



December 2007

A promising p-type transparent conducting material: Layered oxysulfide

Min-Ling Liu

Chinese Academy of Sciences

Li-Bin Wu

Chinese Academy of Sciences

Qiang Chen

Chinese Academy of Sciences

Li-Dong Chen

Chinese Academy of Sciences

I-Wei Chen

University of Pennsylvania, iweichen@seas.upenn.edu

Follow this and additional works at: https://repository.upenn.edu/mse_papers

Recommended Citation

Liu, M., Wu, L., Chen, Q., Chen, L., & Chen, I. (2007). A promising p-type transparent conducting material: Layered oxysulfide. Retrieved from https://repository.upenn.edu/mse_papers/139

Copyright 2007 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. Reprinted in *Journal of Applied Physics*, Volume 102, Issue 11, Article 116108, December 2007.

Publisher URL: <http://dx.doi.org/10.1063/1.2817643>

This paper is posted at ScholarlyCommons. https://repository.upenn.edu/mse_papers/139
For more information, please contact repository@pobox.upenn.edu.

A promising p-type transparent conducting material: Layered oxysulfide

Abstract

$\text{Sr}_3\text{Cu}_2\text{Sc}_2\text{O}_5\text{S}_2$, a layered oxysulfide, composed of anti-PbO-like $[\text{Cu}_2\text{S}_2]$ slabs alternating with perovskitelike $[\text{Sr}_3\text{Sc}_2\text{O}_5]$ slabs, was systematically studied as a p-type transparent conducting material. The material has a wide energy gap of 3.1 eV and a p-type electrical conductivity of 2.8 S cm^{-1} at room temperature. The hole mobility of $+150 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ at room temperature, which is much higher than the typical value of $\sim 10^{-1} - 10 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ found in other copper compounds. The performances of bulk undoped $\text{Sr}_3\text{Cu}_2\text{Sc}_2\text{O}_5\text{S}_2$ show the promise of copper oxysulfides as a class of p-type transparent conductive materials that is essential for optoelectronic applications.

Keywords

copper compounds, energy gap, hole mobility, optoelectronic devices, strontium compounds, wide band gap semiconductors

Comments

Copyright 2007 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. Reprinted in *Journal of Applied Physics*, Volume 102, Issue 11, Article 116108, December 2007.
Publisher URL: <http://dx.doi.org/10.1063/1.2817643>

A promising *p*-type transparent conducting material: Layered oxysulfide [Cu₂S₂][Sr₃Sc₂O₅]

Min-Ling Liu,^{a)} Li-Bin Wu,^{b)} Fu-Qiang Huang,^{b)} and Li-Dong Chen
*State Key Laboratory of High Performance Ceramics and Superfine Microstructures,
 Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050,
 People's Republic of China*

I.-Wei Chen

*Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia,
 Pennsylvania 19104-6272, USA*

(Received 2 October 2007; accepted 2 October 2007; published online 12 December 2007)

Sr₃Cu₂Sc₂O₅S₂, a layered oxysulfide, composed of anti-PbO-like [Cu₂S₂] slabs alternating with perovskitelike [Sr₃Sc₂O₅] slabs, was systematically studied as a *p*-type transparent conducting material. The material has a wide energy gap of 3.1 eV and a *p*-type electrical conductivity of 2.8 S cm⁻¹ at room temperature. The hole mobility of +150 cm² V⁻¹ S⁻¹ at room temperature, which is much higher than the typical value of ~10⁻¹–10 cm² V⁻¹ S⁻¹ found in other copper compounds. The performances of bulk undoped Sr₃Cu₂Sc₂O₅S₂ show the promise of copper oxysulfides as a class of *p*-type transparent conductive materials that is essential for optoelectronic applications. © 2007 American Institute of Physics. [DOI: 10.1063/1.2817643]

