Thermodynamic investigation of the systems $LnSe_2$–$LnSe_{1.5}$ (Ln = La, Nd)

L. N. Zelenina · T. P. Chusova · I. G. Vasilyeva

Abstract A detailed thermodynamic study of the systems $LnSe_2$–$LnSe_{1.5}$ (Ln = La, Nd) was performed by static method of vapour pressure measurement using quartz membrane-gauge manometers within the temperature range 713–1,395 K. The p_{Se}–T–x dependences obtained in this study have shown that the phase regions in composition intervals studied consist of discrete phases: $LnSe_{1.95}$ $LnSe_{1.90}$, $LnSe_{1.85}$, $LnSe_{1.80}$ (Ln = La, Nd). The enthalpies and the entropies for the stepwise dissociation process were calculated from the experimental data. The standard enthalpies of formation and the absolute entropies were estimated for the compounds investigated using literature data.

Keywords Nd- and La-polyselenides · Vapour pressure measurements · Phase diagram · Enthalpy of formation · Absolute entropy

Introduction

Polyselenides of rare-earth metals are of interest due to their ability to electronic-structural transitions [1]. The probability of such transitions increases for polyselenides with low selenium content. This phenomenon is predicted in theory [1] but experimental investigation is not realized owing to lack of high-quality crystals. The preparation of such crystals is a difficult problem without knowledge of the thermodynamic parameters ($p_{Se}(T, x)$), which define the condition of crystals growth. Numerous literature data have fragmentary and contradictory information about quantity of polyselenide phases and their real nonstoichiometry [2–5].

Earlier we have investigated the systems $LnSe_{2-x}$–$LnSe_{1.5}$ (Ln = Pr, Gd), where the intermediate individual phases $GdSe_{1.85}$, $GdSe_{1.71}$, $PrSe_{1.9}$, $PrSe_{1.85}$, and $PrSe_{1.8}$ [6] were detected. The aim of this study is to obtain the reliable data on compositions and homogeneity regions of intermediate phases in the $LnSe_2$–$LnSe_{1.5}$ (Ln = La, Nd) systems with respect to p_{Se}, T, and x and to calculate the thermodynamics of the dissociation processes.

