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Copper sulfides CuS have been synthesized by a reaction between [Cu(en)_2]^+ (en = ethylenediamine) and thiourea in alkaline solutions at different temperatures. The product obtained at 10°C (CuS-10) was amorphous and showed semiconductive properties with an electrical conductivity of 0.1 S cm^-1 at 298 K and 3.6 × 10^-3 S cm^-1 at 108 K, whereas the product at 30°C (CuS-30) was a crystalline CuS (covellete) that exhibited a metal-like temperature dependence with a conductivity of 92 S cm^-1 at 304 K and 104 S cm^-1 at 104 K. CuS-10 was changed to a crystalline CuS when annealed at 100–150°C. The resulting CuS had a higher crystallinity than that of CuS-30, and the electrical conductivity showed a metal-like temperature dependence: 27.5 cm^-1 at 299 K and 31 S cm^-1 at 98 K. When the reactions were conducted with an immersed polymer film in the solution, CuS films were formed on the substrate surface. The CuS-30 film and the annealed CuS-10 film were electroconductive and transparent in the visible spectral region. The synthesis of amorphous CuS followed by thermal treatment is a new method for the fabrication of metal sulfide films of high quality.

Metal sulfides show novel optical and electrical properties, and some of them are used for the fabrication of devices. Copper sulfides can be obtained with different stoichiometries. Their complex structures and valence states result in their interesting physical properties. 1-5 CuS, known as covellete, attracts special interest because it shows a metal-like electrical conductivity down to the liquid-helium temperature. 6 When a metal sulfide is deposited on a polymer substrate that is flexible and transparent, the resulting coated polymer film is expected to be useful for electronic and optical device applications. 6-10 CuS films on polymer substrates have been fabricated by a variety of techniques. 6-9 When a water-soluble copper(ii) compound that is dissociated readily reacts with an alkali-metal sulfide, a colloidal-like solid is formed at the first reaction stage and it is immediately converted to covellete. If, therefore, a highly stable copper(ii) chelate is used instead of the ionic copper(ii) compounds, a copper sulfide that is metastable at a metastable state is expected to be isolated. We have reported that a reaction between [Cu(cyclam)]^{+}Cl (cyclam: 1,4,8,11-tetraazacyclododecanec) and Na_2S gives CuS that has physical properties which differ from those of covellete. 11,12 The resulting CuS is amorphous and can be obtained in the form of a thin film supported on a polyester substrate. Thiourea has been reported to be a good sulfur source for the preparation of metal sulfides in an alkaline solution. 13 In the use of thiourea for the fabrication of a CuS film on a polymer substrate, a copper(ii) compound that exchanges with an adequate stability constant in solution are needed. In this paper, we report that a reaction between thiourea and bis(ethylenediamine)copper(ii) [Cu(en)_2]^+, gives two types of CuS depending on the reaction conditions. These copper sulfides have been characterized by electrical resistivity measurements, electronic spectroscopy, X-ray powder diffraction and scanning electron microscope (SEM) imaging.

Experimental
To an 8 mmol dm^-3 aqueous solution (125 cm^3) of Cu(en)_2Cl_2·2H_2O, a 1 mol dm^-3 NaOH solution (40 cm^3) was added, and then a 0.1 mol dm^-3 thiourea solution (40 cm^3) was added slowly. The resulting mixture was allowed to stand for 5.5 h at a controlled temperature. A green solid was obtained when the reaction was carried out at 30°C, and a brown solid was obtained at 10°C. Hereafter, the materials were represented by CuS-30 and CuS-10 in accordance with the reaction temperature. The solids obtained were washed with water and dried under vacuum at room temperature. Reaction at an intermediate temperature gave a heterogeneous mixture of the two materials. Cu(en)_2Cl_2·2H_2O was prepared by the addition of an ethanol solution containing CuCl_2·2H_2O (2.2 g, 6 mmol) to ethylenediamine (0.7 g, 12 mmol) in 20 cm^3 of ethanol. After the reaction mixture was allowed to stand for 0.5 h, the purple crystals formed were separated by filtration, washed with ethanol and dried under vacuum.

When the above reaction between Cu(en)_2Cl_2·2H_2O and thiourea was conducted with a polymer film immersed in a solution of Cu(en)_2Cl_2·2H_2O, the product was deposited on the surface of the substrate; a brown film and a green film were obtained at the reaction temperatures of 10°C and 30°C, respectively. Reactions at an intermediate temperature gave a heterogeneous film which was green and brown non-uniformly. The film was rinsed with water several times and dried under vacuum at room temperature. Polystyrene (PS), polyethylene terephthalate (PET) and 6-Nylon films were used as substrates. The polymer films were washed with detergent, rinsed well with water and washed with water in an ultrasonic cleaner. These pretreated films were washed with acetone in an ultrasonic cleaner before use.

