

Thermodynamic study of the systems PrSe_{2.00}–PrSe_{1.50} and GdSe_{1.875}–GdSe_{1.50}

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Received 18 September 2006; received in revised form 29 December 2006; accepted 29 December 2006

Available online 25 February 2007

Abstract

A detailed thermodynamic study of the systems PrSe_{2.00}–PrSe_{1.50} and GdSe_{1.875}–GdSe_{1.50} was performed using a static method membrane-gauge manometer within the temperature range 675–1296 K. High-quality crystals of PrSe_{2.00} and GdSe_{1.875} were investigated. The p – T – x diagrams obtained in this study show that the regions between the boundary compositions PrSe_{2.00} and PrSe_{1.80}, GdSe_{1.86} and GdSe_{1.77} which were previously described as non-stoichiometric, consist of discrete stoichiometric phases such as PrSe_{1.90}, PrSe_{1.85}, PrSe_{1.80} and GdSe_{1.85}, GdSe_{1.80}, GdSe_{1.71}, respectively. The compositions of the polyselenides were evaluated from the static data to the accuracy of ± 0.02 formula units. From the enthalpy and the entropy of thermal dissociation, the standard heats of formation and the absolute entropies were estimated for each polyselenide.

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Keywords: Pr- and Gd-polyselenides; Vapour pressure measurements; Phase diagram; Enthalpy of formation; Absolute entropy

1. Introduction

The determination of homogeneity regions in crystalline phases deviating from stoichiometry and the examination of their thermodynamic properties as a function of composition are of major interest in modern solid-state chemistry. These problems are important for the preparation of crystalline samples with well-defined physicochemical properties. A distinct knowledge of the nature of rare earth polyselenides is absent. These compounds were considered as essentially non-stoichiometric phases where selenium vacancies are randomly distributed, for example, PrSe_{2– x} ($x = 0.2$) [1], PrSe_{1.87– x} ($x = 0.07$) [2] or GdSe_{1.86– x} ($x = 0.09$) [3]. Some compositions were determined to be individual stoichiometric phases such as Pr₄Se₇ (PrSe_{1.75}) [1], PrSe_{1.90} and PrSe_{1.79} [4–7], for which vacancy ordering is most likely to take place. Based on very low ordering rates in solids, the diversity of polyselenide phases mentioned above may be explained by non-equilibrium states in many of them. So, it is necessary to start the reinvestigation of polyselenide systems using high-quality crystals as samples and applying the

static tensimetric method, which provides reliability and sensitivity of the measurements of vapour pressure, temperature and composition of intermediate phases.

2. Experimental

The samples of PrSe_{2.00} and GdSe_{1.875} were synthesized and identified in the Institute of Inorganic Chemistry of the Technical University of Dresden, Germany. Syntheses were performed as described in ref. [8–10]; pure single crystals were obtained, as confirmed by X-ray powder analysis and by Energy Dispersive X-ray Analysis (EDXA).

The static tensimetric-membrane-method was chosen, because it is suitable for the investigation of systems in the equilibrium state, even if the process goes very slowly. The method 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 vapourization in a closed system. The vapour pressure was measured by the static method using a quartz-membrane zero-manometer, as described by Suvorov [11]. The error of the pressure measurement ranged from 40 Pa at low temperature (300–1000 K) to 400 Pa at high temperature due to the appearance of irreversible drift. The error of the temperature measurement estimated from calibration against mercury, naphthalene and argon did not exceed 0.5 K. The accuracy in the determination of the sample mass was 0.05 mg. The volume of the membrane-gauge manometer was defined as a difference between the manometer filled with water and an empty one, with the accuracy of 0.1 cm³ (with the exception of experiment Nos. 1 and 4 in GdSe _{x} -system; in these cases volumes were estimated by geometrics). The scheme and the main characteristics of the experimental unit are described in detail in ref. [12].

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The investigated compound was loaded into the membrane-zero-manometer and was heated at 373 K under dynamic vacuum for 1 h; then it was sealed. Pressure measurements were recorded after reaching the equilibrium at a given temperature. The time of the solid phase–gas equilibrium establishment varied from 32–40 days at low temperatures (670–700 K) to 1 h at high temperatures.

