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Preparation and structure of the light rare-earth copper selenides $Ln\mathrm{CuSe}_2$ (Ln = La, Ce, Pr, Nd, Sm)

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Abstract

The ternary selenides $Ln\mathrm{CuSe}_2$ (Ln = La, Ce, Pr, Nd, Sm) have been synthesized by the reaction at 1173 K of Ln, Cu, and Se in a KBr or KI flux. The compounds, which are isostructural with LaCuS_2, crystallize with four formula units in the space group $P2_1/c$ of the monoclinic system. The structure may be thought of as consisting of layers of CuSe_4 tetrahedra separated by double layers of $Ln\mathrm{Se}_7$ monocapped trigonal prisms along the a-axis. Cell constants (Å or deg) at 153 K are: LaCuSe_2, 6.8142(5), 7.5817(6), 7.2052(6), 97.573(1)°; CeCuSe_2, 6.7630(5), 7.5311(6), 7.1650(6), 97.392(1)°; PrCuSe_2, 6.740(1), 7.481(1), 7.141(1), 97.374(2)°; NdCuSe_2, 6.7149(6), 7.4452(7), 7.1192(6), 97.310(1)°; SmCuSe_2, 6.6655(6), 7.3825(7), 7.0724(6), 97.115(1)°. There are no Se–Se bonds in the structure of $Ln\mathrm{CuSe}_2$; the formal oxidation states of Ln/Cu/Se are $3+/1+/2-$.

Keywords: Synthesis; Crystal structure; Solid-state compound; Rare-earth copper selenide

1. Introduction

The ternary rare-earth copper chalcogenides $LnCuQ_2$ (Ln = rare-earth element, Sc, Y; Q = S, Se, Te) show structural diversity and interesting optical, magnetic, and thermoelectric properties [1–6]. Nevertheless, only a few such compounds have been characterized by means of single-crystal diffraction techniques. The light rare-earth copper sulfides $Ln\mathrm{CuS}_2$ (Ln = La, Sm) crystallize in space group $P2_1/c$ of the monoclinic system [7,8], whereas YCuS_2 crystallizes in space group $Pnma$ of the orthorhombic system [9]. Recently, the structures of the mixed-chalcogen phases LaCuSTe and SmCuSTe were reported [10]. LaCuSTe is closely related to LaCuS_2 and adopts the same space group, whereas SmCuSTe crystallizes a new structure type in space group $Pbca$ of the orthorhombic system. The structures of the sulfides and mixed-chalcogenides comprise layers of $\mathrm{Cu}Q_4$ tetrahedra separated by Ln atoms. In contrast, the non-stoichiometric compounds $\mathrm{LaCu}_{0.28}\mathrm{Te}_2$ [11] and $Ln\mathrm{Cu}_x\mathrm{Te}_2$ (Ln = La, Nd, Sm, Gd, and Dy) [6] are isostructural and crystallize in space group $Pbcm$ of the orthorhombic system. These materials adopt a three-dimensional structure that contains infinite linear Te–Te chains.

Insofar as we know, no single-crystal data have been reported for the corresponding selenides, $Ln\mathrm{CuSe}_2$. Typically, the methods for crystal growth employed in the syntheses of these materials have led to poor quality or twinned crystals [12,13]. We have successfully synthesized single crystals of the light rare-earth copper selenides, namely LaCuSe_2, CeCuSe_2, PrCuSe_2, NdCuSe_2, and SmCuSe_2, from high-temperature reactions of the constituent elements and the use of a KBr or KI flux. Here, we report these syntheses and the structural characterization of these five compounds.

