., *Problems of Physical-Chemical Petrology*. Academy of Sciences, USSR, in press.
- Colby, J. W. (1971) *MAGIC IV, a computer program for quantitative electron microprobe analysis*. Bell Telephone Laboratories, Allentown, Pennsylvania.
- Condit, R. H., R. R. Hobbins and C. E. Birchenall (1974) Self-diffusion of iron and sulfur in ferrous sulfide. *Oxid. Met.*, 8, 409-455.
- de Silva, L. C. C. and R. F. Mehl (1951) Interface and marker movements in diffusion in solid solutions of metals. *Trans. AIME*, 191, 155-173.
- Dickson, F. W. (1964) Stability of cinnabar in Na₂S solutions at 50 to 250°C and 1-1800 bars with geologic applications. *Econ. Geol.*, 59, 625-635.
- Gobrecht, H., H. Nelkowski, J. W. Baars and M. Weigt (1967) Self diffusion of sulfur in zinc sulfide. *Solid State Comm.*, 5, 777-778.
- Jost, W. (1950) Bemerkung zur mathematischem Behandlung komplizierter Diffusionsprobleme. *Z. Phys.*, 127, 163-167.
- Kumar, V. and F. A. Kroger (1971) Self diffusion and the defect structure of CdS. *J. Solid State Chem.*, 3, 387-400.
- Matano, C. (1933) On the relation between the diffusion coefficients and concentrations of solid metals. *Jap. J. Phys.*, 8, 109-113.
- Stevenson, D. A. (1973) Diffusion in the chalcogenides of Zn, Cd, and Pb. In D. Shaw, Ed., *Atomic Diffusion in Semiconductors*, p. 431-542. Plenum Press, New York.
- Sysoev, L. A., A. Y. Gel'fman, A. D. Kovaleva and N. G. Kravchenko (1969) Measurements of the coefficients of self diffusion of sulfur in CdS microcrystals. *Izv. Akad. Nauk SSSR Neorg. Mater.*, 5, 2208-2209.

*Manuscript received, October 15, 1979;
accepted for publication, April 14, 1980.*