3. Results and discussion

The total pressure over PrSe_{2.00} and GdSe_{1.875} samples was measured as a function of temperature. Under heating, the initial composition shifted in the direction of Pr₂Se₃ and Gd₂Se₃ due to the transition of selenium into the vapour phase. The composition of the condensed phases was calculated using the ideal gas equation:

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

where $x = (N_{\text{Se}}/N_{\text{Ln}})_{ij}$ is the molar ratio in the condensed phase at a temperature T_{ij} for any data point i of experiment j , $N_{\text{Se},j}$ the initial amount of Se in g-atom in the sample, $p_{\text{Se}(n)ij}$ the partial pressure of Se_{*n*} calculated from the experimental total pressure based on the values of equilibrium constants for the reaction Se_{*n*} = *n*Se taken from ref. [13], *n* number of atoms in Se_{*n*} molecule, V_j the volume of the membrane vessel, m_j the initial sample mass, M its molecular mass and R is the gas constant.

The accuracy of determining the composition, estimated from the accuracies of p , T , m , V and from the accuracy of the initial compositions, was 0.02 formula units.

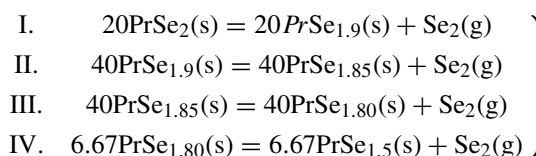
To scan the whole compositional range from PrSe₂ (GdSe_{1.875}) to Pr₂Se₃ (Gd₂Se₃), 20 experiments were performed

in a wide temperature interval (with temperature steps of 5–10 K) with different values of crystal mass (m) and vessel volume (V) and thus, ratios of V (Table 1).

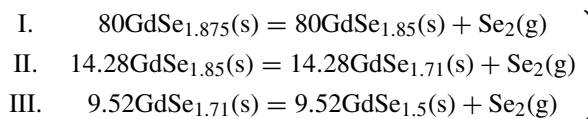
The experimental p – T – x data are plotted as two-dimensional $\log p$ – $1/T$ and x – $1/T$ diagrams in Fig. 1a, 1b and Fig. 2a, 2b, correspondingly. Each experiment is denoted by its own symbol.

Based on the analysis of these diagrams, we can interpret the obtained dependences as follows. The points lying on the solid lines (labeled as I, II, III and IV) correspond to monovariant three-phase equilibria between two adjacent solid polyselenides and the selenium vapour phase. The breaks (the departures from the solid lines) occur at the temperatures where the three-phase equilibria change to two-phase equilibria with a polyselenide–vapour. The two-phase points are located between each pair of neighbouring lines.

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



for PrSe_{*x*}-system



for GdSe_{*x*}-system

Table 1
Conditions and results of tensimetric experiments in PrSe_{*x*}- and GdSe_{*x*}-systems

