

Optical band gaps of selected ternary sulfide minerals

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ABSTRACT

Optical band gaps for a set of 23 ternary and quaternary sulfide minerals have been measured by diffuse reflectance spectroscopy. Comparison of band gaps measured by diffuse reflectance with band gaps determined by single-crystal methods for 12 binary sulfides demonstrates that the diffuse reflectance measurement produces results accurate to within 0.1 eV. Unlike the band gaps of binary sulfides that plot linearly with various measures of bond energy, the ternary and quaternary sulfides cluster within ranges determined by the chemical composition. The band gaps for the ternary and quaternary sulfides tend to lie between the band gaps of the component binary sulfides.

INTRODUCTION

Many sulfide minerals are classed as semiconductors (see e.g., Shuey 1975). They have substantial electrical conductivity, high refractive indices, and often a metallic luster. A fundamental property of semiconductor compounds is the band gap, the energy separation between the filled valence band constructed mainly from sulfur p-orbitals, and the empty conduction band constructed mainly from empty cation orbitals. The bonding arrangement for sulfide minerals, particularly ternary sulfide minerals, is often quite complicated (see e.g., Vaughan and Craig 1978).

Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorptivity at the wavelength corresponding to the gap energy. This feature in the optical spectrum is known as the optical absorption edge. For those structures with band gaps in the range of 0.5 to 3 eV, the optical absorption edge can be easily measured by conventional optical spectroscopy. The complete band structure includes states spanning 30 to 50 eV (Vaughan 1985). The optical absorption edge gives only the lowest energy of this group of states.

The present paper presents optical absorption edges for a selection of ternary sulfide minerals, mainly sulfosalts, and discusses the estimated band gaps in relation to the chemical bonding in these structures.

EXPERIMENTAL METHODS

Sources of minerals

The minerals used in this investigation were obtained from various museum and commercial sources (Table 1). Identification and phase purity of all minerals were checked by X-ray diffraction. In a few cases, electron microprobe analyses were made to determine phase com-

position. For the binary compounds, reagent grade chemicals were used and the crystal structures were checked by X-ray diffraction.

Some compounds of interest, which were not available as natural minerals, were synthesized. The appropriate binary sulfides were mixed in stoichiometric proportions, ground together under acetone, pressed into pellets, and fired in sealed evacuated silica tubes. Details are given in Table 2.

Diffuse reflectance spectroscopy

Samples were ground to a fine powder under acetone and packed into shallow aluminum sample plaques. The spectra were measured with a Beckman DK-2A spectrophotometer equipped with an integrating sphere diffuse reflectance attachment. The sphere was coated with a Kodak BaSO₄ optical paint. A sample plaque coated with the optical paint was also used as the reference. A PbS solid state detector was used from 2700 nm to 500 nm. A photomultiplier detector was used at wavelengths shorter than 500 nm. Only the diffuse component of the reflected light was collected.

Diffuse reflectance data are often converted to absorptivities by the Kubelka-Munk function (Wendlandt and Hecht 1966).

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{\alpha}{s} \quad (1)$$

where $R_{\infty} = (I/I_0)_{\text{diffuse}}$, the diffuse reflectivity from an infinitely thick layer of powder (about 2 mm for typical sulfides), α = absorptivity in units of cm^{-1} , and s = scattering factor largely independent of wavelength for particle sizes larger than the wavelength of light. However, it was found that a plot of $\log(I_0/I_{\text{diffuse}})$ against wavelength gave an acceptably accurate representation of the spectrum. This quantity is termed "absorbance" in the figures and is defined as

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TABLE 1. Sources of minerals

