

Optical properties of the new potential infrared-detectors $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Cu, Fe, Mn, and Cd}$) series and the influence of M(II) exchange

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Abstract

The optical absorption of mixed-valence sulfites such as $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ [$\text{M} = \text{Cu, Fe, Mn, or Cd}$] were studied and the influence of the M(II) cation on this parameter. A transmission spectroscopy technique was used to measure the optical band gap energies (E_g) in the infrared region and the E_g of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cu(II)SO}_3 \cdot 2\text{H}_2\text{O}$ was estimated using a numerical fitting method that can be described empirically by $E_g(\chi_P) = -0.62\chi_P^2 + 1.88\chi_P - 0.5$, where χ_P is Pauling's electronegativity of metal M. The obtained values were in the interval 0.85–0.95 eV, representing a narrow E_g , which can identify these compounds as potential infrared-detectors.

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1. Introduction

Chevreur's salt, $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cu(II)SO}_3 \cdot 2\text{H}_2\text{O}$, and Chevreur's salt derivatives, $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ [$\text{M} = \text{Fe, Mn, or Cd}$], are known as stable mixed-valence sulfites forming an isomorphic series [1–8]. An X-ray study has shown the presence of two kinds of metal atoms: one with a distorted octahedral coordination [$\text{M(II)O}_4(\text{H}_2\text{O})_2$] and the other with a distorted tetrahedral coordination [$\text{Cu(I)O}_3\text{S}$], linked together to form a three-dimensional network with monoclinic structure pertaining to the $P2_1/n$ spatial group [1]. X-ray diffraction data also provided evidence of the replacement of Cu(II) by Mn(II), Fe(II), or Cd(II) in Chevreur's salt [2–7].

This system is of considerable interest in chemistry. Besides sulfite ion in Chevreur's salts being stable to air oxidation, as determined by XPS [8], the properties of mixed-valence compounds rarely represent the sum of separate

ions, but depend on the M(II) ionic radii. The selectivity of M(II) incorporation during salt formation has shown that replacement of Cu(II) with M(II) takes place preferentially in a decreasing order of hardness [3]. In this isomorphic series, the unit cell volume exhibits proportionality with the M(II) ionic radii ($R = 0.9585$) and the thermal conductivity decreases with the ionic radii of M(II) cations ($R = 0.9992$) [5].

There is evidence that Cu(I) and Cu(II) cations interact strongly. The electronic spectrum of Chevreur's salt shows an intervalence transfer transition band at 500 nm from the tetrahedral Cu(I) ions to the empty $3d_{x^2-y^2}$ level of e_g symmetry of the Cu(II) ions [6]. In addition to being responsible for the salt's red color, this band explains the linear correlation with the thermal conductivity observed when one considers the weighted average (88 pm) of the ionic radius of Cu(I) and Cu(II) [5,7]. Clearly, therefore, the properties of these compounds are strongly influenced by the divalent cation nature [4–7].

Mixed-valence sulfites can be useful as radiation detectors. Although Ge and Si radiation detectors were developed quite some time ago, the development of mixed

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element and compound semiconductors was fraught with difficulties, particularly because of micro-crystallinity, high defect densities, impurities and stoichiometric imbalances [9]. Compound semiconductors are generally derived from elements from groups 12 to 16 of the periodic table [8]. Most of the elements in these groups are soluble within each other and form homogenous solid solutions without alteration of their crystal structure. Because the atoms can form solid solutions over large ranges of miscibility, the basic problem in producing compound semiconductors is to obtain materials with an exact stoichiometry. Our previous findings confirm that the mixed-valence sulfites here have an exact stoichiometry [3–7].

A semiconductor is usually chosen as a radiation detector according to its mechanical and electrical properties, which must match the particular radiation measurement to be performed. In radiation detector applications, for instance, room temperature operations require a large band gap energy to reduce thermally generated leakage currents, while high-resolution radiation spectroscopy requires a small band gap energy [10]. In this case, the semiconductor must be cooled to reduce the carrier concentrations in the conduction band, keeping the thermal noise level acceptable. Hence, the band gap is a crucial factor in the design of electronic and optoelectronic devices [9–15].

This Letter reports on the optical absorption of mixed-valence sulfites such as $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ [$\text{M} = \text{Cu, Fe, Mn, or Cd}$] in the region of the fundamental band edge and the influence of the M(II) cation on this parameter. Transmission and photoacoustic spectroscopy techniques were used to determine those band gaps (E_g) at room temperature.

