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Synthesis and Properties of Cobalt Sulfide Phases: CoS₂ and Co₉S₈

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Dedicated to Professor C. N. R. Rao on the Occasion of His 80th Birthday

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Abstract. Single phase cobalt disulfide (CoS₂) nanoparticles were prepared by thermal decomposition of cobalt-thiourea complex at a low temperature (400 °C). CoS₂ nanoparticles exhibit ferromagnetic ordering at 122 K below which the temperature dependent resistivity of cold pressed nanoparticles deviates from metallic behavior and shows a broad maximum. Just below $T_{\rm C}$, it also exhibits a large magnetoresis-

Introduction

Transition metal sulfides are very important class of materials known for their rich structural diversities along with interesting and technologically relevant electronic and magnetic properties.^[1] One additional advantage is that they are cheap and abundant, many of which are found in nature in the form of minerals such as heazlewoodite (Ni₃S₂), chalcocite (Cu₂S), pyrite (FeS₂) etc. Among all, sulfides which crystallize in pyrite structure (FeS₂, CoS₂, NiS₂, CuS₂, and ZnS₂) show great variation in electronic properties by changing transition metal ion and also by substituting Se or Te in the anion site.^[2-4] According to the band theory FeS2 and ZnS2 are semiconducting while CoS₂ and CuS₂ are metallic.^[2] NiS₂ is a Mott insulator.^[5] In CoS₂, Co²⁺ remains in the low spin state with one electron in the eg sub-band. Because of the intermediate strength of the e_g electron correlation, ferromagnetic transition temperature (Curie temperature, T_C) is found to be less (120 K) with fractional magnetic moment (0.85 B.M.).^[6-8] The electrons, which are responsible for ferromagnetic interaction, also give rise to electronic conduction in CoS₂.

The phase diagram of cobalt sulfide is fairly complex containing Co₄S₃, Co₉S₈, CoS, Co₃S₄, Co₂S₃, and CoS₂ phases.^[9] Bulk polycrystalline materials of these phases are synthesized by heating elemental sulfur and cobalt together in silica ampoules. Corresponding single crystals are prepared by adding a flux such as CoBr₂ to the elemental reactants. Recently, chemical synthesis of nanoparticles and submicron sized partance effect (6.5%). A mixture of CoS and Co₉S₈ phases were obtained between the temperature interval 400 °C < T < 1000 °C. At 1000 °C, a pure bulk Co₉S₈ phase was obtained. It exhibits magnetic hysteresis typical of a ferromagnet at room temperature and a peak in magnetization at low temperature with a strong relaxation indicating possible spin glass state.

ticles of phases like CoS2, CoS, and Co2S8 are carried out hydrothermally at relatively lower temperatures (120–230 °C). Bao et al. demonstrated bio-assisted CoS nanowires synthesis by hydrothermal method using cysteine as the sulfur source.^[10] The same sulfur source is used to synthesize CoS₂ nanoparticles on graphene surface.^[11] CoS nanocrystals are grown on graphene hydrothermally starting with thioacetamide as the sulfur source for supercapacitor applications.^[12] Other sulfur sources used for the synthesis of cobalt sulfide nanostructures are thiourea,^[13] H_2S ,^[14] Na_2S ,^[15,16] $Na_2S_2O_3$,^[17] etc. High electrial conductivity in many cobalt sulfide phases has made these materials ideal for many energy devices like dye sensitized solar cells (DSC), Li-ion batteries, and supercapacitors. Phases like CoS₂, CoS, and Co₉S₈ have been used as counter electrode in DSC, where it collects electrons from the external circuit and speeds up the reduction of I3- for dye degradation.^[18–22] CoS_2 and Co_9S_8 are also used as anode material in Li-ion battery.^[23,24] Wang et al. have shown discharge capacity as large as 1210 mAhg⁻¹ and good cyclability for CoS₂ hollow spheres.^[23] Cobalt sulfides can also store charge as pseudocapacitors in redox processes during charging and discharging. Different morphologies and composite of cobalt sulfide with graphene have been tried for supercapacitor applications.^[12,25-29] Nanocrystalline CoS2 phase has also been tried to be used as a material for electrocatalysis of oxygen reduction reaction in fuel cell.^[30]

Pyrite type CoS_2 is particularly interesting in the cobaltsulfur phase diagram for its interesting magnetic and electronic properties. Properties of bulk polycrystals and single crystals have been extensively studied but studies of corresponding properties of nanocrystalline CoS₂ are scarce in the literature. Herein, we have demonstrated the synthesis of CoS₂ nanoparticles from a single source precursor, namely, cobalt-thiourea complex, by decomposing it at 400 °C. The electrical and mag-

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netic properties of the CoS₂ nanoparticles resemble that of the bulk sample. We have also investigated electrical and magnetic properties of bulk Co₉S₈ prepared by heating the complex at 1000 °C.

