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Short communication

$La_5Cu_6O_4S_7$, a p-type material with high conductivity prepared using La_2S_3

Wu Libin [*], Liu Minling, Huang Fuqiang, Chen Lidong, Gao Xiangdong

Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, PR China

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Abstract

A new layered oxysulfide $La_5Cu_6O_4S_7$, composed of anti-PbO-like [Cu_2S_2] slabs alternating with PbO-like [$La_{10}O_8S_2$] slabs and exhibiting high p-type conductivity, was fabricated by solid-state reaction method using La_2S_3 and characterized for the first time. The compound exhibited optical band gap of 2.0 eV, p-type electrical conductivity of 2.17 S cm^{-1} at room temperature, and metallic-like conducting behavior in the range of 150–450 K. $La_5Cu_6O_4S_7$ has presented another new and feasible way in achieving high conductivity, only partly structure-distortion rather than acceptor-doping, for applicable p-type semiconductor.

Keywords: Copper oxysulfide; p-Type; Transport properties; Crystal structure; Semiconductors

1. Introduction

The layered oxysulfide LaCuOS was firstly prepared through the oxidization of $LaCuS_2$ by Palazzi in 1981 [1]. It is a wide-gap p-type semiconductor ($E_g = 3.1$ eV) that exhibits exceptional properties compared with other wide-gap semiconductors such as ITO or AZO due to its unique crystal structure, *namely* alternately stacking of two-dimensional layers like [La_2O_2]/[Cu_2S_2] slabs, and conducting path of [Cu_2S_2] which introduces Cu 3d states to the top valence band and provides conducting carriers [2]. Until now, mostly promising p-type semiconductors have been searching in oxychalcogenides under the direction of this idea [2–4].

However, optoelectronic devices based on p–n junctions would required both p- and n-type transparent conducting materials (TCMs). Compared with the typical n-type oxides such as Sn- or Mo-doped indium oxides and Al-doped zinc oxides [5,6], whose conductivities in the range of $\sim 10^4$ S cm^{-1} are similar to those of degenerate semiconductors, the situation of the shortage for applicable p-type TCMs with high conductivity remained unchanged, and much more efforts were demanded in this field. Therefore, to discover new p-type TCMs with high conductivity has become a major research focus in the field of optoelectronic materials. Different from the commonly adopted method to improve the conductivity of semiconductors, *i.e.* ion-doping to increase carrier concentration *n*, structure-distortion of $La_5Cu_6O_4S_7$ presented another new and feasible way.

In this paper, we reported the high conductivity of $La_5Cu_6O_4S_7$ by partly modulating its crystal structure and the p-type conduction for the first time. For comparison, we also prepared LaCuOS as a reference material (RM) to discuss the different optical, conducting and structural properties.

2. Experimental

Powder of $La_5Cu_6O_4S_7$ was prepared by solid-state reaction of CuO (99.5%), Cu_2O (99.5%) and La_2S_3 (99.5%) powders in a sealed fused silica tube evacuated to ≤ 1 Pa argon. The sample was slowly heated to 973 K in 18 h, kept at that temperature for 24 h, and naturally cooled to room temperature. The harvested powders were grounded, sealed and again calcined at 1073 K for 48 h. The final powders were orange and densified under a pressure of 60 MPa in a graphite die (Ø10 mm) mounted in a spark plasma sintering (SPS) furnace, which was held at 1023 K for 3 min under an argon atmosphere. Reference material of LaCuOS was prepared by a similar way except for the increased holding and densifying temperature (1123 and 1073 K, respectively).

X-ray powder diffraction (XRD) patterns of the bulk samples were obtained (Rigaku D/max 2550 V) using Cu Ka

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[*] Corresponding author.
E-mail address: wlb@mail.sic.ac.cn (W. Libin).

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radiation (λ = 0.15418 nm). The scan speed was 4°/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–vis-NIR spectrometer (Hitachi UV-3010PC) equipped with an integrating sphere. Electrical conductivity was measured by four-probe method from 150 to 500 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 slop of the thermopower to the temperature gradients of 3–5 K, and the thermocouple was made of Pt and Pt/Rh filament.