Mineral	Composition	Source	Locality
Boulangerite	5PbS·2Sb ₂ S ₃	SWMS	Zacatecas, Mexico
Bournonite	2PbS·Cu ₂ S·Sb ₂ S ₃	MU	Mineral King Mine, British Columbia
Cylindrite	Pb ₃ Sn ₄ Sb ₂ S ₁₄	MI	Poopo, Bolivia
Enargite	Cu ₃ As ₄	MI	Zacatecas, Mexico
Franckeite	Pb ₂ Sn ₃ Sb ₂ S ₁₄	MI	Itos Mine, Oruro, Bolivia
Fülöppite	3PbS·4Sb ₂ S ₃	MU	Baia Mare, Romania
Gratonite	9PbS·2As ₂ S ₃	W	Cerre de Pasco, Peru
Livingstonite	HgSb ₇ S ₈	W	Unknown
Lorandite	Tl ₂ S·As ₂ S ₃	W	Allchar, Macedonia
Meneghinite	Cu ₂ S·26PbS·7Sb ₂ S ₃	W	Barrie Twp., Ontario
Miargyrite	AgSbS ₂	MU	Santa Fe Mine, Red Mt. Randsburg mining district
Owyheeite	5PbS·Ag ₂ S·3Sb ₂ S ₃	MU	Near Gabbs, Nye Co., Nevada
Plagionite	5PbS·4Sb ₂ S ₃	USNM	Wolfsberg, Harz, Germany
Proustite	3Ag ₂ S·As ₂ S ₃	W	Marienberg, Saxony, Germany
Pyrrargyrite	3Ag ₂ S·Sb ₂ S ₃	W	Highland Bell Mine, Beaverdell, British Columbia
Semseyite	9PbS·4Sb ₂ S ₃	W	Herja, Romania
Stephanite	Ag ₃ SbS ₄	W	Freiberg, Saxony, Germany
Zinckenite	6PbS·7Sb ₂ S ₃	W	Stevens Co., Washington

Note: MI = Penn State Mineral Museum; MU = Minerals Unlimited, Ridgecrest, CA; SWMS = Southwest Mineral Supplies; USNM = National Museum of Natural History, Washington, DC; W = Wards, Rochester, NY.

$$\text{abs} = \log \left[\frac{\text{diffuse reflectance of BaSO}_4}{\text{diffuse reflectance of sample}} \right] \quad (2)$$

A basic assumption in diffuse reflectance spectroscopy is that light is transmitted through the powder particles a number of times combined with multiple reflections as the light moves from grain to grain into the powder layer and back out again. When the powder is highly absorbing, surface reflectivity of the grains becomes a dominant effect and the observed spectrum becomes more like a specular reflectance spectrum than an absorption spectrum. For this reason, diffuse reflectance measurements at very high absorbances are not true measures of the absorbance. This effect is responsible for the slight bending over of some of the spectra near the top of the absorbance scale.

In a few of the spectra, the "absorbance" drops below zero in the low absorbance region. This is an artifact due to spectral regions in which the reflectance of the sample is greater than the reflectance of the BaSO₄ reference. The small dips near 1400 and 1900 nm are due to tiny amounts of water adsorbed on the reference material.

TABLE 2. Conditions for synthesis

Mineral	Composition	
—	Ag ₂ S·Sb ₂ S ₃ (cubic)	Heated for 45 h at 450 °C and cooled slowly for 2 h to room temperature.
Dufrenoyite	2PbS·As ₂ S ₃	Heated at 620 °C for 24 h, then quenched in water. Annealed for 4 days at 200 °C.
Jordanite	27PbS·7As ₂ S ₃	Heated for 60 h at 450 °C and cooled for 2 h to room temperature.
Proustite	3Ag ₂ S·As ₂ S ₃	Heated for 30 h at 450 °C and cooled slowly.
Pyrrargyrite	3Ag ₂ S·Sb ₂ S ₃	Heated for 48 h at 450 °C.
Smithite	AgAsS ₂	Heated at 595 °C for 14 h and quenched. The resulting material was powdered and annealed for 14 h at 380 °C.

Extraction of the optical absorption edge

An ideal semiconductor or insulator, with no defects or impurities, has an intrinsic absorptivity in the range of 10⁻² to 10⁻⁴/cm at wavelengths between the Urbach tail of the electronic edge at the short wavelength limit and the phonon edge at the long wavelength limit. The phonon edge is determined by the multiphonon tail of the intrinsic vibrational modes. The phonon edge occurs at roughly twice the highest wavenumber longitudinal phonon (White 1990). For sulfides the phonon edge occurs in the range of 1000–1500 cm⁻¹, well beyond the range of the present measurements. The diffuse reflectance at the long wavelength end of the measured spectra is dominated by reflection and scattering due to the high refractive index of the sulfide compounds.