Optoelectronics based on wide-gap materials is one of the most important fields in materials science and engineering. Transparent conductive materials (TCMs) which are widely used as electrodes are especially being concerned. Among them, they are typically *n*-type semiconductors such as Sn-doped indium oxide,¹ Al-doped zinc oxide,² and Mo-doped indium oxide.³ Their conductivities in the range of ~10⁴ S cm⁻¹ are similar to those of degenerate semiconductors. In contrast, *p*-type TCMs known to date generally suffer from poor conductivities or inadequate transparency. Yet transparent optoelectronic devices based on semiconductor *p*-*n* junctions would require *both* transparent *n*-type and *p*-type materials. This has, in turn, hindered the development of useful devices that require *p*-type conduction. Therefore, discovering an excellent *p*-type TCM has become a major research focus in the field of transparent optoelectronic materials.

Since the first reported one, CuAlO₂, was found in 1997,⁴ a series of Cu-based compounds such as CuMO₂ (*M*=Al, Sc, Ga, In, and Y)^{5–9} and SrCu₂O₂ (Ref. 10) were reported as *p*-type TCMs. The essence of these compounds is the introduction of the copper 3*d* states to the top valence band, which provides conducting carriers. This idea is also applicable to chalcogenides. For example, in BaCu₂S₂, the *p*-type doped sulfide has a rather high hole mobility and electrical conductivity, although its band gap is too narrow (about 2.3 eV)¹¹ for TCM applications. Another sulfide, CuAlS₂, has already shown a promising performance in our work.^{12,13} On the other hand, when S partially substitutes for O as in oxysulfides, the band gap generally widens. For example, the layered oxysulfide LaCuOS containing layered [Cu₂S₂] slabs has a wider band gap (3.1 eV) (Refs. 14 and

15) than that of BaCu₂S₂.^{11,16} Therefore, oxysulfides may provide some new, promising TCM candidates. Indeed, Sr-doped LaCuOS (Ref. 15) has a relatively good combination of transparency and conductivity, and the mobility increases as the atomic number of chalcogen increases.¹⁷

Here, Sr₃Cu₂Sc₂O₅S₂ (SCSOS) was investigated as a new oxysulfide structural platform to simultaneously achieve optical transparency and *p*-type conductivity. The compound contains the same two-dimensional [Cu₂S₂] conducting slabs,¹⁸ as seen in BaCu₂S₂ and LaCuOS, but it also has the perovskitelike [Sr₃Sc₂O₅] slabs (see inset of Fig. 1) made of highly ionic components (Sr²⁺, Sc³⁺, and O²⁻) that widen the optical band gap. It may be further doped by cation substitution in the provskitelike slabs to optimize optoelectronic properties. Since no physical properties (optical and transport) of this material have been reported yet, we investigated its optical transparency and electrical conductivity in this paper.

Powder of SCSOS was prepared by solid-state reaction of SrS (99.5%, SinoReag.), Cu₂S (99.5%, SinoReag.), Sc₂O₃ (99.99%, SinoReag.), and freshly calcined SrO obtained from the decomposition of SrCO₃ (99.99%, SinoReag.) at

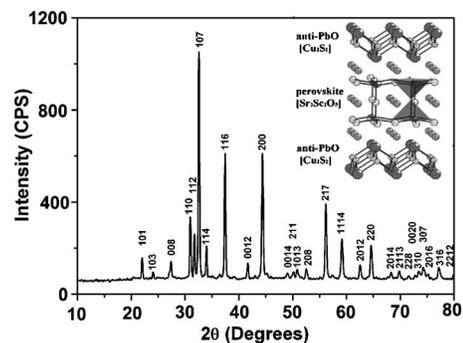


FIG. 1. XRD pattern and absorption spectrum (inset) of Sr₃Cu₂Sc₂O₅S₂. Inset: Crystal structure of Sr₃Cu₂Sc₂O₅S₂ layered oxysulfide.

^{a)}Also at Graduate School of Chinese Academy of Science, Beijing, 100039, People's Republic of China.

^{b)}Author to whom correspondence should be addressed. Electronic mail: huangfq@mail.sic.ac.cn.

