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Crystal structures of the $R_3CuGeSe_7$ (R = Ce, Pr, Nd, Sm, Gd, Tb and Ho) compounds

L.D. Gulay [a,*], O.S. Lychmanyuk [a], I.D. Olekseyuk [a], A. Pietraszko [b]

[a] *Department of General and Inorganic Chemistry, Volyn State University, Voli Ave 13, 43009 Lutsk, Ukraine*
[b] *W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna str. 2, P.O. Box 1410, 50-950 Wrocław, Poland*

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Abstract

The crystal structures of the $R_3CuGeSe_7$ compounds (R = Ce, Pr, Nd, Sm, Gd, Tb and Ho) (La_3CuSiS_7 structure type, space group $P6_3$, Pearson symbol $hP24$) were determined by means of X-ray single crystal diffraction ($a = 1.0643(1)$ nm, $c = 0.60973(7)$ nm, $R1 = 0.0269$ for $Ce_3CuGeSe_7$; $a = 1.0559(1)$ nm, $c = 0.6084(1)$ nm, $R1 = 0.0301$ for $Pr_3CuGeSe_7$; $a = 1.0519(1)$ nm, $c = 0.60707(9)$ nm, $R1 = 0.0305$ for $Nd_3CuGeSe_7$) and X-ray powder diffraction ($a = 1.04216(3)$ nm, $c = 0.60447(3)$ nm, $R_{Bragg} = 0.0862$ for $Sm_3CuGeSe_7$; $a = 1.03491(8)$ nm, $c = 0.60395(7)$ nm, $R_{Bragg} = 0.0932$ for $Gd_3CuGeSe_7$; $a = 1.02940(5)$ nm, $c = 0.60387(4)$ nm, $R_{Bragg} = 0.0734$ for $Tb_3CuGeSe_7$; $a = 1.01978(7)$ nm, $c = 0.60612(6)$ nm for $Ho_3CuGeSe_7$). The R atoms are surrounded by distorted trigonal prisms. A triangular surrounding exists for the Cu atoms. A tetrahedral surrounding exists for the Ge atoms.

Keywords: Chalcogenides; Rare earth compounds; Cu compounds; Ge compounds; Se compounds; Crystal structure; X-ray single crystal diffraction; X-ray powder diffraction

1. Introduction

Production of the compounds with increasingly complex compositions, such as ternary, quaternary, etc., has become a principle direction in a modern science of materials [1]. Among the multicomponent systems an important place belongs to the complex rare earth chalcogenides with various physical properties. The rare earth chalcogenide materials have aroused a certain interest over last years due to their thermal, electrical and optical properties. Therefore, the synthesis and the investigation of the crystal structures of new complex chalcogenides is important step in a search for new materials.

The existence of quaternary $R_3CuGeSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds (La_3CuSiS_7 structure type, space group $P6_3$) has been reported in Ref. [2]. Only lattice parameters have been determined for these compounds. Complete crystal structure determinations of the $Y_3CuGeSe_7$ [3], $La_3CuGeSe_7$ [4] and $Dy_3CuGeSe_7$ [5] compounds have been reported.

This paper presents part of the systematic investigations of complex rare earth chalcogenides. The crystal structures of quaternary $R_3CuGeSe_7$ (R = Ce, Pr, Nd, Sm, Gd, Tb and Ho) compounds are determined and discussed.

2. Experimental details

The synthesis of the samples was realized with the use of high purity elements (the purity of the ingredients was better than 99.9 wt.%). The calculated amounts of the components were sealed in evacuated silica ampoules. The synthesis was realized in a tube furnace. The ampoules were heated with a heating rate of 30 K/h to the maximal temperature, 1420 K. They were kept at the maximal temperature during 3 h. After that they were cooled slowly (10 K/h) to 870 K and annealed at this temperature for 240 h. After annealing the ampoules with the samples were quenched in cold water.

