Chemistry of Metals and Alloys

Chem. Met. Alloys 9 (2016) 105-112
Ivan Franko National University of Lviv
www.chemetal-journal.org

The quasi-ternary system La_2S_3–Er_2S_3–Ga_2S_3 and quaternary compounds of the composition $La(Pr)_{1.5}Tb(Y, Ho)_{1.5}Ga_{1.67}S_7$

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Received September 15, 2016; accepted December 28, 2016; available on-line August 14, 2017

The isothermal section of the La_2S_3–Er_2S_3–Ga_2S_3 system at 770 K was investigated by XRD. $La_3Ga_{1.67}S_7$ forms a solid solution range extending to 50 mol.% "$Er_3Ga_{1.67}S_7$", *i.e.* $La_{1.5}Er_{1.5}Ga_{1.67}S_7$ is the boundary composition of this solid solution. The unit cell parameters vary linearly from *a* = 1.0180(4) nm, *c* = 0.6055(2) nm for $La_3Ga_{1.67}S_7$ to *a* = 0.9820(5) nm, *c* = 0.6228(3) nm for the sample of composition 27 mol.% La_2S_3 – 37 mol.% Er_2S_3 – 36 mol.% Ga_2S_3 (50 mol.% "$Er_3Ga_{1.67}S_7$"). The crystal structures of $La_{1.5}Y_{1.5}Ga_{1.67}S_7$, $Pr_{1.5}Tb_{1.5}Ga_{1.67}S_7$, and $Pr_{1.5}Ho_{1.5}Ga_{1.67}S_7$ were determined by powder XRD; they belong to the structure type $Ce_3Al_{1.67}S_7$, space group *P*6_3. A continuous solid solution series (CSSS) with this hexagonal structure was observed in the quasi-ternary system La_2S_3–Tb_2S_3–Ga_2S_3 along the concentration line 36 mol.% Ga_2S_3. The unit cell parameters vary from *a* = 0.9670(3) nm, *c* = 0.6083(2) nm for $Tb_3Ga_{1.67}S_7$ to *a* = 1.0180(4) nm, *c* = 0.6055(2) nm for $La_3Ga_{1.67}S_7$, with the *c*-parameter having a maximum at the composition $La_{1.5}Tb_{1.5}Ga_{1.67}S_7$.

Rare-earth metals / Phase equilibria / Crystal structure / Chalcogenides / X-ray powder diffraction

Introduction

The La(Pr)$_2S_3$–Y(Tb, Ho, Er)$_2S_3$–Ga_2S_3 systems are of interest for researchers because their binary components are widely used in various fields of modern semiconductor technology [1]. According to literature reports [2-8], the Ln_2S_3–Ga(In)$_2S_3$ systems feature the formation of Ln_3Ga(In)$_{1.67}S_7$ compounds (*Ln* = La, Ce, Y, Tb, Ho) that melt congruently and crystallize in the $Ce_3Al_{1.67}S_7$ structure type (space group *P*6_3) [2]. Among the best known rare-earth chalcogenides, there is a large family of compounds Ln_3BCX_7 (*Ln* = Y, rare earth, *B* = 6-coordinated element, *C* = 4-coordinated element, *X* = S, Se), which also crystallize in the $Ce_3Al_{1.67}S_7$ structure type. They are of great interest as potential IR non-linear optical (NLO) materials, magnetic materials and ionic conductors [9-13]. This family of compounds can tolerate various combinations of *B* and *C*. The most common are: 1) B^{I}, C^{IV} [11]; 2) B^{II}, C^{III} [14,15]. These two types of combination demand that the sum of the valence of *B* and *C* is equal 5. Despite adopting the same crystal structure type, its members show distinctively different NLO properties. This is quite unusual and the intrinsic reason remains unknown. We have earlier investigated the crystal structure of the compound $La_{1.5}Tb_{1.5}Ga_{1.67}S_7$, space group *P*$6_3$, $Ce_3Al_{1.67}S_7$ structure type [16]. The number of known isotypic compounds suggests the possible formation of solid solutions such as $Ln1_{3-x}Ln2_x$GaS$_7$, where *Ln*1 = La, Pr; *Ln*2 = Y, Tb, Ho, Er, with different extensions in the La(Pr)$_2S_3$–Y(Tb, Ho, Er)$_2S_3$–Ga_2S_3 systems, which crystallize in the $Ce_3Al_{1.67}S_7$ structure type and may have interesting optical properties. Changing the composition allows varying the physical properties over a wide range with the possibility to satisfy the requirements of non-linear optics, and may help understanding the differences in the NLO properties.