The electrical conductivities of powder samples were determined on compressed pellets by the van der Paw four-probe method in the temperature range 100-300 K. The surface electrical conductivities of films were measured with a standard two-probe method, and the temperature dependence of the electrical conductivity was determined by using the van der Paw four-probe method. The electrical contacts were made with silver paint. X-Ray powder diffraction patterns were obtained with a CuKα radiation (λ = 1.542 Å) on a Rigaku Geigerflex operated with a Ni filter. Thermal behaviour was studied by using a Perkin-Elmer DSC-4 differential scanning calorimeter and a Perkin-Elmer TGS-2 thermogravimetric analyzer under a nitrogen gas flow. The electronic spectra of CuS films were obtained with a Perkin-Elmer Lambda 2 UV-VIS spectrometer; the transmittance was compensated by a substrate film in the reference light path. The scanning electron microscope (SEM) images were obtained with a Hitachi 'Nanob' 35 kV SEM.

Results and Discussion
We studied reactions between some copper(II) chelates with different stability constants and some sulfur compounds. The
copper(II) compounds employed were: Cu(cyclohexyl)(ClO\textsubscript{4})\textsubscript{2}, Cu(en\textsubscript{2})(ClO\textsubscript{4})\textsubscript{2}, Cu(pyrazine)(NO\textsubscript{3})\textsubscript{2}, III; the order of the stabilities of the chelates is I > II > III. The sulfur compounds used were: Na\textsubscript{2}S, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} and thiourea. A reaction between [Cu(en)\textsubscript{2}]\textsuperscript{2+} and thiourea gave uniform CuS films deposited on a polymer substrate. A reaction between thiourea and I in the same condition gave a heterogeneous film on a polymer substrate, and a reaction with III gave a green solid but no film was formed on a polymer substrate. Reactions between Na\textsubscript{2}S and the copper(II) chelates gave copper sulfide, but only a reaction with I gave a film on a polymer substrate, as reported previously.\textsuperscript{13} Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} did not react with stable copper(II) chelates, I and II. A reaction with III gave a pale-green powder in a very low yield, and no film was formed on a polymer surface. Thus, the selection of a copper(II) chelate with an adequate formation constant is an important controlling factor.

The reaction between [Cu(en)\textsubscript{2}]\textsuperscript{2+} and thiourea gave two types of CuS with different colours depending on reaction temperature: CuS-10 (brown) was obtained at 10\textdegree C and CuS-30 (green) at 30\textdegree C. Fig. 1 and 2 show the X-ray powder diffraction patterns found for these materials. CuS-10 showed broad peaks characteristic of amorphous materials (Fig. 1). In contrast, CuS-30 exhibited well-defined peaks that were attributed to covellite (Fig. 2). Elemental analyses for C, H and N indicated the presence of an organic component in these materials (C, 0.94; H, 1.51; N, 0.70% for CuS-30; C, 2.47; H, 0.89; N, 4.20% for CuS-10); the elemental analyses were performed by Desert Analytics (Tucson, AZ).

The differential scanning calorimetry (DSC) diagram of CuS-10 showed an exotherm in the temperature range 95-175\textdegree C. On reheating, the compound showed no thermal anomaly in the temperature range investigated (40-250\textdegree C). The exotherm observed for the first heating shows that an irreversible phase-transition occurs. In the plotted thermogravimetry diagram, a mass loss initiated at 100\textdegree C and the total mass loss between 100 and 175\textdegree C was 5%. This mass loss is probably due to the evaporation of organic components involved, which accompanies the irreversible phase transition. The X-ray powder patterns (b) and (d) in Fig. 1 were obtained for CuS-10 annealed at 6 h under vacuum at 100 \textdegree C and 150\textdegree C, respectively. The annealed CuS-10 showed well-defined peaks, and all the observed peaks were assignable to covellite.\textsuperscript{14} In the temperature range corresponding to the exotherm in DSC, therefore, the amorphous CuS that is in a metastable state was changed to the crystalline CuS which is thermodynamically more stable. Note that peaks observed for the annealed CuS-10 are sharper than the corresponding peaks of the as-prepared CuS-30: the full width at half maximum (FWHM) of the peak at 20 = 48.04\textdegree was 0.50 for annealed CuS-10, and 1.5\textdegree for as-prepared CuS-30. The diffraction peaks of CuS-30 were also sharpened by thermal treatment (patterns (b) and (e) in Fig. 2), but were still broader than the corresponding peaks of the annealed CuS-10: FWHM = 1.0\textdegree for the 48.04\textdegree peak of the annealed CuS-30. Moreover, some peaks that could not be assigned to covellite were observed at low angles. This suggested that CuS-30 underwent in part a thermal decomposition upon annealing. In fact, a 10% mass loss was observed between 70 and 150\textdegree C in the thermogravimetry; the mass loss is larger than the quantity of the organic component determined by elemental analyses. The obtained C:H:N ratio is almost identical with the ratio predicted for an equimolar mixture of thiourea and ethylenediamine; other hydrogen sources, such as water, are negligible. The evaporation of these organic components probably induces the thermal decomposition for CuS-30. Such decomposition was not significant for CuS-10. The preparation of amorphous CuS followed by thermal treatment, therefore, provides covellite with a higher purity and a higher crystallinity.