At the absorption edge, the absorptivity rises rapidly to values in the range of 10⁵ to 10⁶/cm due to the strongly allowed transition moments of the interband transitions. Measurement of the entire interband absorption spectrum by direct transmission requires films with thicknesses of 10 to 100 nm. Alternatively the spectra can be measured by specular reflectance followed by deconvolution of the reflectance curves to separate the real and imaginary parts of the refractive index.

Diffuse reflectance spectroscopy can be used to determine the optical absorption edge but not much more of the interband spectrum although Wood and Strens (1979) attempted to use diffuse reflectance measurements to the edge of the vacuum ultraviolet at 200 nm. The ideal diffuse reflectance spectrum (for example, the spectra of wurtzite and greenockite in Fig. 1) consists of a nearly flat, low absorbance region at long wavelengths that abruptly transforms to a steeply rising absorption edge at shorter wavelengths.

The most direct way of extracting the optical band gap is to simply determine the wavelength at which the extrapolations of the base line and the absorption edge

TABLE 3. Comparison of measured band gaps with literature values

Compound	E_g (ex)	E_g (McL)	E_g (lit)	Method	Reference
Ag ₂ S	0.92	—	—	Diffuse Reflectance	This investigation
As ₂ S ₃	—	—	2.37	Transmission	Evans and Young (1967)
CdS (h)	2.30	2.43	2.452	Electroreflectance	Cardona et al. (1967)
GaAs	1.32	1.38	1.435	Transmission	Sturge (1962)
GaSb	0.648	0.672	0.74	Faraday Effect	Piller et al. (1963)
Ge	0.67	0.616	0.74	Transmission	Dash and Newman (1955)
HgS	1.97	1.98	1.99	Transmission	Dovgii and Bilen'kii (1966)
			2.02	Transmission	Nakada (1975)
InP	1.22	1.26	1.34	Electroreflectance	Cardona (1961)
			1.351	Absorption	Turner et al. (1964)
PbS	—	—	0.37	Transmission	Schoolar and Dixon (1965)
Sb ₂ S ₃	—	—	1.72	Transmission	Efstathiou and Levin (1968)
Si	1.03	0.987	1.07	Reflectivity	Cardona (1961)
SnS	1.01	0.87	1.07	Transmission	Albers (1960)
ZnS(c)	—	—	3.64	Transmission	Brafman and Steinberger (1966)
ZnS (h)	3.55	—	3.74(II)	Transmission	Brafman and Steinberger (1966)
			3.71(L)		
ZnSe(c)	2.45	—	2.67	Reflectance	Cardona (1961)
ZnTe(c)	2.16	—	2.25	Electroreflectance	Cardona et al. (1967)

Note: All entries are in units of eV. E_g (ex) obtained by direct extrapolation of measured optical absorption edge. E_g (McL) obtained by McLean analysis. E_g (lit) entries are taken from the literature as noted. Most of the literature values were from measurements on single crystals or thin films. h = hexagonal, c = cubic.

cross. This measurement was first applied by Fochs (1956) to Se, Si, and Ge and was used successfully by Keester and White (1969) for the lead oxides, by Tandon and Gupta (1970) for a variety of binary compounds, and by Schevciw and White (1983) for a series of rare earth sulfides.

In non-cubic crystals, the optical absorption edge is dependent on crystallographic direction producing a pronounced pleochroism if the edge is in the visible region. Diffuse reflectance measurements on powders, therefore, give an average edge. Defects and impurities introduce

trap states just below the conduction band or just above the valence band. Absorption by defect and impurity states cause a smearing of the absorption edge and thus a less precise estimation of the optical band gap.