3. Result and discussion

The XRD patterns of the obtained pellets are shown in Fig. 1, which were indicative of only a single phase LaCuOS (JCPDS: No. 84-0261) and the expected phase $La_5Cu_6O_4S_7$. The pulverized $La_5Cu_6O_4S_7$ powder was stable in air, with a color of orange. Fig. 2 shows the optical absorption spectra of LaCuOS and $La_5Cu_6O_4S_7$ powder, which feature a sharp drop at about 400 and 620 nm, respectively, corresponding to their fundamental absorption edges of 3.1 and 2.0 eV in energy. The energy gap (E_g) of $La_5Cu_6O_4S_7$ has also been derived from the plot of $(\alpha h\nu)^2 \sim h\nu$ in the range of 1.5–2.8 eV, inserted in Fig. 2. By extrapolation of linear dependence of $(\alpha h\nu)^2$ versus $h\nu$, the value of E_g is found to be 2.0 eV, consistent with the typical value to orange color of $La_5Cu_6O_4S_7$ and indicating the material is a directly allowed transition [7]. Compared with E_g (3.1 eV) of LaCuOS (see Fig. 2), $La_5Cu_6O_4S_7$ has shown a smaller energy gap. The difference had witnessed the gap modulating by structure-distortion, resulting from *P*4/*nmm* of LaCuOS to I*mma* of $La_5Cu_6O_4S_7$ due to one fifth O atoms are substituted by S atoms along the [0 1 0] direction [8].

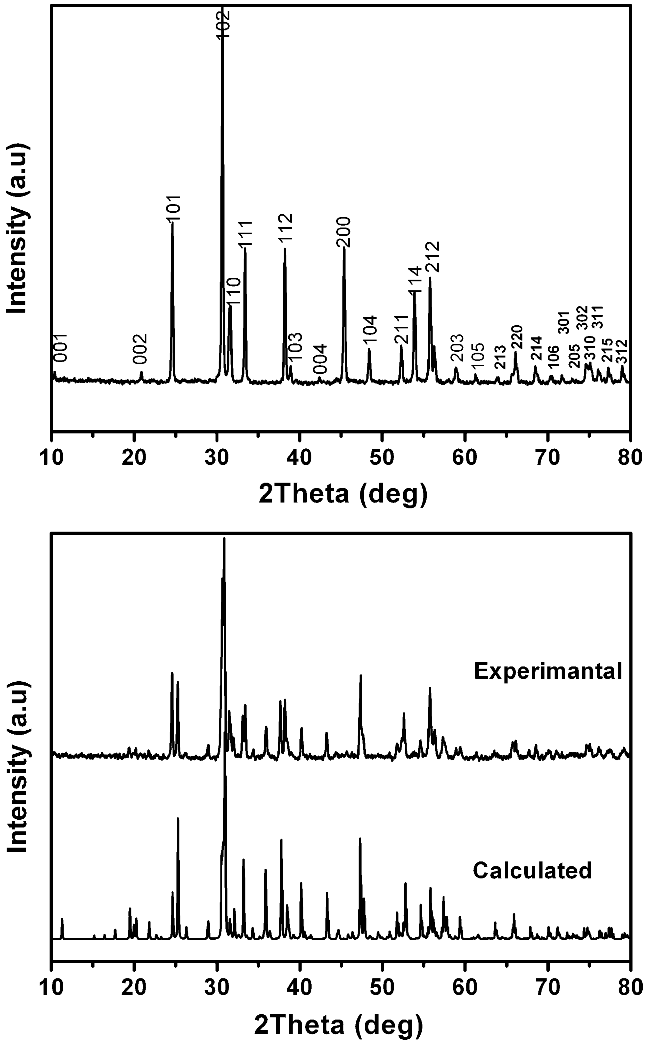

Fig. 1. X-ray diffraction spectra for LaCuOS (top) and $La_5Cu_6O_4S_7$ (bottom).

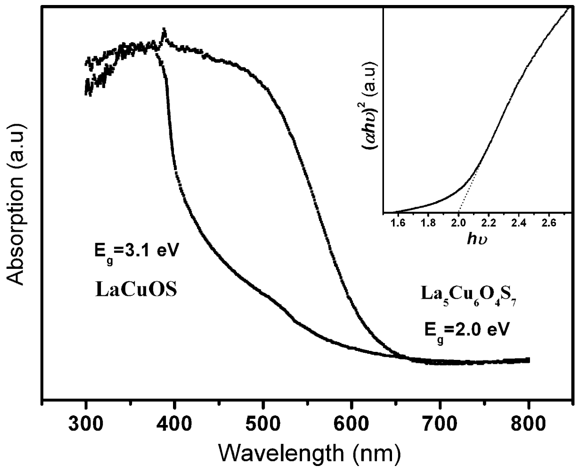

Fig. 2. Optical absorption spectra of powdered LaCuOS and $La_5Cu_6O_4S_7$ in the wavelength range of 300–800 nm. Inset shows the plot of $(\alpha h\nu)^2$ against $h\nu$ for estimation of directly allowed optical gap for $La_5Cu_6O_4S_7$.