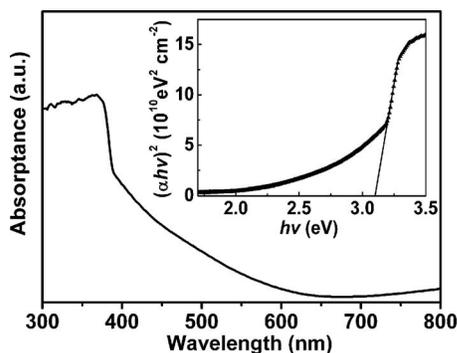


FIG. 2. Optical absorption spectra of the SCSOS powder in the wavelength range of 300–800 nm. Inset shows the plot of $(\alpha hv)^2$ against hv for estimation of directly allowed optical gap.

1400 °C. Stoichiometric amounts of the these starting reagents were loaded into a sealed fused silica tube evacuated to ≤ 1 Pa argon. The tube was initially heated to 800 °C for 12 h and naturally cooled to room temperature. The harvested powder was grounded, sealed, and reheated for another two cycles following the same procedure. The final powder was treated in a NaCN solution to remove an undesired Cu_xS phase and then densified under a pressure of 60 MPa in a graphite die ($\Phi 10$ mm) mounted in a spark plasma sintering furnace, which was held at 800 °C for 5 min under an argon atmosphere.

X-ray powder diffraction (XRD) patterns of the bulk sample were obtained (Rigaku D/max 2550 V) using $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418$ nm). The scan speed was $4^\circ/\text{min}$ with the accelerating voltage of 40 kV and emission current of 40 mA. The optical absorption spectra of the pulverized powder were measured at room temperature by an UV–visible–near infrared spectrometer (Hitachi UV-3010PC) equipped with an integrating sphere. Electrical conductivity was measured by four-probe method from 150 to 450 K, and the Hall effect was investigated on Accent HL5500 Hall system at room temperature. Silver paste was used for electrodes, and Ohmic contact was confirmed before detailed measurements were made. The Seebeck coefficient was obtained from the slope of the thermopower to the temperature gradients of 3–5 K, and the thermocouple was made of Pt and Pt/Rh filament.

The XRD pattern of the obtained pellet is shown in Fig. 1, which was indicative of only a single phase. The pulverized powder is stable in air, with a color of brownish white, which is probably due to the color centers of Cu^{2+} defects. Figure 2 shows the optical absorption spectra of the SCSOS powder, which feature a sharp drop at about 398 nm, corresponding to the fundamental absorption edge. The energy gap estimated by $(\alpha hv)^2 \sim hv$ plot inserted in Fig. 2 is about 3.1 eV. This gap is sufficiently wide for transmitting most of the visible light up to deep blue.

The conductivity of SCSOS pellet is about 2.8 S cm^{-1} , which is two orders of magnitude higher than that of undoped LaCuOS bulk ($0.01\text{--}0.1 \text{ S/cm}$) (Ref. 19) and comparable with that of Sr-doped LaCuOS film ($10^{-5}\text{--}0.012 \text{ S/cm}$).¹⁵ Seebeck coefficient of SCSOS bulk is found to be positive ($+93 \mu\text{V K}^{-1}$) at room temperature, as

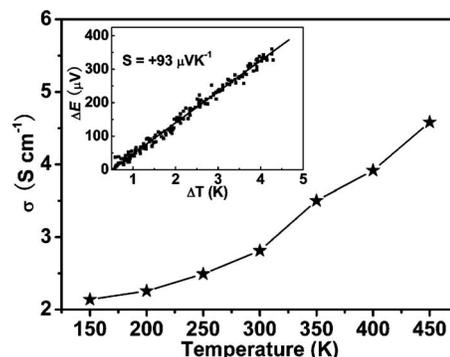


FIG. 3. The electrical conductivity of $\text{Sr}_3\text{Cu}_2\text{Sc}_2\text{O}_5\text{S}_2$ vs temperature and inset shows the temperature difference dependence of thermoelectromotive force near room temperature.

