



The La_2S_3 – LaS_2 system: Thermodynamic and kinetic study

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ABSTRACT

A detailed thermodynamic study of the LaS_2 – La_2S_3 system in the temperature range 350–1000 °C was performed, starting from high quality crystals LaS_2 as the highest polysulfide in the system, and using a sensitive static tensimetric method with a quartz Bourdon gauge and a membrane as a null-point instrument. The p_s – T – x diagram obtained has shown that the phase region covering the composition between LaS_2 and La_2S_3 , which was previously described as a single grossly nonstoichiometric phase, consists of three discrete stoichiometric phases, $\text{LaS}_{2.00}$, $\text{LaS}_{1.91}$, and $\text{LaS}_{1.76}$, where compositions could be determined with an accuracy of ± 0.01 f.u. The thermodynamic characteristics of evaporation of the polysulfides as well as standard heat of LaS_2 formation were calculated. The role of kinetics in the formation of ordered superstructures of sulfur-poorer polysulfides with different formal concentration of vacancies is considered.

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1. Introduction

Nonstoichiometry is known to affect strongly the physical and chemical properties of inorganic compounds. It is generally accommodated by the formation of lattice defects, and the first step in elucidating the properties of materials is to characterize these defects. In recent years, much work has been done to understand nonstoichiometry and order–disorder transitions in polysulfides of rare earth metals (RE). Both the structural and thermodynamic techniques were used to identify the defects, although interpretation of the results was not always correct.

The crystal structure of the LnS_{2-x} compounds is represented by derivatives from the ZrSSi structure type, known also as the PbFCl type [1,2]. This structural type is built from $[\text{LnS}]$ double sheets with NaCl structure, sandwiched with $[\text{S}_2]$ square layers. For the extreme composition LnS_2 , the electro-neutral structural formula is $[\text{Ln}^{3+}\text{S}^{2-}]_2 \cdot [\text{S}_2^{2-}]$, where the anionic layer contains only the sulfur dimers S_2 without any defects. In the sulfur-poorer compounds $\text{LnS}_{2-\square}$, the nonstoichiometry in the anionic layer comes from sulfur vacancies (\square) and isolated anions S^{2-} for charge compensation. Ordering of vacancies and orientation of the sulfur dimers give rise to the formation of a reach family of various superstructures. So, for $\text{LnS}_{1.9}$ with $\square=0.1$, a 10-fold superstructure of the ZrSSi was found, while for the $\text{LnS}_{1.875}$ (Ln_8S_{15}) with $\square=0.125$ it was a 24-fold superstructure of the ZrSSi type [2,3]. On the other hand, when the vacancy concentration increased, unexpected and slightly different

stoichiometries and structures of polysulfides were observed. So, $\text{LnS}_{1.84}$ and $\text{LnS}_{1.76}$ were also referred to the $\text{LnS}_{1.875}$ structural type by inserting an uncertain term δ in the stoichiometric composition $\text{LnS}_{1.875-\delta}$ and assuming incomplete structure ordering [3]. It follows that equilibrium and full superstructure ordering into discrete phases with a high formal concentration of sulfur defects may not be achieved for kinetic reasons resulting in pseudo-nonstoichiometric and metastable products. If the defect ordering in the simulated phase is controlled by kinetics, structural knowledge becomes inadequate for understanding the nonstoichiometry of polysulfides, and thus new insight into defect chemistry of the compounds can be provided by thermodynamic approach.

Thermodynamic studies with very sensitive static vapor pressure measurements by a membrane gauge have already been performed with the systems LnS_2 – $\text{LnS}_{1.5}$, where $\text{Ln}=\text{Pr}$, Nd , Gd , Dy [4,5]. A thorough study of the equilibrium p_s – T – x diagrams showed that the compositional range, which was previously described as a single grossly nonstoichiometric phase, consists of a set of discrete stoichiometric phases that must be fully ordered in the equilibrium state. Identification of the composition of all possible, but previously unknown intermediate phases, especially with the highest vacancy concentration, and determination of the p_s – T phase borders for each of the phases are an obvious advance of the thermodynamic approach and equilibrium diagrams. However, some questions still remain: what is the cause of the variety of intermediate compositions found in these systems, and what is the highest vacancy concentration in the RE polysulfides. It seems that the first attempt to classify these compounds according to structural types and precise chemical compositions will be possible only after a thorough study of the p_s – T – x diagrams of other polysulfide systems.