Experimental

The samples for the investigation were synthesized by step-wise heating the batches to 1420 K at the rate of 10 K/h with 48-h stops at 400 K and 720 K. After 2 h at the maximum temperature they were cooled to 770 K at the rate of 20 K/h and annealed for 300 h. Some samples were pressed into pellets and additionally annealed for 500 h at 770 K for better homogeneity.

X-ray diffraction patterns of the samples were recorded on a DRON 4-13 diffractometer (Cu K_α-radiation), scan step 0.05°, 2 s exposure time. The unit cell parameters were determined using the PDWin 2.0 and POWDER CELL 2.4 software packages. For the determination and refinement of the crystal structures of the quaternary phases by the powder method, diffraction patterns obtained on a DRON 4-13 diffractometer (Cu K_α-radiation) were used, scan step 0.02-0.05°, 15-30 s exposure at each point. During the refinement, the compositions of the statistical mixture and defect positions were fixed in agreement with the stoichiometry, in order to preserve the electric neutrality of the compounds. The refinement included the atom coordinates and isotropic displacement parameters. The determination and refinement of the structures by the powder method were performed using the CSD software package [17].

Results and discussion

Isothermal section of the La_2S_3–Er_2S_3–Ga_2S_3 system at 770 K. The isothermal section of the quasi-ternary system La_2S_3–Er_2S_3–Ga_2S_3 was constructed from the results of XRD of 84 samples (Fig. 1). The existence of a new quaternary phase of the composition $La_{1.5}Er_{1.5}Ga_{1.67}S_7$, which crystallizes in the hexagonal space group $P6_3$, was found. Further investigation showed that $La_{1.5}Er_{1.5}Ga_{1.67}S_7$ is isostructural to $La_3Ga_{1.67}S_7$. The intermediate samples between these compositions are single-phase ($P6_3$), the unit cell parameters vary linearly from $a = 1.0180(4)$ nm, $c = 0.6055(2)$ nm for $La_3Ga_{1.67}S_7$ to $a = 0.9820(14)$ nm, $c = 0.6228(12)$ nm for the composition 27 mol.% La_2S_3 – 37 mol.% Er_2S_3 – 36 mol.% Ga_2S_3 (Fig. 2). This indicates the formation of a solid solution range of $La_3Ga_{1.67}S_7$ extending to 50 mol.% "$Er_3Ga_{1.67}S_7$" *i.e.* the existence of a phase $La_{3-x}Er_xGa_{1.67}S_7$, $0 \le x \le 1.5$, where the sample $La_{1.5}Er_{1.5}Ga_{1.67}S_7$ is the boundary composition of the solid solution. Additionally, the system at 770 K features single-phase regions of the binary compounds Ga_2S_3 (Cc), La_2S_3 ($Pnma$), Er_2S_3 ($P2_1/m$), and the ternary compounds Er_3GaS_6 ($Cmc2_1$) and $LaGaS_3$ ($P2_1/c$). The phase $La_{3-x}Er_xGa_{1.67}S_7$, $0 \le x \le 1.5$, forms equilibria with Ga_2S_3, La_2S_3, Er_2S_3, Er_3GaS_6, and $LaGaS_3$. Two-phase and single-phase fields border the regions of three-phase equilibria.