A bit more information about the lowest energy inter-band transition can be obtained by a McLean analysis of the absorption edge. McLean (1960) derived the equation

$$\alpha h\nu = (h\nu - E_g + E_p)^{1/n} \quad (3)$$

where E_g is the band gap and E_p is the phonon energy for indirect transitions. The analysis consists of fitting the absorption edge to Equation 3 and determining experimental values for E_g and n . A value of $n = 2$ implies a direct allowed transition; $n = 3/2$ implies a direct forbidden transition; $n = 1/2$ implies an indirect allowed transition; $n = 1/3$ implies an indirect forbidden transition.

Literature comparisons of binary compounds

Absorption edges were measured for 12 binary semiconductors for which single crystal optical or electrical band gap measurements were available. Nine of the spectra are shown in Figure 1. Values for the band gap obtained directly from the absorption edge and from a McLean analysis of the measured edge (Table 3) are compared with values reported in the literature. Also included are literature band gaps for the binary sulfides that comprise the components of the ternary sulfides examined here. Several compounds, notably HgS and Ge, give band gaps in good agreement with the single-crystal measurements but most appear to be about 0.1 eV low. In only one compound, ZnSe, was the discrepancy as much as 0.2 eV.

Comparison of the two methods of extracting band gaps from the diffuse reflectance spectra show that the McLean analysis provides no substantial improvement over a simple extrapolation of the absorption edge. Over-

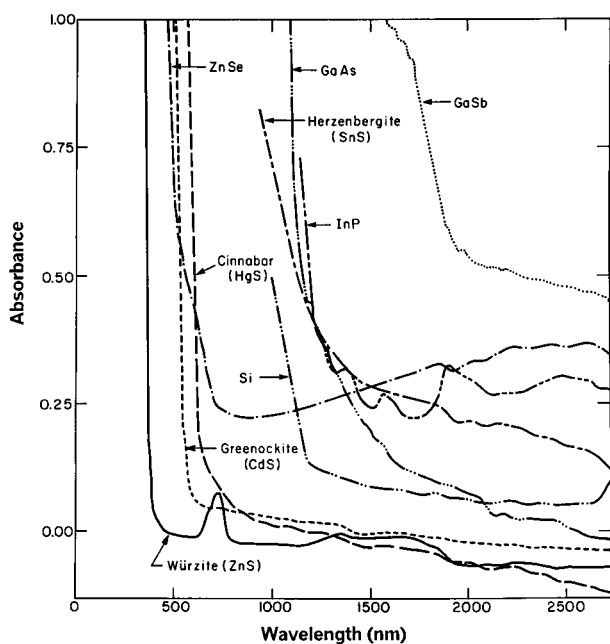


FIGURE 1. Absorption edge spectra for various binary semiconductors. All samples are synthetic.

TABLE 4. Measured band gaps of ternary sulfide minerals

Mineral	Composition	Space group*	E_g (min)	E_g (syn)	E_g (lit)
Boulangerite	$Pb_3Sb_4S_{11}$	$P2_1/a$	1.34	—	1.47†
Bourmonite	$PbCuSbS_3$	$Pnm2_1$	1.23	—	—
Cylindrite	$Pb_3Sn_4Sb_2S_{14}$	$P1$	0.65	—	—
Dufrenoyite	$Pb_2As_2S_5$	$P2_1/m$	—	1.39	—
Enargite	$Cu_3As_4S_4$	$Pmn2_1$	1.28	—	1.46‡
Franckeite	$Pb_2Sn_3Sb_2S_{14}$	$P1$	0.65	—	—
Fülöppite	$Pb_3Sb_4S_{15}$	$C2/c$	1.63	—	—
Gratonite	$Pb_9As_4S_{15}$	$R3m$	1.59	—	—
Jordanite	$Pb_{14}As_6S_{23}$	$P2_1/m$	—	1.38	—
Livingstonite	$HgSb_4S_8$	$A2/a$	1.68	—	—
Lorandite	$TlAsS_2$	$P2_1/a$	1.80	—	2.25§
Meneghinite	$CuPb_{13}Sb_2S_{24}$	$Pnm2_1$	1.44	—	—
Miargyrite	$AgSbS_2$	Aa	1.72	—	—
—	$AgSbS_2(c)$	$Fm3m$	—	1.22	—
Owyheite	$Pb_{10}Ag_3Sb_{11}S_{28}$	$Pnam$	1.39	—	—
Plagionite	$Pb_2Sb_3S_{17}$	$C2/c$	1.53	—	—
Proustite	Ag_3AsS_3	$R3c$	1.85	1.38	—
Pyrrargyrite	Ag_3SbS_3	$R3c$	1.84	1.85	—
Rathite II	$Pb_{19}As_{26}S_{58}$	$P2_1$	1.59	—	—
Semseyite	$Pb_9Sb_4S_{21}$	$C2/c$	1.50	—	—
Smithite	$AgAsS_2$	$A2/a$	—	1.95	—
Stephanite	Ag_3SbS_3	$Cmc2_1$	1.62	—	—
Zinckenite	$Pb_3Sb_2S_{42}$	$P6_3$	1.48	—	—