Diffraction-quality single crystals of the $R_3CuGeSe_7$ (R = Ce, Pr and Nd) compounds for the crystal structure determination were selected from the samples of the respective compositions. The X-ray intensities data were collected on a KUMA diffraction KM-4 four-circle single crystal diffractometer equipped with a CCD camera using graphite-monochromatized Mo Kα radiation (λ = 0.071073 nm). The intensities of the reflections were corrected for Lorentz and polarisation factors. Semiempirical absorption correction was applied. The crystal structure was solved by Patterson methods [6] and refined by full matrix least squares method using SHELX-97 program [7].

* Corresponding author.
E-mail address: gulay@univer.lutsk.ua (L.D. Gulay).

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Table 1
Crystal data and structure refinement details of the $R_3CuGeSe_7$ (R = Ce, Pr and Nd) compounds

	Empirical formula		
	$Ce_3CuGeSe_7$	$Pr_3CuGeSe_7$	$Nd_3CuGeSe_7$
Formula weight	1109.21	1111.58	1121.57
Space group	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)
Unit cell dimensions	$a = 1.0643(1)$ nm, $c = 0.60973(7)$ nm	$a = 1.0559(1)$, $c = 0.6084(1)$ nm	$a = 1.0519(1)$, $c = 0.60707(9)$ nm
Volume	0.5981(1) nm^3	0.5874(1) nm^3	0.5817(1) nm^3
Number of formula units per unit cell	2	2	2
Calculated density	6.159 g/cm^3	6.284 g/cm^3	6.403 g/cm^3
Absorption coefficient	36.658 mm^{-1}	38.142 mm^{-1}	39.342 mm^{-1}
$F(0\,0\,0)$	946	952	958
Crystal size	0.08 mm × 0.09 mm × 0.12 mm	0.06 mm × 0.08 mm × 0.11 mm	0.04 mm × 0.06 mm × 0.10 mm
Θ range for data collection	3.83–29.54	3.86–29.48	3.87–29.57
Index ranges	$-14 \le h \le 14$, $-14 \le k \le 13$, $-8 \le l \le 7$	$-12 \le h \le 14$, $-14 \le k \le 11$, $-8 \le l \le 7$	$-14 \le h \le 13$, $-14 \le k \le 13$, $-8 \le l \le 8$
Reflections collected	8851	8741	8685
Independent reflections	1066 [R(int.) = 0.0951]	1090 [R(int.) = 0.0917]	1090 [R(int.) = 0.0869]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Absolute structure parameter	0.04(4)	0.00(5)	0.00(8)
Data/restraints/parameters	1066/0/37	1090/0/38	1090/0/38
Goodness-of-fit on F^2	1.045	1.025	1.046
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0269$, $wR2 = 0.0553$	$R1 = 0.0301$, $wR2 = 0.0760$	$R1 = 0.0305$, $wR2 = 0.0816$
R indices (all data)	$R1 = 0.0292$, $wR2 = 0.0560$	$R1 = 0.0331$, $wR2 = 0.0779$	$R1 = 0.0398$, $wR2 = 0.0897$
Extinction coefficient	0.0111(4)	0.0125(7)	0.0074(6)
Largest diff. peak and hole × 10^{-3}	1.187 and −1.174 e/nm^3	1.401 and −1.190 e/nm^3	1.932 and −1.446 e/nm^3

X-ray powder diffraction patterns of the $R_3CuGeSe_7$ (R = Ce, Pr, Nd, Sm, Gd, Tb and Ho) compounds were recorded using DRON-4-13 powder diffractometer (Cu Kα radiation, $10^\circ \le 2\Theta \le 100^\circ$, step scan mode with a step size of 0.05° and counting time of 20 s per data point). Crystal structure determinations were performed using Rietveld method with the CSD [8] and DBWS-9411 [9] programs.