The conductivity of $La_5Cu_6O_4S_7$ pellet is about 2.17 S cm^{-1} at room temperature, which is $\sim 10^2$ to 10^3 times higher than that of LaCuOS bulk (0.01–0.1 S cm^{-1} in Ref. [4], 3.9×10^{-3} S cm^{-1} in RM) and comparable with that of Sr-doped LaCuOS film (0.2–7.7 S cm^{-1}) [3]. We also noted that the conductivity along [1 0 0] of a single crystal of $La_5Cu_6O_4S_7$ was previously reported to be 2.6×10^4 S cm^{-1} [8], much greater than that of the sintered pellet. That is not surprising, because $La_5Cu_6O_4S_7$ is anisotropic in its transport properties. From the crystal structure and band structure calculations [8], the conductivity perpendicular to the $[Cu_2S_2]/[La_2O_2]$ layers (along [0 0 1] direction) should be much smaller than that along the layers. In the single crystal of $La_5Cu_6O_4S_7$, the conductivity was determined along the layers, especially in the [1 0 0] direction. In addition, the measurement on the sintered bulk is an average over all orientations, apart from grain boundaries and defects impeding the transport of holes. As for the Seebeck coefficient, $La_5Cu_6O_4S_7$ bulk is found to be positive (+18 μV/K at room temperature), indicating p-type conduction. Furthermore, the Hall coefficient R_H = +15.5 cm^3/C again confirms that the conductivity is p-type, due to hole carriers. The origin of the holes may be ascribed to the formation of a small amount of Cu vacancies in the $[Cu_2Q_2]$ sheet, which has been reported for other oxysulfides and oxytellrides [9–12]. However, in $La_5Cu_6O_4S_7$, the hole carriers could also come from the vicinity

Table 1
Room-temperature electrical conductivity (σ), Hall mobility (μ), hole concentration (n), Seebeck coefficient (S), optical band gap (E_g) of $CuAlO_2$, LaCuOS and $La_5Cu_6O_4S_7$.

Sample	Cond. σ (S cm^{-1})	Hall coeff. μ ($cm^2\ V^{-1}\ s^{-1}$)	Holes n (cm^{-3})	Seebeck coef. S (μVK^{-1})	Band gap E_g (eV)	Ref.
$CuAlO_2$	9.5×10^{-2}	10.4	1.5×10^{17}	+183	3.1	[16]
LaCuOS film	1.2×10^{-2}	~0.5	1.5×10^{17}	+150	3.1	[2,14]
	6.4×10^{-5}	0.20	2.0×10^{15}	+713	3.1	[3]
LaCuOS bulk	3.9×10^{-3}	9.3	2.6×10^{15}	+141	3.1	This work
LaCuOSe bulk	~1			+130		[15]
LaCuOSe:Mg film	24	8	1.9×10^{19}	+230	2.8	[14]
LaCuOTe bulk	1.65	80.6	1.3×10^{17}	310	2.3	[11]
$La_5Cu_6O_4S_7$ bulk	2.17	29.5	4.5×10^{17}	+18	2.2	This work

of Cu^+ (or denoted as $Cu^{+(1+\delta)}$) since the copper atoms in this compound have an average oxidation state of +7/6.

The electrical conductivity (σ) of a bulk ceramic sample of $La_5Cu_6O_4S_7$ is shown in Fig. 3 as a function of temperature (T). The material exhibits metallic-like conducting behavior, whose conductivity decreases with increasing temperature. Although $La_5Cu_6O_4S_7$ is related to the LnCuOQ structure (Ln = rare-earth element; Q = S, Se, Te), belonging to the LaAgOS structure type [13], the variations of the conductivity with temperature increasing (150–500 K) are quite different: LaCuOS (see Fig. 3) and LaCuOSe (not shown) are both typical semiconductors, σ increase with increasing temperature; LaCuOTe may be described as a degenerate semimetal and its conductivity is not sensitive to temperature [11]; $La_5Cu_6O_4S_7$ shows some similar behavior as LaCuOTe and illustrates a metallic conducting characteristic (see Fig. 3). As stated in Ref. [11], the increasing hybridization of Cu 3d and Q np states (n = 3 for S, 4 for Se, 5 for Te) might be responsible for this variation (semiconducting to semimetal, to metallic). Herein more than one S atoms (exactly one plus one fifth) in $La_5Cu_6O_4S_7$ could play the same role as Te of LaCuOTe. Moreover, along with partly structure-distortion [8] the Cu $3d^{9+x}$ configuration of $La_5Cu_6O_4S_7$ would bring more Cu–Cu antibonding 3d states to be unoccupied besides droping the Fermi level, and lead to Cu–Cu more bonding. As a result, the Cu–Cu interactions become bonding and the conducting $[Cu_2S_2]$ layers become metallic. Therefore, we might describe $La_5Cu_6O_4S_7$ as a metal or degenerate semimetal; a similar degenerate conductivity was found in Mg-doped LaCuOSe [14].