Results and Discussion

Several thiourea complexes of cobalt have been reported in the literature. Cotton et al. carried out detailed synthesis and characterization of Co(CH₄N₂S)₂Cl₂, Co(CH₄N₂S)₂Br₂, $Co(CH_4N_2S)_4(NO_3)_2$, $Co(CH_4N_2S)_3SO_4$, and $Co(CH_4N_2S)_4(ClO_4)_2$. Herein, we choose the most volatile of them, $Co(CH_4N_2S)_4(NO_3)_2$, (b.p. 127 °C) for thermal decomposition in order to obtain different phases of cobalt sulfide. Figure 1a shows the TGA data of Co(CH₄N₂S)₄(NO₃)₂ in nitrogen atmosphere obtained by ramping the temperature at a speed of 10 °C·min⁻¹. Till 200 °C the complex is almost stable apart from a small weight loss because of removal of absorbed water and/or alcohol. Near 200 °C there is a sudden weight loss because of the decomposition of the complex with the evolution of gases containing nitrogen and sulfur. This is continued till 280 °C after which the weight loss becomes gradual. The region between 280 °C and 580 °C is perhaps due to the removal of sulfur from already formed cobalt sulfide phases. After 600 °C, the weight loss is very slow which implies that low sulfur content phases like CoS and Co₉S₈ would be stable for wide range of temperature. In contrast, high sulfur containing phase like CoS₂ could be stabilized for a narrow range of temperature because of the steeper change in the weight loss at low temperature.

The complex exhibits paramagnetic behavior down to the lowest measured temperature (2 K). The susceptibility and inverse susceptibility plots are shown in Figure 1b. The effective paramagnetic moment per formula unit is calculated at 300 K by using the relation: $\mu_{\rm eff} = 2.83 \ (\chi_{\rm m} T)^{1/2}$. The observed $\mu_{\rm eff}$ is 4.84 B.M., which is close to the earlier report of 4.75 B.M. for high spin Co²⁺.^[31] This confirms the absence of any magnetic impurity as well as the unreacted starting material.

The thermal decomposition of the cobalt-thiourea complex is carried out at different temperatures in order to obtain different phases of cobalt sulfide. Such strategy to obtain metal sulfides which involves single precursor solution-free approach is not very well explored in the literature. We have recently demonstrated phase evolution of different nickel sulfide phases using this strategy.^[32] When the complex is heated at 400 °C for 2 h in nitrogen atmosphere a cubic CoS₂ phase is obtained. For making other phases of cobalt sulfide, we decomposed the complex at higher temperatures till 1000 °C. Figure 2 shows the XRD patterns of samples obtained at different temperatures. At 500 °C, CoS₂ phase almost disappears with major contributions from an unknown phase and NiAs type hexagonal CoS. This unknown phase does not match to any of the reported phase in the Co-S phase diagram and could be attributed to a nonstoichiometric composition. CoS is the only major phase with a small amount of Co₉S₈ at 600 °C. At 900 °C Co₉S₈ becomes the major phase with small amount of CoS as the secondary phase. At 1000 °C, pure phase of Co₉S₈



Figure 1. (a) TGA and (b) magnetic susceptibility of cobalt-thiourea complex.

is obtained. Therefore, we have investigated the electrical and magnetic properties of CoS2 and Co9S8 phases.



Figure 2. XRD patterns of cobalt sulfide phases obtained at different temperatures.

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Figure 3. (a) XRD pattern and (b) TEM image of CoS_2 nanoparticles with electron diffraction pattern in the inset.

The XRD pattern of CoS_2 nanoparticles is shown in Figure 3a. It crystallizes in cubic pyrite type structure (space group, $Pa\bar{3}$). Crystallite size of the CoS_2 nanoparticles is obtained to be 23 nm using Scherrer's formula.TEM image of CoS_2 nanoparticles is shown in Figure 3b. The average size of the particles is ca. 20 nm with no defined morphology. Spots in the electron diffraction pattern reveal the crystalline nature of the particles.

