



# Thermodynamic properties of dysprosium polyselenides



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## ABSTRACT

A detailed thermodynamic study of the DySe<sub>1.875</sub>–DySe<sub>1.50</sub> system has been performed using a static method within the temperature range 595–1330 K. Single crystals of DySe<sub>1.875</sub> composition grown by chemical transport reactions were investigated as an initial compound. The *p*–*T*–*x* dependences obtained in this study show that the regions between the boundary compositions DySe<sub>1.875</sub> and DySe<sub>1.50</sub> consist of discrete stoichiometric phases whose compositions submit to the same dependence ( $Ln_nSe_{2n-1}$ ) which was found earlier for the other similar systems. A set of standard thermodynamic functions ( $\Delta_f H^\circ_{298}$ ,  $S^\circ_{298}$ ) were determined for each polyselenide using the enthalpy and entropy of stepwise dissociation processes calculated from experimental data. The information obtained was used for thermodynamic simulation of crystal growth processes in the system studied.

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## 1. Introduction

Rare-earth polyselenides are promising for the creation of functional materials with effective optical, magnetic and thermoelectric properties. A characteristic feature of these compounds with  $LnSe_x$  composition ( $1.5 < x < 2.0$ ) is the ability of selenium atoms to create a low-dimensional structure in anion sublattice [1,2]. This ability appears in a rich variety of superstructures whose period grows with decrease of  $x$  [3,4]. The displacement of the selenium atoms in new positions of superstructures leads to charge density wave formation and to the emergence of electronic-structural transitions [5,6]. For experimental investigation of their properties the high-quality crystals of rare-earth polyselenides are needed. These crystals are difficult to obtain without knowledge of the thermodynamic parameters ( $p_{Se}$ – $T$ – $x$ ) which define the conditions of their growth.

Previously, we have studied the polyselenides of cerium group in the systems  $LnSe_{2-6}$ – $LnSe_{1.5}$  ( $Ln = La, Ce, Nd, Pr, Gd, Sm$ ) [7–10] and revealed the regularity ( $Ln_nSe_{2n-1}$ ) in the composition change of solid phases under stepwise removing the selenium atoms from anionic lattice. This work is devoted to the polyselenides of yttrium group, namely DySe<sub>*x*</sub> ( $1.5 < x < 1.875$ ). In the literature, there is generally information only on the boundary compounds of this system. For DySe<sub>1.5</sub> (Dy<sub>2</sub>Se<sub>3</sub>) there are information on synthesis [11] and

structure [12,13] and thermodynamic characteristics of the formation reaction ( $\Delta_f H^\circ_{298}$ ,  $\Delta_f G^\circ_{298}$ ,  $\Delta_f S^\circ_{298}$ ) [14] obtained by calorimetric method. The synthesis and structure of DySe<sub>1.875</sub> (Dy<sub>8</sub>Se<sub>15</sub>) are described in [15]. The only intermediate phase with composition DySe<sub>1.84</sub> is presented in [16] (synthesis) and in [6] (structure). As concerns the other intermediate polyselenides with the selenium content from 1.875 to 1.5 the literature data have sketchy information about the number of phases and their real composition while their thermodynamic properties aren't presented at all.

The aim of this work is to clarify the compositions and homogeneity regions of intermediate phases in the system DySe<sub>1.875</sub>–DySe<sub>1.5</sub>, to obtain a set of standard thermodynamic functions of these phases and to calculate the optimal growth conditions for intermediate phases by thermodynamic simulation.

## 2. Experimental

The samples investigated in this work were synthesized from the elements of mass fraction purity as follows (Dy: 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 [15]. Obtained product was single crystals which have been characterized by X-ray powder diffraction (STOE IPDS-II, MoK $\alpha$  radiation, graphite monochromator), single crystal X-ray diffraction (IPDS-1 Stoe & Cie., MoK $\alpha$ -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 DySe<sub>1.875</sub> (see Appendices, Table A.1).

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The selenium vapor pressure has been measured by the static method with quartz membrane-gauge manometers [17] using an anisothermic [18,19] procedure. The schematic diagram of the experimental setup, the main characteristics of the experimental unit and the procedure of operation were described in more detail in our previous works [9,10,20].

The temperature of manometer inner chamber where the investigated sample was placed is measured by a platinum-(platinum + 0.1 mass fraction of rhodium) thermocouple (type S), preliminarily calibrated with the use of standard substances, with accuracy  $\pm 0.3$  K. 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.

The sensitivity of the membrane gauge-manometers used in the present study varied from 7 to 13 Pa. 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 no more than 133 Pa.

The accuracy in the determination of the sample mass was  $\pm 0.01$  mg. 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  $10^{-4}$  dm<sup>3</sup>. The uncertainty in values of composition ( $x$ ) obtained from uncertainties of pressure (133 Pa), temperature (0.5 K), volume ( $10^{-4}$  dm<sup>3</sup>) and mass (0.01 mg) was 0.01 formula units.

Thus, the standard uncertainties ( $u$ ) in values of pressure, temperature and solid phase composition were 133 Pa, 0.5 K and 0.01 f. u., accordingly.