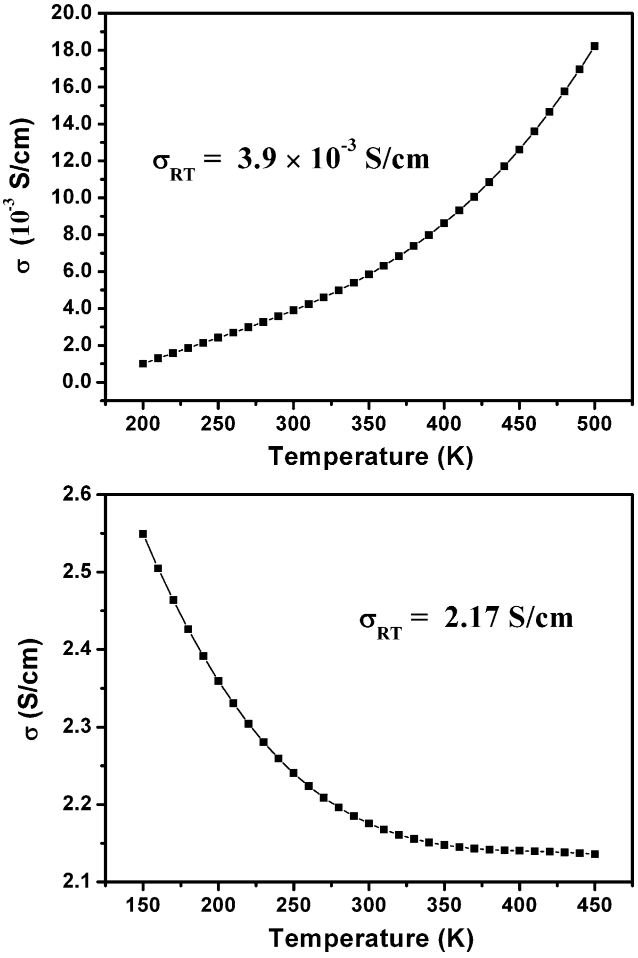

Fig. 3. The electrical conductivity of LaCuOS (top) and $La_5Cu_6O_4S_7$ (bottom) dependence of temperature from 150 to 500 K.

Since the conductivity is usually connected with many parameters such as Hall mobility (μ), carrier concentration (n), electrical quantity of carrier (Q) *etc*., and μ correlates with n each other, it is necessary to compare them with those of some well-known TCMs, to find the difference and discuss the root cause. Table 1 lists some electrical properties for $CuAlO_2$, LaCuOQ (Q = S, Se, Te) and $La_5Cu_6O_4S_7$ at room temperature. The conductivity of the bulk sample of LaCuOS is in the range of the films. The conductivity of the bulk LaCuOTe is about 40 times higher than that of bulk LaCuOS, but much lower than that of the LaCuOSe:Mg film. In another word, LaCuOQ demonstrates an increasing conductivity in the order of S to Se to Te. Although $La_5Cu_6O_4S_7$ is an oxysulfide rather than oxytelluride, the conductivity of 2.17 S cm^{-1} presents a comparable value (much higher) to that of LaCuOTe. On the reason why excellent transport property could be achieved in this oxysulfide, we could find the answer from the relatively higher carrier concentration, 10^{17} in $La_5Cu_6O_4S_7$/LaCuOTe and 10^{15} in LaCuOS, respectively. As for the lower mobility of $La_5Cu_6O_4S_7$ compared to the bulk LaCuOTe, it could find some reasonable interpretation based on the assumption that more carriers would interfere with each other and hinder the holes from moving freely. On the other hand, the larger dispersion of the Cu 3d states and increased distribution of Te 5p states near the VBM are also responsible for the improved hole mobility in LaCuOTe.

4. Conclusions

A high conductivity p-type $La_5Cu_6O_4S_7$ was prepared by solid phase reaction method using La_2S_3, CuO and Cu_2O, and characterized for the first time. $La_5Cu_6O_4S_7$ presented a high conductivity ($2.17\ S\ cm^{-1}$) *via* partly structure-distortion only through one-fifth S atoms substituting for O in LaCuOS. Based on positive Seebeck and Hall coefficients, we elucidated the p-type conduction for $La_5Cu_6O_4S_7$. Associated with a band gap of 2.0 eV, the bulk $La_5Cu_6O_4S_7$ showed a promising p–n junctions application for its excellent transport properties; and what is more, $La_5Cu_6O_4S_7$ has illustrated a good way in pursuit of applicable p-type TCMs by structure-distortion, compared with acceptor-doping to noticeably increase the conductivity.

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