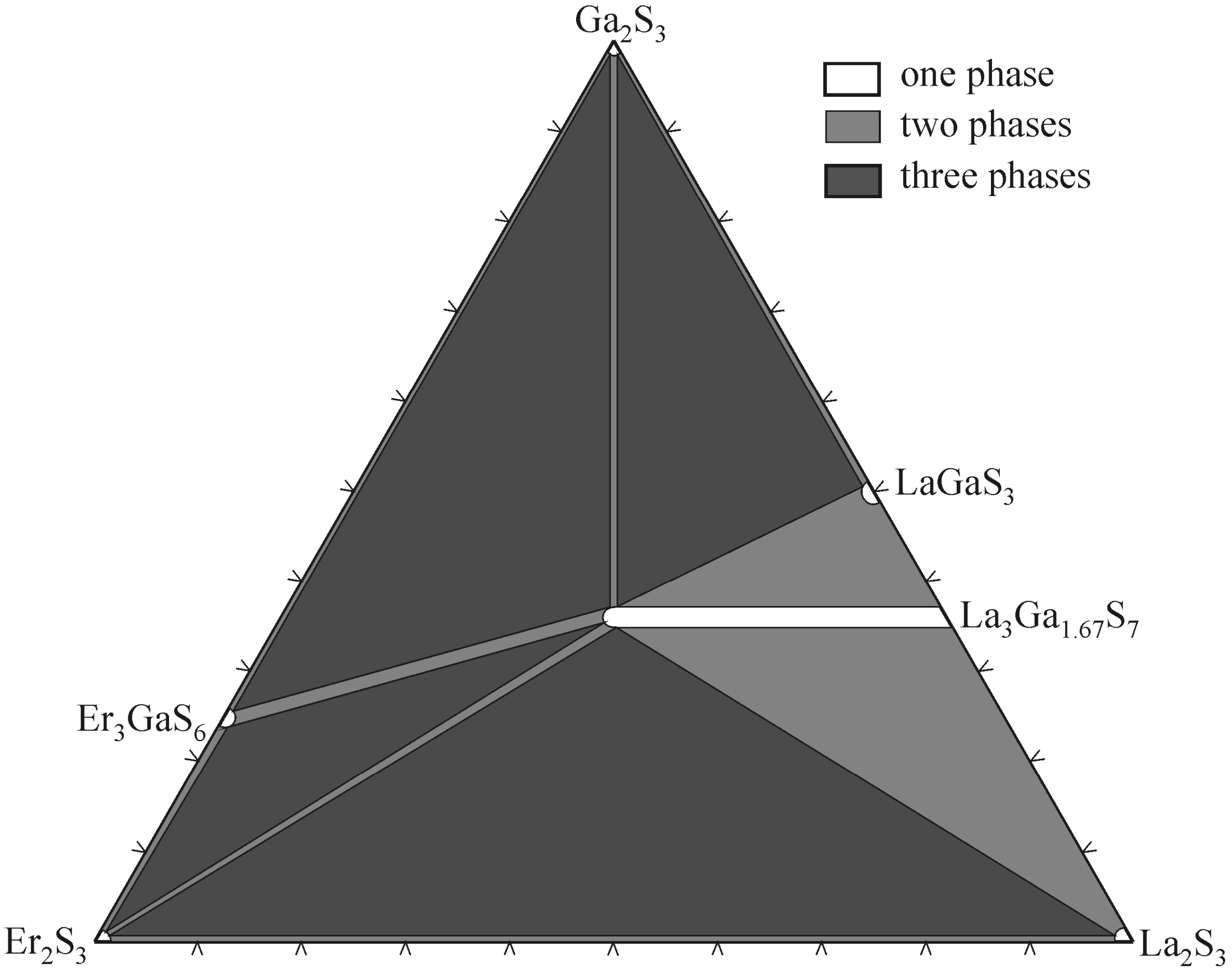

Fig. 1 Isothermal section of the quasi-ternary system La_2S_3–Er_2S_3–Ga_2S_3 at 770 K.

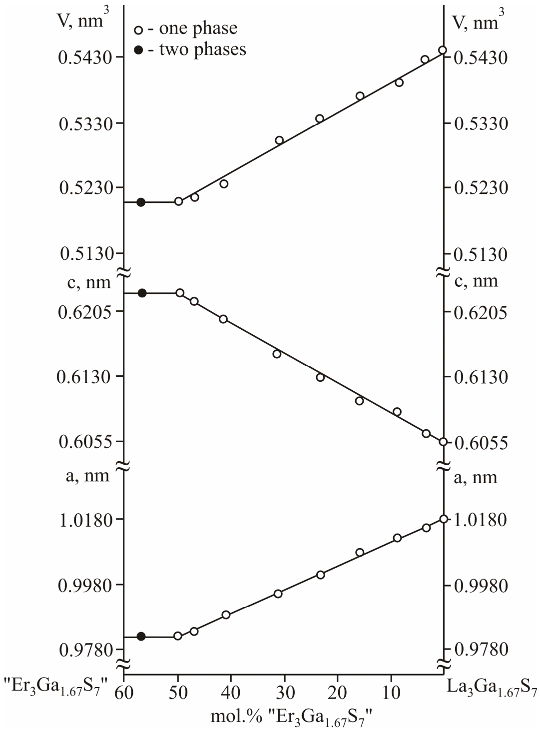

Fig. 2 Variation of the unit cell parameters of the samples along the "$Er_3Ga_{1.67}S_7$"–$La_3Ga_{1.67}S_7$ line (36 mol.% Ga_2S_3).

Crystal structures of the compounds La(Pr)$_{1.5}$Tb(Y, Ho)$_{1.5}$Ga$_{1.67}$S$_7$ determined by X-ray powder diffraction. Samples of compositions La(Pr)$_{1.5}$Tb(Y, Ho)$_{1.5}$Ga$_{1.67}$S$_7$ were synthesized to search for new quaternary compounds with other rare-earths. XRD data showed that these samples are single-phase; the structure analysis showed that they are isostructural to $La_{1.5}Tb_{1.5}Ga_{1.67}S_7$ (*P*6$_3$) [3] and the structure of this compound was chosen as starting model for the refinement. The compositions of the statistical mixture *M* were fixed from the nominal composition of the sample and were not refined. The results of the refinements of the structures of the compounds $La_{1.5}Y_{1.5}Ga_{1.67}S_7$, $Pr_{1.5}Tb_{1.5}Ga_{1.67}S_7$, and $Pr_{1.5}Ho_{1.5}Ga_{1.67}S_7$ are presented in Figs. 3-5 and Tables 1 and 2. Calculated interatomic distances and coordination numbers are given in Table 3.

