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Synthesis and the crystal structure of $CeCuS_2$

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Abstract

Single phase of $CeCuS_2$ has been prepared by the mixture of CeO_2 and Cu_2S at 1000 °C in CS_2/Ar atmosphere. All X-ray diffraction peaks of $CeCuS_2$ are indexed on the basis of the monoclinic system (space group: $P2_1/c$) the same as $LaCuS_2$ and $NdCuS_2$. The lattice parameters obtained by Rietveld analysis are $a = 0.6573(1)$ nm, $b = 0.7256(1)$ nm, $c = 0.6875(1)$ nm, and $\beta = 98.566(1)^\circ$.

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Keywords: Layered rare earth copper sulfide; $CeCuS_2$; New synthesis; Crystal structure

1. Introduction

Ternary copper sulfides expressed as $MCuS_2$ (M = Al, Fe, Ga, and In) are known to have a chalcopyrite structure and show interesting properties such as nonlinear optical properties and photovoltaic properties.

The related compounds of rare earth copper sulfides $LnCuS_2$ (Ln = La, Nd, Sm, Gd, Dy, Ho, Yb, Lu, and Y) have been investigated by Murugesan and Gopalakrishnan [1]. While $LuCuS_2$ belongs to the orthorhombic system with the space group *Pnma*, the other $LnCuS_2$ except $LuCuS_2$ belongs to the monoclinic system with the space group $P2_1/c$. All compounds are p-type semiconductors with band gaps around 2.2–2.5 eV and show red luminescence which is similar to that of II–VI semiconductors.These optical properties are independent of the rare earth ion. The absolute values of the electrical resistivity at room temperature are in the range from 10^3 to $10^5\,\Omega\,\mathrm{cm}$. From these results, $4f$ electrons in these compounds are presumably localized in the valence band. However, the Ce $4f$ orbital is expected to have higher energy than that of other rare earth ions and hybridize with Cu$3d$ and S$3p$ orbitals which constitute the top of the valence band. Therefore, we envisage that cerium copper sulfides may have potentials to show heavy fermion character in the sulfide system.

While the precise crystal structure was investigated for $LnCuS_2$ (Ln = La, Y, Pr, Nd) [2–5], only lattice parameters were reported for other compounds. $LnCuS_2$ are usually synthesized by heating the mixture of Ln_2S_3 and Cu_2S in an evacuated silica tube or heating the mixture under H_2S atmosphere. However, such samples often have a significant amount of impurities and show poor crystallinity. These facts restrict the precise crystal structure determination and the investigation of physical properties. Particularly, the synthesis of bulk single phase $CeCuS_2$ has proved difficult. In this study, we have attempted to synthesize single phase $CeCuS_2$ by the sulfurization with CS_2 vapor. The detailed crystal structure studies were carried out using powder X-ray diffraction.

2. Experimental

Cerium sulfides such as CeS_2 and Ce_2S_3 are non-stoichiometric compounds and a little bit air sensitive. To

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avoid to introduce any unknown factors about stoichiometry ratio, CeO_2 was chosen as a starting material, because it is known as a stable stoichiometric compound.

Cerium copper sulfides were prepared by the solid state reaction in CS_2/Ar atmosphere. The starting powder materials are CeO_2 (Alfa, 99.99 %) and Cu_2S. Firstly, Cu_2S is made from stoichiometric mixture of Cu and S at 700 °C in an evacuated silica tube. The appropriate amount of CeO_2 and Cu_2S with the molar ratio 2:1 were ground for 40 min, and the mixture was placed in an alumina crucible. The crucible was placed in an silica tube, and the sample was heated at 1000 °C for 5 h under CS_2 vapor carried by flowing argon. CS_2 vapor was obtained by the bubbling Ar gas in CS_2 liquid. The products were ground into powders and then sealed in an evacuated silica tube and reheated at 1000 °C for 10 h to improve their crystallinity.

The products were characterized by powder X-ray diffraction measurements with a Rigaku RINT 1100 diffractometer using Cu Kα radiation (40 kV, 30 mA). The X-ray diffraction was measured from 5 to 90° 2θ in 0.01° step with a counting time of 5 s per step. The powder X-ray diffraction profiles were analyzed by Rietveld method using the RIETAN 2000 program [7].

