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Phase equilibria in the NiX–La_2X_3–$Ga(In)_2X_3$ (X = S, Se) systems and crystal structure of the La_3NiGaS_7 compound

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The isothermal sections of the quasi-ternary NiX–La_2X_3–$Ga(In)_2X_3$ (X = S, Se) systems at 770 K were constructed using X-ray diffraction. The crystal structure of the quaternary compound La_3NiGaS_7 (structure type La_3MnGaS_7, Pearson symbol *hP*24, space group $P6_3$, a = 1.01605(4), c = 0.60397(3) nm, R_I = 0.0856, R_p = 0.1897) was determined by X-ray powder diffraction.

Rare-earth elements / X-ray powder diffraction / Crystal structure

Introduction

Chalcogenide systems have been intensively studied in recent years to find new materials for infrared and non-linear optics. The study of phase equilibria and crystal structures of compounds in the quasi-ternary systems NiX–La_2X_3–$Ga(In)_2X_3$ (X = S, Se) will provide clarification of the nature of the chemical interaction of the components in systems of a similar type and the conditions of formation and existence of new phases that will constitute valuable information in the search for new promising materials.

Here we present the results of an investigation of the phase equilibria in the quasi-ternary systems NiX–La_2X_3–$Ga(In)_2X_3$ (X = S, Se) at 770 K.

The components of the investigated systems are binary semiconductor compounds, the crystal structures of which have been studied in detail and reported in the literature (Table 1).

Literature sources also report information on the formation of compounds in the boundary binary systems (Table 2).

Experimental

The samples were synthesized from elements of at least 99.99 wt.% purity in quartz containers in an MP-30 programmable electric muffle furnace. The containers were evacuated to a residual pressure of 10^{-2} Pa and sealed in the flame of an oxygen-gas burner. The samples were synthesized by: 1) heating the mixture to 870 K at the rate of 30 K/h; 2) exposure for 100 h; 3) heating to 1370 K at the rate of 12 K/h; 4) exposure for 2 h; 5) cooling to 770 K at the rate of 12 K/h; 6) homogenizing annealing for 500 h. After having reached the equilibrium state, the samples were quenched into room-temperature water.

X-ray diffraction patterns for phase analysis were recorded on a DRON 4-13 diffractometer in the 2θ range 10-80° (Cu Kα radiation, scan step 0.05°, 4 s exposure at each point). Data processing and the determination of the crystal structure utilized the WinCSD software package [32].

Result and discussion

The existence of ten ternary compounds was confirmed in the boundary binary systems of the investigated quasi-ternary systems at the annealing temperature. These are La_4NiS_7 (space group $I4/mmm$), $La_3Ga_{1.67}S_7$ ($P6_3$), $LaGaS_3$ ($Pna2_1$), $NiGa_2S_4$ (P-3m1), $La_3Ga_{1.67}Se_7$ ($P6_3$), La_3InS_6 ($P2_12_12_1$), $La_3In_{1.67}S_7$ ($P6_3$), $La_4In_{4.67}S_{13}$ ($Pbam$), $La_3In_{1.67}Se_7$ ($P6_3$), and $La_4In_{4.67}Se_{13}$ ($Pbam$).

We have determined the existence of a new quaternary compound, La_3NiGaS_7, in the quasi-ternary system NiS–La_2S_3–Ga_2S_3 (La_3MnGaS_7 structure type [33]). This compound crystallizes with hexagonal symmetry (space group $P6_3$) and the unit cell parameters a = 1.01605(4) nm and c = 0.60397(3) nm.

Table 1 Crystallographic data for the binary compounds.