Note: E_g (min) = optical absorption edge measured on mineral samples; E_g (syn) = optical absorption edge measured on synthetic samples; E_g (lit) values obtained from the literature as noted. All data are in units of eV.

* Anthony et al. (1995).

† Lomelino and Mozurkewich (1989).

‡ Wood and Strens (1979).

§ Bernroider and Amthauer (1994).

all, determination of the optical band gap from diffuse reflectance spectra of the optical absorption edge gives values that are within 0.1 eV of band gaps determined on single crystals by various methods. Measurements of thin films and single crystals by different investigators also vary by about 0.1 eV, depending on the method of measurement.

RESULTS

The measured absorption edge spectra were organized by composition (Figs. 2–7). The extracted values of the optical band gap are listed in Table 4, in separate columns for those measured on natural minerals and those measured on synthetic materials. Table 4 also lists the few measurements that have appeared in the literature.

The absorption edges for ternary sulfides with compositions in the Pb-As-S and Pb-Sb-S systems are reasonably sharp (Figs. 2 and 3). The band gaps for the arsenic and the antimony sulfides are surprisingly similar. As a check, $PbS \cdot Bi_3S_3$ was synthesized and its reflectance spectrum measured. The absorption edge for this compound lies at longer wavelengths than could be reached with the present measurements.

Lorandite is the only thallium-containing mineral in the set, and livingstonite is the only mercury-containing mineral. Both have a crisp and sharp absorption edge (Fig. 4). The sharp edge of lorandite at 682 nm gives the mineral its deep red color. Lorandite was the only mineral measured for which there was a substantial dis-

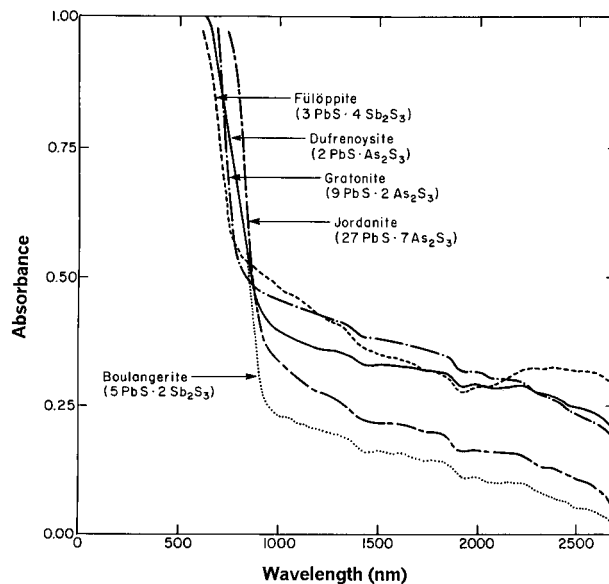


FIGURE 2. Absorption edge spectra for ternary Pb-As-S and Pb-Sb-S sulfide minerals.

crepancy with the literature. Bernroider and Amthauer (1994) reported 2.25 eV from polarized spectra of a single crystal, with a small difference between the absorption edges measured parallel and perpendicular to [010]. Extrapolation of their spectra by the same methods used for the diffuse reflectance spectra gave 2.16 eV. Both values are substantially larger than the band gap of 1.80 eV measured using diffuse reflectance. Careful compar-