2. Experimental procedure

2.1. Material

Mixed-valence sulfites were prepared according to literature. Details of the steps involved in isomorphous series synthesis and characterization and their chemical and physical properties are discussed elsewhere [3–7].

2.2. Apparatus

2.2.1. Transmission and absorption measurements

Transmission spectroscopy measurements [11] were taken with a homemade spectrometer using a halogen lamp as the light source. The polychromatic beam is diffracted by a plane diffraction grating attached to a step-motor. Measurements of transmittance at near-normal incidence were made in the energy range of 0.84–1.4 eV. The transmission intensity was closely monitored to obtain an incidence as close to 90° as possible. The monochromatic light passing through the sample was detected by a germanium photodiode set behind the sample. The sample's weight was determined very carefully in order to produce thin compacted

regular pellets, avoiding significant density variations along the sample's surface, thus ensuring the sample's homogeneity and repeatability.

The photoacoustic spectroscopy (PAS) experiments were performed using a spectrometer consisting of a 1000 W xenon arc lamp whose beam was modulated by a mechanical chopper (SRS, model SR540). This technique is able to give the absorption spectrum of a given sample directly. A monochromator in combination with appropriate absorption filters to eliminate high order effects was used for wavelength selection. The monochromator output beam was then directed into a conventional photoacoustic cell, where a 1/2 in. diameter condenser microphone (Panasonic) was mounted on one of the walls. The microphone signal was preamplified and fed into a lock-in amplifier (SRS, model SR530). The absorption spectra were stored in a personal computer connected to the lock-in amplifier.

3. Results and discussion

Fig. 1 shows the light absorption spectra measured in the energy range of 0.84–1.4 eV for the three mixed-valence sulfites studied: $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Fe(II)SO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Mn(II)SO}_3 \cdot 2\text{H}_2\text{O}$, and $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cd(II)SO}_3 \cdot 2\text{H}_2\text{O}$. The $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cu(II)SO}_3 \cdot 2\text{H}_2\text{O}$ was also investigated by the same spectroscopical method and measuring systems (transmission), but no clear absorption structure was observed for this compound.

To obtain the optical band gap energies, two different analytical methods were applied to the experimental data,

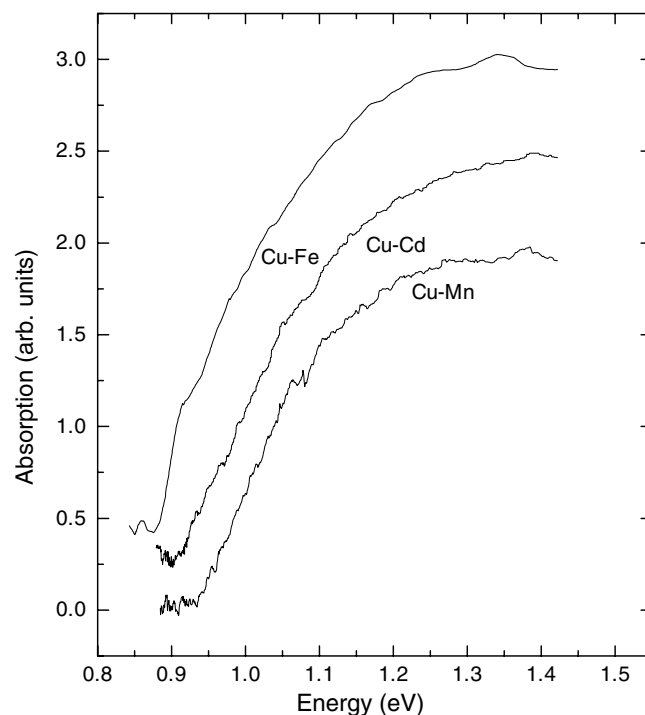


Fig. 1. Absorption spectra of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ [$\text{M} = \text{Fe, Mn, or Cd}$] as a function of photon energy, obtained by transmission spectroscopy.

as follows [12,13]: (i) the geometrical method, which uses the relation below, assuming direct band transitions

$$I = A(h\nu - E_g)^{1/2}, \quad (1)$$

where I is the absorption intensity, A is a coefficient, and $h\nu$ is the photon energy. The value of E_g was obtained by extrapolation of the best linear fit between I^2 and $h\nu$ up to the point where it crosses the ordinate axis; and (ii) evaluation of the absorption intensity derivative near the fundamental absorption edge. The inflection point of the first derivative gives E_g .