The powder electrical conductivities \(\sigma\) are shown as functions of temperature in Fig. 3. The electrical conductivity of a compressed pellet of CuS-10 was 0.10 S cm\textsuperscript{-1} at 298 K, and decreased with decreasing temperature; \(\sigma = 3.6 \times 10^{-2} S \text{ cm}^{-1}\).

![Fig. 1 X-Ray powder diffraction patterns of CuS-10 (a) as-prepared; (b) annealed at 100\textdegree C in vacuum; (c) CuS-10 annealed at 150\textdegree C under vacuum. The diffraction pattern of covellite (ICPDS file no. 6-0464) is shown by vertical lines for comparison.](image1)

![Fig. 2 X-Ray powder diffraction patterns of CuS-30: (a) as-prepared; (b) annealed at 100\textdegree C in vacuum; (c) CuS-30 annealed at 150\textdegree C under vacuum. Vertical lines show diffraction peaks reported for covellite (ICPDS file no. 6-0464).](image2)

![Fig. 3 Electrical conductivities of compressed pellets: (a) CuS-10; (b) CuS-30; (c) CuS-10 annealed at 150\textdegree C under vacuum; (d) CuS-30 annealed at 150\textdegree C in vacuum.](image3)
at 108 K. The $\sigma$ vs. $T$ curve deviates from the Arrhenius relation (activation energy is ca. 0.08 eV at the high-temperature limit) with decreasing temperature, and is well explained, in the entire temperature range investigated, by the variable-range hopping model:  

$$\sigma = \frac{T_0}{T^3} \exp[-(A/kT)^{\beta}]$$  

The parameters determined are: $T_0 = 5.8 \times 10^5$ K and $A/k = 8.5 \times 10^5$ K. CuS-10 annealed at 150 °C for 6 h under vacuum showed a powder conductivity of 278 cm$^{-1}$ at 298 K. The conductivity showed a metal-like temperature dependence throughout the temperature range investigated (110–300 K): $\sigma = 31$ S cm$^{-1}$ at 110 K. The change from semiconductor to metallic by thermal treatment is related to the transition from the amorphous to the crystalline state. The powder conductivity of CuS-30 showed a metal-like temperature dependence: 92 S cm$^{-1}$ at 304 K and 101 S cm$^{-1}$ at 101 K. CuS-30 annealed at 150 °C for 6 h under vacuum showed a conductivity higher than that of the unheated sample: 190 S cm$^{-1}$ at 301 K and 230 S cm$^{-1}$ at 99 K. Such an increase of electrical conductivity upon annealing has been reported for copper sulfides prepared using thiocarbamide. The X-ray powder diffraction results showed that the crystallinity of CuS-30 increased by the thermal treatment, although some thermal decomposition products were formed. The increase of crystallinity may result in the increase of the electrical conductivity.

CuS films were formed on the surface of a polymer substrate, when a polymer film was immersed in a reaction solution; PE, PET and 6-Nylon films were tested. A brown CuS-10 film was obtained at 10 °C and a green CuS-30 film was obtained at 30 °C. Fig. 4 shows the SEM images obtained for CuS-10 on a PE substrate, and Cu-30 on PE and PET films; sample CuS-30 films on the different polymer substrates were made at the same time in the same reaction solution. The CuS films on PE are uniformly uniform, although some cracks were observed for CuS-10. On the surface of films supported on PET, weakly bound particles were observed. It is probable that a conducting layer is formed initially, and then particles formed in solution are attached at later stage. The secondary attached particles are not expected to contribute to electrical conduction. Weakly bound particles were observed for a sample of CuS-30 on Nylon with a higher concentration. The electronic spectra (in transmittance) of CuS-30 films on Nylon are shown in Fig. 5; the nature of the spectrum was independent of the substrates used, CuS-30 has a strong absorption in the near-IR region, where CuS-10 is transparent. When a CuS-10 film was heated at 100 °C for 6 h under vacuum, the resulting film showed an electronic spectrum resembling that of CuS-30. This is consistent with the fact that the amorphous CuS is changed to the crystalline CuS upon annealing. A similar change was observed for CuS films on the PET substrates; the PE substrate was not resistant enough for the thermal treatment. The CuS-30 film that gives the electronic spectrum in Fig. 5b) had a surface electrical resistivity of 10 kΩ at 300 K, and the resistivity decreased with decreasing temperature; the ratio of the surface resistance $R(111)/R(202)$ was close to 0.9. These electrical properties were practically independent of the nature of the substrates used. The electrical resistance of the CuS-10 film that showed the spectrum in Fig. 3b was too high to determine with our conductance meter. On the other hand, the CuS-10 film annealed at 100 °C was a good conductor with a metal-like temperature dependence: $R(101)/R(293) = 0.7$. This is consistent with the change of the corresponding carrier sample upon annealing.