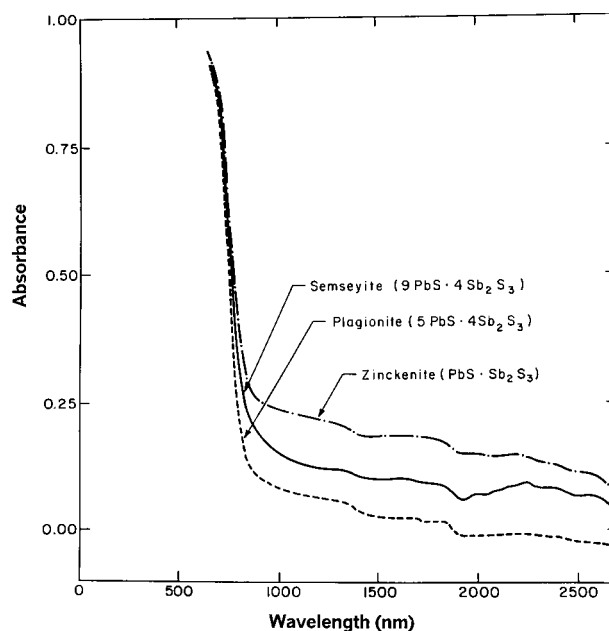


FIGURE 3. Absorption edge spectra for ternary Pb-Sb-S sulfide minerals.

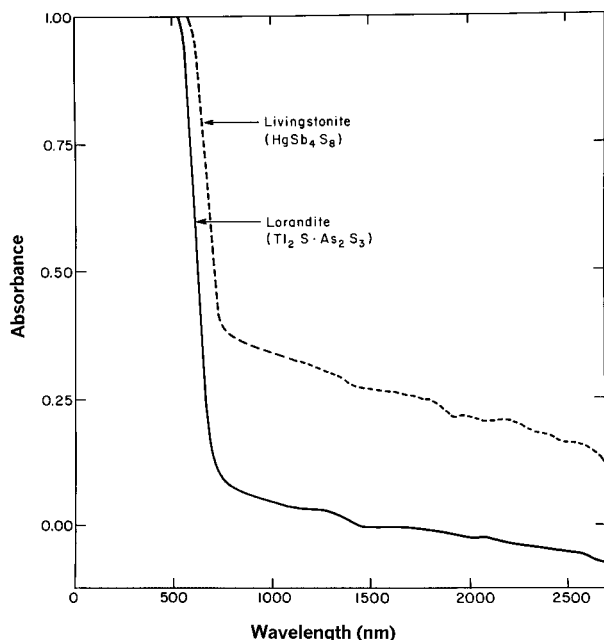


FIGURE 4. Absorption edge spectra for ternary Hg-Sb-S and Tl-As-S minerals.

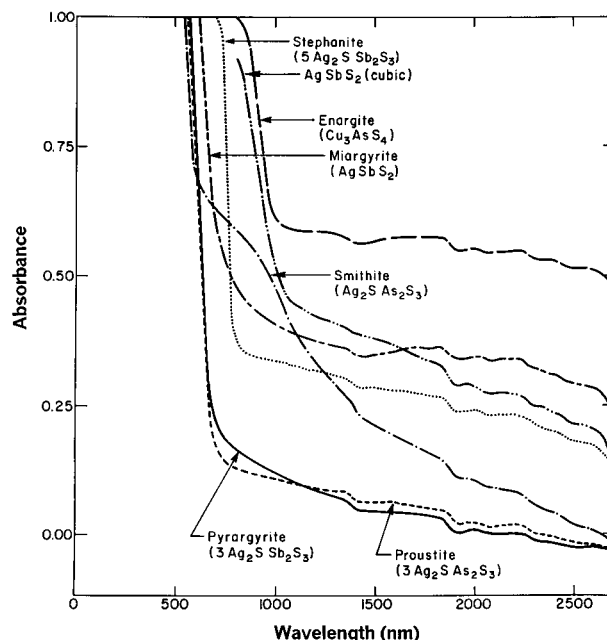


FIGURE 5. Absorption edge spectra for ternary Ag-As-S, Ag-Sb-S, and Cu-As-S minerals.

ison of the spectra revealed no obvious reason for the discrepancy.