Features of the crystal structures of the quaternary compounds La(Pr)$_{1.5}$Y(Tb, Ho, Er)$_{1.5}$Ga$_{1.67}$S$_7$ of the quasi-ternary systems La(Pr)$_2$S$_3$–Y(Tb, Ho, Er)$_2$S$_3$–Ga$_2$S$_3$. As expected, the structures of the studied quaternary compounds $La_{1.5}Y_{1.5}Ga_{1.67}S_7$, $Pr_{1.5}Tb_{1.5}Ga_{1.67}S_7$, and $Pr_{1.5}Ho_{1.5}Ga_{1.67}S_7$ (powder method), belong to the structure type $Ce_3Al_{1.67}S_7$ [2], space group *P*6$_3$, which hosts a large number of compounds such as $La_3In_{1.67}S_7$, $a = 1.01963$ nm, $c = 0.62792$ nm [4], La_3AlSiS_7, $a = 1.0277$ nm, $c = 0.5793$ nm [18], and La_3CuSiS_7, $a = 1.0310$ nm, $c = 0.5794$ nm [19]. The site of the cation *B* is octahedrally coordinated, the cation *C* is tetrahedrally coordinated. In our case, Ga1 has tetrahedral coordination (the 2*a* site is fully occupied), Ga2 has octahedral coordination with a partial site occupation of 2/3 (Table 2). The structures of these compounds may be presented as a series of face-sharing octahedra Ga2S$_6$ and isolated tetrahedra Ga1S$_4$ stretched along the *c*-axis (Figs. 6,7). The coordination polyhedron LaS$_7$ is a single-capped trigonal prism. Similar polyhedra were observed in the structures of $Ce_3Al_{1.67}S_7$ [2] and $La_3In_{1.67}S_7$ [4].

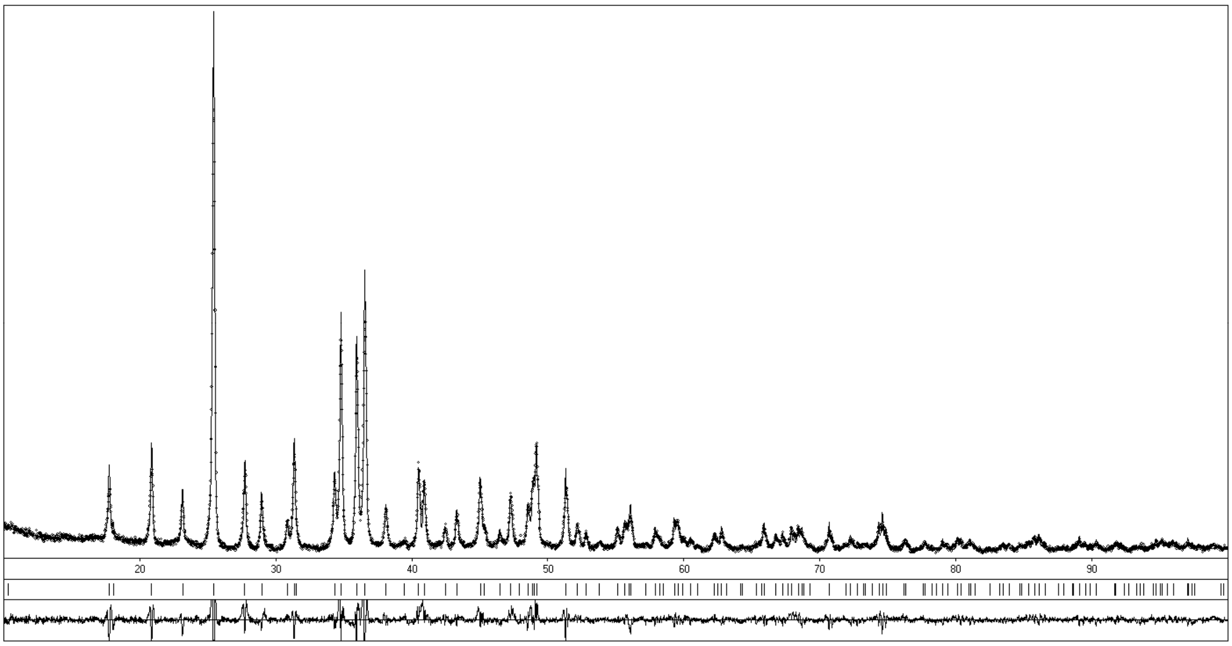

Fig. 3 Experimental (dots), calculated (solid line) and differential (bottom) diffraction patterns of $La_{1.5}Y_{1.5}Ga_{1.67}S_7$.