In conclusion, the crystalline CuS obtained by the annealing of the amorphous CuS has a higher crystallinity than that of the crystalline CuS prepared directly by the reaction in solution. The formation of amorphous CuS followed by thermal treatment is a new method for the fabrication of metal sulfides of high quality.

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Fig. 3 Electronic spectra of CuS deposited on a Nylon film: (a) CuS-30; (b) CuS-10; (c) CuS-10 annealed at 100 °C under vacuum.

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Chemical bath fabrication of CuS/Ag$_2$S-mixed solid films

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Treatment of CuS films with AgNO$_3$ solutions gave CuS/Ag$_2$S films with concentration ratios Cu/Ag of 0.08–0.15. These materials were characterized by scanning electron microscopy and X-ray powder diffraction, and their Cu$^{2+}$-detecting capabilities were studied by a potentiometric method. A uniform secondary-electron image was observed for a CuS/Ag$_2$S film prepared from a CuS film having a high crystallinity. An electrode constructed with the resulting mixed-sulfide film was capable of detecting Cu$^{2+}$ ions down to a concentration as low as 10$^{-7}$ mol dm$^{-3}$. A CuS/Ag$_2$S film obtained from amorphous CuS had a heterogeneous surface and as an electrode was inactive towards Cu$^{2+}$. The rate of reaction between Cu$^{2+}$ and Ag$^+$ is dependent on the crystallinity of CuS, with CuS films of a high crystallinity being resistant to the attack of Ag$^+$ so that the reaction is slow enough to provide a uniform and well-adhering CuS/Ag$_2$S film.

Metal sulfides exhibit important electrical and electrochemical properties, and some sulfides doped with other metal ions show better physical properties (such as electrical and photoelectrical conductivities) than the parent sulfides. An example for the use of doped sulfides in electrochemistry is that membranes of compressed CuS/Ag$_2$S pellets can selectively detect Cu$^{2+}$ ions at lower concentrations than that of CuS membranes. CuS films have been obtained by chemical deposition methods with the objective of fabricating new functional thin films. The principle of chemical deposition is based on control of the rate of reactions between metal ions and sulfur sources. If a metal sulfide film can be doped with other metal ions by a chemical method, the resulting film is expected to be useful for electronic and electrochemical devices. It has been reported that the electrical resistivity of an HgS film is decreased when the film is treated with a Ag$^+$-containing solution this suggests a new method for doping metal sulfides, although the compositions of the doped materials have not been reported.

In our previous paper, we reported that amorphous and crystalline solids of CuS were obtained by reactions between (Cu(en)$_2$)$_2$O (en = ethylenediamine) and thiourea, with their electrical conductivity dependent on the degree of crystallinity. The crystallinity of CuS may also be a controlling factor of the electrical resistance of the material against attack of other metal ions. Amorphous and crystalline CuS solids react with other metal ions, therefore, their reaction rates will be different and the reaction products will show different physical properties. In this work, we have studied the reactions of CuS films with Ag$^+$ and obtained the mixed CuS/Ag$_2$S films. The morphologies and the electrochemical properties of the resulting films are dependent upon the nature of the parent CuS films.

Experimental

Amorphous and crystalline CuS solids were synthesized by the method reported previously: reaction between [Cu(en)$_2$]Cl$_2$ and thiourea in alkaline solution at 10°C gave amorphous CuS (denoted CuS10 according to the reaction temperature), while reaction at 30°C yielded crystalline CuS (CuS30). When a poly(p-toluenesulfonate) film was immersed in the reaction solutions, films of the corresponding sulfides were formed on the polymer substrate. Annealing of CuS10 and CuS30 at 100°C gave crystalline copper sulfides (CuS10A and CuS30A, respectively). CuS30, CuS10A and CuS30A showed X-ray powder diffraction patterns characteristic of crystalline CuS (cavellite, JCPDS 6-464), with CuS10A having the highest crystallinity, as reported previously. These four materials were studied in their reactivity with Ag$^+$. When the CuS films were immersed in a 0.01 M AgNO$_3$ solution at 10°C for 3 h and then at 40°C for 2 h, dark films with metallic luster were obtained. The resulting identically treated films were then washed with water and ethanol, and dried in vacuum. Corresponding powder materials also were obtained under identical reaction conditions, and were used for studies of the bulk electrical resistance and X-ray powder diffraction.

Secondary-electron (SE) images and the compositions of the films were obtained using a JEOL JSM-5400 scanning electron microscope (SEM) equipped with an Oxford EDS analyzer operating at 25 keV. Sample films were coated with Au for observation of morphologies, and uncoated films were used for EDS (energy-dispersive spectroscopy) analyses. X-Ray diffraction patterns were obtained using a Rigaku Geigerflex diffractometer with Cu-K$_\alpha$ radiation and a curved graphite analyzer.