Spectra of the ternary Ag-As-S and Ag-Sb-S minerals (Fig. 5) show a much greater range of absorption edges than was found in the Pb-As-S and Pb-Sb-S minerals (Figs. 2 and 3). The spectrum of synthetic smithite contains a shoulder that masks the onset of the absorption edge. A similar feature exists in the spectrum of synthetic proustite (not shown). These shoulders appear to be due to defect states that introduce additional absorption just below the absorption edge and interfere with optical measurement of the band gap. As a result, the apparent band gap of synthetic proustite is 1.38 eV, substantially lower than the 1.85 eV determined from the sharp absorption edge of the natural specimen. The band gap of miargyrite, AgSbS_2 , is substantially higher than the band gap of the high temperature cubic polymorph of AgSbS_2 demonstrating the effect of structure and cation coordination on the band structure.

Minerals in the quaternary Cu-Pb-Sb-S and Ag-Pb-Sb-S systems have clean sharp absorption edges from which good values of the band gap can be extracted (Fig. 6), whereas for the two examples from the quaternary Pb-Sn-Sb-S system, the absorption increases slowly with decreasing wavelength (Fig. 7). It is impossible to determine whether the observed spectra in Figure 7 represent the intrinsic band edge or only some combination of impurity or defect states. The band gap obtained by extrapolating the absorption edge was 0.65 eV for both minerals, lower than those found for the other lead-antimony minerals.

INTERPRETATION OF ABSORPTION EDGES

Compilations of band gaps of binary compounds exhibit a wide range of values that apparently scale with measures of crystal structure and chemical bonding. It has long been known that the band gap can be considered, in a crude way, to be a measure of the separation between bonding and antibonding orbitals. Duffy (1990) compiled an extensive list of band gaps for binary com-

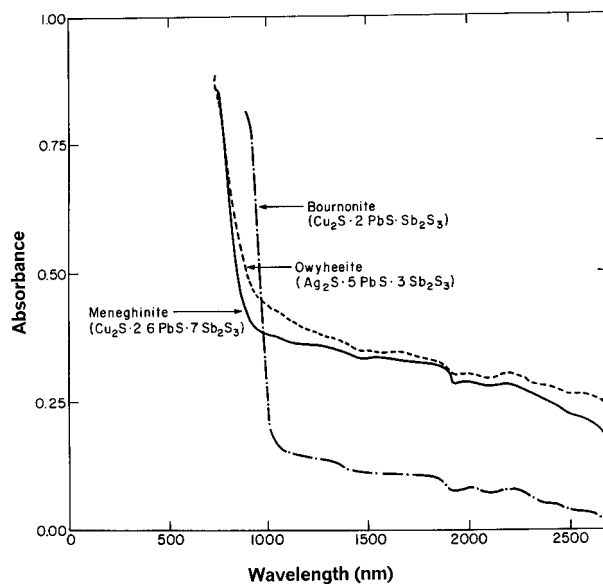


FIGURE 6. Absorption edge spectra for quaternary Ag-Pb-Sb-S and Cu-Pb-Sb-S minerals.

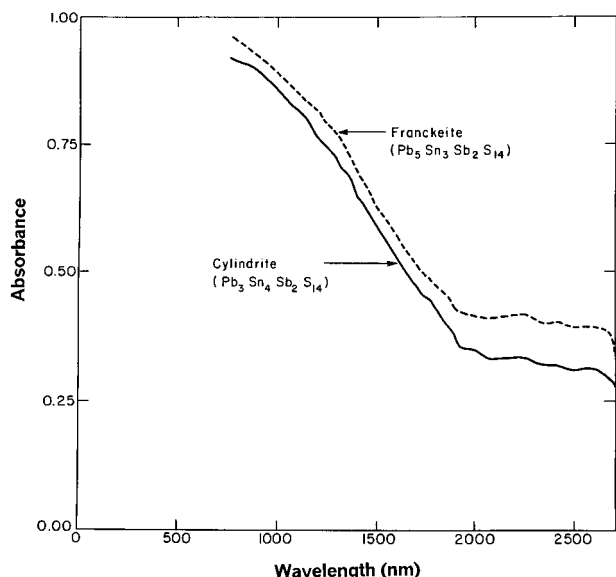


FIGURE 7. Absorption edge spectra for quaternary Pb-Sn-Sb-S minerals.