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In the present work, the equilibrium phase diagram of the $\text{LaS}_{1.50}$ – $\text{LaS}_{2.0}$ system has been determined in detail by the static membrane method, which is an effective tool to control equilibrium in the systems when the solid phases are in equilibrium with vapor [6]. Such study was necessary since the available information concerning the La-polysulfides was quite conflicting, and phase relations have not been thoroughly investigated. Indeed, here the nonstoichiometry was presented as one grossly nonstoichiometric phase covering the composition range $\text{LaS}_{1.76}$ – $\text{LaS}_{1.94}$ [7,8], although there were publications on discrete phases $\text{LaS}_{1.95}$, $\text{LaS}_{1.96}$, $\text{LaS}_{2.0}$, $\text{LaS}_{2.04}$, and $\text{LaS}_{2.33}$ [8–10]. The p_s – T – x projection of this system was studied by a low-sensitive method weighting continuous and X-ray powder analyses of final powder products, which gave the incorrect p_s – T – x diagram with respect to the phase Gibbs rule. Interest in obtaining the equilibrium diagram of the system has quickened, since non-equilibrium states of the powder La-polysulfides were not always established and thus were interpreted quite speculatively. We believe that if precise compositions of equilibrium polysulfides were found, alternative metastable phases could be interpreted more easily in terms of kinetics of the vacancy-ordering process.

2. Experimental

2.1. Samples for thermodynamic study

To provide reliable thermodynamic results, composition of initial crystals should be known precisely and have no impurities, especially volatile. Only high-quality crystals conform to these requirements, and they were grown from a KI flux in sealed quartz ampoules using La_2S_3 +S mixtures in molar ratios ranging from 1 to 4 by a procedure presented in [4]. Although the ratios and high sulfur pressures might provide the synthesis of a higher polysulfide, only the LaS_2 composition was implemented in all these experiments, according to Table 1. Thus, it was concluded that within the used values of temperature and sulfur pressure LaS_2 is the highest polysulfide in the system. Prior to thermodynamic experiments, we selected for individual characterization the grown crystals free from surface contaminations, i.e. sulfur and KI solvent, with the size of $2 \times 4 \times 0.5 \text{ mm}^3$ and weight of $\sim 4 \text{ mg}$.

The powder X-ray diffraction patterns ($\text{CuK}\alpha$ radiation) recorded over the 2θ range from 15° to 80° were indexed, and lattice parameters were calculated with the known values for LaS_2 [9] using the Powder-Cell program. The LaS_2 was found to crystallize in the orthorhombic structure, space group $Pn2_1/a$, with the fully filled La and S sites, lattice parameters $a=8.131(1) \text{ \AA}$, $b=16.338(2) \text{ \AA}$, $c=4.132(1) \text{ \AA}$, and the theoretical density equal to 4.84 g/cm^3 . No impurity peaks were observed in the pattern, showing a single-phase state of the prepared crystals. Experimental density measured by micro-buret method as $4.83 \pm 0.02 \text{ g/cm}^3$ agreed with the theoretical density 4.84 g/cm^3 , which served

Table 1

Composition of crystals grown at different sulfur pressures.

Sulfur pressure (bar)	La (mass%)	S (mass%)	La+S (mass%)	S:La
1	68.4	31.7	100.2	2.01
5		31.5	99.9	2.00
8		31.6	100.0	2.00
10	68.3	31.4	99.7	1.99
15	68.7	31.8	100.5	2.01
Composition of LaS_2	68.4	31.6	100.0	2.00

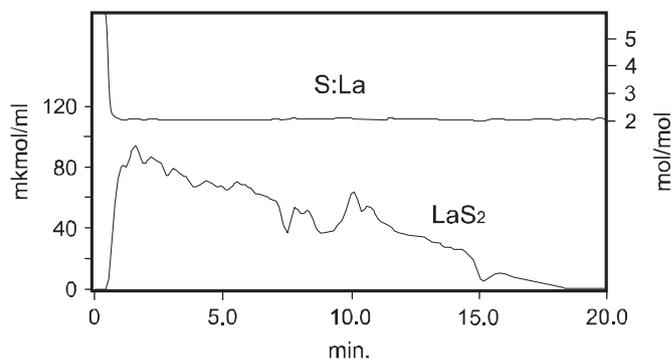


Fig. 1. Kinetic curves of the LaS_2 dissolution in the strong HNO_3 acid (left axis) and the atomic ratio S/La (right axis) versus time. Resolution is 15 \AA , crystal weight is 0.0034 g .

as a good indicator of purity and high spatial homogeneity of the crystals.