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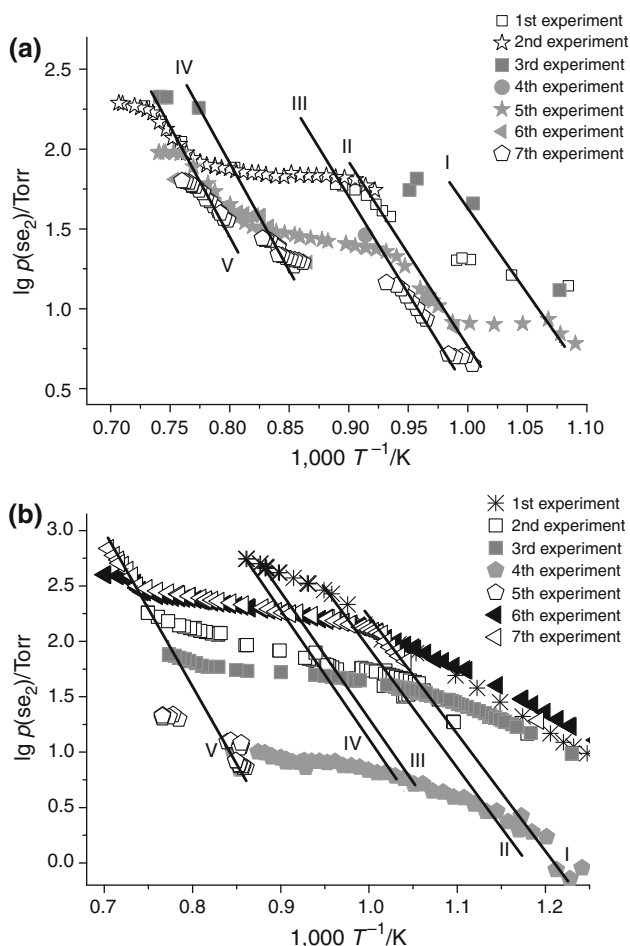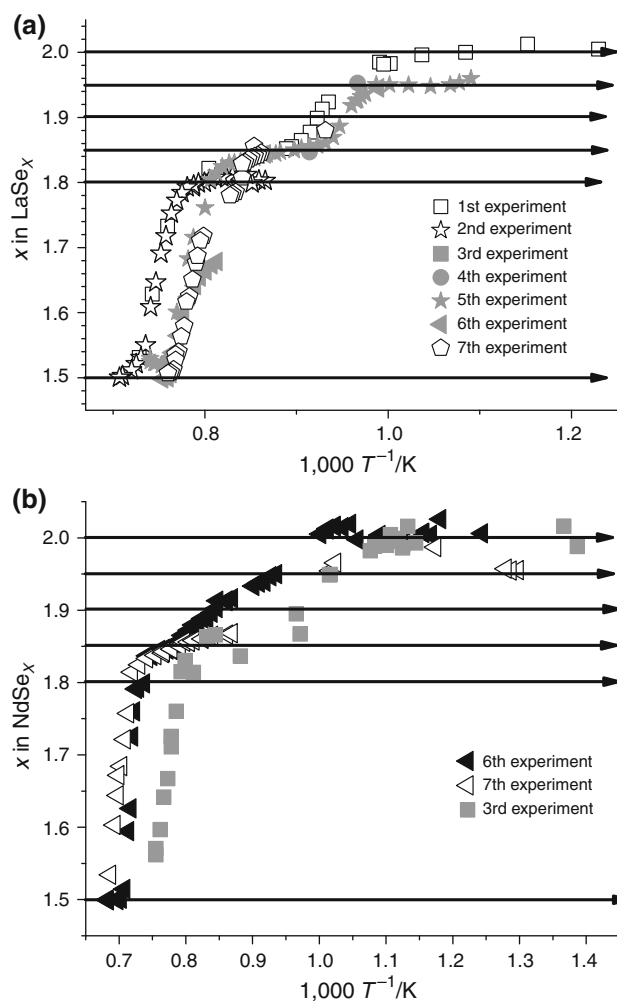Novosibirsk State University, Pirogova street 2,
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Experimental

The samples of $LaSe_{2.0}$ and $NdS_{2.0}$ were got from the Institute of Inorganic Chemistry of the Technical University of Dresden, Germany. The preparation of these samples is described more detail in articles [7–9]. The samples were characterized by X-ray powder diffraction and by EDXA (Energy Dispersive X-ray Analysis). According to the analysis results all samples were pure single crystals.

The vapour pressure investigation has been realized by the static method with quartz membrane-gauge manometers [10] using an isothermic and anisothermic [11] procedure. In the last case the sensitive quartz membrane was kept at constant temperature of 973 K during the whole experiment. This manometer construction allows us to escape the effect of irreversible membrane deformation (plastic quartz

Fig. 1 Temperature dependence of the pressure of LaSe$_x$ (**a**), NdSe$_x$ (**b**) dissociation plotted as lg $p = f(1/T)$. The lines I–V correspond to monovariant three-phase equilibrium between two adjacent solid polyselenides and the selenium vapor phase

Fig. 2 Examples of changes in the condensed phase composition with temperature (**a** for LaSe$_x$, **b** for NdSe$_x$)

deformation at temperatures more then 1,000 K). Moreover, the diffusion both the compensation gas (air) and the gaseous selenium through the membrane was excluded. The main characteristics of the experimental unit and the procedure of operation are described in more detail in [6, 12]. The static method is suitable for the investigation of systems in the equilibrium state, even if the process goes very slowly. It permits to register the transitions from the three-phase to the two-phase equilibrium (and vice versa) by gradual change in composition of the original sample, owing to its incongruent vaporization in a closed system. The limiting errors in measurement of pressure, temperature, and solid phase composition were 1 Torr, 1 K and 0.01 formula units, accordingly. The measurements have been realized in wide intervals of temperature ($713 \leq T$, K $\leq 1,395$) and pressure ($1 \leq p$, Torr ≤ 760). The pressures measured from low to high temperatures and backwards were identical at the same temperature. This procedure guaranteed the achievement of equilibrium. The time of the three-phase equilibrium

establishment in our experiments varied from 120 h at low temperatures (820 K) to 1 h at high temperatures. The composition of the condensed phases was calculated using the ideal gas equation and the equilibrium constants for process Se$_n$(g) $=$ nSe(g) [13].