pounds and showed that there was a rough relationship between band gap and molar refraction. Bailly and Manca (1966) showed that the band gaps for compounds of similar charge and bond character (e.g., the alkali halides, the II-VI semiconductors, the III-V semiconductors, etc.) were linear functions of the Gibbs free energy of sublimation. Similar linear relations are found between band gaps of binary compounds and other measures of bond energy.

The band gaps measured on ternary and quaternary minerals (Fig. 8) are displayed in comparison with the band gaps of the binary component sulfides. The band gaps are arranged by composition in order of decreasing band gap. It is immediately apparent that the band gaps of the ternary compounds span a much smaller range of values that falls within the much larger range of the component binary sulfides. The binary sulfides have band gaps from 0.37 eV for PbS to 2.37 eV for As_2S_3 . All of the ternary minerals examined are arsenic or antimony compounds and in all of them the band gap is lowered substantially from the band gap of As_2S_3 . Some of the antimony minerals, pyrargyrite, miargyrite, gratonite, and fülöppite have band gaps very close to that of Sb_2S_3 itself. The Ag_2S and PbS components have low band gaps that do not persist in the ternary compounds, particularly the lead-arsenic and lead-antimony minerals.

Band gaps generally decrease from silver to lead to quaternary minerals but no distinct relationship exists with the separable details of the chemical bonds. The separation of the valence band from the conduction band is determined by a mixing of the various sulfur to metal transfer states between all of the atomic constituents of the mineral and details of the individual bonds are lost.

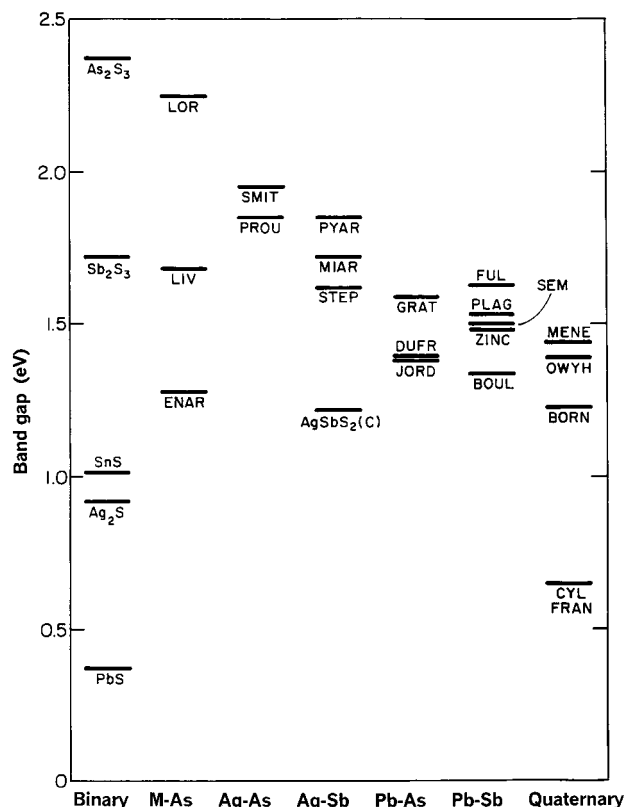


FIGURE 8. Graphic compilation of band gaps. The x axis indicates the compositional families as follows. Binary = compounds that are the components comprising the ternary and quaternary compounds. Ms-As, Ag-As, Ag-Sb, Pb-As, and Pb-Sb = components of the ternary sulfides. Quaternary = quaternary compounds examined here.

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