The chemical homogeneity and stoichiometry of individual crystal were also checked by differential dissolution method [11]. Each crystal was dissolved in a strong oxidative solvent, and the atomic ratio S/La was fixed in a few seconds apart during the full dissolution of the crystal. The kinetic curves of the La and S element dissolution and the atomic ratio S/La are shown in Fig. 1. The S/La ratio equal to 2.00 ± 0.01 , which remained constant within the entire dissolution process, indicates the spatial homogeneity of the crystals. The above results give grounds to take the crystals as strongly stoichiometric disulfide compounds. Only the crystals with identical characteristics were used in further thermodynamic experiments.

2.2. Tensimetric procedure

The $p(T)$ dependences were measured above the $\text{LaS}_{2.00}$ crystals in the pressure interval from 10^{-3} to 2 bar and in the temperature range 655–1260 K by means of a quartz Bourdon gauge with a membrane used as a null-point instrument calibrated previously with metallic cadmium according to the procedure described in [6]. It was impossible to prepare a series of crystals with a given composition within a narrow range between $\text{LaS}_{1.70}$ and $\text{LaS}_{2.00}$.

The vapor above polysulfides was known to consist mainly of S_n species ($n=1-8$), and the initial $\text{LaS}_{2.00}$, losing sulfur in a closed system, is shifted gradually to the composition $\text{LaS}_{1.50}$ (60 at% S), if initial amount of the crystals (m) and the chamber volume ($V \gg V_{\text{solid}}$) are taken in the desired m/V ratios. The total sulfur vapor pressure above the LaS_2 crystals with different m/V values was measured, and the $p=f(T)$ dependences were obtained. Pressure measurements were made at the temperature increasing with step 6 or 10 K; at each temperature the value of pressure was taken to be equilibrium if it remained unaltered within 1 Torr for 24 h.

A large array of experimental points was obtained to fix precisely the transitions from the three-phase (solid–solid–vapor) to the two-phase (solid–vapor) equilibrium. The transitions occurred as inflection points on the straight monovariant lines at a moment changing the phase state of the system: first the initial solid $\text{LaS}_{2.00}$ losing sulfur turned into adjacent sulfur-poorer phase, then this phase losing sulfur became more sulfur-poor and so on until the composition $\text{LaS}_{1.5}$ was acquired. To calculate the composition of the intermediate phases, first the number of sulfur moles in the vapor (N_S^v) based on the known p and T coordinates of the inflection point and the chamber volume is calculated using the equation $N_S = V \sum M_n p_{S_n} / RT M_S$, where M_n is the molecular weight of the sulfur species and p_S is the partial pressure of the

sulfur species. Then, the composition is determined as a difference between the number of sulfur moles in the initial weight of the crystals (N_S^0) and those in the vapor phase (N_S^g) by the following equation:

$$x, \text{at\% S} = 100 \left\{ \frac{N_S^0 - (V \sum M_n p_{S_n}) / (RTM_S)}{N_{\text{La}} + \left\{ N_S^0 - (V \sum M_n p_{S_n}) / (RTM_S) \right\}} \right\} \quad (1)$$

The partial pressures of the sulfur species at the inflection point are determined using a set of equations $p = \sum p_{S_n}$ and $K_n = (p_{S_2})^{n/2} / p_{S_n}$ for $n=1-8$ with the equilibrium constants of sulfur polymerization for a wide temperature range taken from [12].

3. Results and discussion

3.1. Phase relationship in the $\text{LaS}_{1.5}$ – LaS_2 system

Fig. 2a shows the temperature dependences of the sulfur vapor pressure covering the composition region from 66.6 to 60 at% S, based on the six experiments with $m/V=0.0024, 0.0038, 0.0069, 0.008, 0.0091, \text{ and } 0.01 \text{ g/cm}^3$. It is seen that each $\lg p(S_n) - (1/T)$ dependence is a broken line involving several portions of different slopes, which reflects the process of successive transformation of the highest La-polysulfide to the La-sesquisulfide due to sulfur evaporation. The upper straight line 1 corresponds to the three-phase equilibrium of LaS_2 , the adjacent sulfur-poorer polysulfide, and the sulfur vapor. Line 2 reflects equilibrium of the sulfur vapor with the next pair of two intermediate more sulfur-poor phases, while along line 3 there is an equilibrium between the most sulfur-poor intermediate phase, sesquisulfide and sulfur vapor. Equilibrium along lines 1–3 is attained usually during ~ 10

