Synthesis, Structure, and Properties of Layered Sulfide $BaCo_{1-x}Cu_xS_{2-y}$

W. J. Zhu, S. T. Ting, H. H. Feng, and P. H. Hor

Department of Physics and Texas Center for Superconductivity at the University of Houston, Houston, Texas 77204-5932

The Cu-doped layered cobalt sulfides, $BaCo_{1-x}Cu_xS_{2-x/2}$ and $BaCo_{1-x}Cu_xS_2$, have been synthesized with the single-phase region $0 \leq x \leq 0.5$. Both series are semiconducting. The resistivity of $BaCo_{1-x}Cu_xS_2$ decreases drastically with increasing Cu content. Increasing sulfur content has a similar effect in $BaCo_{1-x}Cu_xS_{2-x/2+y}$ with the fixed Cu concentration. In contrast, the resistivity of $BaCo_{1-x}Cu_xS_{2-x/2}$ shows much less variation for different doping levels. Evolution from an antiferromagnetic to spin-glass state was observed for both series. © 1998 Academic Press

Key Words: $Ba(Co, Cu)S_2$; sulfur deficiency; conducting and magnetic properties.

INTRODUCTION

Layered late transition-metal sulfides with square metal–anion lattice have been known only to occur in a few cases. Besides the $ThCr_2Si_2$-type, e.g., AM_2S_2 (A = Tl, alkaline; M = Co, Ni), $BaCu_2S_2$, and related phases $(R_2O_2)Cu_2S_2$ (R = rare earth), $(M_2F_2)Cu_2S_2$ (M = Sr, Ba), and $ACu_{2n}S_{n+1}$ (A = Tl, alkaline), other unusual examples are $BaNiS_2$ and $BaCoS_2$ (1–3), where Ni/Co is in a square–pyramidal sulfur coordination. The sublattice Ni_2S_2 and Co_2S_2 can be viewed as a distorted rock-salt monolayer or a fluorite-type Pb_2O_2 layer. $BaNiS_2$ crystallizes in a tetragonal structure and shows a paramagnetic metallic conducting behavior, while the Mott insulator $BaCoS_2$ is monoclinic and antiferromagnetic with $T_N = 300$ K (2). The sulfur-deficient solid solution $BaCo_{1-x}Ni_xS_{2-y}$ with the composition range $0.05 \leq x \leq 0.20$ and $0.05 \leq y \leq 0.20$ exhibits a first-order transition from an antiferromagnetic insulating to a strongly correlated paramagnetic metallic state (4). The spinel system $Cu_{1+x}Co_{2-x}S_4$ (5) and covellite CuS (6), which are involved with the S $3p$ hole state, have very high conductivity and become superconducting at about 2.3 and 1.5 K, respectively. In this paper, we report the introduction of Cu at the Co site and sulfur deficiency in the layered sulfide $BaCoS_2$ and study their structure and conducting and magnetic properties.

EXPERIMENTAL

Polycrystalline samples $BaCo_{1-x}Cu_xS_{2-x/2}$ and $BaCo_{1-x}Cu_xS_2$ were synthesized by reacting the stoichiometric amounts of BaS, CoS, and Cu_2S or CuS. Reactions were carried out in sealed quartz tubes evacuated to $< 10^{-2}$ Torr, at about 20°C below their melting points. BaS was prepared by hydrogen reduction of $BaSO_4$ at 900°C. Other binary precursors were prepared from elements. To avoid formation of the brown phase Ba_2CoS_3, which is stable at a relatively lower temperature, samples of $BaCoS_2$ and $BaCo_{0.9}Cu_{0.1}S_{1.95}$ were obtained by fast quench in cool water. All others were furnace-cooled to room temperature. Incorporation of Cu at the Co site was observed to stabilize the target phase, and the reaction temperature was considerably reduced as the Cu content increased. For instance, $BaCoS_2$ was prepared at 960°C, while $BaCo_{0.5}Cu_{0.5}S_2$ can be obtained at 680°C. Compared with the sulfur-deficient phase, the sulfur-stoichiometric phase forms at a relatively lower temperature.

The resulting samples were characterized by X-ray diffraction using $CuK\alpha$ radiation. Magnetic measurements were performed at 5000 Oe on a Quantum Design MPMS SQUID magnetometer. Resistivities were measured using a standard four-probe technique, with platinum leads attached to the sample with gold epoxy.

