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Preparation and crystal structure analysis and physical properties of (LaO)CuTe

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Abstract

A single phase of (LaO)CuTe has been synthesized by the solid-state reaction. The lattice constants, a and c, refined by Rietveld analysis are 0.41815 and 0.93417 nm, respectively. The temperature dependence of the electrical resistivity shows a metallic behavior above 150 K and changes to a semiconductive behavior below that temperature. The value of the electronic specific heat coefficient estimated from the T^2 dependence of the C/T was almost zero. The magnetic susceptibility shows diamagnetism which is attributed to the core diamagnetism.

Keywords: Layered oxychalcogenide; Crystal structure; (LaO)CuS; (LaO)CuTe; Physical properties

1. Introduction

The layered oxysulfide (LaO)CuS was recently found to be a transparent p-type semiconductor with wide band gap of 3.2 eV [1,2]. The crystal structure belongs to tetragonal system with space group $P4/nmm$. The La–O and Cu–S layers are alternately stacked along the c-axis as shown in Fig. 1. The Cu–S layer in which Cu ion is surrounded tetrahedrally by four S ions is expected to have a two dimensional character.

Previously, various substitution effects on (LaO)CuS were examined and the physical properties of $(La_{1-x}Sr_xO)CuS$, $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ were investigated by means of electric transport, magnetic [3,4], nuclear magnetic resonance [5], X-ray and ultraviolet spectroscopy [1] studies. Particularly, a semiconductor-metal transition which occurs in the $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ system at $x = 0.03$ is noticeable [4].

On the other hand, the substitution effects on S by heavy chalcogen ion Se were studied in $(LaO)CuS_{1-x}Se_x$ [6,7]. The reduction of the band gap down to 2.8 eV for $x = 1$ was reported. The effect of the substitution for the chalcogen site on the band gap is similar to that of II–VI semiconductors. Moreover, the electrical resistivity of (LaO)CuTe is predicted to decrease by the large spatial extent of the $5p$ orbital of Te ion. In this study, we have attempted to synthesize (LaO)CuTe and investigate the physical properties.

2. Experimental

(LaO)CuS are usually synthesized by solid-state reaction of La_2O_3 (99.9 %), La_2S_3 (99.9 %) and Cu_2S (99.9 %) in evacuated silica tube [1]. In the present study, (LaO)CuTe was prepared under the following procedure. The stoichiometric mixture of La (99.9 %), Cu (99.99 %), Te (99.99 %) and La_2O_3 (99.999 %) powders were put into Ta tube under Ar atmosphere to avoid a reaction between La and silica and sealed in an evacuated silica tube. The mixture was preheated at 700 °C for 40 h and then the reaction was completed by heating at 900 °C for 40 h.

The powder X-ray diffraction (XRD) measurement was carried out at room temperature using an XRD diffractometer with a Cu target (Rigaku Rint 1100). The intensity data collected from $2\theta = 5–90^\circ$ with a scan step of 0.01° were analyzed by the Rietveld method using the program code, RIETAN2000 [8].

The photoluminescence (PL) measurement was carried out at 4 and 300 K using the 325 nm lines from a He–Cd laser.

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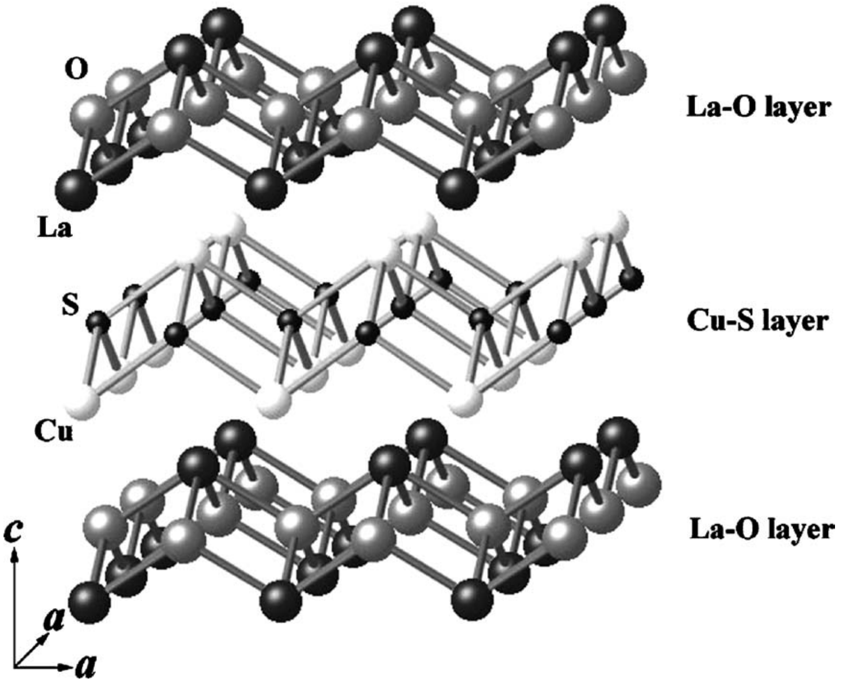

