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Characterization of new copper sulfide materials

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We have reported that the slow reaction between a very stable copper complex, [Cu(cyclam)]$(ClO_4)_2$ (cyclam: 1, 4, 8, 11-tethraazacyclotetradecane), and Na_2S provides a new amorphous copper sulfide, which precipitates in the form of a dark powder, adhering a part of the compound in the form of a thin film on the walls of the reaction vessel. A CuS thin film deposited on a polyethylene substrate showed a metallic like electrical behavior down to 250 K, and was transparent in the visible region of the spectrum. In this work we report the chemical modification of the resulting amorphous copper sulfide. The film and the powders were chemically treated with alkali metal iodides. In addition, the films were treated with iodine in an organic solution. In such a way, the electrical properties of the films were notoriously improved. We report the characterization of the films and powders by using X - ray diffraction, and X-ray photoelectron spectroscopy (XPS) and electrical conductivity measurements.

1. Introduction

Copper sulfides had been widely studied because they form complex structures, with copper atoms in mixed valence states in some of its phases. Such characteristics are responsible of very interesting physical properties, for example, a high electrical conductivity [1,2]. Copper sulfides can be deposited in the form of thin films on different substrates, some of which are polymers [3-5]. These transparent and electroconductive plastic films are potentially useful in the fabrication of electric and electronic devices.

Previously [6,7], we have reported that the slow reaction between a very stable copper complex, [Cu(cyclam)]$(ClO_4)_2$ (cyclam: 1, 4, 8, 11-tethraazacyclotetradecane), and Na_2S provides a new amorphous copper sulfide which was deposited in the form of a thin film on the walls of the reaction vessel. To obtain the films, a polyethylene substrate was immersed into the reaction vessel The CuS films deposited on polyethylene exhibited a metallic-like electrical conductivity down to 250 K and were transparent in the visible range of the electromagnetic spectrum. The metallic properties of the films were performed by treatment with iodine vapor.

These results suggest that CuS films synthesized by using this new method are potentially useful in the fabrication of electric and electronic devices.In this work, we report the chemical modification of the former films with alkali metal iodides in organic solution, as well as the chemical treatment of the powders obtained with alkali metal iodides, in a try to reach materials with better electrical properties.

2. Experimental details

CuS films and powders deposited on polyethylene were prepared by a previously reported method [6]: a polyethylene substrate was immersed in solution containing [(cyclam)]$(ClO_4)_2$] and Na_2S and was allowed precipitation of the powder and deposition of the films was obtained on the polyethylene substrate during 3 h, without stirring, at 300 K.

The treatment of the films with LiI was carried out as follow: a CuS deposited on a polyethylene substrate was immersed in a acetone solution containing LiI at concentrations 0.15, 0.37 and 0.5 M during 3 h in a vessel closed with parafilm. After the tratment, the film was washed with acetone, then air-dried shortly (few minutes) and stored under nitrogen atmosphere. The tratment with NaI in acetone was realized in a similar manner.

The treatment of the CuS powders prepared as described above was carried out by suspending 0.358 g in 75 ml of a 0.15 M LiI acetone solution (CuS:LiI=1:3) or in 75 ml of a 0.15 M NaI acetone solution (CuS:NaI=1:3), and the reaction was stirred slowly for $\approx$ 3 h at room temperature in a vessel closed with parafilm. The treated powder was collected by filtration, washed successively with acetone, water and acetone, and then was dried under vacuum for $\approx$ 3h.

The relative electrical resistance of CuS films on polyethylene substrate, and of the pills prepared with the precipitated powders, at different temperatures, was determined by using the van der Pauw four points probe. The X-ray photoelectron spectra (XPS) for the films were obtained using a Vacuum Generator ESCALAB MKII Spectrometer with a Mg X-ray source.

Relative concentrations of the elements included in a sample material were calculated from the peak areas to which correction of ionization cross section was applied. The X-ray diffraction (XRD) measurements were carried out using a Cu-Kα radiation (λ=1.542 Å) on a Rigaku Geirgerflex diffractometer operated with a Ni filter.