2. Experimental

2.1. Synthesis

The compounds $Ln\mathrm{CuSe}_2$ (Ln = La, Ce, Pr, Nd, Sm) were prepared by the reactions of the rare-earth elements La (Alfa, 99.9%), Nd (Alfa, 99.9%), Ce (Alfa, 99.9%), Pr (Strem, 99.9%), or Sm (Alfa, 99.9%) with Cu (Aldrich, 99.999%) and Se (Aldrich, 99.5%). The synthesis was performed in two steps. First, mixtures

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of 1.0 mmol of *Ln*, 1.0 mmol of Cu, and 2.0 mmol of Se were loaded into carbon-coated fused-silica tubes under an argon atmosphere in a glove box. These tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The samples were heated to 1023 K in 3 days, kept at this temperature for 3 days, and then cooled to 295 K. In the second step, the resultant mixtures were ground thoroughly and 300–400 mg of KBr was added. Next, the samples were heated to 1173 K in 72 h, kept at 1173 K for 4 days, slowly cooled at 0.03°C/min to 953 K, and then cooled to 295 K. The products from each these steps were contaminated with unidentified *Ln*/Se and Cu/Se binaries. The final reaction mixtures also contained powdered $LnCuSe_2$. These reaction mixtures were washed free of halide salts and then dried with acetone. For all reactions dark red block-like crystals were obtained in yields of about ~10%. Selected single crystals were examined with an EDX-equipped Hitachi S-3500 SEM and found to have the stated composition within the accuracy of the method (±5%). These compounds are stable in air for several days. They can also be synthesized with the use of a KI flux.

We used the same procedures in attempted syntheses of $LnCuSe_2$ for the heavier rare-earth elements, specifically for *Ln* = Gd, Tb, Dy, Ho, Er, Tm, and Yb. Only for *Ln* = Gd were any crystals obtained, and these were of very poor quality.

2.2. Crystallography

Single-crystal X-ray diffraction data were obtained with the use of graphite-monochromatized Mo*K*α radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [14]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in three sets of 606 frames at settings of 0°, 120°, and 240° for $PrCuSe_2$, $NdCuSe_2$, and $SmCuSe_2$ and in four sets of 606 frames at settings of 0°, 90°, 180°, and 270°

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $LaCuSe_2$, $CeCuSe_2$, $PrCuSe_2$, $NdCuSe_2$, and $SmCuSe_2$

Atom	*x*	*y*	*z*	U_{eq} (Å^2)[a]
LaCuSe₂				
La	0.30828(5)	0.04995(5)	0.19935(5)	0.0054(2)
Cu	0.0720(1)	0.6621(1)	0.0522(1)	0.0102(2)
Se(1)	0.09587(9)	0.38951(8)	0.27735(8)	0.0059(2)
Se(2)	0.58664(9)	0.27418(8)	0.00057(8)	0.0057(2)
CeCuSe₂				
Ce	0.30802(5)	0.04914(4)	0.19930(4)	0.0067(2)
Cu	0.0717(1)	0.6618(1)	0.0515(1)	0.0113(2)
Se(1)	0.09708(8)	0.38993(8)	0.27863(8)	0.0069(2)
Se(2)	0.58427(8)	0.27451(8)	0.00010(8)	0.0067(2)
PrCuSe₂				
Pr	0.30732(7)	0.04872(7)	0.19902(7)	0.0052(3)
Cu	0.0733(2)	0.6615(2)	0.0512(2)	0.0094(3)
Se(1)	0.0969(1)	0.3898(1)	0.2794(1)	0.0056(3)
Se(2)	0.5819(1)	0.2743(1)	−0.0004(1)	0.0053(3)
NdCuSe₂				
Nd	0.30675(5)	0.04791(5)	0.19867(5)	0.0049(2)
Cu	0.0740(1)	0.6609(1)	0.0508(1)	0.0091(2)
Se(1)	0.0974(1)	0.38968(9)	0.28011(9)	0.0051(2)
Se(2)	0.5803(1)	0.27443(9)	−0.00029(9)	0.0047(2)
SmCuSe₂				
Sm	0.30583(5)	0.04681(5)	0.19861(5)	0.0065(2)
Cu	0.0755(1)	0.6604(1)	0.0504(1)	0.0102(2)
Se(1)	0.0984(1)	0.38962(9)	0.2814(1)	0.0066(2)
Se(2)	0.5768(1)	0.27476(9)	−0.0008(1)	0.0065(2)