Compound	Structure type	Space group	Cell parameters (nm)			Ref.
			a	*b*	*c*	
La_2S_3	La_2S_3	*Pnma*	0.766	0.422	1.588	[1]
La_2S_3	–	*Fd*-3*m*	2.046	–	–	[2]
La_2S_3	Th_3P_4	*I*-43*d*	0.8723	–	–	[3]
La_2Se_3	Th_3P_4	*I*-43*d*	0.90521	–	–	[4]
NiS	NiS	*R*3*m*	0.96071	–	0.31434	[5]
NiS	NiAs	$P6_3/mmc$	0.34395	–	0.53514	[6]
NiSe	NiAs	$P6_3/mmc$	0.3661	–	0.5356	[7]
Ga_2S_3	Ga_2S_3	*Bb*	1.1094	0.9578 γ = 141.15°	0.6395	[8]
Ga_2S_3	Ga_2S_3	$P6_1$	0.6385	–	1.8040	[9]
Ga_2S_3	Ga_2S_3	*Cc*	1.1107	0.6395 β = 121.17°	0.7021	[10]
Ga_2Se_3	Ga_2S_3	*Cc*	0.666	1.165 β = 108.12°	0.666	[11]
Ga_2Se_3	Ga_2Se_3	*F*-43*m*	0.5463	–	–	[12]
In_2S_3	In_2S_3	$I4_1/amd$	0.7623	–	3.236	[13]
In_2S_3	$MgAl_2O_4$	*Fd*-3*m*	1.0728	–	–	[14]
In_2S_3	In_2S_3	*P*-3*m*1	0.3806	–	0.9044	[15]
In_2Se_3	In_2Se_3	*R*-3*m*	0.4025	–	2.8762	[16]
In_2Se_3	Al_2S_3	$P6_1$	0.71286	–	1.9381	[17]
In_2Se_3	Al_2S_3	$P6_5$	0.711	–	1.93	[18]
In_2Se_3	Al_2S_3	$P6_3$	1.600	–	1.924	[19]

[8] is identical to [10] after standardization, [18] to [17]; [11] was published in Bb; Ga_2Se_3 also reported with large tetragonal cell ($I4_1/acd$); Ga_2S_3 also reported with sphalerite structure (*F*-43*m*); [15] contains As or Sb.

The results presented here are part of a systematic investigation of the quasi-ternary systems *AX*–R_2X_3–$Ga(In)_2X_3$ (where *A* = *d*-element, *R* = rare-earth element, *X* = S, Se) [34-36]. The corresponding quasi-binary boundary systems exhibit a decreasing number of ternary compounds within the S→Se series. On the contrary the number of ternary compounds increases within the Ga→In series. Among the studied systems, a quaternary compound only exists in the NiS–La_2S_3–Ga_2S_3 system.

The indium-containing quasi-binary systems NiS(Se)–$In_2S(Se)_3$ feature large solid solution ranges of $In_2S(Se)_3$. The maximum solubility of NiS in the NiS–In_2S_3 system is 30 mol.% and the solid solubility in the selenium-containing system is 25 mol.% NiSe.

Isothermal sections of the investigated systems were constructed from the results of the phase analysis (Figs. 1-4).

The analysis of the *hkl* indices and the intensity of the reflections indicate that the structure of the La_3NiGaS_7 compound is likely to belong to the La_3MnGaS_7 structure type [33]. Experimental details and crystallographic data of La_3NiGaS_7 are presented in Table 3. Refinement of the atom coordinates and isotropic displacement parameters (Table 4) in this model yielded satisfactory values of the reliability factors. Experimental, calculated and differential diffraction patterns of the La_3NiGaS_7 compound are presented in Fig. 5.

The interatomic distances agree well with the sum of the ionic radii (Fig. 6). A projection of the unit cell and the coordination polyhedra of the La, Ni, Ga, S1, S2, and S3 atoms in the La_3NiGaS_7 structure are shown in Figs. 7,8. The surrounding of the La atoms are trigonal prisms with one additional atom, formed by 7 S atoms. The Ni atoms are located at the center of octahedra, and the Ga atoms inside tetrahedra of sulfur atoms. The S1 and S3 atoms also have tetrahedral surrounding, whereas the S2 atoms are surrounded by 5 neighbors.

Table 2 Crystallographic data for the ternary compounds.