The band gap energy values determined by geometrical and derivative methods through transmission for mixed-valence sulfites containing either Cu(I)–Fe(II), Cu(I)–Mn(II), or Cu(I)–Cd(II) are summarized in Table 1. The total determination error of the energy gap is about 3%. The precision of our results is due to the large number of statistics, provided by long-term measuring routines. The errors derive from the absolute deviation of the measuring and the systematic deviation of optics, detectors and detection electronics.

Although the transmission and PA spectroscopy techniques were used efficiently to determine the band gap energies of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Fe(II)SO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Mn(II)SO}_3 \cdot 2\text{H}_2\text{O}$, and $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cd(II)SO}_3 \cdot 2\text{H}_2\text{O}$ in the infrared region, it was not possible to identify the experimental edge absorption energy for $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cu(II)SO}_3 \cdot 2\text{H}_2\text{O}$ in the range of photon energies used here. The energy gap between the valence and conduction states is defined by inter-atomic distance and the electronegativity of the component atoms. Analysis of the experimental data showed band gap energy to be dependent on Pauling's electronegativity of metal M (Fig. 2). This dependence can be given by the phenomenological expression (2)

$$E_g(\chi_P) = a_0\chi_P^2 + a_1\chi_P + c, \quad (2)$$

where χ_P is Pauling's electronegativity of metal M and a_0 , a_1 , and c are free parameters to be adjusted. The band gap energy of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cu(II)SO}_3 \cdot 2\text{H}_2\text{O}$ can be estimated using the above expression and a numerical fitting method. Its value was 0.850 ± 0.026 eV (Table 1). According to the fittings, the free parameters describing the electronegativity dependence of the band gaps of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ [M = Cu, Fe, Mn, or Cd] were determined as $a_0 = -0.62$, $a_1 = 1.88$, and $c = -0.5$.

The relation observed between electronegativity and the forbidden band energy opens up prospects for using this

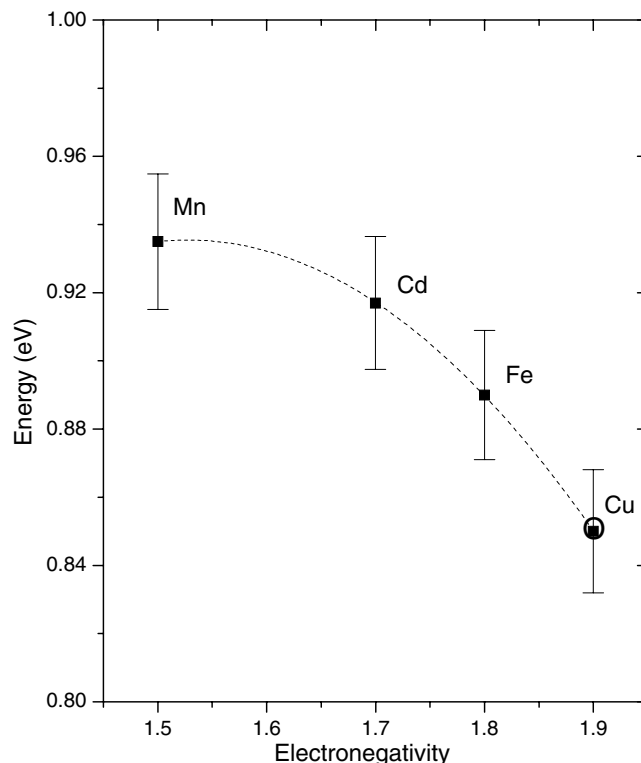


Fig. 2. Dependence of Pauling's electronegativity of metal M on direct band gap energies of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ compounds. At onset, the first point corresponds to manganese (M = Mn), the second point is related to cadmium (M = Cd), the third point is due to iron (M = Fe) and the last point on the right (M = Cu) was determined by numerical calculation.

family of compounds in the production of light detectors. According to Faschinger [9,15], modifying the electronic and chemical formulation of compound semiconductors can result in band gap engineering.

The energy gap varies smoothly from 0.85 to 0.95 eV with the replacement of Cu(II) by M(II), which indicates that the physical nature near the band edge remains reasonably unchanged with different compounds of the isomorphous series. This evidence also indicates that the crystal phase and the band-edge properties of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ [M = Cu, Fe, Mn, or Cd] series are similar.