Results and discussion

The total pressure over LaSe$_{2.00}$ and NdS$_{2.0}$ samples was measured as a function of temperature. To scan the whole compositional range from LnSe$_2$ to LnSe$_{1.5}$, 14 experiments were performed in a wide temperature interval (with temperature steps of 5-10 K) with different values of crystal mass and manometer volume ($0.9 \leq$ m/V, g/dm^3 ≤ 74). The experimental p_{Se}–T–x data are plotted as two-dimensional lg $p - 1/T$ diagrams (Fig. 1a, b) and $x - 1/T$ diagrams (examples of such diagrams are presented in Fig. 2a, b).

Table 1 Temperature dependences of pressure (lg $p(Se_2)$/Torr = A − B/T) and thermodynamic characteristics ($\Delta_r H_{298}$, $\Delta_r S_{298}°$) for the stepwise dissociation process of lanthanum and neodymium polyselenides

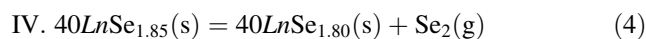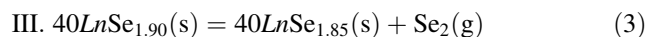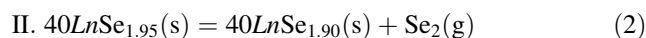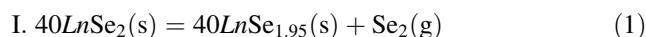| Number of reaction	T/K	A	B	$\Delta_r H_{298}$/kJ mol^{-1}		$\Delta_r S°_{298}$/J mol^{-1} K^{-1}	
				Second law	Third law	Second law	Third law
LaSe$_x$							
I	917–996	12.716	11008.6	210 ± 5	208 ± 5	187 ± 5	185 ± 5
II	996–1,104	12.738	12011.5	229 ± 3	226 ± 3	187.5 ± 2.3	185 ± 5
III	1,016–1,135	12.512	12027.2	230 ± 4	231 ± 4	184.4 ± 3.5	185 ± 5
IV	1,171–1,292	12.509	13244.8	253 ± 2	255 ± 2	183 ± 2	185 ± 5
V	1,257–1,350	12.455	13774.6	265 ± 7	267 ± 7	182 ± 6	185 ± 5
NdSe$_x$							
I	814–1,005	12.687	10,473	199.5 ± 1.8	201.6 ± 1.8	185.5 ± 1.9	188 ± 5
II	853–1,053	12.682	10,737	204 ± 4	207 ± 4	185 ± 4	188 ± 5
III	962–1,141	12.864	11,564	219.7 ± 1.5	220.0 ± 1.5	188.4 ± 1.4	189 ± 5
IV	961–1,162	12.799	11,672	221.8 ± 1.8	223.9 ± 1.8	187.1 ± 1.6	189 ± 5
V	1,207–1,376	12.997	14,231	270.3 ± 5	270.1 ± 5	191 ± 4	190 ± 5

Table 2 Standard enthalpies of formation ($\Delta_f H_{298}$), absolute entropies ($S_{298}°$) and heat capacities ($C_{p,298}°$) of lanthanum and neodymium polyselenides at 298 K

Solid phase	$-\Delta_f H_{298}$/kJ·mol^{-1}	$S_{298}°$/J mol^{-1} K^{-1}	$C_{p,298}°$/J mol^{-1} K^{-1}	$S_{298}°^a$/J mol^{-1} K^{-1}
LaSe$_2$	493	113.9 ± 8	69.5[a]	113
LaSe$_{1.95}$	491	112.4 ± 7	68.5[a]	112
LaSe$_{1.90}$	489	110.9 ± 7	67.5[a]	110
LaSe$_{1.85}$	487	109 ± 6	66.5[a]	109
LaSe$_{1.80}$	484	107.7 ± 6	65.5[a]	107
LaSe$_{1.50}$	466 ± 21 [16]	97.9 ± 1 [15]	59.4 ± 0.5 [15]	–
NdSe$_2$	497	127 ± 6.3	75[a]	126
NdSe$_{1.95}$	495	125.4 ± 6.0	74	124
NdSe$_{1.90}$	494	123.9 ± 4.5	73[a]	123
NdSe$_{1.85}$	492	122.4 ± 4.3	72.5[a]	121
NdSe$_{1.80}$	490	120.9 ± 4.1	71[a]	120
NdSe$_{1.50}$	471 ± 63 [16]	112.5 ± 1 [15]	64.8 ± 0.5 [15]	–