days at each temperature because the vacancy ordering in intermediate phases goes with low mobility of the solid reactants. Independently of the m/V ratio, total pressure of the saturated vapor above the solid polysulfides falls always on the appropriate straight line, which is a direct evidence that the intermediates are of constant composition phases known as “line phases”. According to the Gibbs phase rule, monovariant lines 1, 2, and 3 restrict the phase stability fields of these La-polysulfides.

Between each pair of the monovariant lines, the divariant ranges are located, where experimental points fall on almost horizontal lines, Fig. 2b. No reaction proceeds here and the intermediate phase coexists in equilibrium with the sulfur vapor. But the vapor pressure deviates from a straight line of the vapor thermal expansion, which is explained by the dissociation of polymeric gaseous sulfur species contributing to the total pressure. The dissociation is known to depend both on the total pressure and temperature; thus, this contribution disappeared from the uppermost divariant line, where total content of the S_2 species is as great as 95–98%. Both the dissociation and expansion are high-velocity processes, and here the equilibrium is attained virtually immediately.

The compositions of the intermediate polysulfides in the inflections points were determined using Eq. (1) with an error of about 0.3 at% S or 0.01–0.02 f.u., Table 2. The error was calculated from the measurement error as $\pm 2 \text{ K}$ for the temperature, $\pm 0.0005 \text{ g}$ for the sample weight, $\pm 0.1 \text{ cm}^3$ for the chamber volume, and $\pm 1-4 \text{ Torr}$ for the pressure. The starting composition $\text{LaS}_{2.00}$ and K_{equilib} of the sulfur polymerization reaction were assumed to be “exact” values (their errors being less than the measured ones). We found out also that the terminal phase (column 5) has really the La_2S_3 composition having no region homogeneity on the sulfur side according to [13]. It means that all the desired compositional range was covered in the tensimetric experiments and compositions of the intermediate phases were calculated accurately.

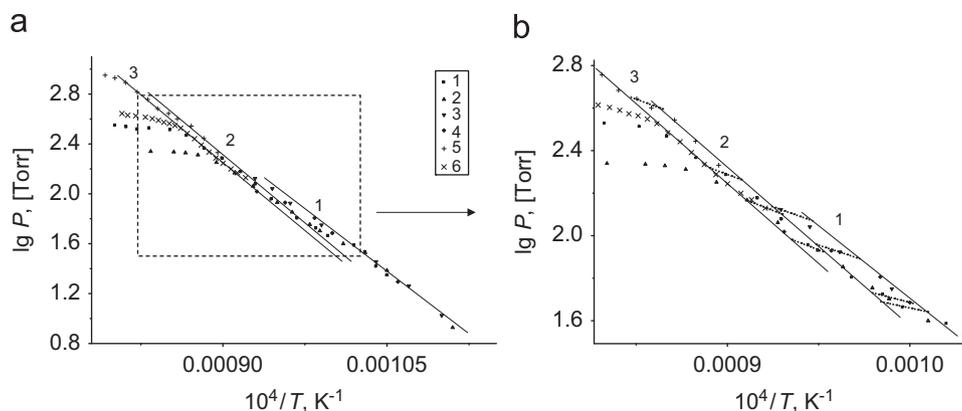


Fig. 2. The general view of monovariant lines (a); the view of the divariant lines (b). $\lg p_S - 1/T$ dependences measured above the LaS_2 crystals with different m/V values: (1) – 0.0038; (2) – 0.0024; (3) – 0.0069; (4) – 0.008; (5) – 0.01; and (6) – 0.0091 in g/cm^3 .

Table 2

Composition of the intermediate La-polysulfides.