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

Table 1
Crystal data and structure refinement for $LaCuSe_2$, $CeCuSe_2$, $PrCuSe_2$, $NdCuSe_2$, and $SmCuSe_2$[a]

Compound	$LaCuSe_2$	$CeCuSe_2$	$PrCuSe_2$	$NdCuSe_2$	$SmCuSe_2$
Formula weight	360.37	361.58	362.37	365.70	371.81
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	6.8142(5)	6.7630(5)	6.740(1)	6.7149(6)	6.6655(6)
b (Å)	7.5817(6)	7.5311(6)	7.481(1)	7.4452(7)	7.3825(7)
c (Å)	7.2052(6)	7.1650(6)	7.141(1)	7.1192(6)	7.0724(6)
β (deg)	97.573(1)	97.392(1)	97.374(2)	97.310(1)	97.115(1)
V (Å^3)	369.00(5)	361.90(5)	357.07(9)	353.02(5)	345.34(5)
d_{calcd} (g/cm^3)	6.487	6.636	6.741	6.881	7.151
lin. abs. coeff. (cm^{-1})	366.40	381.32	395.44	409.04	437.83
Transm. factors	0.023–0.128	0.036–0.107	0.013–0.066	0.051–0.157	0.028–0.135
$R(F)^b(F_o^2) > 2\sigma(F_o^2))$	0.0249	0.0232	0.0350	0.0247	0.0246
$R_w(F_o^2)^c$ (all data)	0.0612	0.0610	0.1031	0.0643	0.0615

[a] For all structures $Z = 4$, $T = 153(2)$ K, and $\lambda = 0.71073$ Å.

[b] $R(F) = \sum \|F_o| - |F_c\| / \sum |F_o|$.

[c] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ for $F_o^2 \geqslant 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leqslant 0$. $q = 0.015$ for La, 0.023 for Ce, 0.045 for Pr, 0.029 for Nd, 0.023 for Sm.

Table 3
Selected bond lengths (Å) for $LaCuSe_2$, $CeCuSe_2$, $PrCuSe_2$, $NdCuSe_2$, and $SmCuSe_2$

$LaCuSe_2$	$CeCuSe_2$	$PrCuSe_2$	$NdCuSe_2$	$SmCuSe_2$
La–Se2 2.9830(7)	Ce–Se2 2.9633(7)	Pr–Se2 2.947(1)	Nd–Se2 2.9330(8)	Sm–Se2 2.9115(8)
La–Se2 3.0002(7)	Ce–Se2 2.9771(7)	Pr–Se2 2.961(1)	Nd–Se2 2.9519(7)	Sm–Se2 2.9268(8)
La–Se2 3.0251(7)	Ce–Se2 3.0072(7)	Pr–Se1 2.995(1)	Nd–Se1 2.9801(8)	Sm–Se2 2.9519(8)
La–Se1 3.0355(7)	Ce–Se1 3.0133(7)	Pr–Se2 2.996(1)	Nd–Se2 2.9809(7)	Sm–Se1 2.9528(8)
La–Se1 3.0419(7)	Ce–Se2 3.0157(7)	Pr–Se2 2.998(1)	Nd–Se2 2.9863(7)	Sm–Se2 2.9663(8)
La–Se2 3.0422(7)	Ce–Se1 3.0255(7)	Pr–Se1 3.010(1)	Nd–Se1 2.9990(7)	Sm–Se1 2.9766(8)
La–Se1 3.2235(7)	Ce–Se1 3.1975(7)	Pr–Se1 3.180(1)	Nd–Se1 3.1630(8)	Sm–Se1 3.1352(8)
Cu–Se2 2.454(1)	2.4496(9)	2.445(2)	2.442(1)	2.434(1)
Cu–Se1 2.482(1)	2.4686(9)	2.460(2)	2.455(1)	2.442(1)
Cu–Se1 2.526(1)	2.521(1)	2.518(2)	2.515(1)	2.512(1)
Cu–Se1 2.619(1)	2.608(1)	2.598(2)	2.589(1)	2.574(1)
Cu⋯Cu 2.716(2)	2.691(2)	2.677(3)	2.659(2)	2.637(2)