3. Results y discussion

Figure 1 shows the relative electrical resistance of the CuS films treated with LiI in acetone, at different temperatures. The electrical properties of the CuS films changed after the treatment, increasing their metallic behavior. The X-ray photoelectron spectra indicated that copper atoms are in the Cu(I) state. The binding energy of the Cu $2p_{1/2}$ peak was computed to be 953.0 eV, and the binding energy of the Cu $2p_{3/2}$ was 932.9 eV, without being accompanied by the shake-up satellite that is characteristic of paramagnetic Cu(II) state. A S 2p peak was observed at 162.1 eV, being this value identical to those values of the observed binding energies for amorphous CuS before the treatment and for covellite. In addition, one S 2p peak was observed at a binding energy of 169.3 eV corresponding to SO_x^{2-} (x=3 or 4) species [7]. The relative concentrations of the elements included in the samples were calculated from the peak areas as: [Li]:[Cu]:[S]:[SO_x^{2-}]=1.61.8:1.0:0.8:0.6.
For iodine: [Cu]:[I]=1.0:0.04-0.07. Since the relative concentrations of elements are independent on the concentration of the LiI, Li and SO_x^{2} solutions, they exists as intrinsec components and probably a new one phase chemical species was formed.

The treatment of the CuS films with NaI in acetone increased the metallic behavior range, as can be noted in Fig. 2. From the relative concentrations of the included elements in those samples, it was founded an important quantity of iodine [Cu]:[I]=1.0:0.1-0.2. The relative concentration of elements included in these samples varied widely with the treatment.

For example, [Na]:[Cu]:[S]:[SO_x^{2-}] was calculated to be 1.2:1.0:0.9:0.7 for a film treated treated with a 0.15 M NaI solution; 0.6:1.0:1.0:0.3 for a 0.37 M solution and 0.9:1.0:0.9:0.4 for a 0.5 M solution.
From these results, it can be concluded that CuS reacts with NaI forming new chemical species whose composition is not a only one phase composition. X ray diffraction (XRD) measurements of the powders indicated a mainly amorphous nature, with a little crystalline part , as can be noted from Fig. 3. From elemental analysis C and H was detected, so that probably exist a part of organic material mixed with copper sulfide. Elemental analysis results for CuS treated with LiI indicated the presence of approximately 4 % I, 61.5 % Cu and 20.6 % S. Li was no founded in the samples.

The quantity of I included is not big enough to change the amorphous nature of CuS, but it could suggest that, because the treatment with LiI, CuS was doped with I, which would explain the increased electrical conductivity after the treatment, as can be noted in fig. 4.

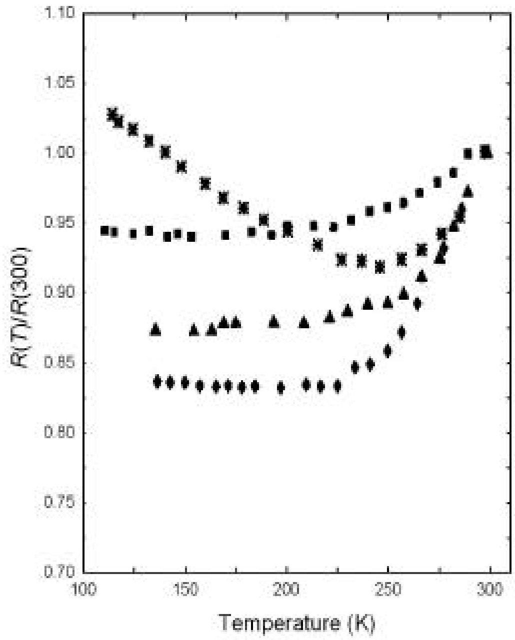

Fig. 1. Temperature dependence of relative electrical resistances of CuS films treated with LiI in acetone at concentrations of 0.15 M (♦), 0.37 M (▲) and 0.5 M (■). Also is shown, for comparison, the relative electrical resistance of the untreated film (✳).