The investigated sample was loaded into the inner chamber of membrane-gauge manometer and it was heated at 373 K under dynamic vacuum for one hour; then it was sealed. Pressure measurements were recorded after reaching the equilibrium at a given temperature. The measurements have been realized in wide intervals of temperature ( $595 \leq T/K \leq 1330$ ), pressure ( $0.06 \leq p/\text{kPa} \leq 58.0$ ) and composition ( $1.5 \leq x/\text{f. u.} \leq 1.875$ ). 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 to one hour at high temperatures.

### 3. Results and discussion

The total pressure over DySe<sub>1.875</sub> samples was measured as a function of temperature at fixed volume in four experiments. These experimental data are presented in Appendices (Fig. A.1). As can be seen from this figure all samples along with DySe<sub>1.875</sub> monocrystals contained free selenium, which is X-ray amorphous substance. 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) [21]. The initial Se/Dy ratio is presented in the legend of the Fig. A.1 for each experiment.

The composition of the condensed phases ( $x$  in DySe <sub>$x$</sub> ) was calculated according to the equation:

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

where  $x = (N_{\text{Se}}/N_{\text{Dy}})_{ij}$  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 selenium  $g$ -atom in the sample;  $p_{\text{Se}(n)_{ij}}$  is partial pressure of Se <sub>$n$</sub>  calculated from the experimental total pressure using equilibrium constants for the reaction Se <sub>$n$</sub>  =  $n$ Se taken from [21];  $n$  is number of atoms in Se <sub>$n$</sub>  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.

Four experiments with different values of crystal mass and manometer volume ( $2.38 \leq m/V, \text{g/dm}^3 \leq 14.77$ ) were carried out to scan the whole compositional range from DySe<sub>1.875</sub> to DySe<sub>1.5</sub>. Total pressure was recalculated on partial pressure of Se<sub>2</sub>(g) as this species is predominant in the gas phase under experimental conditions. The obtained  $p(\text{Se}_2)$ - $T$ - $x$  dependencies plotted as two-dimensional  $\lg p-1/T$  and  $x-1/T$  diagrams are presented in Fig. 1a, b.

As well as in earlier studied systems [7–10] the experimental data have a step-like form (Fig. 1a). It means that in the system studied there are intermediate phases of constant composition. The compositions of these solid phases were established from the  $x-1/T$  diagram (Fig. 1b). After transforming to stoichiometry these compositions submit to earlier found regularity  $L_n\text{Se}_{2n-1}$  with  $n = 3$  (DySe<sub>1.67</sub>), 4 (DySe<sub>1.75</sub>), 5 (DySe<sub>1.80</sub>) and 7 (DySe<sub>1.85</sub>).

The points from different experiments (Fig. 1a), lying on one straight line (I–V), 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:

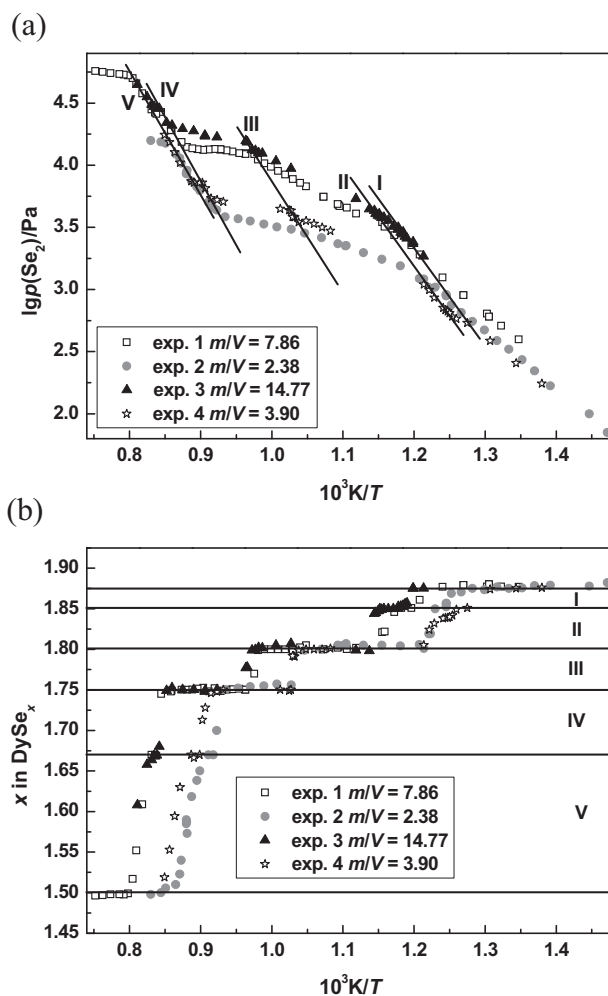


Fig. 1. Temperature dependence of Se<sub>2</sub> pressure (a) and solid phase composition (b) for DySe <sub>$x$</sub>  dissociation plotted as  $\lg p = f(1/T)$  and  $x = f(1/T)$ . The lines I–V (a) and regions I–V (b) correspond to monovariant three-phase equilibrium between two adjacent solid polyselenides and the selenium vapor phase. Sample mass and manometer volume (m/V, g/dm<sup>3</sup>) are presented in the legend of this figure for each experiment.

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