

## Semiconducting band gaps of three lead-antimony sulfosalts

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### ABSTRACT

Electronic properties of three sulfosalts (natural boulangerite, jamesonite, and heteromorphite, and synthetic boulangerite) were examined. All three materials are conventional semiconductors. Photoconductivity band gaps fall in the range 1.4 to 1.5 eV. Room-temperature resistivities are also given.

### INTRODUCTION

This note reports measurements of electronic band gaps  $2\Delta$  and resistivities  $\rho$  in the lead-antimony sulfosalts boulangerite, jamesonite, and heteromorphite. These materials were studied as part of an effort to find new sliding charge-density-wave materials. Sliding charge-density waves arise from metal-insulator transitions in some quasi-one-dimensional compounds (Monceau, 1985; Grüner and Zettl, 1985). Most of the known materials have acicular morphology and metallic luster, as do many sulfosalts (Kostov and Minčeva-Stefanova, 1982). Therefore an examination of sulfosalts was undertaken.

Above its phase transition, a charge-density-wave material is metallic; below the transition, it is a semiconductor with a small band gap, of order 0.1 eV. The three sulfosalts that we have examined have band gaps between 1.4 and 1.5 eV. Thus they are conventional semiconductors without charge-density waves.

### SPECIMENS

Naturally occurring and laboratory-grown specimens were examined. The Smithsonian Institution provided natural specimens of boulangerite (catalogue no. 115863, from Zacatecas, Mexico), jamesonite (161768, Zacatecas, Mexico), and heteromorphite (B4676, Příbram, Czechoslovakia). A second specimen of jamesonite, also from Zacatecas, was obtained from a commercial mineralogical supply house (Burminco Minerals, Monrovia, California).

Boulangerite was grown by vapor transport in sealed, evacuated quartz tubes containing a roughly stoichiometric mixture of the starting materials PbS powder (purity 99.9%), Sb pellets (99.999%), and S powder (99.999%). A transparent, homemade furnace produced a temperature gradient from 400 to 600 °C across the 30-cm length of the tubes. Over the course of several days, small needles of boulangerite grew in fibrous patches in the hotter half of the tube. In the same tube, large needles of the binary compound stibnite ( $\text{Sb}_2\text{S}_3$ ) grew near the cool end. The compounds were identified by comparing X-ray powder-diffraction patterns to published data (McClune, 1982). Patterns from the laboratory-grown boulangerite speci-

mens were also compared to a pattern produced from the Smithsonian specimens; peaks were located at the same angles, but the relative intensities of several peaks differed.

### EXPERIMENTAL TECHNIQUES

For room-temperature electrical resistance measurements, each specimen was mounted between the center conductors of two parallel, semirigid coaxial cables whose outer conductors were soldered together. Electrical contact was made with water-dispersed graphite (Aquadag). Measurements were made with a General Radio electrometer. Specimens were measured in the dark to avoid photoconduction.

An attempt was made to determine the band gaps from Arrhenius plots of  $\log \rho$  vs.  $1/T$ . The specimens were heated to 250 °C in air. To avoid thermoelectric effects, an audio-frequency voltage was applied across the specimen, and the resulting current was measured with a Princeton Applied Research current-sensitive amplifier and phase-sensitive detector. Although some boulangerite specimens gave straight-line plots with slopes translating into an energy gap  $2\Delta \approx 1.4$  eV, reliable gaps were not obtained for most specimens because the plots usually were not straight or depended on thermal history. Apparently the specimens were adversely affected by heating, perhaps by driving off the S.

To obtain band gap values without heating the samples, photoconductivity was measured at room temperature. The specimens were mounted as for the  $\rho$  measurement, a dc voltage was applied, and ac response to chopped light was monitored using the current amplifier. Because the onset of photoconductivity was not sharp owing to band tailing (Pankove, 1971), the gap was taken to be the photon energy at which the photocurrent reached half its maximum value.

### RESULTS

All specimens showed semiconducting electrical behavior near room temperature: their resistivities  $\rho$  ranged in order of magnitude from  $10^4$  to  $10^8 \Omega\text{-cm}$ , and  $\rho$  decreased with increasing temperature.

TABLE 1. Band gaps and resistivities

Material	Formula	Source	$2\Delta$ (eV)	$\rho$ ( $\Omega \cdot \text{cm}$ )
Boulangerite	$\text{Pb}_5\text{Sb}_4\text{S}_{11}$	Smithsonian	1.47	$4 \times 10^7$
		synthetic	1.43*	$3 \times 10^8$
Jamesonite	$\text{FePb}_3\text{Sb}_6\text{S}_{14}$	Smithsonian	1.49	$4 \times 10^7$
		Burminco	1.47	$\leq 1 \times 10^7$
Heteromorphite	$\text{Pb}_7\text{Sb}_6\text{S}_{19}$	Smithsonian	1.41	$6 \times 10^8$
Stibnite**	$\text{Sb}_2\text{S}_3$	synthetic	1.58	$6 \times 10^4$

Note:  $2\Delta$  = band gap from photoconductivity threshold.  $\rho$  = approximate room-temperature electrical resistivity.  
 \* Weak photo response.  
 \*\* Included for comparison.