Compound	Structure type	Space group	Cell parameters (nm)			Ref.
			a	*b*	*c*	
La_4NiS_7	La_4NiS_7	*I*4/*mmm*	0.40801	–	1.6334	[20]
La_4NiS_7	La_3CuSiS_7	$P6_3$	1.0264	–	0.5744	[21]
$NiGa_2S_4$	$FeGa_2S_4$	*P*-3*m*1	0.36249	–	1.19956	[22]
$LaGaS_3$	$LaGaS_3$	$P2_1/c$	1.517	1.056 β = 137.70°	1.282	[23]
$LaGaS_3$	Ag_8SiS_6	$Pna2_1$	1.04045	2.19835	0.60565	[24]
$La_3Ga_{1.67}S_7$	La_3CuSiS_7	$P6_3$	1.015	–	0.608	[25]
$La_3Ga_{1.67}Se_7$	La_3CuSiS_7	$P6_3$	1.067	–	0.610	[26]
La_3InS_6	La_3InS_6	$P2_12_12_1$	1.6912	1.3946	0.4079	[27]
$La_3In_{1.67}S_7$	La_3CuSiS_7	$P6_3$	1.01963	–	0.62792	[28]
$La_4In_{4.67}S_{13}$	$Nd_4In_5S_{13}$	*Pbam*	2.1280	1.1795	0.40380	[29]
$La_3In_{1.67}Se_7$	$Ce_3Al_{1.67}S_7$	$P6_3$	1.050	–	0.650	[30]
$La_4In_{4.67}Se_{13}$	$Nd_4In_5S_{13}$	*Pbam*	1.2442	2.2146	0.41969	[31]

[21] also reported as $La_3Ni_{1.67}S_7$ ($Ce_3Al_{1.67}S_7$ type); [23]: $P2_1/b$, a = 1.033, b = 1.282, c = 1.056 nm, γ = 98.90°; [26]: a = 1.053, c = 0.639 nm; monoclinc $La_3In_5S_{12}$ was reported in 2001.