RESULTS AND DISCUSSION

Single phases were obtained for the samples $BaCo_{1-x}Cu_xS_{2-x/2}$ and $BaCo_{1-x}Cu_xS_2$ with the composition range $0.0 \leq x \leq 0.5$, as manifested in their X-ray diffraction patterns (Fig. 1). The samples with higher copper contents contain other phases. The major impurity is $BaCu_2S_2$. The substitution of 10% Cu for Co is able to stabilize the tetragonal structure, as in $BaCo_{1-x}Ni_xS_2$ with the substitution of Ni for Co. The phase with 5% Cu dopant still crystallizes with monoclinic distortion. The structure for the highly sulfur-deficient phase $BaCo_{0.5}Cu_{0.5}S_{1.75}$ is also not tetragonal. The reflection (112) apparently splits into two

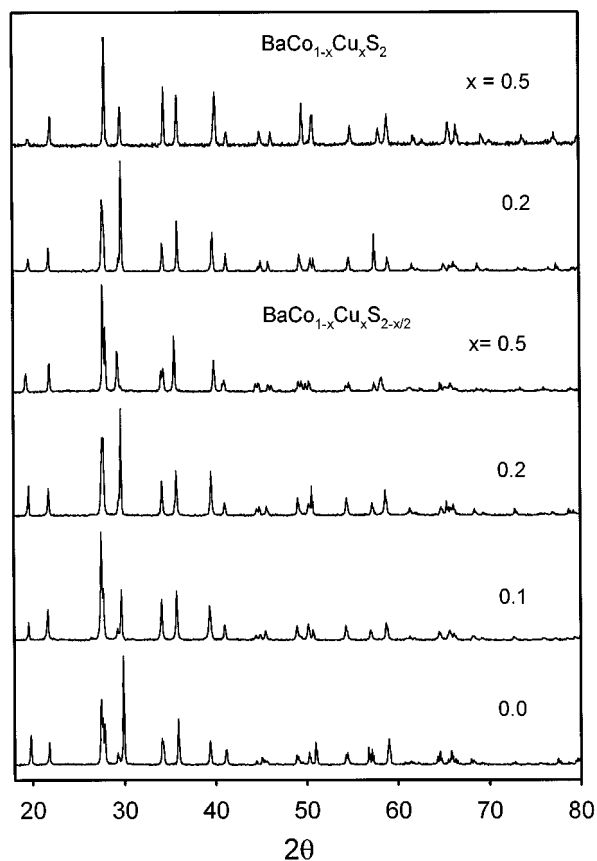**FIG. 1.** X-ray diffraction patterns for $BaCo_{1-x}Cu_xS_{2-x/2}$ and $BaCo_{1-x}Cu_xS_2$.

with the same Cu content, the sulfur-deficient phase has the longer a and b axes, as also observed in $BaCo_{0.9}Ni_{0.1}S_{2-y}$. The sulfur deficiency is expected to locate in the $(Co,Cu)_2S_2$ layer. The small cations Co and Cu were usually tetrahedral coordinated with sulfur. The apical sulfur deficiency is relatively unlikely considering minimization of repulsion among the coordination sulfur anions.

Electrical resistivities for $BaCo_{1-x}Cu_xS_{2-x/2}$ and $BaCo_{1-x}Cu_xS_2$ are shown in Fig. 2. All these samples show semiconducting behaviors. For $BaCo_{1-x}Cu_xS_{2-x/2}$ where Co, Cu, and S have the normal valences $+2$, $+1$ and -2, respectively, the value does not vary significantly in the high-temperature region (above ~ 150 K). The temperature dependence is greater for the sample with the lower Cu content. This is also true for the sulfur-stoichiometric system $BaCo_{1-x}Cu_xS_2$. The resistivity for this latter series decreases drastically as the Cu concentration increases. The resistivity ratio of $BaCoS_2$ to $BaCo_{0.5}Cu_{0.5}S_2$ is about 10^3 at 200 K. Similarly, for the series with the fixed Cu content, the resistivitiy is remarkably reduced with increasing sulfur content, especially in the high Cu composition region. At 200 K, the resistivity ratios of sulfur-deficient to stoichiometric samples with the Cu contents of 0.2 and 0.5 are about 10^2 and 10^3, respectively.