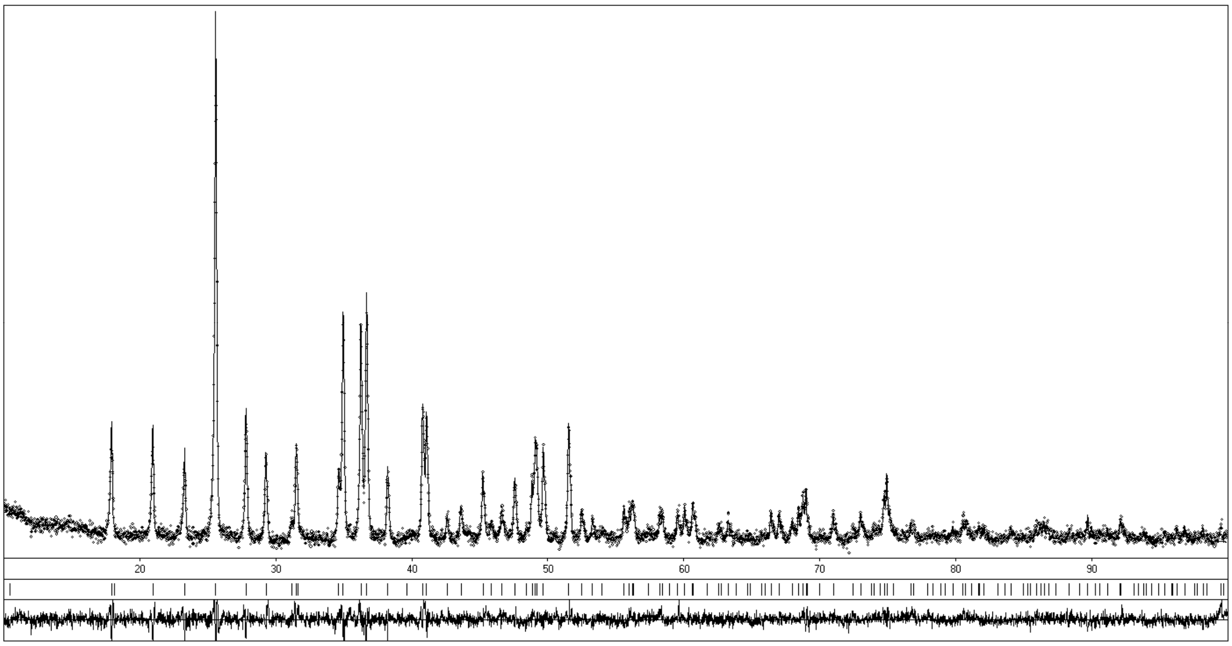

Fig. 4 Experimental (dots), calculated (solid line) and differential (bottom) diffraction patterns of $Pr_{1.5}Tb_{1.5}Ga_{1.67}S_7$.