Points on line 1		Points on line 2		Points on line 3	
Composition	T (K)	Composition	T (K)	Composition	T (K)
$\text{LaS}_{1.89(1)}$	987	$\text{LaS}_{1.78(2)}$	1053	$\text{LaS}_{1.51(1)}$	1140
$\text{LaS}_{1.92(2)}$	1004	$\text{LaS}_{1.76(1)}$	1091	$\text{LaS}_{1.52(2)}$	1174
$\text{LaS}_{1.92(2)}$	1045	$\text{LaS}_{1.75(1)}$	1176	$\text{LaS}_{1.51(1)}$	1196
$\text{LaS}_{1.90(1)}$	1058			$\text{LaS}_{1.53(2)}$	1262
Average $\text{LaS}_{1.91(1)}$	987–1058	Average $\text{LaS}_{1.76(1)}$	1053–1176	Average $\text{LaS}_{1.51(1)}$	1140–1262

The general view of the p_S - T - x diagram obtained here with confidence for the $\text{LaS}_{1.50}$ - $\text{LaS}_{2.0}$ system allows us to conclude the following:

- in a wide temperature region, three discrete polysulfide phases separated by two-phase regions exist without the region homogeneity within the limit of experimental error, < 0.5 at%, instead of a single grossly nonstoichiometric phase covering the $\text{LaS}_{1.91}$ - $\text{LaS}_{1.76}$ composition range according to the previous study [8];
- the $p(T)$ dependences of monovariant lines 1–3 in our experiments are located more below than those measured in [8].

This fact points to a metastable view of the previous p_S - T - x diagram, studied with non-equilibrium powders samples. Equilibrium for such samples is known to attain with difficulty and to require annealing for a long time. We believe that several days taken for synthesis of the samples by the reaction solid-vapor used in [8] were too short to prepare spatially homogeneous powders. In our tensimetric experiments, the equilibrium of sulfur entering the process, inverse to losing, was attained only for 40–50 days even at a temperature of 1000 K. Therefore, such powders are usually heterogeneous owing to inclusions of free sulfur, and the consideration of the $\text{LaS}_{2.04}$ and $\text{LaS}_{2.33}$ compositions determined chemically as the individual phases in [8] is clearly incorrect. Besides it should be remembered on the well-known high ability of polysulfide powders to absorb sulfur [14]. Our experiment showed that in this system hyper-stoichiometric polysulfides are generally absent.

According to the diagram obtained, thermodynamically stable phases $\text{LaS}_{1.91}$ and $\text{LaS}_{1.76}$ are stoichiometric; thus, their fractional formulas were converted to the integral ones to give $\text{La}_{10}\text{S}_{19}$ and La_4S_7 . Besides, these phases must be also fully ordered under equilibrium conditions. Then, combining these thermodynamic results with the structural data for the compounds may provide important information on kinetics of the sulfur vacancy ordering in the anionic layers. So, single-crystal studies carried out for $\text{La}_{10}\text{S}_{19}$ in [3,4] showed that the superstructures of the ZrSSi type are indeed fully ordered. Preparing crystals of La_4S_7 ($\text{LaS}_{1.76}$) with the higher vacancy concentration was impossible previously without knowing the p and T values providing the stability of this phase. As long as single crystals of La_4S_7 phase are not obtained, the structure features may be considered for $\text{DyS}_{1.76}$ with the same vacancy concentration. Here, an increasing disorder in defective planar polysulfide layer of the superstructure based on the ZrSSi type was established due to partially filled positions of the polymerized sulfur and partially disordered sulfur atoms in the vacant position [15]. But one question remains to be solved: in what level this partially disordered structure is controlled by kinetics and whether or not equilibrium conditions were established during of the crystal growth.

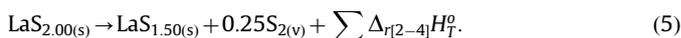
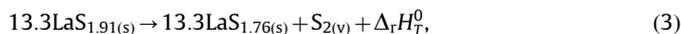
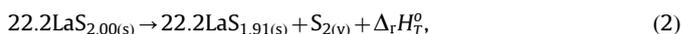
According to the general mechanism of formation of sulfur-poor phases suggested in [2] the sulfur-poor phases can be obtained from the bulk composition $\text{La/S}=24:48$ by removal of one, two or more sulfur atoms and statistical distribution of the remaining atoms over a lattice that is 24 times as large as the

parent one. However, complete ordering in layered compounds is difficult and hardly obtainable. This is due to the necessity of longer exposure of crystals to high temperatures and slows cooling during growth.