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction profile of the sample obtained in this work. First, we supposed that this compound has the isostructure with $LaCuS_2$ [2] belonging to the monoclinic system with space group $P2_1/c$ and then this profile was analyzed by RIETAN 2000 program in the range of 20–60 °. The isotropic thermal parameters determined for $NdCuS_2$ [5] were used and were not refined in this analysis. The calculated results are in good agreement with the experimental results with $R_{\mathrm{wp}} = 10.51\%$ and $S = 1.81$ as shown in Fig. 1, where the solid line indicates the calculated results and the residual error between the observed and the calculated ones is shown at the bottom of the figure. S value is defined with an expected R factor R_{e} as $R_{\mathrm{wp}}/R_{\mathrm{e}}$. These results reveal that this compound has the same structure as $LaCuS_2$. As no impurity phase is observed, we have firstly succeeded to obtain a single phase of $CeCuS_2$ in the bulk form. The lattice parameters obtained from Rietveld analysis are listed in Table 1. The fractional atomic coordinates and the occupancy factor are shown in Table 2.

Fig. 2 shows the change of the lattice parameters of $LnCuS_2$ (Ln = La, Ce, Nd) with the kind of Ln. They decrease linearly with increasing the atomic number (lanthanide contraction). This indicates that all Ce ions in this compound are trivalent and Ce $4f$ electrons localize in the valence band.

Fig. 3 shows the crystal structure of $CeCuS_2$. This structure contains a double-tetrahedron, which consists of two single-tetrahedra with sharing a common edge, as a basic building unit (Fig. 3(a)). Each copper atom is surrounded by one S(1) and three S(2), and each double-tetrahedron

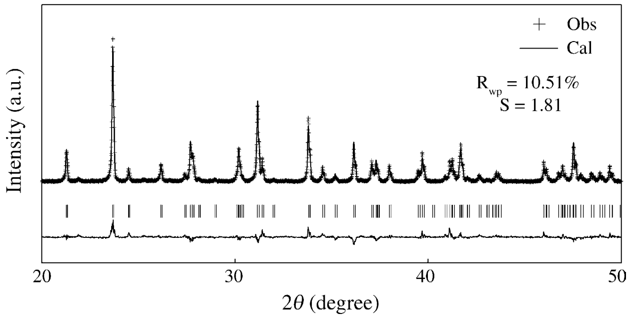

Fig. 1. X-ray powder diffraction profile of $CeCuS_2$ together with the final Rietveld refinement profile. Bottom spectrum is the difference of the observed and calculated intensities. The vertical bars indicate the position of Bragg reflections.

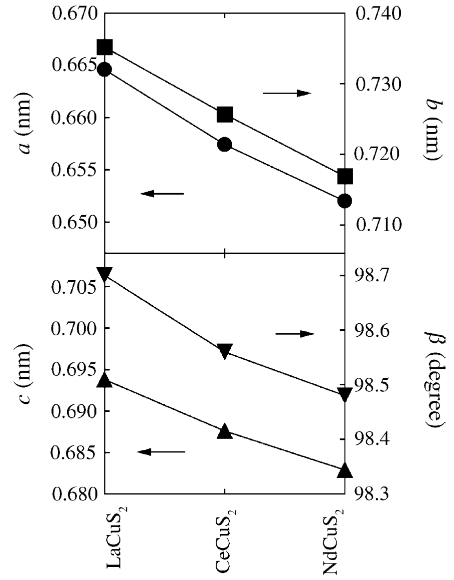

Fig. 2. Lattice parameters (a, b, c and β) for $LnCuS_2$ (Ln = La, Ce, Nd) [2,5].