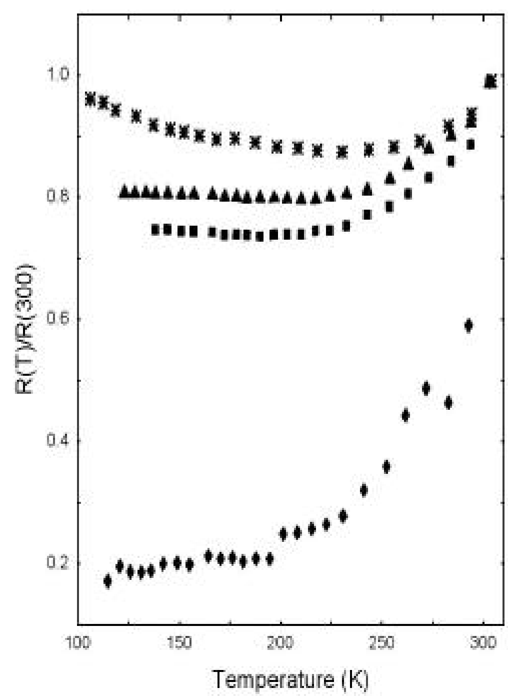

Fig. 2. Temperature dependence of relative electrical resistances of CuS films treated with NaI in acetone: at concentrations of 0.15 M (♦),(♦), 0.37 M (▲) and 0.5 M (■). Also is shown, for comparison, the relative electrical resistance of the untreated film (✳).

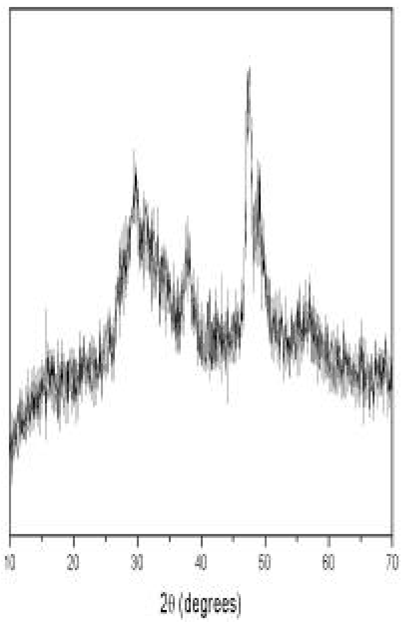

Fig. 3. X-ray diffraction pattern of the amorphous CuS powder.

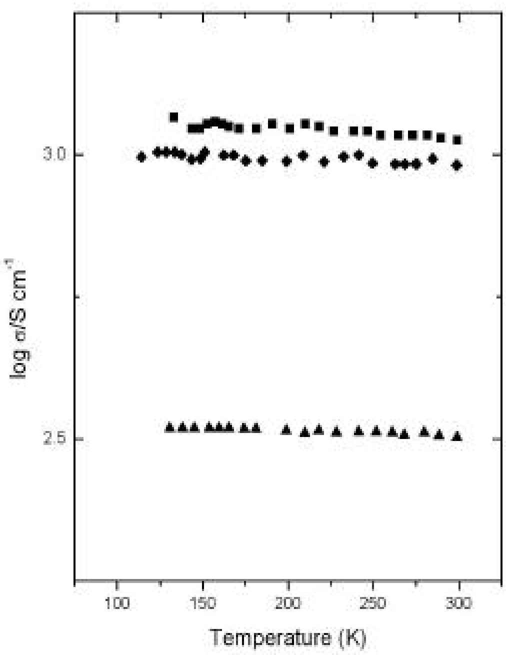

Fig. 4. Temperature dependence of conductivities of CuS powders: untreated (▲), treated with LiI (■) and treated with NaI (♦).

4. Conclusions

This work suggests a new method for preparing a new kind of copper sulfide by chemical treatment with alkali halides metals. Amorphous CuS chemically active and their chemical modifications provide new materials, although the new species obtained are dificult to characterize completely.

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