Figure 4a shows the zero field cooled (ZFC) and field cooled (FC) magnetizations of CoS2 nanoparticles obtained at an applied magnetic field of 100 Oe. It undergoes a ferromagnetic transition at 122 K $(T_{\rm C})$ which is consistent with the previous studies of bulk CoS₂ phases. Surprisingly, Lei et al.^[33] reported a $T_{\rm C}$ of 140 K for a composition $\rm CoS_{1.93}$ and attributed the increase in the $T_{\rm C}$ to the sulfur vacancies as compared to the bulk CoS₂. There are no further reports of magnetic properties of CoS_2 nanoparticles. The fact that the T_C of the present sample is 122 K rules out the possibility of nonstoichiometry. Energy dispersive X-ray spectroscopy (EDX) shows the composition to be CoS_{2.04} for our sample. Another main feature of the ZFC-FC magnetizations is the large divergence at low temperature compared to the bulk material, which can be attributed to the surface anisotropy of the nanoparticles. According to Coey and co-workers,^[34] due to the competition between surface and bulk magnetocrystalline anisotropy the spins at the surface tend to orient normal to the surface while the spins



Figure 4. (a) ZFC-FC magnetizations and (b) isothermal magnetization of CoS_2 nanoparticles with inset showing the enlarged view of magnetization near the origin.

inside the bulk remain parallel to each other. The effect of surface anisotropy is also observed in the magnetic hysteresis of nanocrystalline CoS_2 as shown in Figure 4b. Inset of Figure 4b shows the enlarged view of the magnetization near the origin. The value of coercive field (H_C) is about 100 Oe at 2 K, which is otherwise non hysteretic in the bulk form. The value of H_C decreases as the temperature is increased and almost vanishes near T_C . Unlike the bulk phase where the saturation magnetization (M_S) is 0.84 B.M., CoS_2 nanocrystals exhibit a value of 0.61 B.M. which is around 25% less. Such a decrease in the magnetization is often observed in the ferromagnetic nanoparticles because of the surface disorder.

 CoS_2 is known to be a metallic ferromagnet. Figure 5a shows the resistivity of CoS_2 nanoparticles as a function of temperature in the cold pressed form using four probe technique. Interestingly, connectivity among the nanoparticles is sufficient enough to exhibit metallic behavior down to the magnetic transition temperature. Such a behavior is rare in the bulk electrical resistivity measurements of otherwise intrinsically conducting nanoparticles and they are often observed to be showing semiconducting property because of electron hopping between loosely connected grains. We observe an anomaly in the resistivity corresponding to the ferromagnetic transition (120 K). A broad hump is observed because of the increase in the resistivity below the transition temperature which again decreases at low temperature. Similar but much sharper hump is observed in bulk CoS_2 . The origin of this



Figure 5. (a) Resistivity as a function of temperature and (b) magnetoresistance at fixed temperatures.

anomaly is because of a very interesting property of CoS₂, namely, the transformation to a half metal below $T_{\rm C}$. Turning to a half metal implies that due to exchange splitting the density of states for minority spins near the Fermi level decreases drastically, which therefore increases the resistivity. Effect of magnetic field on resistivity of bulk CoS2 has been studied in detail but the same has not been explored in nanoparticles.^[6,35-37] Figure 5b shows magnetoresistance of cold pressed CoS₂ nanoparticles in a configuration where the magnetic field is applied perpendicular to the current direction. Magnetoresistance of 6.5% is observed at 115 K and 5 T, which varies almost linearly with respect to field. At 70 K there is a negative contribution at low field but as the field is increased positive contribution takes over. At a temperature significantly higher than the $T_{\rm C}$, resistivity does not depend on the magnetic field. The negative contribution is due to the spin orientation effect of H, while the positive contribution can be explained by the Lorentz force magnetoresistance. It has also been shown that magnetoresistance diverges near the transition temperature.^[6] Co₉S₈ is the high temperature phase in the Co-S phase diagram, which is formed peritectically at 835 °C. We obtain a pure phase of Co₉S₈ on decomposing the Cothiourea complex at 1000 °C. Co₉S₈ crystallizes in a face centered cubic structure (space group, $Fm\bar{3}m$). It consists of cubic closed packed sulfur atoms with one cobalt atom in each of the tetrahedral holes and the ninth cobalt atom occupies an



Figure 6. (a) XRD pattern and (b) temperature dependent resistivity of Co_9S_8 .