Fig. 1. Crystal structure of LaO(CuS). La–O layer and Cu–S layer are alternately stacked along the *c*-axis.

The electrical resistivity was measured by the four-probe method. The specific heat and magnetization measurements were carried out using Quantum Design PPMS 7N system.

3. Results and discussion

The measured XRD pattern and the fitted pattern by the Rietveld analysis in the 2θ range between 20° and 60° are shown in Fig. 2. The values of R_{wp} and S were 8.24 and 1.23 %, respectively. All the X-ray diffraction peaks were indexed on the base of the tetragonal system with the lattice constants $a = 0.41824$ nm and $c = 0.93432$ nm. The lattice constants of (LaO)CuTe are longer than those of (LaO)CuS [9]. The lattice constants and fractional coordinates refined by the Rietveld analysis are summarized in Tables 1 and 2, respectively.

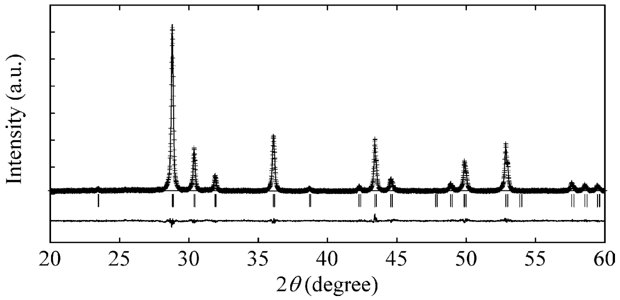

Fig. 2. XRD pattern of (LaO)CuTe. Observed pattern (+) and calculated pattern (solid line) are shown along with their difference. The vertical bars indicate the position of Bragg reflections.

In PL spectra, the strong green emission band is observed in the wavelength range between 520 and 580 nm at 4 K. This green emission does not disappear even at room temperature. This strong emission at 4 K has been known to correspond to the emission from the band edge in (LaO)CuS [1,10]. This indicates that (LaO)CuTe is a semiconductor with band gap of 2.3 eV.

Fig. 3 shows the temperature dependence of the electrical resistivity. The resistivity shows metallic behavior from 300 K to about 150 K and upturns at lower temperature. The absolute value of the resistivity of (LaO)CuTe is about three order of magnitude smaller than that of (LaO)CuS [1]. This decrease of resistivity is attributed to the large spatial extent of the $5p$ orbital of Te ion. From optical and electrical properties, (LaO)CuTe can be regarded as a degenerate semiconductor.

Table 1
Summary of refinement data and lattice parameters for (LaO)CuTe

Space group	$P4/nmm$
Lattice constants	
a (nm)	0.41815 (3)
c (nm)	0.93417 (7)
Unit cell volume (nm^3)	0.16334 (3)
R_{wp} (%)	8.24
S	1.23

Table 2
Site occupancy and fractional coordinates for (LaO)CuTe

Atom	WN	g	x	y	z
La	2c	1.0	0.25	0.25	0.1276 (1)
O	2a	1.0	0.25	0.75	0.0
Cu	2b	1.0	0.25	0.75	0.5
Te	2c	1.0	0.25	0.25	0.6762 (1)