[a] Our estimation from the dependence of properties on the molecular weights

Based on the analysis of the $x − 1/T$ diagrams (Fig. 2a, b), we can interpret the obtained dependences as follows. The points lying on the solid lines (labeled as I, II, III, IV, V) correspond to monovariant three-phase equilibria between two adjacent solid polyselenides and the selenium vapor phase. Bivariant two-phase regions are situated between these lines. The phase regions in composition intervals investigated consist of discrete intermediate phases as in case of PrSe$_2$–PrSe$_{1.5}$ system investigated by us previously [6]. Our study does not confirm the existence of homogeneity regions, which were described earlier in [2, 3].

The monovariant three-phase equilibria may be described according the following formal reactions:

I. $40LnSe_2(s) = 40LnSe_{1.95}(s) + Se_2(g)$ (1)

II. $40LnSe_{1.95}(s) = 40LnSe_{1.90}(s) + Se_2(g)$ (2)

III. $40LnSe_{1.90}(s) = 40LnSe_{1.85}(s) + Se_2(g)$ (3)

IV. $40LnSe_{1.85}(s) = 40LnSe_{1.80}(s) + Se_2(g)$ (4)

V. $6.67LnSe_{1.80}(s) = 6.67LnSe_{1.50}(s) + Se_2(g)$.   (5)

For these processes, the partial pressure of Se$_2$ is expressed by equation:

$$p = p_{st}\exp\left[-\Delta_r H°_{298}/RT + \Delta_r S°_{298}/R + \varphi\left(\Delta_r C°_p, T\right)\right],\quad(6)$$

where p_{st} is the standard pressure of 101.325 kPa, $\Delta_r H°_{298}$, $\Delta_r S°_{298}$ are the enthalpy and the entropy of the

process, respectively, at $T = 298$ K $\cdot \varphi \left(\Delta_r C_p^\circ, \ T \right)$ is some function of temperature which is determined by difference in heat capacities of reaction ingredients.

The processing of the experimental data was carried out by least-squares method with criterion function from [14] on the basis of the second and third law of thermodynamics. It means that in the case of the second law, enthalpy and entropy at 298.15 K were the sought quantities. When carrying out the treatment according to the third law, the entropy of the reaction was considered to be known. The results of the calculation are presented in Table 1.

As follows from Table 1, the thermodynamic properties obtained by using the second-law approach are in good agreement with the same values calculated on the third-law method. This fact indicates an absence of systematic errors both in the experimental data and in the estimated values for third-law treatment.

The thermodynamic characteristics of the dissociation processes $\left(\Delta_r H_{298}^\circ, \Delta_r S_{298}^\circ \right)$ from Table 1, obtained by second-law treatment, were used to calculate the standard enthalpies of formation and the absolute entropies of neodymium and lanthanum polyselenides. The obtained values are presented in Table 2. In the same table are also indicated the experimental [15, 16] and estimated values of absolute entropies and heat capacities used at calculations.

Conclusions

According to the results obtained the phase regions in $Ln\mathrm{Se}_2$–$Ln\mathrm{Se}_{1.5}$ systems, where Ln = La, Nd, consist of discrete intermediate phases of constant composition, e.g. $Ln\mathrm{Se}_{1.90}$, the phases of $Ln\mathrm{Se}_{1.95}$, $Ln\mathrm{Se}_{1.85}$, $Ln\mathrm{Se}_{1.80}$ composition being detected for the first time. As a result of this study, the fundamental thermodynamic characteristics $\left(\Delta_f H_{298}, S_{298}^\circ \right)$ were obtained for the compounds investigated (Table 2) and the thermodynamic parameters p_{Se} and T, which define the fields of stability and the growth conditions of homogeneous La and Nd polyselenides phases of a specified composition, were determined (Fig. 1a, b).

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