Element doping is expected to affect the Co $3d$ antiferromagnetic ordering in $BaCoS_2$. Figure 3 shows the magnetic susceptibility of $BaCo_{1-x}Cu_xS_{2-x/2}$ measured at zero field (ZFC) and field (FC) cooling modes. For the undoped sample, The Néel temperature T_N is about 300 K, as
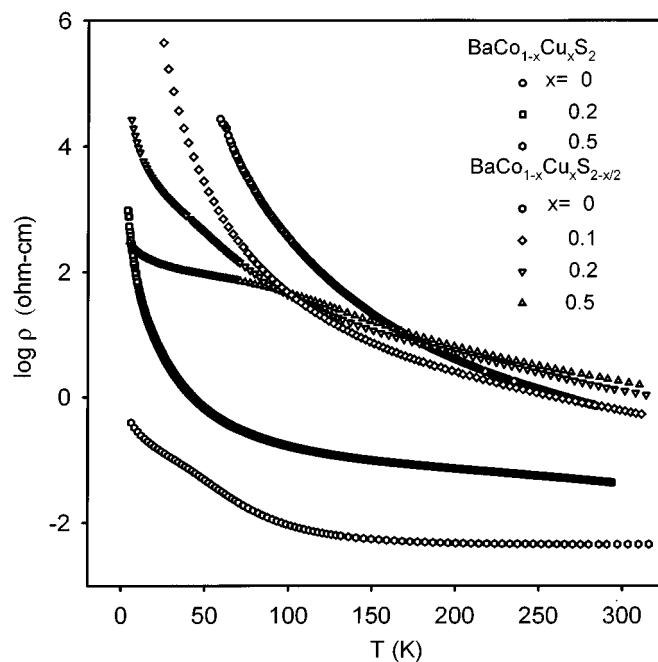
peaks. Its pattern can be indexed on a monoclinic lattice as in $BaCoS_2$ (3). Sulfur deficiency around cation Co/Cu leads to its quartacoordination, which will reconstruct to the preferred tetrahedral configuration, resulting in the structure distortion within the layer from tetragonal symmetry. In contrast, the corresponding sulfur-stoichiometric phase $BaCo_{0.5}Cu_{0.5}S_2$ keeps the tetragonal structure. Its diffraction peaks are much sharper. Table 1 lists the lattice parameters for $BaCo_{1-x}Cu_xS_{2-x/2}$ and $BaCo_{1-x}Cu_xS_2$. For both series, the a and b axes contract with increasing Cu content, while the c axis is elongated. It is interesting that

TABLE 1
Lattice Parameters for $BaCo_{1-x}Cu_xS_{2-x/2}$ and $BaCo_{1-x}Cu_xS_2$(*)

x	a (Å)	b (Å)	c (Å)	γ (°)	V (Å^3)
0.0	4.571(1)	4.571(1)	8.951(2)	90.34(3)	187.02(12)
0.1	4.570(1)		9.004(3)		188.05(14)
0.2	4.550(1)		9.017(2)		186.67(12)
*0.2	4.525(1)		8.968(2)		183.62(13)
0.5	4.513(1)	4.513(1)	9.117(3)	90.61(4)	185.68(14)
*0.5	4.491(1)		9.002(2)		181.56(12)

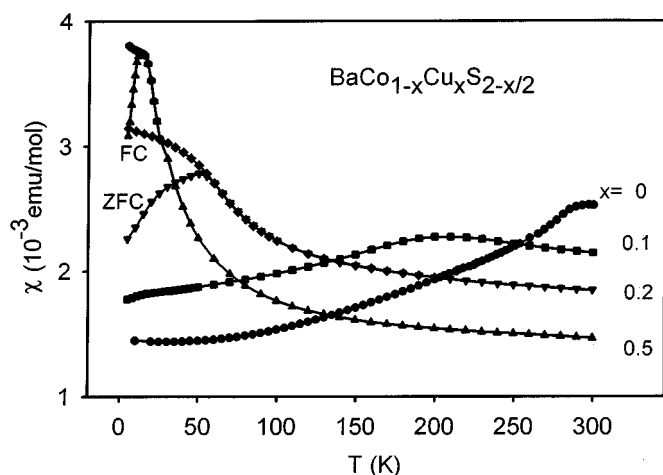**FIG. 2.** Temperature dependence of resistivity for $BaCo_{1-x}Cu_xS_{2-x/2}$ and $BaCo_{1-x}Cu_xS_2$.

FIG. 3. ZFC magnetic susceptibility versus temperature for Ba $Co_{1-x}Cu_xS_{2-x/2}$, with FC data for $x = 0.2$ and 0.5.

FIG. 4. Field dependence of ZFC and FC magnetic susceptibility for $BaCo_{0.5}Cu_{0.5}S_{1.75}$.

reported in Ref. (3). Doping only 10% Cu drives T_N to 200K with a rather broad peak. Suppression of AFM ordering of localized Co $3d$ spin is faster then that of the Ni-doped system $BaCo_{1-x}Ni_xS_2$. The sulfur deficiency further weakens the coupling of Co magnetic moments. For the sample $x = 0.2$, a relatively sharper peak shows up with maximum at about 50 K in its ZFC magnetic susceptibility. This is identified as a feature of spin-glass, because ZFC and FC magnetic susceptibilities clearly split at the above freezing temperature T_f. Such a maximum becomes much sharper and shifts down to about 12 K for the sample $x = 0.5$ with higher Cu content and more sulfur deficiencies. As shown in Fig. 4, this peak becomes broadened with increasing applied field. The normal-state magnetic susceptibility is larger for the sample with the higher Co concentration. This is reasonable, for Cu^+ and S^{2-} are nonmagnetic, the contribution solely comes from Co^{2+}. The sulfur-stoichiometric series $BaCo_{1-x}Cu_xS_2$ exhibits similar magnetic behavior. With increasing Cu content, the AFM ordering was suppressed and a spin-glass state occurs at low temperature.