Table 1
Lattice parameters for $LnCuS_2$ (Ln = La, Ce, Nd)

	$CeCuS_2$	$LaCuS_2$	$NdCuS_2$
a (nm)	0.6573(1)	0.6646	0.652
b (nm)	0.7256(1)	0.7352	0.7169
c (nm)	0.6875(1)	0.6938	0.6829
β (°)	98.566(1)	98.7	98.48
Remark	This work	[6]	[5]

Table 2
Wyckoff notation in, occupation factors, fractional atomic coordinates and isotropic thermal parameters of $CeCuS_2$

Atom	WN	g	x	y	z	B
Ce	4e	1.0	0.6934(3)	0.0548(2)	0.3029(2)	0.41
Cu	4e	1.0	0.0893(6)	0.1518(5)	0.0705(5)	0.4
S(1)	4e	1.0	0.410(1)	0.234(1)	0.998(1)	0.5
S(2)	4e	1.0	0.912(1)	0.3764(9)	0.224(1)	0.5

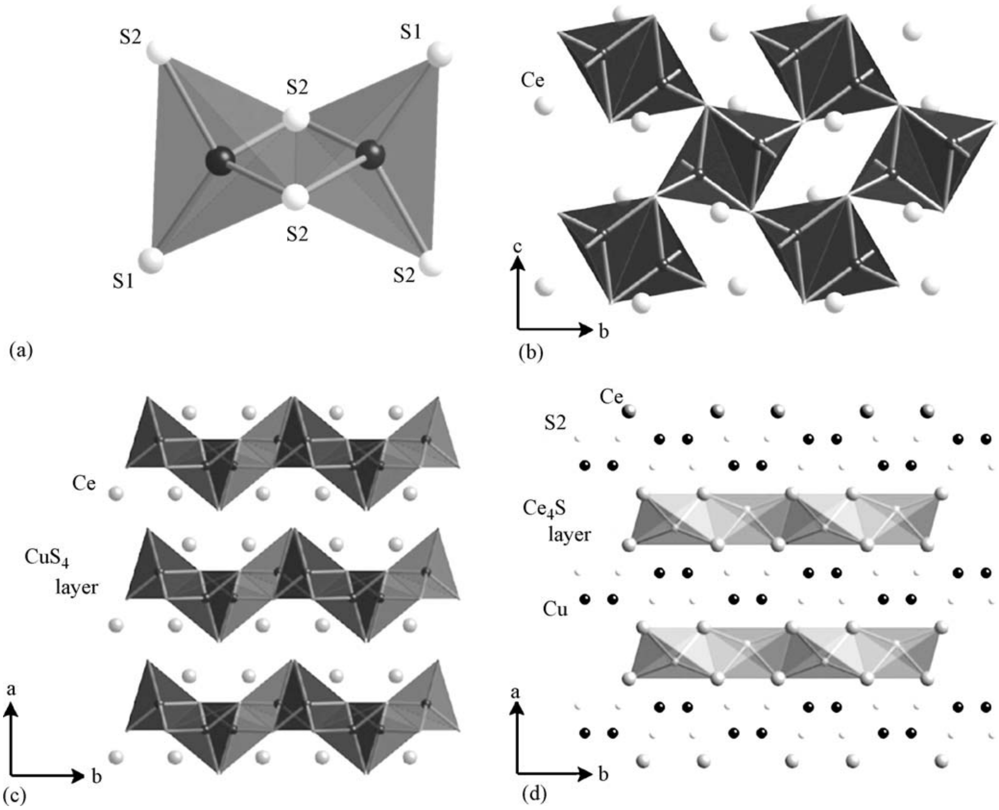

Fig. 3. Projection of atomic arrangement of $CeCuS_2$ ($P2_1/c$): (a) basic constitution unit, (b) CuS_4 layers in *c*–*b* plane, (c) CuS_4 layers in *a*–*b* plane and (d) Ce_4S layers in *a*–*b* plane.

shares corners through S(2) producing puckered layers with the chemical composition CuS as shown in Fig. 3(b). S(2) is coordinated by three copper atoms, while S(1) is coordinated by only one copper atom. The puckered CuS_4 layers, which are separated by Ce ions, are stacked along *a*-axis (Fig. 3(c)). Four Ce ions surround one S(1) to form layers with the chemical composition CeS as presented in Fig. 3(d). Fig. 3(c) and (d) reveal that $CeCuS_2$ has an alternating arrangement of CuS and CeS slabs along the *a*-axis.

In conclusion, we have succeeded in the synthesis of single phase $CeCuS_2$ for the first time. The properties of this compound are under investigation.

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