octahedral hole. Figure 6a shows the XRD pattern of the sample obtained at 1000 °C, which can be fitted with Co₂S₈ phase. Cell parameter of Co₉S₈ as obtained from Lebail fitting is 9.9282(9) Å. We cold-press the powder and measure the resistivity as a function of temperature by employing four probe technique. It shows metallic behavior throughout the temperature range with a resistivity value of 3.5 m Ω ·cm⁻¹ at 300 K as shown in Figure 6b. Figure 7a shows ZFC-FC magnetizations of Co₉S₈ at 100 Oe applied field. Unlike the finding of Lotgering et al.,^[38] wherein Curie-Weiss law is observed between 150 and 300 K, we find an entirely different behavior. There is a strong irreversibility between ZFC-FC curves and hysteresis at room temperature indicating ferromagnetism at room temperature. The observation of high magnetic ordering temperature in transistion metal sulfides is uncommon. Therefore, the observed ferromagnetism could be due to cobalt metal. However, we do not see any impurity peak in X-ray diffraction pattern. Moreover, the obtained saturation magnetization at room temperature is ca. 10% of the cobalt metal. Such a high amount of cobalt metal should be seen in X-ray diffraction. EDX analysis for the compound at different regions provides an average composition of Co₉S_{7.95}, which again rules out the possibility of ca. 10% Co metal impurity in the sample. It requires further investigation to know the exact ordering temperature and origin of magnetic ordering. At low temperature (about 5 K), a peak in the ZFC magnetization is observed. To

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Figure 7. (a) ZFC-FC magnetization of Co_9S_8 at 100 Oe with inset showing room temperature hysteresis and (b) magnetization vs. time plot in ZFC and FC conditions at 2 K and 200 Oe.

verify whether this peak indicates a spin glass state, we have performed relaxation measurements. At 2 K and under ZFC conditions, a strong relaxation is observed in the magnetization vs. time plot, while under FC conditions there is almost no relaxation (Figure 7b). The relaxation behavior under ZFC conditions is fitted with the equation $M = -1 + 2t^{\gamma}$, where γ signifies the extent of relaxation. We obtain a *g* value of 0.0037, which is comparable to alloys like Au₈₂Fe₁₈ known for exhibiting strong relaxation behavior.^[39] At 30 K, we do not observe any relaxation under ZFC conditions, which confirms the low temperature peak (5 K) to be due to spin freezing.

Conclusions

Decomposition of a Co-thiourea complex at 400 °C leads to the formation of pyrite type cubic CoS_2 nanoparticles. It exhibits metallic behavior with a ferromagnetic transition at 122 K. Near this transition, a magnetoresistance of 6.5% is observed, which might have contributions from both intrinsic as well as extrinsic effects. At moderate temperatures a mixture of CoS and Co_9S_8 phases is obtained. Bulk Co_9S_8 obtained at 1000 °C exhibits metallic behavior and ferromagnetic ordering at room temperature. It shows spin glass behavior below 5 K with strong relaxation.

Experimental Section

Synthesis of [Co(tu)₄.(NO₃)₂]: Synthesis of [Co(tu)₄.(NO₃)₂] was carried out following a previously reported procedure.^[31] In a typical synthesis, Co(NO₃)₂·6H₂O (2.91 g, 0.01 mol) was dissolved in red hot butanol (25 mL). Thiourea (3.04 g, 9.04 mol) was added and the mixture was heated to boiling, until all solid had dissolved. The color of the solution changed from red to blue. On cooling, a blue solid separated. This was suction filtered, washed with diethyl ether, dried under vacuum, and recrystallized from ethyl acetate. This produced large green-blue crystals, which were dried in vacuum at 100 °C.

Synthesis of Cobalt Sulfide Phases: The complex was heated at different temperatures between 400 and 1000 °C for 2 h in nitrogen atmosphere to obtain several phases of cobalt sulfide.

Characterization: X-ray diffraction patterns were obtained with Bruker D8 Discover and Rigaku 99 diffractometers. Rietveld refinement was carried out using FullProf software. Transmission electron microscopy images were taken from JEOL JEM 3010 fitted with Gatan CCD camera operating at accelerating voltage of 300 kV. Magnetic properties were studied with SQUID VSM, Quantum Design, USA. DC electrical resistivity measurements were carried out in Physical Property Measurement System (PPMS), Quantum Design, USA. Experiments for thermogravimetric analysis (TGA) were conducted with a Mettler Toledo Star system.

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