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The crystal structure of $Er_{2.34}La_{0.66}Ge_{1.28}S_7$ and the $La_xR_yGe_3S_{12}$ phases (R – Tb, Dy, Ho and Er)

M. Daszkiewicz [a], O.V. Smitiukh [b], O.V. Marchuk [b, *], L.D. Gulay [c]

[a] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P. O. Box 1410, 50-950 Wrocław, Poland
[b] Department of Inorganic and Physical Chemistry, Eastern European National University, Voli Ave 13, 43025 Lutsk, Ukraine
[c] Department of Ecology and Protection of Environment, Eastern European National University, Voli Ave 13, 43025 Lutsk, Ukraine

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ABSTRACT

Isothermal section of the Er_2S_3–La_2S_3–GeS_2 system at 770 K was investigated. The phase boundaries of the solid solution $La_{4-4x}R_{4x}Ge_3S_{12}$ (x = 0–0.75, R – Tb, Dy, Ho and Er) were determined, and their structure was investigated by single crystal and powder X-ray diffraction. The existence of new quaternary compound $Er_{2.34}La_{0.66}Ge_{1.28}S_7$ was established and its crystal structure was determined by X-ray single crystal diffraction (space group $P6_3$, Pearson symbol $hP24$–1.44, a = 0.96934(3) nm, c = 0.58680(2) nm, R_1 = 0.0220).

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1. Introduction

The development of modern inorganic chemistry and semiconductor material science is associated with the design of new materials that would possess pre-set functional properties. One approach to find new substances with semiconductor properties is to study the interaction of the components of complex chalcogenide systems [1].

The study of the composition-structure-property relationship of a substance as well as the determination of its thermodynamic conditions of existence is one of the tasks of physico-chemical analysis.

The information about the crystalline structure of a compound not only provides some data on interatomic distances and the coordination surrounding of atoms but also makes possible certain assumptions and conclusions about the mechanisms of chemical transformations and predictions on the synthesis of new substances. The crystal structure is one of the fundamental characteristics of a compound that determines a range of its physico-chemical properties.

The accumulation of experimental data on the conditions for the formation and existence of compounds makes the process of designing new materials on their basis more purposeful [2].

Presented work is one of the stages of the systematic study of the interaction of components in complex sulfide systems R_2S_3–R'_2S_3–$D^{IV}S_2$ (D^{IV} – Si, Ge, Sn; R – Lanthanide) and of determination of the crystal structure of the compounds formed therein [3].

Principal crystallographic characteristics of the binary and of the ternary components of the quasi-quaternary system Er_2S_3–La_2S_3–GeS_2 are shown in Table 1.

2. Experimental details

A total of 63 samples were synthesized for the investigation of the system. The samples for the studies were prepared of the individual components of semiconductor purity. The alloys were synthesized in evacuated quartz containers in an MP-30 programmable electrical muffle furnace by heating to 1423 K at a rate of 12 K/h; exposure at 1423 K for 4 h; cooling to 770 K at a rate of 12 K/h; homogenizing and annealing at 770 K for 240 h; and finally quenching into cold water.

Powder XRD patterns to determine the phase composition of synthesized alloys were recorded at a DRON 4-13 diffractometer in the range 2Θ = 10–80° (CuKα radiation, scan step 0.05°, 4 s exposure at each point). The data were processes using WinCSD

* Corresponding author.
E-mail address: Oleg_M_1974@i.ua (O.V. Marchuk).

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Table 1
Crystallographic characteristics of the binary and of the ternary components of the quasi-quaternary system Er_2S_3–La_2S_3–GeS_2.

Compound	Space group	Lattice parameters, nm			Ref.
		a	*b*	*c*	
Er_2S_3	$P2_1/m$	1.0072	0.3976 $\beta = 98.66°$	1.7389	[4]
La_2S_3	*Pnma*	0.766	0.422	0.1595	[5]
GeS_2	$P2_1/c$	0.6720	1.6101 $\beta = 90.88°$	1.1436	[6]
GeS_2	*Fdd*2	1,68	2238	0,687	[7]
$Er_3Ge_{1.33}S_7$	$P6_3$	1.02970	–	0.58120	[8]
La_2GeS_5	$P2_1/c$	0.7641	1.2702 $\beta = 101.39°$	0.7893	[9]
$La_3Ge_{1.25}S_7$	$P6_3$	1.0297	–	0.58120	[8]
$La_4Ge_3S_{12}$	*R*3*c*	1.940	–	0.810	[9]
$ErLaS_3$	*Pnma*	1.6510	0.3996	2.12597	[10]
Er_3LaS_6	$P2_1/m$	1.095	1.126 $\beta = 108.6°$	0.398	[11]

software package [12].

The investigation of the crystal structure of the quaternary phases was performed using X-ray single crystal diffraction. The X-ray intensities data were collected on a Oxford Diffraction X'calibur four-circle single-crystal X-ray diffractometer with CCD Atlas detector, using graphite-monochromatized MoK_α radiation ($\lambda = 0.071073$ nm). The raw data were treated with the CrysAlis Data Reduction program taking into account an absorption correction. The intensities of the reflections were corrected for Lorentz and polarization factors. The crystal structure was solved by Patterson methods and refined by the full-matrix least-squares method using SHELXL-2014 [13]. Acentric space groups were checked with the PLATON program, and no additional symmetry elements were found [14].