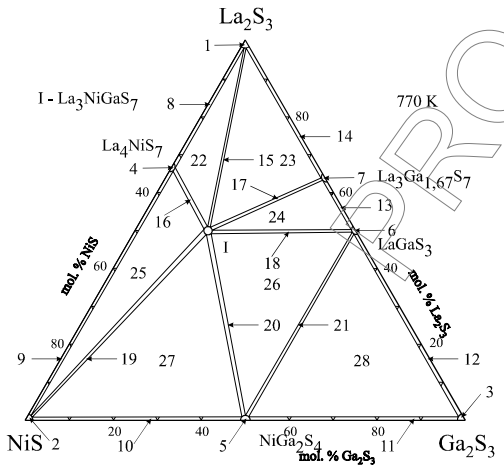

Fig. 1

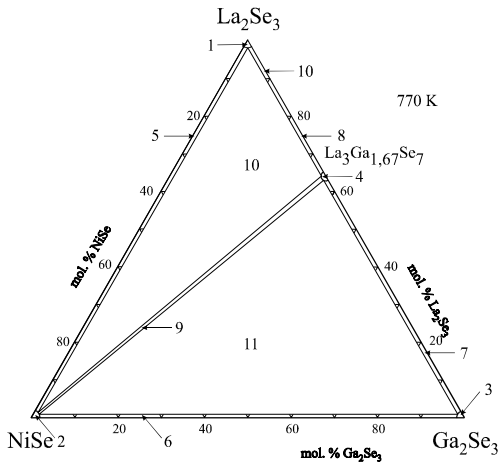

Fig. 2

Isothermal section of the NiS–La_2S_3–Ga_2S_3 system at 770 K: 1 – La_2S_3; 2 – NiS; 3 – Ga_2S_3; 4 – La_4NiS_7; 5 – $NiGa_2S_4$; 6 – $LaGaS_3$; 7 – $La_3Ga_{1.67}S_7$; 8 – La_2S_3 + La_4NiS_7; 9 – NiS + La_4NiS_7; 10 – NiS + $NiGa_2S_4$; 11 – Ga_2S_3 + $NiGa_2S_4$; 12 – Ga_2S_3 + $LaGaS_3$; 13 – $LaGaS_3$ + $La_3Ga_{1.67}S_7$; 14 – La_2S_3 + $La_3Ga_{1.67}S_7$; 15 – La_2S_3 + La_3NiGaS_7; 16 – La_4NiS_7 + La_3NiGaS_7; 17 – $La_3Ga_{1.67}S_7$ + La_3NiGaS_7; 18 – $LaGaS_3$ + La_3NiGaS_7; 19 – NiS + La_3NiGaS_7; 20 – $NiGa_2S_4$ + La_3NiGaS_7; 21 – $NiGa_2S_4$ + $LaGaS_3$; 22 – La_2S_3 + La_4NiS_7 + La_3NiGaS_7; 23 – La_2S_3 + $La_3Ga_{1.67}S_7$ + La_3NiGaS_7; 24 – $LaGaS_3$ + $La_3Ga_{1.67}S_7$ + La_3NiGaS_7; 25 – NiS + La_4NiS_7 + La_3NiGaS_7; 26 – $LaGaS_3$ + $NiGa_2S_4$ + La_3NiGaS_7; 27 – NiS + $NiGa_2S_4$ + La_3NiGaS_7; 28 – Ga_2S_3 + $NiGa_2S_4$ + $LaGaS_3$.

Isothermal section of the NiSe–La_2Se_3–Ga_2Se_3 system at 770 K: 1 – La_2Se_3; 2 – NiSe; 3 – Ga_2Se_3; 4 – $La_3Ga_{1.67}Se_7$; 5 – NiSe + La_2Se_3; 6 – NiSe + Ga_2Se_3; 7 – Ga_2Se_3 + $La_3Ga_{1.67}Se_7$; 8 – La_2Se_3 + $La_3Ga_{1.67}Se_7$; 9 – NiSe + $La_3Ga_{1.67}Se_7$; 10 – NiSe + La_2Se_3 + $La_3Ga_{1.67}Se_7$; 11 – NiSe + Ga_2Se_3 + $La_3Ga_{1.67}Se_7$.