Exp. no.	M (g)	V (cm ³)	$(m \times 1000)/V$	Se/Ln ratio		Intermediate phases
				Start	Final	
PrSe _{<i>x</i>} -system						
1	0.1748	4.5	38.8	2.00	1.90	PrSe _{1.90}
2	0.1270	10.1	12.6	2.016	1.85	PrSe _{1.90} , PrSe _{1.85}
3	0.0451	22.4	2.02	3.237	1.805	PrSe _{1.90} , PrSe _{1.85} , PrSe _{1.80}
4	0.0550	72.8	0.75	3.200	1.90	PrSe _{1.90}
5	0.0573	59.4	0.96	2.153	1.500	PrSe _{1.90} , PrSe _{1.85} , PrSe _{1.80}
6	0.0332	59.4	0.56	2.060	1.561	PrSe _{1.90} , PrSe _{1.85} , PrSe _{1.80}
7	0.0410	17.8	2.3	2.00	1.80	PrSe _{1.90} , PrSe _{1.85} , PrSe _{1.80}
8	0.15845	14.1	11.26	2.008	1.81	PrSe _{1.90} , PrSe _{1.85} , PrSe _{1.80}
GdSe _{<i>x</i>} -system						
1	0.0557	6.0 ^a	9.27	1.875	1.692	GdSe _{1.85} , GdSe _{1.80} , GdSe _{1.71}
2	0.0577	16.8	3.434	1.875	1.565	GdSe _{1.85} , GdSe _{1.80} , GdSe _{1.71}
3	0.0391	20.7	1.88	1.854	1.500	GdSe _{1.85} , GdSe _{1.80} , GdSe _{1.71}
4	0.2483	1.0 ^a	248.3	1.875	1.850	GdSe _{1.85}
5	0.0275	103.5	0.266	1.875	1.500	GdSe _{1.85} , GdSe _{1.80} , GdSe _{1.71}
6	0.2049	27.2	7.541	1.875	1.850	GdSe _{1.85}
7	0.1014	17.9	5.665	1.850	1.710	GdSe _{1.85} , GdSe _{1.80} , GdSe _{1.71}
8	0.0708	20.0	3.54	1.850	1.52	GdSe _{1.85} , GdSe _{1.80} , GdSe _{1.71}
9	0.0708	20.0	3.54	1.85	1.84	GdSe _{1.85}
10	0.0708	20.0	3.54	1.85	1.82	GdSe _{1.85}
11	0.0708	20.0	3.54	1.85	1.72	GdSe _{1.85} , GdSe _{1.80}
12	0.0708	20.0	3.54	1.85	1.69	GdSe _{1.85} , GdSe _{1.80} , GdSe _{1.71}

^a Estimation by geometrics.

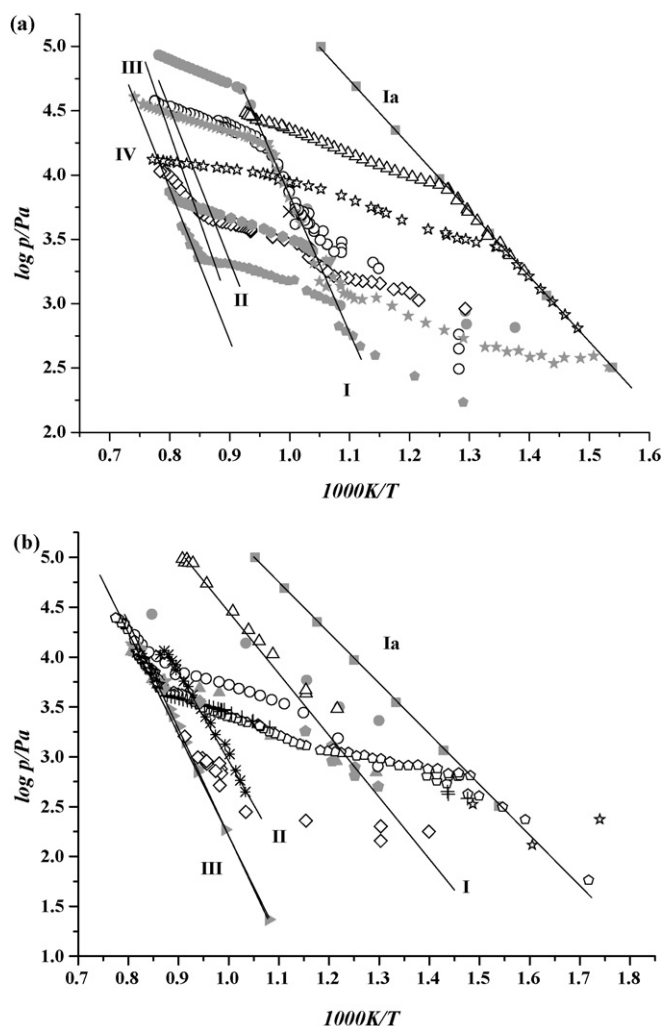


Fig. 1. (a) Temperature dependence of the pressure of PrSe_x dissociation plotted as $\log p = f(1/T)$. Ia is literature data for Se(s) vapour pressure [13]. The lines I–IV correspond to monovariant three-phase equilibrium between two adjacent solid polyselenides of Pr and the selenium vapour phase and (b) temperature dependence of the pressure of GdSe_x dissociation plotted as $\log p = f(1/T)$. Ia is literature data for Se(s) vapour pressure [13]. The lines I–III correspond to monovariant three-phase equilibrium between two adjacent solid polyselenides of Gd and the selenium vapour phase.