Electrical resistivities were determined by the standard two-probe method. The electrode potential induced for a sulfide film or an Ag/AgCl reference electrode was measured at 25°C by the use of a Keithley 614 electrometer (input impedance >5 x 10$^{13}$ Ohm). A CuS film of dimensions 8.5 x 28 mm was vertically mounted on a Teflon holder, together with a double junction reference electrode at a separation of 1 cm. The top edge of the CuS film was connected to a Cu wire with Aquadag, and the bottom area of 8.5 x 18 mm was immersed in the sample solution. Sample solutions were prepared by dissolving CuClO$_4$·6H$_2$O in 0.1 M KNO$_3$, and standardized by colorimetry with neocuproine (2,9-dimethyl-1,10-phenanthroline).

Results and Discussion

All four CuS films reacted with Ag$^+$ ions and gave dark films with a metallic luster. The parent CuS films were initially characterized by SEM, since their reactivities towards Ag$^+$ differed. Fig. 1 and 2 show the SE images of the films studied. The images of CuS10 and CuS30 show the formation of a fairly uniform surface. The particle size of amorphous CuS10 is smaller than that of CuS30. On the surface of each material, weakly bound large particles are observed as white images. The
Cu:S ratios determined by EDS analyses on the entire surface of CuS10 and CuS30 were ca. 0.7:1, and all the regions of the white areas had a practically identical composition. It is probable that CuS particles formed at a later reaction stage were weakly attached. The SE images of the annealed materials resemble that of CuS30. The compositions of the annealed materials are: Cu:S=1.3 for CuS10A and 0.7 for CuS30A. The surface of CuS10A has the highest uniformity among the four CuS films and is responsible for the low surface electrical resistivity (10 kΩ at 300 K). These observations show that the synthesis of amorphous CuS followed by annealing is a better method for the fabrication of CuS films than the direct chemical deposition of crystalline CuS.

For all films treated with Ag⁺-containing solutions, EDS analyses showed that the Ag:S ratio was ca. 2:1, and that Cu was present at a Cu/Ag ratio of 0.08 for a film obtained from CuS10 while this ratio was 0.15 for the other three CuS films; no other elements were detected by EDS analyses. The X-ray powder diffraction patterns of the corresponding powder materials showed the formation of monoclinic Ag₃S (acanthite, JCPDS 14-72), while diffraction peaks assignable to crystalline CuS (cubelite) were weak and masked by the peaks of Ag₃S, as shown in Fig. 3. These observations indicate that a large part of Cu atoms in CuS were replaced by Ag during treatment with Ag⁺-containing solutions, and that Ag₃S doped with CuS (acanthite mixed with cubelite) was formed; these materials are thus denoted Ag₃S/CuS10, Ag₃S/CuS10A, Ag₃S/CuS30 and Ag₃S/CuS30A. Ag₃S/CuS10 obtained from amorphous CuS10 has a low crystallinity compared with the other Ag₃S/CuS solids (Fig. 3). The SE images show that the surface of the Ag₃S/CuS10 film is heterogeneous whereas the other films are fairly uniform (Fig. 1 and 2). For each film, weakly bound particles are observed as white images. These particles had a lower Cu concentration than that of the overall film; the Cu/Ag ratio was 0.05 for Ag₃S/CuS10, 0.1 for Ag₃S/CuS30, 0.08 for Ag₃S/CuS10A and 0.05 for Ag₃S/CuS30A. The uniformities of the Ag₃S/CuS films are related to the crystallinities of the parent CuS films. CuS10A, which has the highest crystallinity, is the most resistant towards attack by Ag⁺, and hence the replacement of Cu by Ag occurs slowly enough to result in good adherence of CuS/Ag₃S-mixed solids on the substrate. By contrast, amorphous CuS10 is highly reactive, and hence its reaction with Ag⁺ proceeds too fast to lead to the formation of a uniform surface and formation of crystalline particles. The surface electrical resistivities of all the Ag₃S/CuS films were
Fig. 4 Electrode potentials of CuS10A (●) and Ag/S/CuS10A (▲) films vs. an Ag/AgCl reference electrode in 0.1 M KNO₃ at 25 °C. The straight line indicates the Nernst relation with a slope of 33 mV.

> 200 GΩ. The bulk electrical resistivities of the corresponding powder materials were of the order of 2 MD at 300 K, except for Ag/S/CuS10 the resistivity of which was > 100 MΩ cm. Electrical conduction in the other three Ag/S/CuS materials is a result of Ag/S being doped homogeneously by CuS, since pure Ag/S is an electrical insulator. On the other hand, Ag/S/CuS10 is probably a heterogeneous mixture of Ag/S and CuS, which results in its high electrical resistivity.

A combination of a CuS film and a reference electrode leads to a Cu²⁺-sensing electrode. The induced potential of the electrode obeyed the Nernst equation, \( E = E_0 - \frac{RT}{nF} \log [Cu^{2+}] \) (C=27–30 mV) down to [Cu²⁺] = 10⁻³ M in 0.1 M KNO₃. Fig. 4 shows the potential observed for a film of CuS10A. The response times of all the films studied were <5 min throughout the concentration range for which the Nernst relation was valid. Electrodes prepared from CuS30 and CuS10A films showed high stability of electrical readings and a rapid response in comparison with the CuS10 film. These better properties of the former two electrodes are related to their low impedances owing to the high electrical conductivities of the constituent materials.