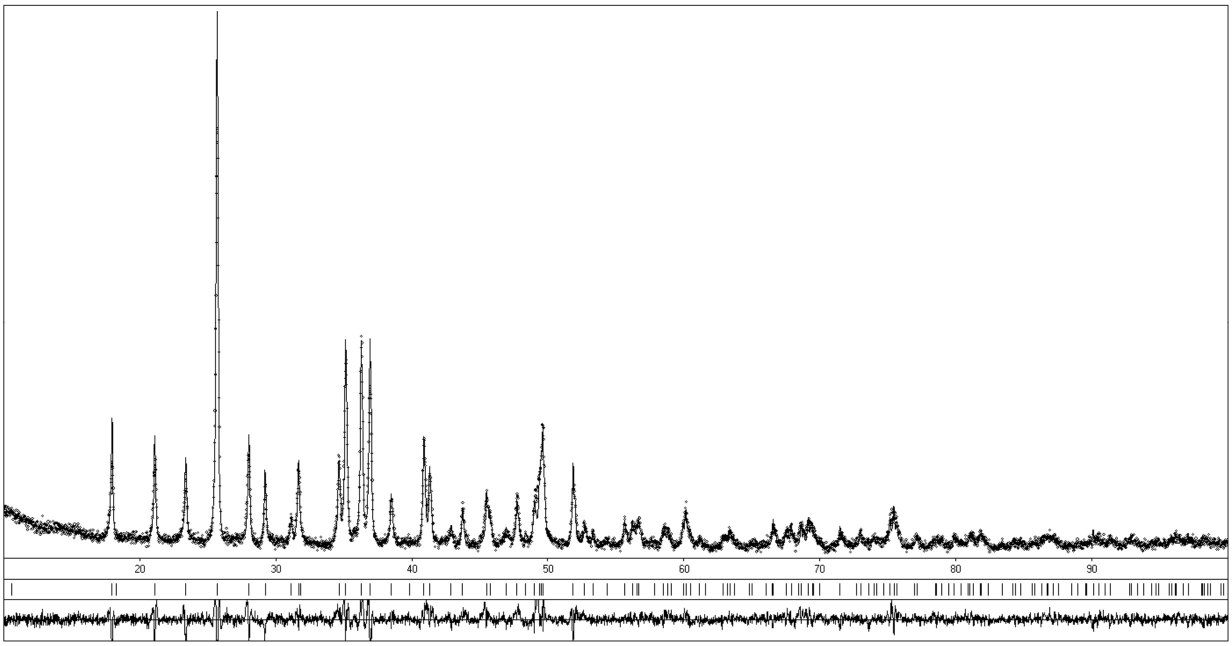

Fig. 5 Experimental (dots), calculated (solid line) and differential (bottom) diffraction patterns of $Pr_{1.5}Ho_{1.5}Ga_{1.67}S_7$.

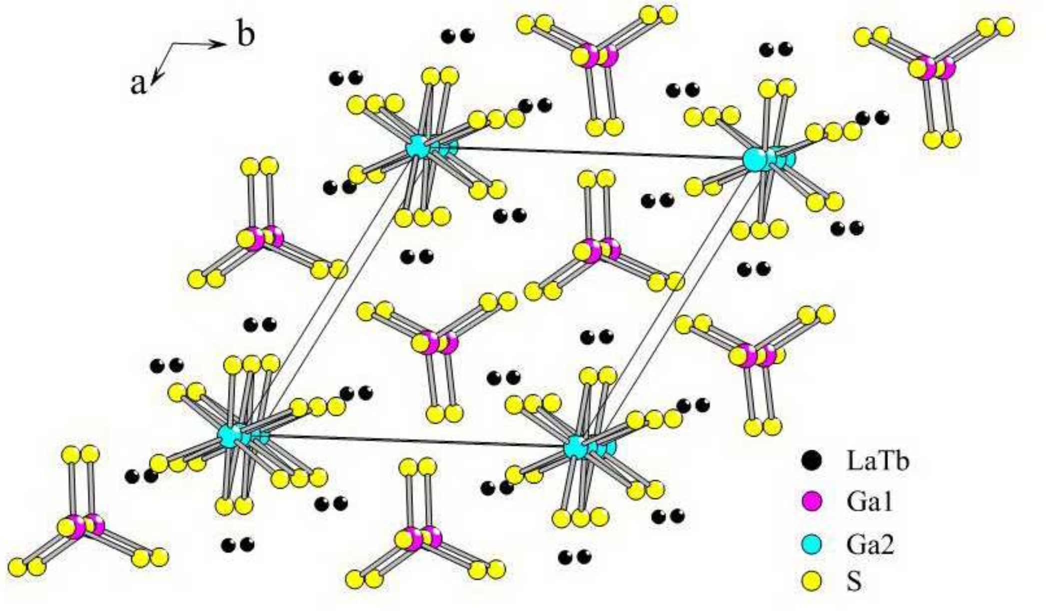

Fig. 6 Crystal structure of $La_{1.5}Tb_{1.5}Ga_{1.67}S_7$ along the crystallographic direction *c*.

Table 1 Crystallographic characteristics of the structures of the compounds $La(Pr)_{1.5}Y(Tb, Ho)_{1.5}Ga_{1.67}S_7$.

Sample composition	$La_{1.5}Y_{1.5}Ga_{1.67}S_7$	$Pr_{1.5}Tb_{1.5}Ga_{1.67}S_7$	$Pr_{1.5}Ho_{1.5}Ga_{1.67}S_7$
Space group	$P6_3$	$P6_3$	$P6_3$
Unit cell, nm	a = 0.98276(2), c = 0.61658(2)	a = 0.97973(2), c = 0.61008(2)	a = 0.97373(3), c = 0.61179(3)
V, nm^3	0.51572(4)	0.50714(4)	0.50236(5)
Number of atoms per unit cell	23.34	23.34	23.34
Calculated density, g/cm^3	4.3953(3)	5.1769(5)	5.2858(5)
Absorption coefficient, 1/cm	752.26	1159.63	900.96
Radiation; wavelength, nm	Cu Kα; 0.154178	Cu Kα; 0.154178	Cu Kα; 1.54185
Diffractometer	DRON 4-13	DRON 4-13	DRON 4-13
Computation mode	full profile	full profile	full profile
Number of free parameters	20	20	20
R_I; R_p	0.0666; 0.2169	0.0907; 0.2460	0.1027; 0.2793
Scale factor	0.36414(4)	0.5375(4)	0.4741(3)
Texture axis and parameter	[011]; 1.86(2)	[110]; 0.52(2)	[100]; 0.96(3)

Table 2 Atomic coordinates of the structures of the compounds $La(Pr)_{1.5}Y(Tb, Ho)_{1.5}Ga_{1.67}S_7$.