shown in the inset of Fig. 3), indicating p -type conduction. Moreover, the positive Hall coefficient $R_H = +56.8 \text{ cm}^3 \text{ C}^{-1}$ again confirms that the conductivity is p -type, due to holes. The origin of the hole carriers may be ascribed to the formation of a small amount of Cu vacancies in the Cu_2S_2 sheet, which has been reported for other oxysulfides.^{20,21} However, in SCSOS, it could also come from cation vacancies (e.g., at Sr site) in the perovskitelike $[\text{Sr}_3\text{Sc}_2\text{O}_5]$ slabs. As shown in Fig. 3, the conductivity increases with increasing temperature, exhibiting a semiconducting behavior. The hole mobility (μ) and carrier concentration (n_p) dependent on temperature (150–450 K) were displayed in Fig. 4(a). Indeed, the room-temperature hole mobility of $150 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ of SCSOS exceeds those of BaCu_2S_2 ($3.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),¹¹ Na-doped $\text{Sr}_2\text{Cu}_2\text{ZnO}_2\text{S}_2$ ($0.74 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),²² CuAlO_2 ($0.13\text{--}10.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),^{4,5} and CuGaO_2 ($0.23 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),⁷ and is the highest ever reported for any p -type TCM. The mobility is higher than that of n -type Mo-doped indium oxide ($130 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),³ which is the highest value reported. Such

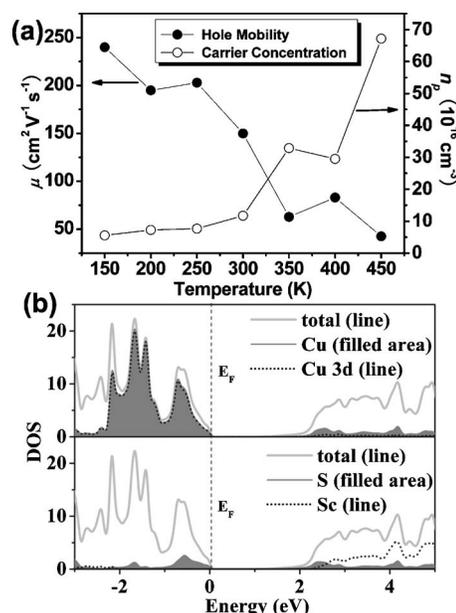


FIG. 4. (a) The hole mobility and carrier concentration dependence of temperature from 150 to 450 K. (b) Total and partial density of states of $\text{Sr}_3\text{Cu}_2\text{Sc}_2\text{O}_5\text{S}_2$, where TVB is dominated by Cu 3d states and BCB is composed of the hybridized Cu 4s and S 3p states.

a remarkable hole mobility is partly responsible for the relatively high electrical conductivity since the carrier concentration in undoped SCSOS is relatively low ($\sim 1 \times 10^{17} \text{ cm}^{-3}$).

As pointed out, the hole carriers might derive from the deficiencies of Cu sites or Sr sites in SCSOS. The latter defaults would have little structural disturbance on the $[\text{Cu}_2\text{S}_2]$ slabs, preserve the conduction path intact, and accordingly enhance the hole mobility due to low defect scattering. Actually, the thick perovskitelike $[\text{Sr}_3\text{Sc}_2\text{O}_5]$ slabs not only provide a robust tolerance for various dopant but also promise a much higher tendency of the cation-site deficiency (e.g., at Sr^{2+} “A” site) over that of $[\text{Cu}_2\text{S}_2]$ slabs, *namely*, the Cu-site vacancies. In contrast to the facility of Sr-site deficiency in perovskite slabs, cation vacancies are rather difficult to form in $[\text{La}_2\text{O}_2]$ or $[\text{Ba}_2\text{F}_2]$ slabs in LaCuOS or BaCuFS, for example. The unique perovskitelike $[\text{Sr}_3\text{Sc}_2\text{O}_5]$ slab assures a much high hole transmission in SCSOS. The very low mobilities, reported in other $[\text{Cu}_2\text{S}_2]$ -containing compounds (BaCu₂S₂, LaCuOS, etc.) could partly ascribe to the low crystallinity of their nonstoichiometric film, as derived from the broad peaks of their XRD.^{11,23,24}