An electrode constructed with the AgS/CuS10A film followed the Nernst relation down to a Cu²⁺ concentration of 5 x 10⁻⁷ M, as shown in Fig. 4. This concentration is much lower than that for the parent CuS film (CuS10A) and is comparable to that of commercially available Cu²⁺-sensing electrodes consisting of compressed CuS/AgS pellets. The AgS/CuS10A electrode was electrically less stable than that of CuS10A, and showed a relatively large fluctuation in the potential readings which is due to the high surface electrical resistivity (> 200 GΩ). The other AgS/CuS10A films did not show a Nernst-type response with respect to Cu²⁺ concentration. Since the Cu:Ag ratio of the four films are practically identical, the Cu²⁺-sensing capability is related to physical properties (such as contact between CuS/AgS particles in the conducting layer) rather than chemical properties (such as chemical composition). The most sensitive electrode, Ag/S/CuS10A, has the highest uniformity in the dark SE image area that is believed to be responsible for the good Cu²⁺-sensing capability, and has the lowest surface electrical resistivity.

In conclusion, the formation of amorphous CuS followed by annealing gives superior films of crystalline CuS (correlate). The high crystallinity of such films reduces the rate of the reaction with Ag⁺, resulting in the formation of a uniform CuS/AgS film, which is beneficial for sensing Cu²⁺. Since any metal ions that are nobler than Cu²⁺ can replace Cu atoms in CuS films, such reactions are expected to be useful for the fabrication of a variety of doped metal sulfide films.

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References
Note
Spectroscopic and magnetic properties of Chevreul's salt, a mixed valence copper sulfite \( \text{Cu}_3(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O} \)

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Abstract

Chevreul's salt, a mixed valence copper sulfite \( \text{Cu}_3(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O} \), was synthesized by a reaction between \( \text{CuSO}_4 \) and \( \ce{NaHSO_3} \), and characterized by X-ray photoelectron spectroscopy, magnetic susceptibility, EPR and electronic spectroscopy. These magnetic and spectroscopic studies consistently proved the validity of the formulation \( (\text{Cu}^{+})_2\text{SO}_4\text{Cu}^{2+} \cdot 2\text{H}_2\text{O} \). Between \( \text{Cu}^{+} \) and \( \text{Cu}^{2+} \) ions an intervalence transition occurs with an energy of 23 500 cm\(^{-1}\). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Copper sulfite; Mixed valence state

1. Introduction

A number of copper sulfites with different compositions have been reported, but some of them are unstable and have no definite composition [1]. Chevreul's salt is known as a stable mixed-valence sulfite, and attracts interest because of its intense red color as well as its highly stable mixed-valence state [1,2]. The precipitation of this complex is a key stage in a hydrometallurgical process [3]. An X-ray crystal study has shown the presence of two kinds of copper atoms: one has a distorted octahedral coordination and the other a distorted tetrahedral coordination [2]. The former is supposed to be in the Cu(I) state and the latter in the Cu(II) state, and hence the compound can be formulated as \( (\text{Cu}^{+})_2\text{SO}_4\text{Cu}^{2+} \cdot 2\text{H}_2\text{O} \). Despite this interesting structural property and the intense color, other physical properties have not been reported in detail. The most common synthetic method for the preparation of this compound consists of passing a \( \text{SO}_2 \) stream in an aqueous \( \text{CuSO}_4 \) solution at 70°C. This reaction, however, has been reported to yield byproducts depending on the reaction conditions: a decrease in the \( \text{Cu}^{2+} \) concentration with the progression of reduction, for example, facilitates coprecipitation of metallic copper [1]. An X-ray photoelectron spectroscopy (XPS) study has shown that metallic copper and elemental sulfur deposit on the surface of the material obtained by the reduction of \( \text{CuSO}_4 \) with \( \text{SO}_2 \) at elevated temperatures [3]. On the other hand, a red product obtained by bubbling \( \text{SO}_2 \) into an ammonia/\( \text{CuSO}_4 \) solution exhibits an XPS spectrum that is consistent with the formula proposed by the X-ray study [3]. The ultimate product of this reduction, however, has been reported to be a colorless ammonium copper(II) sulfite, \( \text{NH}_4\text{CuSO}_3 \) [4]. These difficulties in the control of the composition of Chevreul's salt have probably obstructed further studies of its intrinsic physical properties. In this paper we report that a reaction between \( \text{CuSO}_4 \) and \( \text{NaHSO}_3 \) yields a pure Chevreul's salt which shows reproducible XPS, magnetic moment, EPR and electronic spectra, and all these properties are consistently interpreted by the mixed valence state of copper.

