Optical band gaps of selected ternary sulfide minerals

STEVEN I. BOLDISH* and WILLIAM B. WHITE†

Intercollege Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

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 composition. 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).

\[ F(R_s) = \frac{(1-R_s)^2}{2R_s} = \frac{\infty}{s} \]  (1)

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