At higher energies in the visible region the compounds exhibit a second light absorption structure starting at 1.2 eV. In Fig. 3, we can see the photoacoustic spectra for all compounds, clearly showing the second absorption

Table 1
Band gap energy values of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ [M = Cu, Fe, Mn, or Cd] determined by geometrical, derivative and fitting methods

Band gap energy (eV)	$\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$			
	M = Cu	M = Mn	M = Fe	M = Cd
Geometrical (infrared range)	–	0.935 ± 0.028	0.890 ± 0.027	0.917 ± 0.028
Derivative (infrared range)	–	0.952 ± 0.020	0.898 ± 0.027	0.931 ± 0.028
Calculation (infrared range)	0.850 ± 0.026	–	–	–
Geometrical (visible range)	1.306 ± 0.039	2.162 ± 0.065	1.861 ± 0.055	2.172 ± 0.065

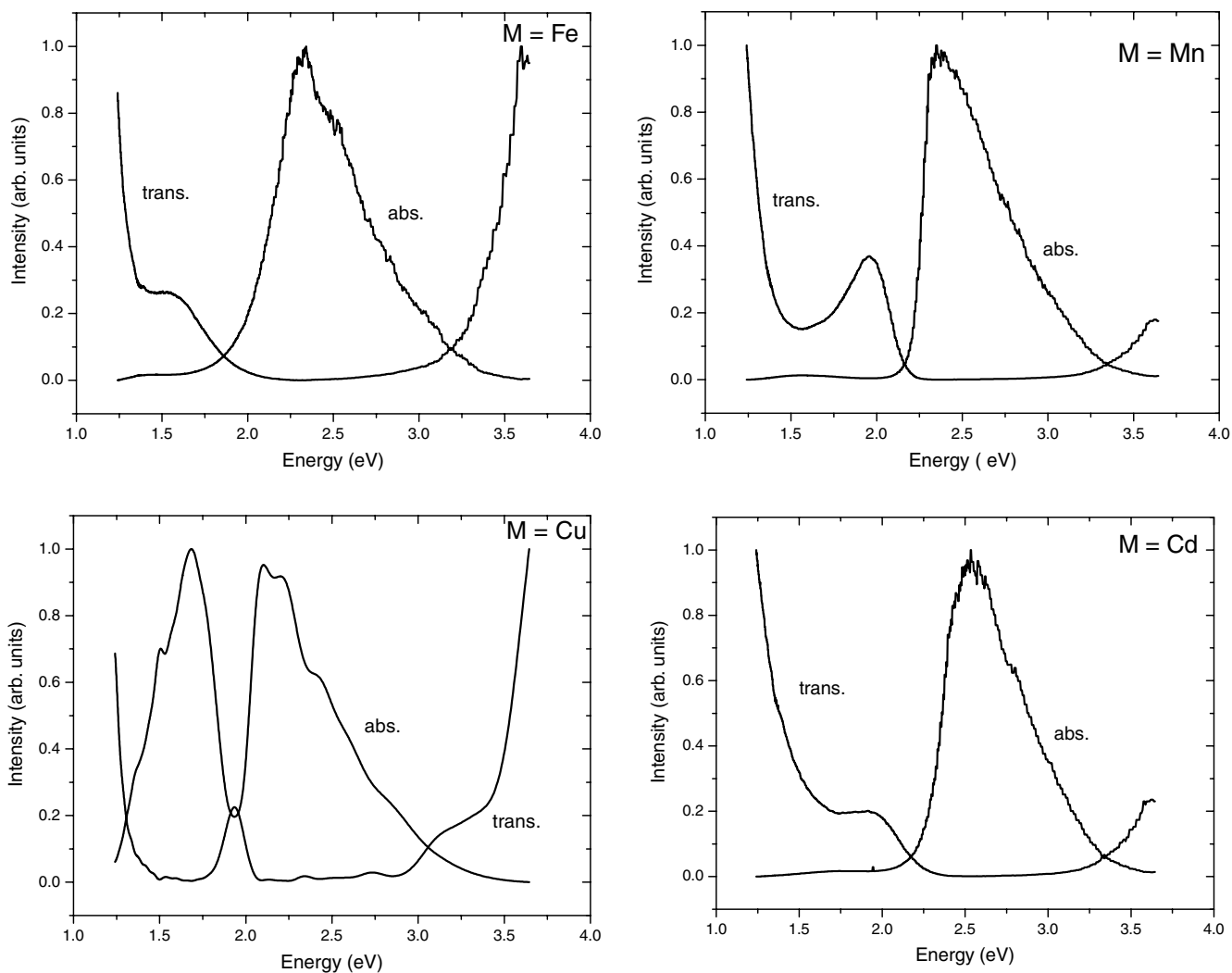


Fig. 3. Absorption and transmission spectra of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)SO}_3 \cdot 2\text{H}_2\text{O}$ [$\text{M} = \text{Cu}, \text{Fe}, \text{Mn}, \text{or Cd}$].

structure, especially attested to by an abrupt increase in the sample's light transmission at 1.9 eV for the $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cu(II)SO}_3 \cdot 2\text{H}_2\text{O}$ compound.

An analysis of the experimental data showed that the energy of this second band was also dependent on Pauling's electronegativity of metal M (see Fig. 4), just as were the results obtained for the gap energies presented in Fig. 2. The band gap energy values determined by geometrical method through PA spectroscopy for mixed-valence sulfites containing either Cu(I)–Cu(II), Cu(I)–Fe(II), Cu(I)–Mn(II), or Cu(I)–Cd(II) in the visible light are also summarized in Table 1.