Mean resistivity values are given in Table 1. For boulangerite, heteromorphite, and stibnite, the standard deviation between specimens from the same source was about 30% of the mean. Resistivities were consistently an order of magnitude larger for synthetic as opposed to natural boulangerite. Jamesonite results were especially variable. The standard deviation was nearly 75% of the mean for those from the Smithsonian, and resistivities ranged so widely for the Burminco samples as to make the mean meaningless—only the largest value is quoted here. Presumably the variations are due to impurities.

Photoconductive gap values are also given in Table 1. All three sulfosalts had gaps in the range 1.4 to 1.5 eV, somewhat smaller than the value of 1.58 eV for  $\text{Sb}_2\text{S}_3$ . Our stibnite value may be compared with that from optical transmission through thin films, which varied from 1.72 eV for stoichiometric  $\text{Sb}_2\text{S}_3$  through 1.60 eV with S deficiency (Efstathiou and Levin, 1968); other reported values range from 1.55 to 1.92 eV (Skubenko and Lapshii, 1962; Tandon and Gupta, 1970). Stibnite and the natural specimens showed strong photoresponses. However the photocurrent in synthetic boulangerite was very weak, indicating rapid recombination processes.

## DISCUSSION

All materials examined obey the  $(8 - N)$  valence rule, ascribing +3 to Sb, +2 to Pb and Fe, and -2 to S. Their conventional semiconducting behaviors indicate that all bonds are indeed satisfied, despite the complex structures and despite the presence of transition-metal ions in jamesonite. If charge-density-wave materials are to be found among sulfosalts, attention should be directed toward compounds containing more complex arrays of transition-metal ions or to the possibility of Te substitution for S.

Several differences were observed between the natural and synthetic boulangerite. Besides differences in intensities of some X-ray peaks, the synthetic specimens had substantially larger resistivities and substantially weaker photoconductivity. The differences should probably be attributed to impurities or defects. In the absence of chemical analysis, it is difficult to guess the identities of the active impurities, and the nature of point defects in sulfosalts is a completely open question. The existence of

active impurities or defects could be established by photoabsorption or photoluminescence.

Furthermore, it is not apparent whether the differences should be attributed to impurities or defects in the natural materials or to defects in the synthetic ones, which were grown rapidly under very nongeological conditions. The effect of impurities can be either to increase the resistivity (by compensating other impurities, or perhaps by increasing scattering) or to decrease it (by acting as donors or acceptors). Independently of the effect on  $\rho$ , the impurities can strengthen the photoresponse by increasing the recombination time, a process known as "sensitizing" (Bube, 1960; Rose, 1963), or the impurities can weaken the photoresponse by introducing additional recombination centers. Sensitization can sometimes be identified by observing a supralinear dependence of photocurrent on light intensity (Rose, 1963, p. 48). Our apparatus was not suited to such quantitative measurements. Thus we cannot be specific about the reasons for the differences between the natural and synthetic specimens. Our current guess is that impurities in the natural specimens are sensitizing them. We base this guess on (1) the high purity of our starting materials, (2) the fact that the apparent nonstoichiometry of our stibnite (as indicated by its gap of 1.58 eV) did not adversely affect the strength of its photoresponse, and (3) the great variability of  $\rho$  in the natural jamesonite.

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## REFERENCES CITED

- Bube, R.H. (1960) Photoconductivity of solids, 461 p. Wiley, New York.  
 Efstathiou, A., and Levin, E.R. (1968) Optical properties of  $\text{As}_2\text{Se}_3$ ,  $(\text{As}_x\text{Sb}_{1-x})_2\text{Se}_3$ , and  $\text{Sb}_2\text{S}_3$ . Journal of the Optical Society of America, 58, 373-377.  
 Grüner, G., and Zettl, A. (1985) Charge density wave conduction: A novel collective transport phenomenon in solids. Physics Reports, 119, 117-232.  
 Kostov, I., and Minčeva-Stefanova, J. (1982) Sulphide minerals, 212 p. Nägele and Obermiller, Stuttgart.  
 McClune, W.F. (1982) Powder diffraction file, inorganic phases, 977 p. International Centre for Diffraction Data, Swarthmore, Pennsylvania.  
 Monceau, P. (1985) Electronic properties of inorganic quasi-one-dimensional compounds, part II, 323 p. Reidel, Dordrecht, Netherlands.  
 Pankove, J.I. (1971) Optical processes in semiconductors, 422 p. Prentice-Hall, Englewood Cliffs, New Jersey.  
 Rose, A. (1963) Concepts in photoconductivity and related problems, 168 p. Interscience, New York.  
 Skubenko, A.F., and Lapshii, S.V. (1962) Optical properties of  $\text{Sb}_2\text{S}_3$  single crystals. Soviet Physics Solid State, 4, 327-330.  
 Tandon, S.P., and Gupta, J.P. (1970) Measurement of forbidden energy gap of semiconductors by diffuse reflectance technique. Physica Status Solidi, 38, 363-367.