



Thermodynamic properties of samarium and gadolinium polyselenides



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ABSTRACT

The thermodynamic characteristics ($\Delta_f H_{298}$, $\Delta_f S_{298}^\circ$) for the stepwise dissociation processes in the systems $\text{SmSe}_{1.9}$ – $\text{SmSe}_{1.5}$ and $\text{GdSe}_{1.875}$ – $\text{GdSe}_{1.5}$ were calculated from $p_{\text{Se}}-T-x$ dependences obtained by the static method with quartz membrane-gauge manometers. Solid phase compositions in the systems studied submit to the same dependence ($\text{Ln}_n\text{Se}_{2n-1}$) which was found by us earlier for the other similar systems. Estimations of entropies and heat capacities of the intermediate polyselenides were carried out by the additive rule with use as reference values of $\text{LnSe}_{1.5}$ thermodynamic characteristics. In this regard, data obtained earlier for the phases GdSe_x ($x = 1.85, 1.875$) were reprocessed. From the presented information the existence of individual linear phases of polyselenides was proved and a set of standard thermodynamic functions ($\Delta_f H_{298}$, S_{298}° , $\Delta_f G_{298}^\circ$) were determined for each polyselenide.

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1. Introduction

Rare-earth polyselenides with layered low-dimensional structure in the composition interval LnSe_2 – $\text{LnSe}_{1.5}$ have tendency to formation of intermediate individual phases [1]. These phases are realized in various superstructures with basic structure pattern at the expense of vacancies ordering and specific orientation of Se_2^2 dimers in anionic sublattice [2–4]. Thanks to this phenomena rare-earth polyselenides show anisotropy of physical properties [5] and have ability to the some interesting properties due to variety of superstructures. The displacement of selenium atoms in new positions of superstructures results to electron density redistribution and charge density wave formation [6]. Under external fields the electronic-structural transitions can take place in such superstructures. But experimental investigation of these superstructures is not realized owing to lack of high-quality crystals of rare-earth polyselenide phases.

The phases with the minimum and maximum selenium content have been mainly obtained in the polyselenides systems of $\text{LnSe}_{2-\delta}$ – $\text{LnSe}_{1.5}$ composition by present time. Minimum selenium content (1.5) corresponds to stoichiometric compounds Ln_2Se_3 . They do not contain a distinct selenium layer and consequently cannot form superstructures. The phases with maximum selenium content are synthesized under excess of selenium. By this way the

diselenide phases were obtained for light rare-earth elements (La, Ce, Pr, Nd) [7–9]. For heavy rare-earth elements at such synthesis the maximum selenium content is less than 2. For example x in LnSe_x is equal 1.9 for samarium [10] and 1.875 for gadolinium [11]. These phases are already superstructures: $\text{Sm}_{10}\text{Se}_{19}$ is a 10-fold and $\text{Gd}_8\text{Se}_{15}$ is a 24-fold superstructure of the ZrSi type. But the crystals of intermediate phases in $\text{LnSe}_{2-\delta}$ – $\text{LnSe}_{1.5}$ systems are difficult to obtain without knowing the thermodynamic parameters ($p_{\text{Se}} - T$) _{$x=\text{const}$} which define the conditions of their growth. Literary data on phase diagrams of rare-earth polyselenides have sketchy and contradictory character both about the number of phases, and their real composition [12–14]. It is connected with experimental difficulties in obtaining the equilibrium phases and lack of effective methods for proving an equilibrium achievement.

Earlier we have investigated the systems $\text{LnSe}_{2-\delta}$ – $\text{LnSe}_{1.5}$ ($\text{Ln} = \text{La, Ce, Nd, Pr, Gd}$) [15–17] and revealed the regularity in the composition change of solid phases under stepwise removing the selenium atoms from anionic lattice: $\text{Ln}_n\text{Se}_{2n-1}$ where n is equal to 5, 7, 10, 20.