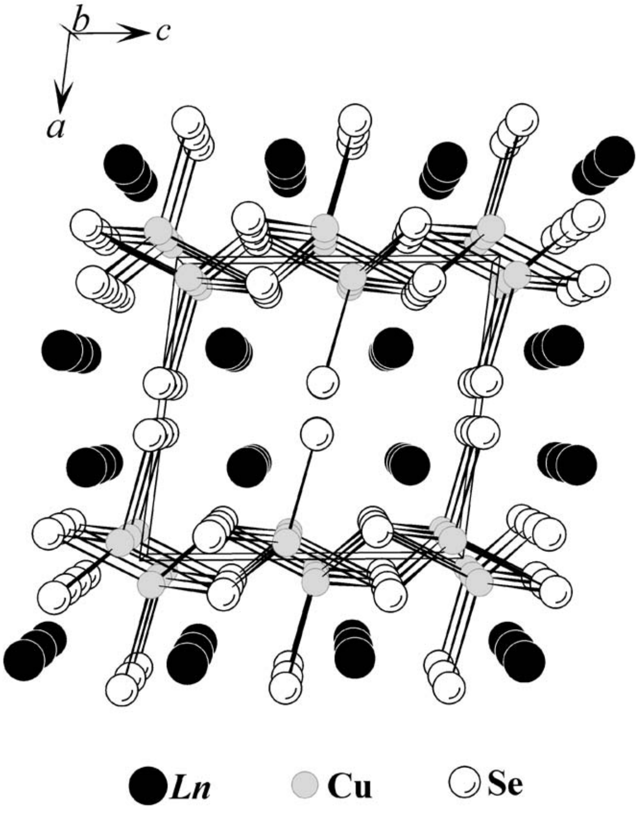

Fig. 1. Unit cell of LnCuSe$_2$ viewed down the b-axis. For clarity, the Ln–Se bonds are not shown.

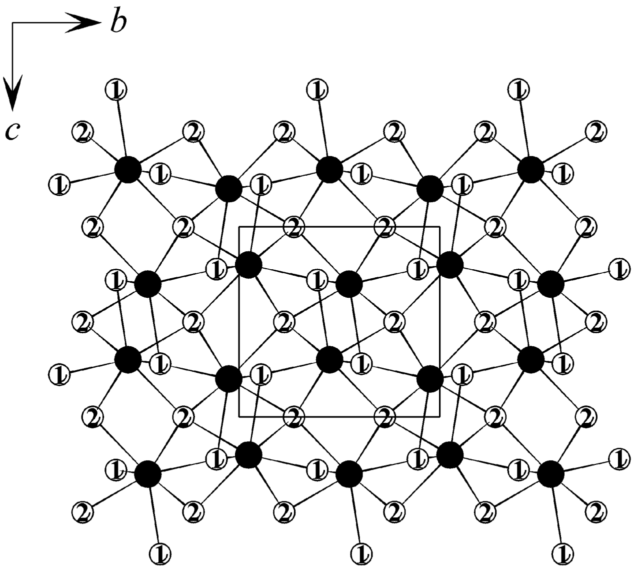

Fig. 2. LnSe$_7$ layer viewed down the a-axis.

for $LaCuSe_2$ and $CeCuSe_2$. The exposure times were 15 s/frame for $LaCuSe_2$, $CeCuSe_2$, and $PrCuSe_2$, and 10 s/frame for $NdCuSe_2$ and $SmCuSe_2$. The collection of intensity data on the Bruker diffractometer was carried out with the program SMART [14]. Cell refinement and data reduction were carried out with the use of the program SAINT [14] and face-indexed absorption corrections were carried out numerically with the program XPREP [15]. Then the program SADABS [14] was employed to make incident beam and decay corrections.