As mentioned already, the $[\text{Cu}_2\text{S}_2]$ slabs in SCSOS is responsible for the *p*-type electrical conduction. This is due to the highly hybridized band between the Cu 3*d* and S 3*p* states, which is common for Cu₂S, LaCuOS, and SCSOS. The compound Cu₂S is a well-known *p*-type semiconductor that has a three-dimensional structure, whereas LaCuOS has a layered structure composed of conducting $[\text{Cu}_2\text{S}_2]$ separated by ionic $[\text{La}_2\text{O}_2]$ slabs. The reduced dimensions of the latter result in decreased hybridization which is reflected in the larger band gap, $E_g \approx 3.1 \text{ eV}$, in LaCuOS compared to $< 2.0 \text{ eV}$ in Cu₂S.²⁵ Obviously, SCSOS can be understood in a similar way in view of its similar layered structure. This was confirmed by first-principles calculations (tight binding linear muffin-tin orbital). As shown in Fig. 4(b), the inclusion of the thick perovskitelike $[\text{Sr}_3\text{Sc}_2\text{O}_5]$ gives moderate band dispersion at the top valence bands and bottom conduction bands. Meanwhile, the highly ionic components of Sr^{2+} , Sc^{3+} , and O^{2-} maintain the wide band gap necessary for optical transparency. Importantly, since the structurally robust perovskitelike $[\text{Sr}_3\text{Sc}_2\text{O}_5]$ slab, which is isolated from the conducting $[\text{Cu}_2\text{S}_2]$ slab, is amenable to various doping schemes (at either Sr^{2+} A site or Sc^{3+} “B” site),²⁶ the SCSOS platform should offer considerable freedom for tuning the transparent and conducting performance of this class of TCM. In a word, more feasible dopants on the cation sites (Sr or Sc site) in SCSOS than on only La site in LaCuOS would promise more options and better performance from the compound. For example, SCSOS should be possible to dramatically increase the hole concentration without affecting its electronic band structure, which has been validated by our preliminary results. More details are being under investigation still.

In summary, we have observed both wide band gap ($\sim 3.1 \text{ eV}$) and excellent *p*-type transport properties in trans-

parent SCSOS, which contains chemically versatile perovskitelike ionic $[\text{Sr}_3\text{Sc}_2\text{O}_5]$ slabs alternating with anti-PbO-like conducting $[\text{Cu}_2\text{S}_2]$ slabs. The bulk electrical conductivity ($\sim 3 \text{ S cm}^{-1}$ at room temperature) and hole mobility ($40\text{--}240 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from 150 to 450 K) of undoped SCSOS are already orders of magnitude higher than those of other well-known *p*-type TCMs reported to date. Moreover, its perovskitelike $[\text{Sr}_3\text{Sc}_2\text{O}_5]$ slabs offer the additional possibility of cation doping for further electrical and optical property tuning. Since TCM thin film typically possesses better properties than the bulk, we suggest that doped, transparent *p*-type SCSOS thin film devices could be a very promising candidate for optoelectronic applications.

Financial supports from 973 Program of China Grant No. 2007CB936704, and NSF of China Grant No. 20471068 are acknowledged.

¹S. P. Harvey, T. O. Mason, Y. Gassenbauer, R. Schafrank, and A. Klein, *J. Phys. D* **39**, 3959 (2006).

²T. Minami, H. Nanto, and S. Takata, *Jpn. J. Appl. Phys., Part 2* **23**, L280 (1984).

³W. N. Miao, X. F. Li, Q. Zhang, L. Huang, Z. J. Zhang, L. Zhang, and X. J. Yan, *Thin Solid Films* **500**, 70 (2006).