Atom	Wyckoff site	*x/a*	*y/b*	*z/c*	Occupation	$B_{iso}\times10^2$, nm^2
			$La_{1.5}Y_{1.5}Ga_{1.67}S_7$			
*M*1	6*c*	0.1597(2)	0.3779(1)	0.0540(5)	0.50La + 0.50Y	1.72(2)
Ga1	2*b*	⅓	⅔	0.6221(6)	1	1.17(4)
Ga2	2*a*	0	0	0.2657(13)	0.667	3.34(4)
S1	2*b*	⅓	⅔	0.2755(13)	1	0.67(4)
S2	6*c*	0.1066(6)	0.2446(5)	0.4725(8)	1	0.85(4)
S3	6*c*	0.4650(7)	0.9091(5)	0.7669(8)	1	1.39(4)
			$Pr_{1.5}Tb_{1.5}Ga_{1.67}S_7$			
*M*1	6*c*	0.1535(2)	0.3788(2)	0.0466(8)	0.50Pr + 0.50Tb	0.54(3)
Ga1	2*b*	⅓	⅔	0.6037(11)	1	0.83(7)
Ga2	2*a*	0	0	0.2657(13)	0.667	3.49(7)
S1	2*b*	⅓	⅔	0.255(2)	1	0.37(7)
S2	6*c*	0.1006(8)	0.2398(8)	0.4990(14)	1	0.78(7)
S3	6*c*	0.4798(11)	0.9110(9)	0.7714(13)	1	0.66(7)
			$Pr_{1.5}Ho_{1.5}Ga_{1.67}S_7$			
*M*1	6*c*	0.1562(2)	0.3797(2)	0.0423(7)	0.50Pr + 0.50Ho	1.21(3)
Ga1	2*b*	⅓	⅔	0.6174(9)	1	0.66(6)
Ga2	2*a*	0	0	0.2657(13)	0.667	1.65(7)
S1	2*b*	⅓	⅔	0.273(2)	1	0.92(7)
S2	6*c*	0.1065(9)	0.2447(8)	0.4646(12)	1	0.60(6)
S3	6*c*	0.4751(11)	0.9038(9)	0.7653(12)	1	0.73(6)

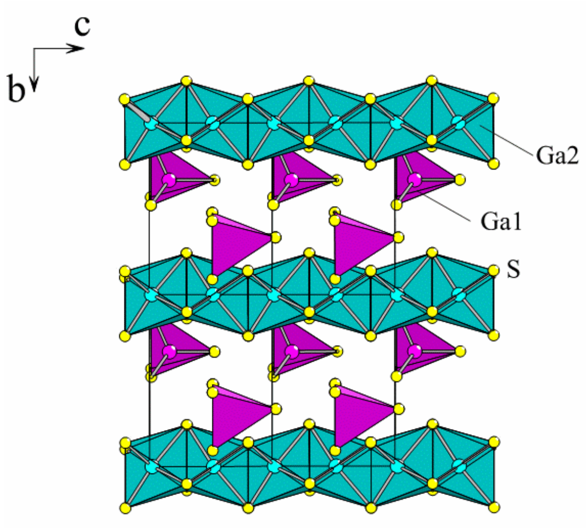

Fig. 7 Polyhedral representation of the crystal structure of $La_{1.5}Tb_{1.5}Ga_{1.67}S_7$.

Taking into account the formation in the quasi-ternary system La_2S_3–Tb_2S_3–Ga_2S_3 of the compounds $Tb_3Ga_{1.67}S_7$ and $La_3Ga_{1.67}S_7$, both having the same hexagonal structure, space group $P6_3$, samples along the concentration line 36 mol.% Ga_2S_3 were prepared. They show the existence of a continuous solid solution series with the hexagonal structure, with the unit cell periods varying from $a = 0.9670(3)$ nm, $c = 0.6083(2)$ nm for $Tb_3Ga_{1.67}S_7$ to $a = 1.0180(4)$ nm, $c = 0.6055(2)$ nm for $La_3Ga_{1.67}S_7$ (Fig. 8).

