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Synthesis, structure, and optical properties of the new lanthanum copper oxysulfide $La_3CuO_2S_3$

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Abstract

The new quaternary lanthanum copper oxysulfide $La_3CuO_2S_3$ has been synthesized by the reaction of La_2S_3 and CuO at 1223 K. This compound crystallizes in space group *Pnma* of the orthorhombic system with four formula units in a cell of dimensions at 153 K of $a = 14.0318(7)$ Å, $b = 3.9342(2)$ Å, and $c = 12.5212(6)$ Å. The structure of $La_3CuO_2S_3$ consists of a three-dimensional framework of interconnected LaO_nS_{8-n} bicapped trigonal prisms and CuS_4 tetrahedra. Optical absorption measurements on a $La_3CuO_2S_3$ single crystal led to derived band gaps of 2.01 eV in both the [010] and [001] directions.

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1. Introduction

With the discovery of high-T_c superconductivity in copper-based materials, the structures, crystal chemistry, and physical properties of layered cuprates have been thoroughly investigated [1–3]. Partial replacement of oxygen by chalcogen atoms (Q= S, Se, Te) leads to the formation of metal oxychalcogenides, a family of compounds that have received comparatively little attention. The first representatives were quaternary rare-earth copper oxychalcogenides LnCuOQ (Q= S, Se) [4–7] with the tetragonal LaAgOS-type structure [4]. This layered structure can be regarded as a "filled" version of the PbFCl structure [8] or as the intergrowth of fluorite-like $[Ln_2O_2]$ and antifluorite-like $[Cu_2Q_2]$ layers. More recently, the substitution of some O atoms with S atoms in the $[Ln_2O_2]$ layer led to the formation of $La_5Cu_6O_4S_7$, a compound in which Cu has an average oxidation state of +7/6 [9]. This orthorhombic phase crystallizes with a layered structure closely related to the tetragonal LnCuOS structure [4].

As an extension of this family of oxychalcogenides, we describe here the synthesis, structure, and optical properties of the new quaternary lanthanum copper oxysulfide $La_3CuO_2S_3$.

2. Experimental

2.1. Synthesis

Deep-red needles of $La_3CuO_2S_3$ were obtained in the reaction of La_2S_3 (2.0 mmol, Strem, 97%) and CuO (1.5 mmol, Alfa, 99.9%) in a fused-silica tube with KI (3.5 mmol, Aldrich, 99.99%) added to promote crystal growth. The materials were mixed and sealed in an unprotected tube that was then evacuated to 5×10^{-5} Torr. The tube was heated to 1223 K at 0.25 K/min, kept at 1223 K for 5 days, cooled at 0.05 K/min to 923 K, and then the furnace was turned off. The reaction mixture was washed free of iodide salts with water and then dried with acetone. Semiquantitative analyses were performed with a Hitachi 3500N SEM. Oxygen was detected but could not be quantified. EDX results for the heavier elements confirmed the presence of La, Cu, and S in the approximate ratio 3:1:3.

2.2. Crystallography

Single-crystal X-ray diffraction data were collected on a 0.30 mm × 0.040 mm × 0.052 mm needle with the use of graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [10]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting

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Table 1
Crystal data and structure refinement for $La_3CuO_2S_3$

Formula weight	608.45
Space group	*Pnma*
a (Å)	14.0318(7)
b (Å)	3.9342(2)
c (Å)	12.5212(6)
V (Å^3)	691.22(6)
Z	4
T(K)	153 (2)
λ (Mo$K\alpha$)	0.71073
ρ_c (g/cm^3)	5.847
Crystal dimensions (mm)	0.300 × 0.052 × 0.040
μ (cm^{-1})	220.1
Transmission factors	0.041–0.433
$R(F)$[a]	0.0244
$R_w(F_o^2)$[b]	0.0592