The high conductivity of sulfur-stoichiometric $BaCo_{1-x}Cu_xS_2$ is related to the incorporation of unfilled S $3p$ state, where S is within the $(Co,Cu)_2S_2$ layer. As is known in CuS (7) and $TlCu_4S_3$ (8), the conduction states are Cu–S antibonding and primarily composed of S $3p$, with a small component of Cu $3d_{x^2-y^2}$. For the Mott insulator $BaCoS_2$, S $3p$ lies below the antibonding Co $3d_{x^2-y^2}$. Electron doping, e.g., Ni doping or sulfur deficiency, will partially fill this σ^* state, while hole doping, as in $BaCo_{1-x}Cu_xS_2$, removes electrons from Co–S and Cu–S antibonding states with primarily the S $3p$ character, which accounts for the above-observed lattice contraction for the sulfur-stoichiometric phase as compared with the sulfur-deficient phase. High mobility of holes in th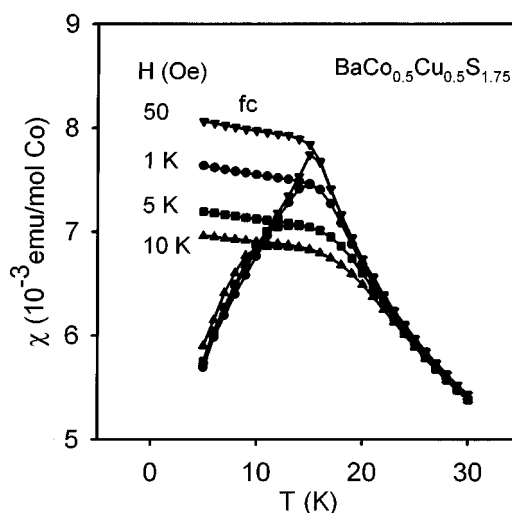ese states is responsible for substantial increase of conductivity in this series $BaCo_{1-x}Cu_xS_{2-y}$ with increasing sulfur content or Cu^+ doping concentration.

In summary, Cu has been successfully doped in $BaCoS_2$. Magnetic and conducting properties strongly depend on the Cu content and sulfur deficiency. In the normal valent series $BaCo_{1-x}Cu_xS_{2-x/2}$, antiferromagnetic coupling of the Co^{2+} moments is suppressed by Cu^+ and sulfur deficiency. The intermediate valent system $BaCo_{1-x}Cu_xS_2$ exhibits much lower resistivity. Both series develop into a spin-glass state as the doping level increases. The upper limit of phase stability $BaCo_{0.5}Cu_{0.5}S_2$ and $BaNi_{0.5}Cu_{0.5}S_2$ indicates that the maximum S $3p$ hole number doped is one per unit M_2S_2 ($M = Cu, Co, Ni$). An alternative substitution study is underway to achieve high hole concentration in the pure Co_2S_2 layer without inclusion of the impurity Cu^+ and sulfur deficiency.

ACKNOWLEDGMENT

REFERENCES

1. I. E. Grey and H. Steinfink, *J. Am. Chem. Soc.* **92,** 5093 (1970).
2. G. J. Snyder, M. C. Gelabert, and F. J. DiSalvo, *J. Solid State Chem.* **113,** 355 (1993).
3. N. C. Baenziger, L. Grout, L. S. Martinson, and J. W. Schweitzer, *Acta Crystallogr. C* **50,** 1375 (1994).
4. L. S. Martinson, J. W. Schweitzer, and N. C. Baenziger, *Phys. Rev. Lett.* **71,** 125 (1993).
5. Y. Furukawa, S. Wada, K. Miyatani, T. Tanaka, M. Fukugauchi, and M. Ishikawa, *Phys. Rev. B* **51,** 6159 (1995).
6. W. Buckel and R. Hilsh, *Z. Physik* **128,** 324 (1950).
7. H. Nozaki, K. Shibata, and N. Ohhashi, *J. Solid State Chem.* **91,** 306 (1991).
8. G. V. Vajenine and R. Hoffmann, *Inorg. Chem.* **35,** 451(1996).