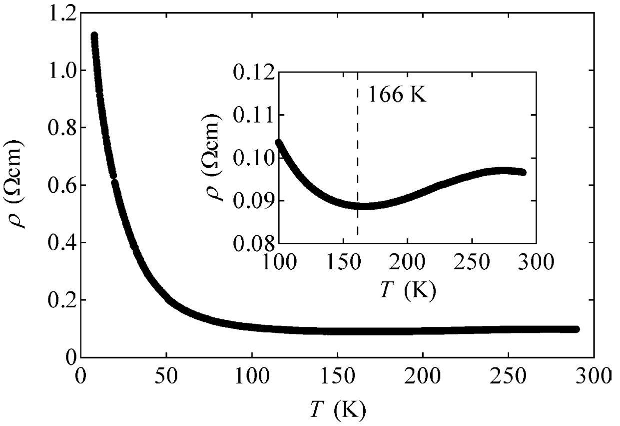

Fig. 3. Temperature dependence of the electrical resistivity of (LaO)CuTe. The inset shows that between 100 and 300 K.

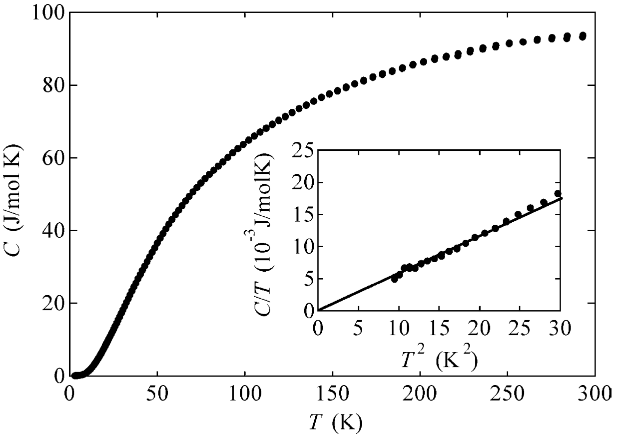

Fig. 4. Temperature dependence of molar specific heat of (LaO)CuTe. The inset shows the T^2 dependence of the C/T at low temperature.

The temperature dependence of molar specific heat is shown in Fig. 4. The value at 300 K is 93 J/mol K, which corresponds to 12*R* (*R*, gas constant). The inset is the T^2 dependence of the C/T at low temperature and shows that the electronic specific heat coefficient is almost zero and the phonon term obeying the Debye T^3-law is observed, in which Debye temperature is 233 K.

Fig. 5 shows the temperature dependence of the magnetic susceptibility. In the whole temperature range, the magnetic susceptibility is diamagnetic and almost temperature independent. The magnitude corresponds to the core diamagnetism. The increase at low temperature is considered to be caused by paramagnetic impurities in the starting materials.

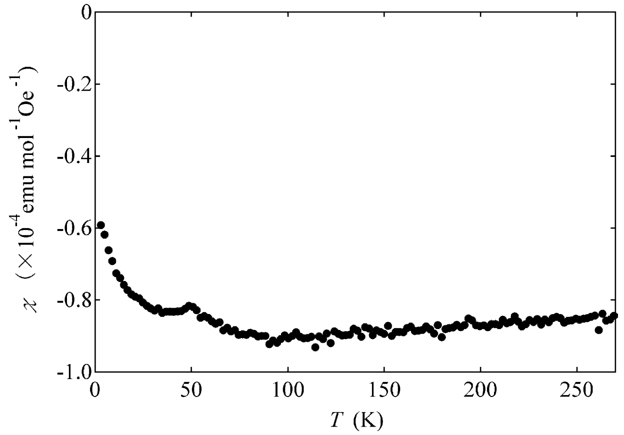

Fig. 5. Temperature dependence of magnetic susceptibility of (LaO)CuTe. The applied magnetic field was 7 T.

4. Conclusion

We have succeeded to obtain a single phase of (LaO)CuTe. The results of the optical and electrical measurements show that (LaO)CuTe is a degenerated semiconductor with the band gap of 2.3 eV. The temperature dependence of molar specific heat indicates that the electronic specific heat coefficient is almost zero. The almost temperature independent diamagnetism is attributed to the core diamagnetism.

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