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

[b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.04 \times F_o^2)^2$ for $F_o^2 \geqslant 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Table 2
Atomic coordinates[a] and equivalent isotropic displacement parameters for $La_3CuO_2S_3$

Atom	x	z	U_{eq} (Å^2)[b]
La(1)	0.13201(2)	0.40327(2)	0.0060(1)
La(2)	0.20765(2)	0.11266(3)	0.0055(1)
La(3)	0.42251(2)	0.40037(2)	0.0051(1)
Cu	0.08592(5)	0.67155(5)	0.0093(2)
S(1)	0.2195(1)	0.7900(1)	0.0064(3)
S(2)	0.4136(1)	0.0666(1)	0.0064(3)
S(3)	0.4441(1)	0.7339(1)	0.0072(3)
O(1)	0.0730(2)	0.0071(3)	0.0056(7)
O(2)	0.2711(3)	0.5072(3)	0.0066(7)

[a] The y-coordinate of all atoms is 1/4.

[b] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected interatomic distances (Å) and angles (deg) for $La_3CuO_2S_3$

La1–O2	2.346(4)	La3–O1 × 2	2.379(2)
La1–S2 × 2	2.909(1)	La3–O1	2.409(4)
La1–S3 × 2	3.083(1)	La3–O2	2.511(4)
La1–S2	3.088(1)	La3–S1 × 2	3.122(1)
La1–S1 × 2	3.198(1)	La3–S3 × 2	3.194(1)
La1–Cu	3.4208(7)	La3–Cu × 2	3.4774(6)
La2–O1	2.306(4)	Cu–S3	2.316(2)
La2–O2 × 2	2.388(2)	Cu–S2 × 2	2.366(1)
La2–S2	2.947(1)	Cu–S1	2.390(1)
La2–S1 × 2	3.138(1)	S2–Cu–S1	110.03(4)
La2–S3 × 2	3.272(1)	S2–Cu–S2	112.51(6)
La2–Cu × 2	3.5782(6)	S3–Cu–S2	106.64(4)
		S3–Cu–S1	110.90(5)

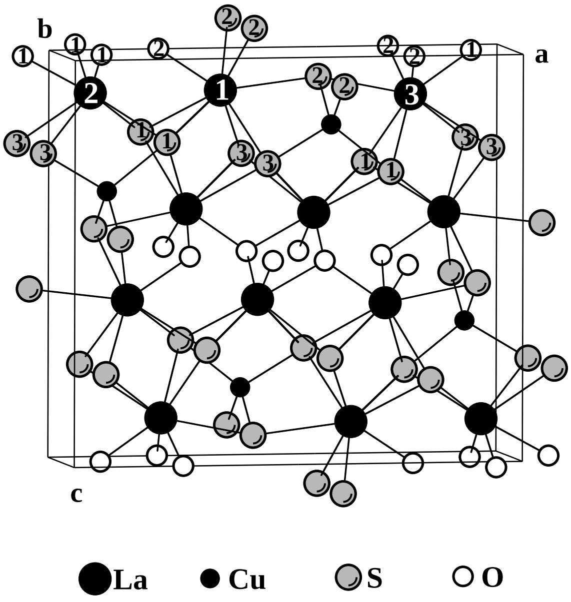

Fig. 1. Unit cell of $La_3CuO_2S_3$.

50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606, 606, 606, and 606 frames at ϕ settings of 0°, 90°, 180°, and 270°. The exposure times were 15 s/frame. The collection of intensity data was carried out with the program SMART [10]. Cell refinement and data reduction were carried out with the use of the program SAINT [10], and a face-indexed absorption correction was performed numerically with the use of the program XPREP [11]. The program SADABS [10] was then employed to make incident beam and decay corrections.