3. Results and discussion

The existence of $R_3CuGeSe_7$ compounds was determined during the investigation of the phase relations in the R_2Se_3–Cu_2Se–$GeSe_2$ (R = Ce, Pr, Nd, Sm, Gd, Tb and Ho)

Table 2
Atomic coordinates and temperature factors for the $R_3CuGeSe_7$ (R = Ce, Pr and Nd) compounds

Atom	Position	x/a	y/b	z/c	$U_{eq.} \times 10^2$ (nm^2)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$Ce_3CuGeSe_7$											
Ce	6(c)	0.12985(4)	0.35612(4)	0.7486(3)	0.0117(1)	0.0121(2)	0.0098(2)	0.0132(2)	0.0009(2)	0.0007(2)	0.0053(1)
Cu	2(a)	0	0	0.7190(5)	0.0188(4)	0.0142(5)	0.0142(5)	0.028(1)	0	0	0.0071(2)
Ge	2(b)	1/3	2/3	0.3333[a]	0.0116(3)	0.0127(4)	0.0127(4)	0.0096(7)	0	0	0.0063(2)
Se1	2(b)	1/3	2/3	0.9534(3)	0.0135(3)	0.0143(4)	0.0143(4)	0.0119(7)	0	0	0.0072(2)
Se2	6(c)	0.83778(7)	0.09358(8)	0.7327(3)	0.0123(1)	0.0114(3)	0.0109(3)	0.0140(4)	−0.0006(3)	−0.0012(3)	0.0050(3)
Se3	6(c)	0.48020(8)	0.90023(9)	0.4866(3)	0.0124(1)	0.0106(3)	0.0119(4)	0.0141(4)	−0.0002(3)	0.0010(3)	0.0052(3)
$Pr_3CuGeSe_7$											
Pr	6(c)	0.13040(5)	0.35606(5)	0.7482(3)	0.0134(1)	0.0134(2)	0.0112(2)	0.0154(3)	0.0004(3)	0.0005(3)	0.0060(1)
Cu	2(a)	0	0	0.7161(6)	0.0209(5)	0.0146(6)	0.0146(6)	0.033(1)	0	0	0.0073(3)
Ge	2(b)	1/3	2/3	0.3333[a]	0.0138(4)	0.0144(5)	0.0144(5)	0.0126(8)	0	0	0.0072(3)
Se1	2(b)	1/3	2/3	0.9525(4)	0.0146(4)	0.0154(5)	0.0154(5)	0.0129(9)	0	0	0.0077(2)
Se2	6(c)	0.8376(1)	0.0945(1)	0.7310(3)	0.0136(2)	0.0124(4)	0.0119(4)	0.0156(5)	−0.0003(4)	−0.0011(4)	0.0053(3)
Se3	6(c)	0.4804(1)	0.9013(1)	0.4881(4)	0.0136(2)	0.0115(4)	0.0131(4)	0.0152(5)	−0.0004(4)	0.0009(4)	0.0054(4)
$Nd_3CuGeSe_7$											
Nd	6(c)	0.22504(6)	0.35612(6)	0.7486(4)	0.0153(1)	0.0160(3)	0.0147(3)	0.0142(3)	0.0005(3)	0.0001(3)	0.0068(2)
Cu	2(a)	0	0	0.7149(8)	0.0233(7)	0.0188(7)	0.0188(7)	0.033(2)	0	0	0.0094(4)
Ge	2(b)	1/3	2/3	0.3333[a]	0.0152(5)	0.0172(7)	0.0172(7)	0.011(1)	0	0	0.0086(3)
Se1	2(b)	1/3	2/3	0.9521(5)	0.0165(4)	0.0185(6)	0.0185(6)	0.012(1)	0	0	0.0093(3)
Se2	6(c)	0.9045(1)	0.1623(1)	0.7300(4)	0.0158(3)	0.0155(5)	0.0160(5)	0.0154(5)	0.0009(5)	0.0007(5)	0.0075(4)
Se3	6(c)	0.4214(1)	0.9021(1)	0.4895(4)	0.0155(3)	0.0156(5)	0.0169(6)	0.0146(5)	0.0002(5)	−0.0013(5)	0.0087(4)

$U_{eq.}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The anisotropic temperature factor exponent takes the form: $-2\pi^2[h^2a \times {}^2U_{11} + \cdots + 2hka \times b \times U_{12}]$.

[a] Fixed.