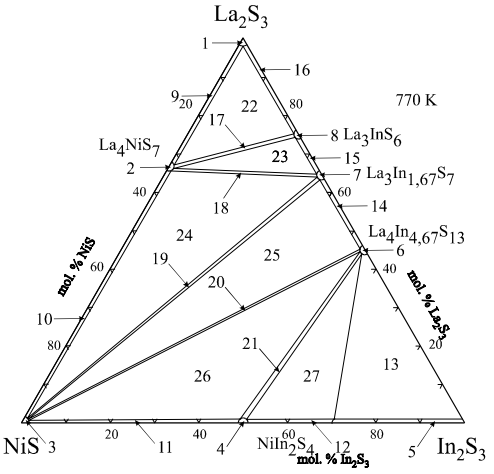

Fig. 3

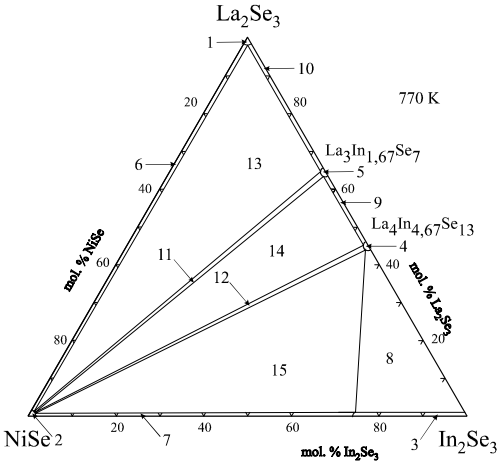

Fig. 4

Isothermal section of the NiS–La_2S_3–In_2S_3 system at 770 K: 1 – La_2S_3; 2 – La_4NiS_7; 3 – NiS; 4 – $NiIn_2S_4$; 5 – In_2S_3; 6 – $La_4In_{4.67}S_{13}$; 7 – $La_3In_{1.67}S_7$; 8 – La_3InS_6; 9 – La_2S_3 + La_4NiS_7; 10 – NiS + La_4NiS_7; 11 – NiS + $NiIn_2S_4$; 12 – $NiIn_2S_4$ + In_2S_3; 13 – In_2S_3 + $La_4In_{4.67}S_{13}$; 14 – $La_3In_{1.67}S_7$ + $La_4In_{4.67}S_{13}$; 15 – La_3InS_6 + $La_3In_{1.67}S_7$; 16 – La_2S_3 + La_3InS_6; 17 – La_4NiS_7 + La_3InS_6; 18 – La_4NiS_7 + $La_3In_{1.67}S_7$; 19 – NiS + $La_3In_{1.67}S_7$; 20 – NiS + $La_4In_{4.67}S_{13}$; 21 – $NiIn_2S_4$ + $La_4In_{4.67}S_{13}$; 22 – La_2S_3 + La_4NiS_7 + La_3InS_6; 23 – La_4NiS_7 + La_3InS_6 + $La_3In_{1.67}S_7$; 24 – NiS + La_4NiS_7 + $La_3In_{1.67}S_7$; 25 – NiS + $La_3In_{1.67}S_7$ + $La_4In_{4.67}S_{13}$; 26 – NiS + $NiIn_2S_4$ + $La_4In_{4.67}S_{13}$; 27 – In_2S_3 + $La_4In_{4.67}S_{13}$ + $NiIn_2S_4$.

Isothermal section of the NiSe–La_2Se_3–In_2Se_3 system at 770 K: 1 – La_2Se_3; 2 – NiSe; 3 – In_2Se_3; 4 – $La_4In_{4.67}Se_{13}$; 5 – $La_3In_{1.67}Se_7$; 6 – La_2Se_3 + NiSe; 7 – NiSe + In_2Se_3; 8 – In_2Se_3 + $La_4In_{4.67}Se_{13}$; 9 – $La_3In_{1.67}Se_7$ + $La_4In_{4.67}Se_{13}$; 10 – La_2Se_3 + $La_3In_{1.67}Se_7$; 11 – NiSe + $La_3In_{1.67}Se_7$; 12 – NiSe + $La_4In_{4.67}Se_{13}$; 13 – NiSe + La_2Se_3 + $La_3In_{1.67}Se_7$; 14 – NiSe + $La_3In_{1.67}Se_7$ + $La_4In_{4.67}Se_{13}$; 15 – NiSe + In_2Se_3 + $La_4In_{4.67}Se_{13}$.

Table 3 Experimental details and crystallographic data of La_3NiGaS_7.

Compound		La_3NiGaS_7
Structure type		La_3MnGaS_7
Pearson symbol		*hP*24
Space group		$P6_3$
a (nm)		1.01605(4)
c (nm)		0.60397(3)
Cell volume (nm^3)		0.53998(6)
Calculated density (g/cm^3)		4.7328(6)
Radiation and wavelength (nm)		Cu Kα 0.154185
Diffractometer		DRON 4-13
Mode of refinement		Full profile
Program		WinCSD
Number of free parameters		19
2θ(°) and $\sin\theta/\lambda$ max. (1/nm)		100.02 4.97
Reliability factors	R_I	0.0856
	R_p	0.1897
Scale factor		0.21900(1)

Table 4 Atomic coordinates, equivalent displacement parameters and site occupancies for La_3NiGaS_7.