The mixed-valence sulfites investigated proved to be narrow band gap semiconductors. Although wide band gap ($E_g > 3 \text{ eV}$) compounds are able to operate at room temperature, narrow band gap materials offer the potential to compete with the spectral response of both Si and Ge [10]. In terms of material development, our preliminary results appear to indicate that these compounds have a certain potential in NIR radiation spectroscopy detectors.

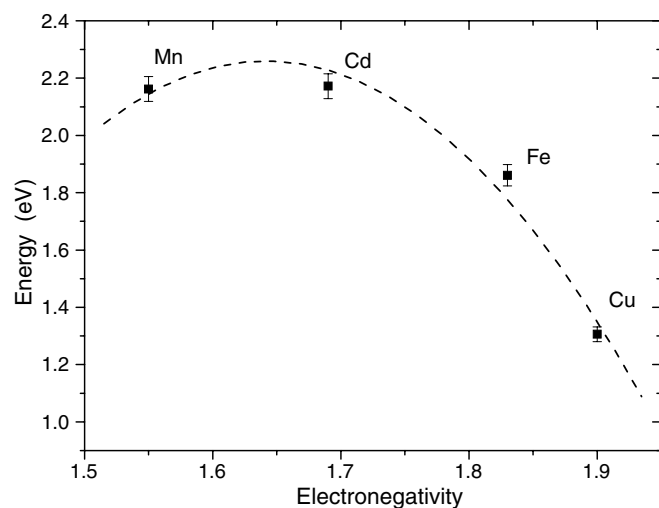


Fig. 4. Dependence of Pauling's electronegativity for a given metal M in the $\text{Cu(I)}_2\text{SO}_3 \cdot \text{M(II)} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$ compounds as a function of the second absorption structure energy from PA spectra.

4. Conclusions

The mixed-valence sulfites investigated by transmission and PA spectroscopy techniques and by two different methods to determine the fundamental band edge showed a semiconductor behavior. They exhibited a room temperature band gap in the interval of 0.85–0.95 eV. Changing the metal cation in the crystal structure of the mixed-valence sulfite changed the energy gap smoothly, which can be described empirically by $E_g(\chi_P) = a_0\chi_P^2 + a_1\chi_P + c$. The band gap energy of $\text{Cu(I)}_2\text{SO}_3 \cdot \text{Cu(II)SO}_3 \cdot 2\text{H}_2\text{O}$ was also estimated using this empirical model. The band gap energy values determined at higher energies (1.3–2.2 eV) were also dependent on Pauling's electronegativity of metal M, similarly to the results obtained at lower energies. The results in some aspects corroborate to the molecular modeling calculation carried out in Ref. [6] by two of the authors. Future improvements on the theory of electronic structure showing such transitions in this range of energy might be obtainable along the line of that calculation in a future work. The mixed-valence sulfites investigated here showed a narrow band gap and, in terms of material development, these compounds show a promising potential as infrared-detectors.

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