The structure was solved and refined in the orthorhombic space group *Pnma*. After the positions of the heavy atoms (La, Cu, S) were determined by direct methods with the program SHELXS of the SHELXTL-PC suite of programs [11] the positions of the O atoms were found in a difference electron-density map. The structure was refined by full-matrix least-squares techniques with the use of the program SHELXL [11]. Additional experimental details are given in Table 1. The program STRUCTURE TIDY [12] was used to standardize the positional parameters. Fractional coordinates and equivalent atomic displacement parameters are listed in Table 2. Table 3 presents selected interatomic distances and bond angles.

2.3. *Optical measurements*

Optical absorption measurements on a $La_3CuO_2S_3$ single crystal were performed with the use of an Ocean Optics model S2000 spectrometer over the range 400 nm (3.10 eV) to 800 nm (1.55 eV) at 293 K. The spectrometer was coupled by fiber optics to a Nikon TE300 inverted microscope. White light originated from the TE300 lamp and passed through a polarizer before reaching the sample. The crystal was positioned at the focal point above the 20 × objective by means of a goniometer mounted on translation stages (Line Tool Company). The light transmitted through the crystal was then spatially filtered before being focused into the 400 μm core diameter fiber coupled to the spectrometer. Fine alignment of the microscope assembly was achieved by maximizing the transmission of the lamp profile. The excitation white light was polarized perpendicular to the crystal *a*-axis. The optical band gap was calculated from the absorption spectrum by means of a simple inflection point analysis that does not require a correction for crystal thickness or a spot size fill factor. Although this method may slightly overestimate the location of the band edge, it is much more reproducible than the one used previously [13], and it is independent of the spectral baseline.

3. Results and discussion

The compound $La_3CuO_2S_3$ crystallizes in new structure type. A labeled view of the unit cell is provided in Fig. 1. The asymmetric unit cell contains three crystallographically independent La atoms, one Cu atom, three S atoms, and two O atoms, all located at sites with *m* symmetry. The structure consists of a three-dimensional framework of LaO_nS_{8-n} bicapped trigonal prisms and CuS_4 tetrahedra. The La(1)OS_7 bicapped trigonal prism has one S atom and one O atom cap; the La(2)O_3S_5 bicapped trigonal prism has one S atom and one O atom cap; the La(3)O_4S_4 trigonal prism has two O atom caps. Each La(1)OS_7 and La(3)O_4S_4 polyhedron has two triangular face-sharing neighbors along [010] and two edge-sharing ones along [100] whereas two La(2)O_3S_5 bicapped trigonal prisms share faces along [010] (Fig. 2). The Cu atom is coordinated to a slightly distorted tetrahedron of S atoms (Fig. 1 and Table 3). The CuS_4 tetrahedra form one-dimensional double isolated $^1_\infty[CuS_3^{5-}]$ chains along [010] by the sharing of vertices (S(2)) with two neighboring tetrahedra. Such $^1_\infty[CuS_3^{5-}]$ chains have been found in ALn_2CuS_4 (*A*= K, Rb, *Ln*= Nd, Sm, Gd) [14,15] and Ba*Ln*CuS_3 (*Ln*=rare earth or Sc) [16,17]. Each CuS_4 tetrahedron in the $^1_\infty[CuS_3^{5-}]$chains links by edge sharing with three La(1)OS_7, two La(2)O_3S_5, and two La(3)O_4S_4 bicapped trigonal prisms.

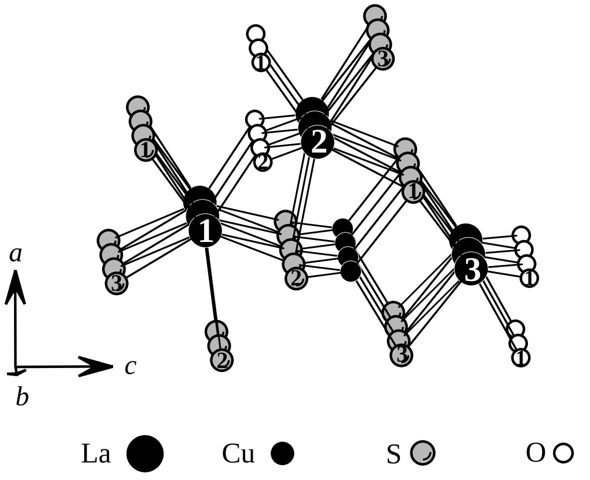

Fig. 2. The connection of LaO_nS_{8-n} and CuS_4 polyhedra in the structure of $La_3CuO_2S_3$.