2. Experimental

Chevreul's salt was synthesized by heating a solution containing \( \text{CuSO}_4 \) and \( \text{NaHSO}_3 \) at a temperature be
tween 60 and 70°C for 3 h [1]. The concentration of CuSO₄ was altered between 0.6 and 0.8 M, and the NaHSO₃/ CuSO₄ mole ratio between 1.1 and 1.7. All materials obtained under these different conditions reproduced all the magnetic and spectroscopic properties reported in this work. The formation of Chevreul's salt was confirmed by X-ray powder diffraction.

The X-ray powder diffraction pattern was obtained by a Rigaku Geigerflex diffractometer with Cu Kα radiation. The XPS spectrum was obtained by a Kratos 165 Ultra spectrometer with Mg Kα radiation. A sharp peak of oxygen 1s core-electrons was observed with a full width at half maximum (FWHM) of 1.9 eV. The binding energy of this peak was assumed to be 532.4 eV [3], and it was used as a reference for determination of the binding energies of other peaks. The EPR spectrum was obtained for the powdered sample with a Bruker ESP 300 X-band EPR spectrometer. The g factors were determined by using a computer simulation program [5]. The magnetic susceptibility was determined by a Johnson Matthey automagnetic susceptibility balance calibrated by water (0.720 × 10⁻⁶ emu cm⁻³). The nolar susceptibility χ was corrected for diamagnetic contributions from SO₄²⁻ (38 × 10⁻⁶ emu mol⁻¹) and H₂O (13 × 10⁻⁶ emu mol⁻¹) [6,7]. The magnetic moment was calculated from the relation μ = 2.83gμB [8] of BM, without correction of the temperature-independent paramagnetism. The electronic spectrum was recorded by a Varian DMS 80 UV–Vis spectrometer equipped with a diffuse reflectance adaptor. The IR spectrum was obtained for the powdered sample with a Perkin–Elmer 1600 FT IR spectrometer equipped with a Specro-Tech diffuse reflectance unit under a nitrogen atmosphere. The vibrational bands of SO₄²⁻ were assigned by comparing the spectra of the samples treated and untreated with D₂O.

3. Results and discussion

The XPS showed copper 2pₓᵧ core-electron peaks at 933.3 and 935.6 eV accompanied by a shake-up satellite. The former peak is attributed to Cu(I) and the latter to Cu(II) [5,8]. For sulfur 1s core electrons, a single peak was centered at 168.6 eV. Although a tail extends from the higher binding energy side and the FWHM was as large as 2.5 eV, no peak assignable to atomic sulfur was observed. The reduction of CuSO₄ with NaHSO₃ is therefore not accompanied by deposition of metallic copper or elemental sulfur on the surface of the product and differs from the reduction with SO₂. The use of copper(II) sulfate yielded a heterogeneous green-yellow solid at room temperature; the nature of the counterions that regulate the pH of the reaction system is one of the factors that control the composition of the product.

The EPR spectrum of the powdered sample showed a pattern of orthorhombic symmetry, and the g factors were determined as shown in Table 1. The spectrum obtained at liquid nitrogen temperature gave identical g values. The magnetic susceptibility was determined to be 3.71(±0.03) × 10⁻⁵ emu g⁻¹ at 295 K. When all the copper atoms are assumed to be magnetically equivalent, the magnetic susceptibility gives a magnetic moment of 1.10 BM per Cu⁺ if the proposed formula Cu⁺(Cu⁺)₂(SO₄)²⁻(H₂O)₃ is valid, the magnetic susceptibility gives the magnetic moment 1.90 BM for each paramagnetic Cu⁺ ion. The latter value agrees with the magnetic moment μ(BM) = μₑₙ(3(5 + 1))¹/₂ = 1.90 calculated from the EPR g factors (gₑₙ is the mean of the three g component values). These magnetic properties support the formula Cu⁺(Cu⁺)₂(SO₄)²⁻(H₂O)₃ in which no valence interconversion occurs at the EPR frequency and magnetic interaction between Cu⁺ ions is much weaker than the thermal energy at temperatures studied.

The electronic diffuse reflectance spectrum of the powdered sample showed two well-defined bands at 785 and 425 nm with the relative absorbance ratio A₇₈₅/A₄₂₅ approximately 1.23 (Fig. 1). The 785 nm band arises from the d-d transition of Cu⁺⁺ ions. The 425 nm band is assigned to the intercalation transition between Cu⁺⁺(I) (i.e. Cu⁺⁺ with tetrahedral coordination) and Cu⁺⁺(II) (Cu⁺⁺ with octahedral coordination); obviously this transition is responsible for the deep-red color. The energy 23 500 cm⁻¹ of the 425 nm band corresponds to the energy difference between the ground state Cu⁺⁺(I)Cu⁺⁺(I) and the excited state Cu⁺⁺(I)Cu⁺⁺(II). This intercalation transition is supposed to occur through bridging sulfate ions; the strongest Cu˂sub>₉₋₁Ο₉> Cu˂sub>₉₋₁Ο₉> linkage is formed with the interatomic distances r(Cu˂sub>₉₋₁Ο₉> = 2.034 Å and r(Cu˂sub>₉₋₁Ο₉> = 2.140 Å [2]. The octahedral coordination around a Cu⁺⁺ ion is distorted to D₃d symmetry so that three EPR g compo-