The aforesaid is true for $\text{LaS}_{1.96}$ composition with $\text{La/S}=1.958 \approx 1.96$ where one sulfur atom is removed and the remaining 47 sulfur atoms are statistically distributed over the lattice. Structural data and details of experiments on refining the structure $\text{LaS}_{1.96}$ are given in [10]. With precise absorption correction on shape and size, the positions of the sulfur atoms in the anionic layer of the crystal were found to be incompletely occupied, and the nonstoichiometry polysulfide $\text{LaS}_{1.96}$ was treated as a spatially averaged, disordered individual phase. The disorder is caused by a temperature of 1090 K, from which these crystals were quenched during the growth from the molten solution in KI. These crystals formed outside the stability fields in the equilibrium diagram that allow us to refer this polysulfide $\text{LaS}_{1.96}$ to a metastable phase. From this point of view it is clear that for lanthanum polysulfides, the ordering process is still unclear and investigation of polysulfide crystals quenched from different temperatures would obviously be useful.

3.2. Thermodynamics of the evaporation reactions

Each of the La-polysulfides evaporates incongruently and takes part in the appropriate monovariant reactions (2–5) regarding 1 mol of S_2 . To calculate thermodynamic properties of the reactions, the dependences $\lg p_{S_2} - 1/T$ were transformed to the $p_{S_2} - 1/T$ lines, and the following equations appear to give a reliable description of the vaporization equilibrium:



The least squares treatment (95% confidence limit, Student distribution) gives the temperature dependence of the equilibrium pressure, standard dispersion, the enthalpy, and the entropy calculated from the second law, Table 3.

The heat of LaS_2 formation from S(solid) and La(solid) was then determined using the appropriate thermo-chemical cycles and thermodynamic properties of La, S, La_2S_3 as well as the values of heat capacity of LaS_2 at 298 and 900 K taken from [16,17] (Table 4). The heat of LaS_2 formation was calculated to be $\Delta_f H_{298}^0 = -593 \pm 8.4$ kJ/mol, which was very close to the value known from the literature and determined calorimetrically as $\Delta_f H_{298}^0 = -604 \pm 8.5$ kJ/mol [18]. Good agreement between these values means that the quality of the LaS_2 crystals was adequate and there were no substantial errors in our thermodynamic measurements. Since the calorimetric value includes some uncertainty, the preference should be given to the thermodynamic experiment and the heat of LaS_2 formation equal to -593 ± 8.4 kJ/mol can be recommended as a more reliable value.

Table 3
Thermodynamic characteristics of the vaporization reactions (2–5).

Reaction	$\lg p_{S_2}$ (bar) $\pm 2\sigma$	Temperature (K)	$\Delta_r H_T^0$ (kJ/mol)	$\Delta_r S_T^0$ (J/mol K)
(2)	$(5.19 \pm 0.11) - (6370 \pm 100)/T$	897–1058	121.9 ± 2.0	99.2 ± 2.1
(3)	$(5.65 \pm 0.09) - (6920 \pm 100)/T$	1004–1176	132.4 ± 1.9	108.0 ± 1.8
(4)	$(5.87 \pm 0.04) - (7230 \pm 50)/T$	1078–1233	138.4 ± 0.9	112.6 ± 0.8
(5)		897–1233	33.4 ± 0.8	

Table 4

Thermodynamic characteristics of substances taking part in thermo-chemical cycles.

Substance	C_p 298 (J/mol K)	C_p 900 (J/mol K)	$\Delta_f H_{298}^0$ (kJ/mol)
La (s)	–	–	0
S (s)	–	–	0
S ₂ (g)	0.0324	0.0366	127.5 ± 2.1
La ₂ S ₃ (s)	0.1209	0.1297	–1180 ± 17
LaS ₂ (s)	0.0704	~0.076 ^a	–

^a Estimation from a series PrS₂–SmS₂ [16,17].

4. Conclusions

The thermodynamic study of the LaS₂–La₂S₃ system and the general view of the p_S – T – x diagram give a strong indication of the existence of three discrete polysulfide phases LaS_{2.00}, LaS_{1.90}, and LaS_{1.76} separated by two-phase regions and having no homogeneity region within the error limit of < 0.5 at% S. The thermodynamic static method used in the study of evaporation of the highest polysulfide LaS₂ grown as high quality crystals showed itself as an effective tool to attain progress in establishment of the phase relationships for the rare earth metals polysulfide systems controlled kinetically. To reveal the potential of these low-dimensional RE polysulfides as new and unusual materials, thermodynamic and structural investigations remain to be the primary task.

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