⁴H. Kawazoe, M. Yasukawa, H. Hyodou, M. Kurita, H. Yanagi, and H. Hosono, *Nature (London)* **389**, 939 (1997).

⁵B. J. Ingram, G. B. González, T. O. Mason, D. Y. Shahriari, A. Barnabè, D. Ko, and K. R. Peopelmeier, *Chem. Mater.* **16**, 5616 (2004).

⁶N. Duan, A. W. Sleight, M. K. Jayaraj, and J. Tate, *Appl. Phys. Lett.* **77**, 1325 (2000).

⁷K. Ueda, T. Hase, H. Yanagi, H. Kawazoe, H. Hosono, H. Ohta, H. Orita, M. Orita, and M. Hirano, *J. Appl. Phys.* **89**, 1790 (2001).

⁸H. Yanagi, T. Hase, S. Ibuki, K. Ueda, and H. Hosono, *Appl. Phys. Lett.* **78**, 1583 (2001).

⁹B. J. Ingram, B. J. Harder, N. W. Hrabe, T. O. Mason, and K. R. Peopelmeier, *Chem. Mater.* **16**, 5623 (2004).

¹⁰A. Kudo, H. Yanagi, H. Hosono, and H. Kawazoe, *Appl. Phys. Lett.* **73**, 220 (1998).

¹¹S. Park, D. A. Keszler, M. M. Valencia, R. L. Hoffman, J. P. Bender, and J. F. Wager, *Appl. Phys. Lett.* **80**, 4393 (2002).

¹²M. L. Liu, F. Q. Huang, L. D. Chen, Y. M. Wang, Y. H. Wang, G. F. Li, and Q. Zhang, *Appl. Phys. Lett.* **90**, 072109 (2007).

¹³M. L. Liu, Y. M. Wang, F. Q. Huang, L. D. Chen, and W. D. Wang, *Scr. Metall.* **57**, 1133 (2007).

¹⁴K. Ueda, S. Inoue, H. Hirose, H. Kawazoe, and H. Hosono, *Appl. Phys. Lett.* **77**, 2701 (2000).

¹⁵H. Hiramatsu, M. Orita, M. Hirano, K. Ueda, and H. Hosono, *J. Appl. Phys.* **91**, 9177 (2002).

¹⁶Y. M. Wang, M. L. Liu, F. Q. Huang, L. D. Chen, H. L. Li, X. P. Lin, W. D. Wang, and Y. J. Xia, *Chem. Mater.* **19**, 3102 (2007).

¹⁷M. L. Liu, L. B. Wu, F. Q. Huang, L. D. Chen, and J. A. Ibers, *J. Solid State Chem.* **180**, 62 (2007).

¹⁸K. Otzsch, H. Ogino, J. Shimoyama, and K. Kishio, *J. Low Temp. Phys.* **117**, 729 (1999).

¹⁹K. Takase, M. Koyano, T. Shimizu, K. Makihara, Y. Yakahashi, Y. Takano, and K. Sekizawa, *Solid State Commun.* **123**, 531 (2002).

²⁰W. J. Zhu and P. H. Hor, *J. Solid State Chem.* **134**, 128 (1997).

²¹K. Ueda and H. Hosono, *Thin Solid Films* **411**, 115 (2002).

²²K. Ueda, S. Hirose, H. Kawazoe, and H. Hosono, *Chem. Mater.* **13**, 1880 (2001).

²³H. Hiramatsu, K. Ueda, H. Ohta, M. Orita, M. Hirano, and H. Hosono, *Appl. Phys. Lett.* **81**, 598 (2002).

²⁴H. Yanagi, S. Park, D. A. Keszler, and J. Tate, *J. Solid State Chem.* **175**, 34 (2003).

²⁵S. Inoue, K. Ueda, and H. Hosono, *Phys. Rev. B* **64**, 245211 (2001).

²⁶H. Tanaka and M. Misono, *Curr. Opin. Solid State Mater. Sci.* **5**, 381 (2001).