| Table 1 |
| EPR g factors and Cu-O distances of [CuO(OH)₂(OH)₃] in Chevreul's salt and [Cu(OH)₃] in the low-temperature phase of Tuton's salt |
| [CuO(OH)₂(OH)₃] | [Cu(OH)₃] |
| gₓ | 2.656 | 2.066 |
| gᵧ | 2.168 | 2.117 |
| gₑ | 2.363 | 2.466 |
| Cu-Oₓ (Å) | 1.924 b | 1.966 |
| Cu-Oᵧ (Å) | 2.034 b | 2.022 |
| Cu-Oᵧ (Å) | 2.467 b | 2.310 |

* Ref. [8]
* Ref. [2]
* Cu-OH₁ bond.
Fig. 1. Diffuse reflectance spectrum observed for Chevrel’s salt, CuSO₄Cu(SO₄)₂·2H₂O. The 785 nm band is assignable to d-d transition of Cu(II), and the 425 nm band to the intervalence transition between Cu(I) and Cu(II).

nents are observed. The g factors are related to the crystal field parameters as follows [9,10]:

\[ g_x = 2 - (8j^2) \alpha_{3xy} \Delta E_{xy} \]  \hspace{1cm} (1)

\[ g_y = 2 - (2j^2) \alpha_{3yz} \Delta E_{yz} \]  \hspace{1cm} (2)

\[ g_z = 2 - (2j^2) \alpha_{3zx} \Delta E_{zx} \]  \hspace{1cm} (3)

where \( \alpha \) is the spin–orbit coupling constant, \( k \) the orbital reduction constant along the \( i \) axis, and \( \Delta E_{xy}, \Delta E_{yz} \), and \( \Delta E_{zx} \) are the energy differences of the \( xy, yz \) and \( zx \) d-orbital levels from the \( x^2 - y^2 \) level, respectively. A similar \( D_{2h} \) coordination geometry has been reported for \([Cu(OH)_4]^{2-}\) in Tutton’s salt [9,11]. Recent structural and EPR studies have shown that the \([Cu(OH)_4]^{2-}\) unit undergoes a thermal equilibrium between two phases in which the directions of the Jahn–Teller distortion are different so that the \( g \) tensor (including the axes and the values of the components) is temperature-dependent [12,13]. Such a dynamic Jahn–Teller effect is supposed to be insignificant in Chevrel’s salt, because the EPR \( g \) factors were unchanged at 300 and 77 K. The low-temperature phase of Tutton’s salt is frozen at 77 K, and the EPR and structural parameters at \( T \leq 77 K \) (shown in Table 1) are characteristic of the \([Cu(OH)_4]^{2-}\) ion [12,13]. The Cu-O₂ distance along the \( z \) axis in Chevrel’s salt is longer than that in the low-temperature phase of Tutton’s salt, and the differences in Cu-O₂ and Cu-O₃ are not significant. The elongation along the \( z \) axis stabilizes the \( xy \) and \( yz \) levels so that \( \Delta E_{xy} \) and \( \Delta E_{yz} \) increase (leading to \( g_y \) and \( g_z \) closer to 2.00), while \( E_{zx} \) (consequently \( g_x \)) is not significantly influenced. This simple theory explains the reason why the \( g \) value of Chevrel’s salt is smaller than that of Tutton’s salt, but the \( g_x \) and \( g_z \) values of the two salts have irregular relations without following the above simple theory. Since the \( y \) and \( z \) axes are along the oxygen atoms that form Cu²⁺-O-Cu²⁺ links, it is probable that an electron delocalization through the Cu²⁺-O-Cu²⁺ linkages influences the orbital reduction constants \( k_x \) and \( k_z \), and consequently the \( g_x \) and \( g_z \) values.

The vibrational bands of SO₄²⁻ were observed at 1024(vs), 976(90), 858(m), 690(m) and 631(m) cm⁻¹. In this IR region, free SO₄²⁻ with \( C_{4v} \) symmetry shows three bands at 967(A₁), 933(E) and 620(A₁) cm⁻¹ [14]. Coordination of a SO₄²⁻ ion at the sulfur atom shifts the vibrational bands to higher frequencies and coordination at the oxygen atom to lower frequencies [14]. In Chevrel’s salt, all SO₄²⁻ ions are crystallographically equivalent, and all the atoms of each sulfite ion coordinate one or two copper ions. This bridging coordination results in the irregular shifts of the vibrational bands.

In conclusion, Chevrel’s salt synthesized by a reduction of CuSO₄ with NaHSO₃ showed reproducible magnetic and spectroscopic properties. The valence states of Cu atoms are definitely in the Cu(I) and Cu(II) states, as consistently confirmed by the XPS, magnetic moment and EPR spectroscopy. Between the atoms of the two valence states an intervalence transition occurs with an energy of 23500 cm⁻¹ resulting in the characteristic deep color.

References