Atom	Wyckoff position	*x/a*	*y/b*	*z/c*	Occ.	$B_{iso}\times10^2$ (nm^2)
La	6*c*	0.3737(2)	0.1430(2)	0.2308(6)	1	0.95(5)
Ni	2*a*	0	0	-0.007(2)	1	0.3(2)
Ga	2*b*	⅓	⅔	0.1533(7)	1	0.73(14)
S1	6*c*	0.1012(6)	0.5164(8)	0.0023(9)	1	0.6(3)
S2	6*c*	0.1438(7)	0.2327(6)	0.2675(14)	1	1.5(3)
S3	2*b*	⅓	⅔	0.513(2)	1	1.0(3)

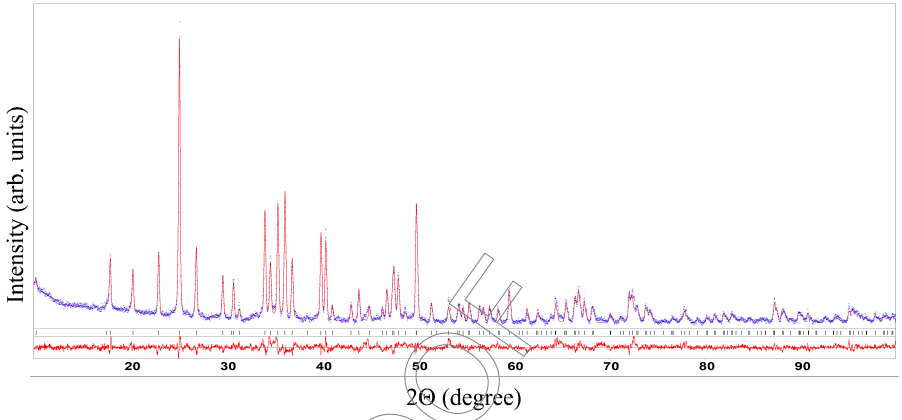

Fig. 5 Experimental and theoretical diffraction patterns of La_3NiGaS_7 and their difference.

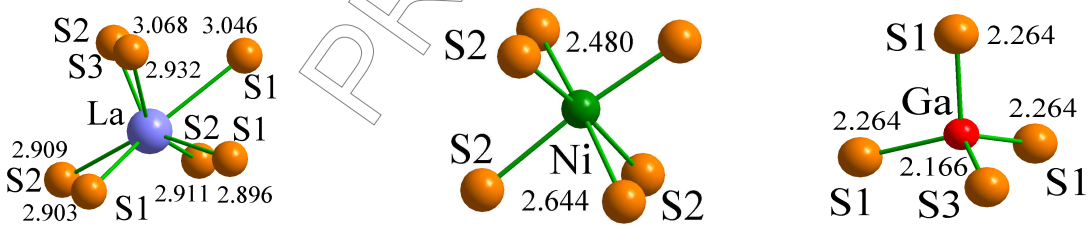

Fig. 6 Coordinations and interatomic distances (Å) in the La_3NiGaS_7 structure.

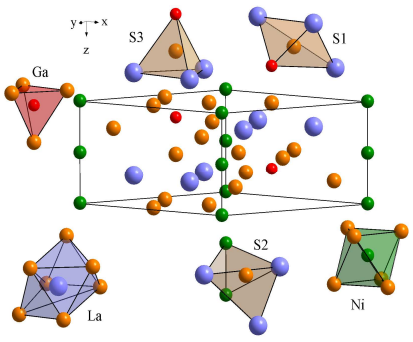

Fig. 7 Unit cell and coordination polyhedra of the atoms in the La_3NiGaS_7 structure.

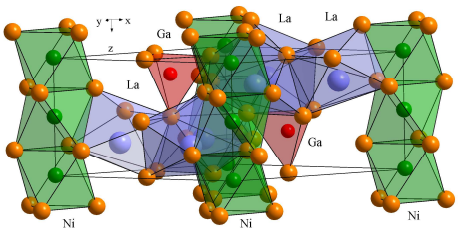

Fig. 8 Packing of polyhedra in the structure of the La_3NiGaS_7 compound.

Conclusions

Isothermal sections of the phase diagrams of the NiX–La_2X_3–$Ga(In)_2X_3$ (X = S, Se) systems were investigated. The existence of compounds reported in the literature was confirmed. The crystal structure of the new quaternary compound La_3NiGaS_7 was determined.

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