Selected bond distances for $La_3CuO_2S_3$ are displayed in Table 3. The distances La–O (2.306(4)–2.511(4) Å) and La–S (2.909(1)–3.272(1) Å) found in $La_3CuO_2S_3$ may be compared with those found in LaCuOS (La–O, 2.367(3); La–S, 3.253(4) Å) [5] and $La_5Cu_6O_4S_7$ (La–O, 2.337(2)–2.446(3) Å; La–S, 2.969(5)–3.231(1) Å) [9]. The Cu–S bond lengths are reasonable, from 2.316(2) to 2.390(1) Å, compared with 2.372(1)–2.398(1) Å and 2.315(2)–2.624(3) Å in $BaLaCuS_3$ [16] and KBi_2CuS_4 [18], respectively. The S–Cu–S angles are in the range 106.64(4)–112.51(4)° indicating a slight distortion of the CuS_4 tetrahedra.

The three-dimensional structure of $La_3CuO_2S_3$ results in the following coordination geometries about O and S: O(1)—tetrahedrally coordinated by three La(3) and one La(1); O(2)—tetrahedrally coordinated by one La(1), two La(2), and one La(3); S(1) and S(3)—surrounded by six La in a trigonal prism capped by one Cu; S2—irregular octahedral geometry constructed from four La and two Cu atoms.

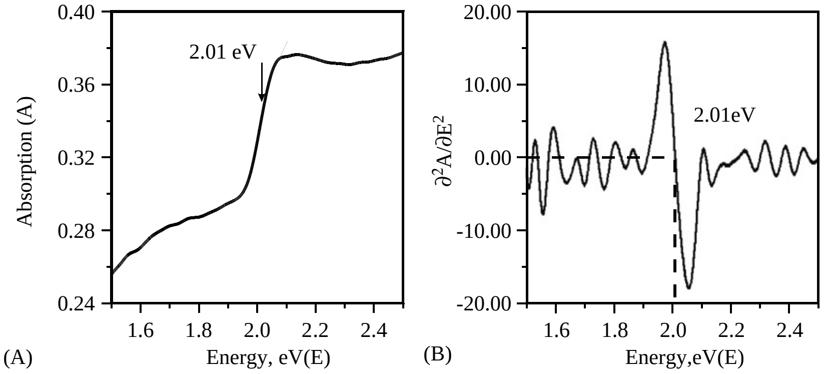

Fig. 3. Optical absorption spectrum (A) and band gap calculation (B) for $La_3CuO_2S_3$. The light is in the [001] direction.

Because the shortest S–S interactions are 3.229(2) Å there is no S–S bonding in $La_3CuO_2S_3$. Charge balance is therefore achieved with the expected formal oxidation states of La^{3+}, Cu^{+}, S^{2-}, and O^{2-}.

Fig. 3 shows the optical absorption spectrum and its second derivative for light impinging on the (001) crystal face of a $La_3CuO_2S_3$ single crystal. Analysis leads to a band gap of 2.01 eV. Similar analysis of the absorption spectrum obtained with light in the [010] direction also leads to a band gap of 2.01 eV. This lack of variation with direction is to be contrasted with the earlier results for members of the Cs*Ln*ZnSe$_3$ series [13].

Single-crystal materials, such as $La_3CuO_2S_3$ discussed here, with large optical densities and well-defined optical band gap energies may find application in optical waveguides [19] and optical filters [20].

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