3. Results and discussion

Literature sources report the existence of GeS_2 in two modifications, with the phase transition temperature of 770 K. We have identified at the annealing temperature the monoclinic modification of GeS_2 ($P2_1/c$). The investigation of the quasi-quasiternary system Er_2S_3–La_2S_3–GeS_2 confirms the existence of three ternary compounds, $La_4Ge_3S_{12}$ (space group *R*3*c*, own structure type), La_2GeS_5 (space group $P2_1/c$, own structure type), $La_3Ge_{1.25}S_7$ (space group $P6_3$, structure type $Dy_3Ge_{1.25}S_7$). No ternary compounds were observed in the Er_2S_3–GeS_2 section. A part of the isothermal section of the Er_2S_3–La_2S_3–GeS_2 system at 770 K is presented in Fig. 1.

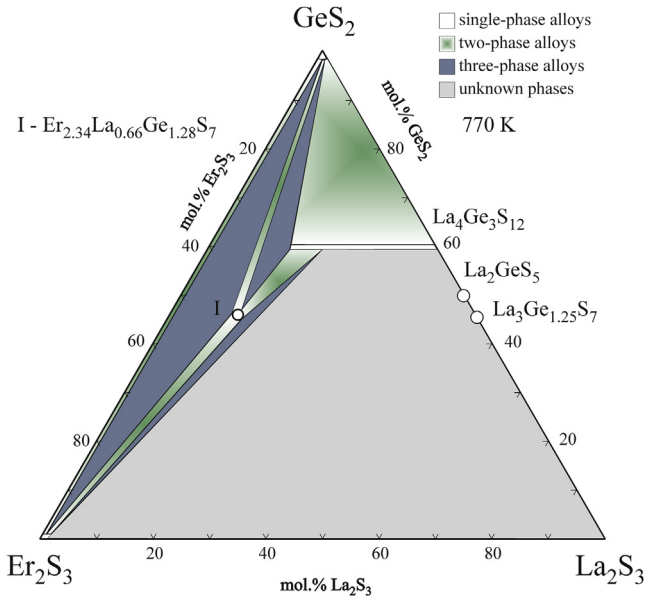

Fig. 1. Isothermal section of the quasi-ternary system Er_2S_3–La_2S_3–GeS_2 at 770 K.

Table 2
Crystallographic data and structure refinement details for the $Er_{2.34}La_{0.66}Ge_{1.28}S_7$ compound.

Empirical formula	$Er_{2.34}La_{0.66}Ge_{1.28}S_7$
Formula weight	800.45
Space group	$P6_3$ (No 173)
Unit cell dimensions:	
a (nm)	0.96934(3)
c (nm)	0.58680(2)
V (nm^3)	0.47749(3)
Number of formula units per unit cell	2
Calculated density	5.572
Absorption coefficient	28.754
F(000)	700
Crystal color	black
Crystal size	0.055 × 0.029 × 0.024 mm
Θ range for data collection	2.426–26.702
Index ranges	$-12 \le h \le 12$ $-12 \le h \le 12$ $-7 \le l \le 7$
Reflections collected	7908
Independent reflections	686 [R(int.) = 0.0490]
Refinement method	Full-matrix least-square on F^2
Absolute structure parameter	0.35(2)
Data/restraints/parameters	686/1/40
Goodness-of-fit on F^2	1.062
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.0220$ $wR_2 = 0.0448$
R indices (all data)	$R1 = 0.0229$ $wR_2 = 0.0450$
Extinction coefficient	–
Largest diff. peak and hole × 10^{-3}	0.683 and −0.974 e/nm^3

A ternary phase $Er_3Ge_{1.33}S_7$ was reported in Ref. [8] in the Er–Ge–S system outside the Er_2S_3–GeS_2 section. We synthesized and annealed nine alloys of the composition $Er_{3-x}La_xGe_{1.25}S_7$ ($x = 0–0.7$) and tested their phase composition. The synthesis of samples was according to the procedure described in the Experimental section. The formation of new quaternary compound of approximate composition $Er_{2.4}La_{0.6}Ge_{1.25}S_7$ was observed. A single crystal from the $Er_{2.4}La_{0.6}Ge_{1.25}S_7$ sample was selected to study its crystalline structure. Performed investigation determined the composition of the new quaternary phase as $Er_{2.34}La_{0.66}Ge_{1.28}S_7$ (structure type $Dy_3Ge_{1.25}S_7$, space group $P6_3$, Pearson symbol *hP*24–1.44). Crystallographic data and structure refinement details for the $Er_{2.34}La_{0.66}Ge_{1.28}S_7$ compound are given in Table 2. Atomic coordinates and thermal displacement parameters are given in Table 3, and the interatomic distances are listed in Table 4. The position M of the mixture of randomly distributed La and Er atoms in the $Er_{2.34}La_{0.66}Ge_{1.28}S_7$ structure corresponds to the position of Dy in the structure of $Dy_3Ge_{1.25}S_7$. The positions of Ge and S are the same in both structures. The unit cell projection and the coordination environment of atoms in the structure of the compound $Er_{2.34}La_{0.66}Ge_{1.28}S_7$ are depicted in Fig. 2. The atoms of the statistical mixture M (Er+La) occupy the 6*c* site and are located in monocapped trigonal prisms with coordination number (6 + 1). The Ge atoms are located in sites 2*b* and 2*a* which have octahedral and tetrahedral surrounding of sulfur atoms respectively. Sulfur atoms (6*c* and 2*b* sites) are coordinated by tetrahedra of cations.

The existence at 770 K of the solid solution range of $La_4Ge_3S_{12}$ (space group *R*3*c*, Pearson symbol *hR*38) was found in the quasi-ternary system Er_2S_3–La_2S_3–GeS_2; its extent is $La_{4-4x}Er_{4x}Ge_3S_{12}$ ($x = 0–0.63$).

Additionally, we studied the extent of solid solutions in the

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