The aim of this work is to clarify the implementation of this regularity for SmSe_x ($1.5 < x < 1.9$) and GdSe_x ($1.5 < x < 1.85$) and to obtain a set of standard thermodynamic functions of polyselenides in the systems $\text{SmSe}_{1.9}$ – $\text{SmSe}_{1.5}$ and $\text{GdSe}_{1.875}$ – $\text{GdSe}_{1.5}$.

2. Experimental

The samples of $\text{SmSe}_{1.9}$ and $\text{GdSe}_{1.875}$ were synthesized from the elements of mass fraction purity as follows (Sm: 0.9999,

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powder, Alfa; Gd: 0.9999, powder Strem; Se: 0.9999, powder, Fluka) in the Institute of Inorganic Chemistry of the Technical University of Dresden, Germany by the way described in detail in [10,18]. All samples were characterized by X-ray powder diffraction (STOE IPDS-II, MoK α radiation, graphite monochromator) and by EDXA (Zeiss scanning electron microscope 982 Gemini with Noram Voyager analytic unit). According to the analysis results the samples were pure single crystals with composition SmSe_{1.90} or GdSe_{1.875} (see Appendices table A.1).

The selenium vapor pressure has been measured by the static method with quartz membrane-gauge manometers [19] using an isothermic [20] and anisothermic [21,22] procedure. The schematic diagram of the experimental setup, main characteristics of the experimental unit and the procedure of operation were described in more detail in our previous works [17,20–24].

The temperature of manometer inner chamber where the investigated sample was placed is monitored by a platinum-(platinum + 0.1 mass fraction of rhodium) thermocouple (type S) with accuracy ± 0.3 K. The thermocouple was preliminarily calibrated with the use of standard substances (In, Sn, Pb and Sb). During measurements the temperature in a furnace where the chamber with the sample was placed is kept constant within ± 0.1 K by using three independent type S thermocouples and heat-control devices. A radial and linear gradient of the temperature in the furnace does not exceed 0.5 K throughout the volume occupied by the inner chamber. This gradient increases to 1 K in the case of anisothermic procedure of measurement.

The compensating pressure is measured by use of mercury manometer (inner diameter 25 mm) and cathetometer, with an error of less than 5 Pa. The other instrumental errors were the following: (1) a compensation error ($dp = 30$ Pa), (2) an amendment on temperature drift of zero position of a membrane owing to a difference in coefficients of thermal expansion of separate parts of the manometer ($dp = 60$ Pa) and (3) an amendment on the irreversible drift of zero position caused by plastic deformation of quartz which is varied from 40 to 133.3 Pa.

The samples are weighed on the balance HP-200 with the resolution of ± 0.0001 g. The volume of the membrane-gauge manometer was defined as a difference between the weight of the manometer filled with water and an empty one, with the accuracy of 10^{-4} dm³. The uncertainty in values of composition (x), which are obtained from uncertainties of pressure (150 Pa), temperature (1 K), volume (10^{-4} dm³) and mass (0.01 mg), is 0.01 formula units.

Thus, the standard uncertainties (u) in values of pressure, temperature and solid phase composition were 150 Pa, 1 K and 0.01 formula units, accordingly.

The measurements have been realized in wide intervals of temperature ($715 \leq T/K \leq 1298$), pressure ($0.13 \leq p/\text{kPa} \leq 24.0$) and composition ($1.5 \leq x/f. u. \leq 1.9$). 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 100 h at low temperatures (758 K) to one hour at high temperatures (1300 K).

3. Results and discussion

The total pressure over SmSe_{1.9} and GdSe_{1.875} samples was measured as a function of temperature at fixed volume. These experimental data are presented in Appendices (figure A.1a and b). As can be seen from these figures all samples along with SmSe_{1.9} and GdSe_{1.875} monocrystals contained free selenium, which is X-ray amorphous substance. This is not surprising since the syntheses were carried out in an excess of selenium. But thanks to the static method, we could accurately determine the amount of

free selenium in each experiment. This amount was calculated at the points of exit in unsaturated vapor from monovariant equilibrium line Se(l) = Se(g) [25] for the 1–3 experiments with SmSe_{1.9} and for 1–2 experiments with GdSe_{1.875}. In the 4–5 experiments with SmSe_{1.9} the amount of selenium was determined from the points of bivariant equilibrium SmSe_{1.5}(s) + Se₂(g). The initial Se/Sm ratio is presented in the legend of the figure A.1 a and b for each experiment.