A comparison of the extent of the solid solutions along the concentration line 36 mol.% Ga_2S_3 in the La_2S_3–Ga_2S_3–Er_2S_3 and La_2S_3–Ga_2S_3–Tb_2S_3 systems (Figs. 2,8) is of interest. The solubility of $La_3Ga_{1.67}S_7$ in the erbium-containing system is limited. The terbium-containing system features a continuous solid solution series (CSSS) between the isostructural compounds $La_3Ga_{1.67}S_7$ and $Tb_3Ga_{1.67}S_7$. The unit cell parameter *a* and the volume vary with a minor deviation from linearity with composition, whereas the *c*–parameter shows a maximum at the composition $La_{1.5}Tb_{1.5}Ga_{1.67}S_7$ (Fig. 8).

Table 3 Interatomic distances and coordination numbers of atoms in the structure of the compounds $La(Pr)_{1.5}Y(Tb,Ho)_{1.5}Ga_{1.67}S_7$.

Atoms		Distance, nm	C.N.
		$La_{1.5}Y_{1.5}Ga_{1.67}S_7$	
*M*1	1S3	0.2804(6)	7
	1S2	0.2816(6)	
	1S1	0.2835(4)	
	1S2	0.2872(5)	
	1S2	0.2881(5)	
	1S1	0.2943(6)	
	1S1	0.3107(6)	
Ga1	1S3	0.2208(9)	4
	3S1	0.2271(5)	
Ga2	3S2	0.2416(7)	6
	3S2	0.2734(8)	
		$Pr_{1.5}Ho_{1.5}Ga_{1.67}S_7$	
*M*1	1S3	0.2769(9)	7
	1S2	0.2802(9)	
	1S1	0.2811(7)	
	1S2	0.2818(8)	
	1S1	0.2884(10)	
	1S2	0.2888(8)	
	1S1	0.3064(10)	
Ga1	1S3	0.2246(14)	4
	3S1	0.2190(8)	
Ga2	3S2	0.2335(10)	6
	3S2	0.2854(9)	
		$Pr_{1.5}Tb_{1.5}Ga_{1.67}S_7$	
*M*1	1S3	0.2763(9)	7
	1S2	0.2826(9)	
	1S1	0.2829(7)	
	1S2	0.2854(8)	
	1S1	0.2855(10)	
	1S2	0.2976(8)	
	1S1	0.3003(10)	
Ga1	1S3	0.2185(14)	4
	3S1	0.2328(8)	
Ga2	3S2	0.2482(10)	6
	3S2	0.2563(9)	

A similar phenomenon was also observed in the study of the Cu_2FeSnS_4–Cu_2ZnSnS_4 system [20]. This was explained by the ordered location of the cations with the formation of a superstructure, as in the case of the solid solution in the Ag_3PS_4–Cu_3PS_4 system [21]. No superstructure reflections were observed in the diffraction patterns of the samples of the $La_3Ga_{1.67}S_7$–$Tb_3Ga_{1.67}S_7$ system within the CSSS. The maximum deviation from Vegard's rule falls on the composition $La_{1.5}Tb_{1.5}Ga_{1.67}S_7$. This leads us to conclude that partial ordering of the cations in the structure may exist at this composition. Clearly, the difference in the character of the interactions in the systems La_2S_3–Ga_2S_3 and Er_2S_3–Ga_2S_3, and the absence of a ternary compound $Er_3Ga_{1.67}S_7$, limit the extent of the solid solutions in this case.

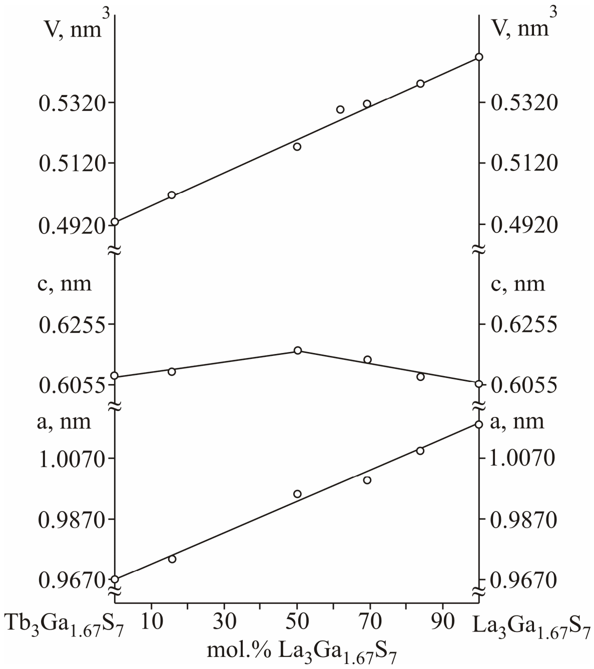

Fig. 8 Variation of the unit cell parameters of the samples of the $Tb_3Ga_{1.67}S_7$–$La_3Ga_{1.67}S_7$ system (36 mol.% Ga_2S_3).

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