The structures were solved with the direct methods program SHELXS and refined with the full-matrix least-squares program SHELXL of the SHELXTL suite of programs [15]. The final refinements included anisotropic displacement parameters and secondary extinction corrections. These displacement parameters do not suggest the presence of non-stoichiometry. Indeed, for all of these structures the site occupancy for the Cu atom when refined did not differ significantly from unity. A summary of the selected crystallographic data is listed in Table 1. The program STRUCTURE TIDY [16] was used to standardize the positional parameters; these

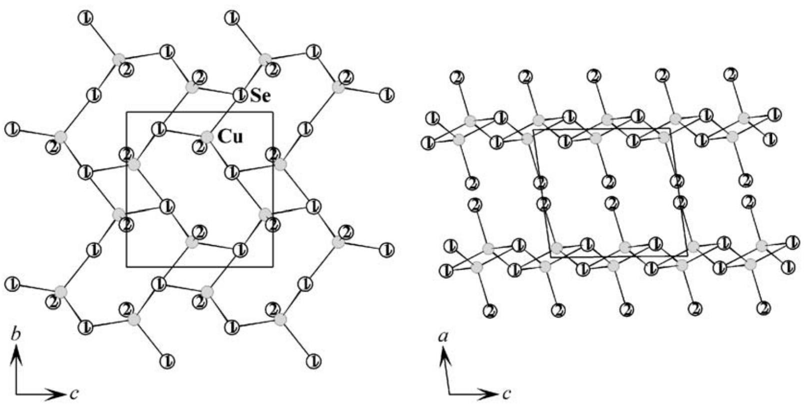

Fig. 3. $CuSe_4$ mixed octagonal/quadrilateral nets viewed along the *a*- and *b*-axis, respectively.

are given in Table 2. Table 3 presents selected bond distances and angles.

3. Results and discussion

The structure of the isostructural *Ln*$CuSe_2$ (*Ln* = La, Ce, Pr, Nd, Sm) compounds, which is of the $LaCuS_2$ structure type [7], is illustrated in Fig. 1; for clarity, the *Ln*–Se bonds are not shown. Each *Ln* atom is surrounded by seven Se atoms (3Se(1) + 4Se(2)) to form a monocapped trigonal prism. These prisms share edges and caps to form double layers that stack perpendicular to the *a*-axis (Fig. 2). These double layers are separated by layers of Cu atoms, each Cu atom being tetrahedrally coordinated by four Se atoms (3Se(1) + 1Se(2)). Alternatively, the structure may be thought of as consisting of $CuSe_2$ sheets separated by *Ln* atoms along the *a*-axis. A more detailed illustration of the $CuSe_2$ sheets is depicted in Fig. 3. The sheets are composed of edge-sharing dimers of $CuSe_4$ tetrahedra (Cu_2Se_6). Each dimer shares corners with neighboring dimers to form mixed octagonal/quadrilateral nets that stack along the *a*-axis to form channels in which the *Ln* atoms reside.

The *Ln*–Se distances, which range from 2.9115(8) to 3.2235(7) Å, are reasonable and decrease from La to Sm, as expected from the lanthanide contraction (Table 3). These *Ln*–Se bond lengths are consistent with those in other materials that contain seven-coordinate *Ln* atoms, for example with those of 3.023(2)–3.210(2) Å for La–Se in $KLaGeSe_4$ [17], 2.900(1)–3.216(1) Å for Ce–Se in $Ce_{3.67}Ti_2O_3Se_6$ [18], 2.911(2)–3.079(2) Å for Pr–Se in Pr_3InSe_6 [19], 2.864(1)–3.209(1) Å for Nd–Se in $Nd_{3.67}Ti_2O_3Se_6$ [18], and 2.911(1)–2.969(1) Å for Sm–Se in Sm_2Se_3 [20]. The Cu–Se bond lengths are also reasonable and vary from 2.434(1) to 2.619(1) Å in *Ln*$CuSe_2$ compared with 2.478(2)–2.577(2) Å for Cu–Se in β-$BaLaCuSe_3$ [21]. The smallest contact distance between Se anions is beyond the bonding range. Therefore, the formal oxidation states of *Ln*/Cu/Se are 3+/1+/2−. These charge-balanced materials are expected to be semiconductors, as was predicted for $LaCuS_2$ and LaCuSTe [10].

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