The composition of the condensed phases (x in LnSe _{x}) was calculated according to the equation:

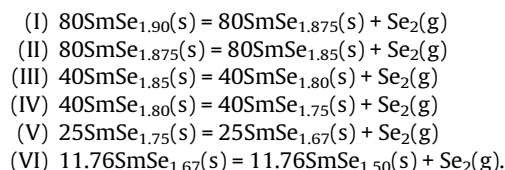
$$X = (N_{\text{Se}}/N_{\text{Ln}})_{ij} = \frac{N_{\text{Se}j} - \sum_{n=1}^8 n \left(\frac{p_{\text{Se}(n)ij} V_j}{RT_{ij}} \right)}{m_j/M}, \quad (1)$$

where $x = (N_{\text{Se}}/N_{\text{Ln}})_{ij}$ is the atomic ratio in the condensed phase at a temperature T_{ij} for any data point i of experiment j ; $N_{\text{Se}j}$ is the initial amount of Se in g-atom in the sample; $p_{\text{Se}(n)ij}$ is partial pressure of Se _{n} calculated from the experimental total pressure using equilibrium constants for the reaction Se _{n} = n Se taken from [25]; n is number of atoms in Se _{n} molecule and V_j is manometer volume; m_j is the initial sample mass and M is its molecular mass; R is the gas constant.

Five experiments with different values of crystal mass and manometer volume ($1.53 \leq m/V, \text{ g/dm}^3 \leq 3.33$) were carried out to scan the whole compositional range from SmSe_{1.9} to SmSe_{1.5}. Total pressure was recalculated on partial pressure of Se₂(g) as this species is predominant in the gas phase under experimental conditions. The $p(\text{Se}_2) - T - x$ data plotted as two-dimensional $\lg p - 1/T$ and $x - 1/T$ diagrams are presented in figure 1a and b for SmSe_{1.9}–SmSe_{1.5} system.

As well as in earlier studied systems [15–17] experimental data have a step-like form (figure 1a). It means that in the SmSe_{1.9}–SmSe_{1.5} system there are not solid solutions, but only individual phases of constant composition. The compositions of these solid phases were established from the $x-1/T$ diagram (figure 1b). After transforming to stoichiometry these compositions submit to the earlier found regularity Ln _{n} Se _{$2n-1$} with $n=3$ (SmSe_{1.67}), 4 (SmSe_{1.75}), 5 (SmSe_{1.80}), 7 (SmSe_{1.85}) and 8 (SmSe_{1.875}). It should be noted that the set of n values differs from the set obtained earlier for light rare earth polyselenides ($n=5, 7, 10, 20$ [17]).

The points from different experiments (figure 1a), lying on one straight line (I)–(VI), belong to monovariant three-phase equilibrium between two adjacent solid polyselenides and the selenium vapor phase. The monovariant three-phase equilibria in this system can be represented by following formal reactions:



The GdSe_{1.875}–GdSe_{1.5} system was investigated by us earlier [15]: three intermediate phases (GdSe_{1.85}, GdSe_{1.80}, GdSe_{1.71}) were detected and for two of them (GdSe_{1.85}, GdSe_{1.71}) the standard thermodynamic characteristics ($\Delta_f H_{298}$, S_{298}°) were obtained from the experimental data on dissociation processes and literary data for GdSe_{1.5} [26,27]. At that time we did not have enough experimental data to calculate the thermodynamic parameters of GdSe_{1.80} phase. In this work, to clarify the situation, we carried out two more experiments with GdSe_{1.875}. The experimental conditions were chosen so that to investigate solid phases with the composition on selenium from 1.85 to 1.5: $(m/V)_1 = 3.5$ and $(m/V)_2 = 4.7 \text{ g/dm}^3$. The experimental data together with data from [15] are presented in figure 2a and b as $\lg p-1/T$ and $x-1/T$ diagrams.

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