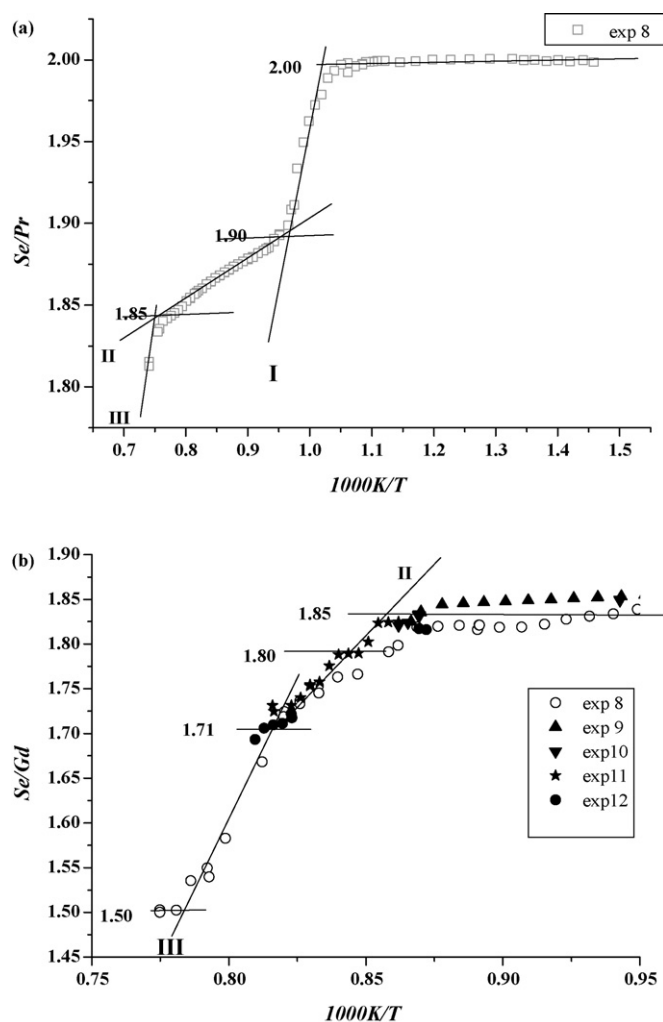


Fig. 2. Examples of changes in the condensed phase composition with temperature (a) for PrSe_x and (b) for GdSe_x .

Table 2

Temperature dependence of dissociation pressure ($\log p(\text{Se}_2)/\text{Pa} = (A-B)/T$) of the praseodymium and gadolinium polyselenides

Number of reaction	Temperature interval (K)	A	B	$\Delta_r H_{298}^\circ$		$\Delta_r S_{298}^\circ$	
				Second law	Third law	Second law	Third law
PrSe_x-system							
I	933–1096	14.365	10660	205.6 ± 8	206.5 ± 8	181 ± 8	181.5 ± 5
II	1071–1229	14.485	12302.5	236 ± 11	236 ± 11	181 ± 8	182 ± 5
III	1111–1269	14.627	12856.4	246 ± 8	243.9 ± 8	184 ± 7	182 ± 5
IV	1179–1325	16.594	15945.9	306.4 ± 3.5	308 ± 3.5	223.2 ± 5.6	224.5 ± 0.9
GdSe_x-system							
I	827–1100	11.332	7058.1	156.9 ± 3	162.4 ± 3	158.5 ± 2.8	163.7 ± 5
II	968–1157	11.390	8371.0	184.9 ± 2.8	185.2 ± 2.8	162.4 ± 2.6	162.4 ± 5
III	926–1291	11.373	8925.7	198.3 ± 3.8	196.0 ± 3.2	164.6 ± 3.2	162.7 ± 5

$\Delta_r H_{298}^\circ$, Enthalpy of dissociation in kJ (mole Se_2)⁻¹; $\Delta_r S_{298}^\circ$, entropy of dissociation in J (mole Se_2)⁻¹ K⁻¹.

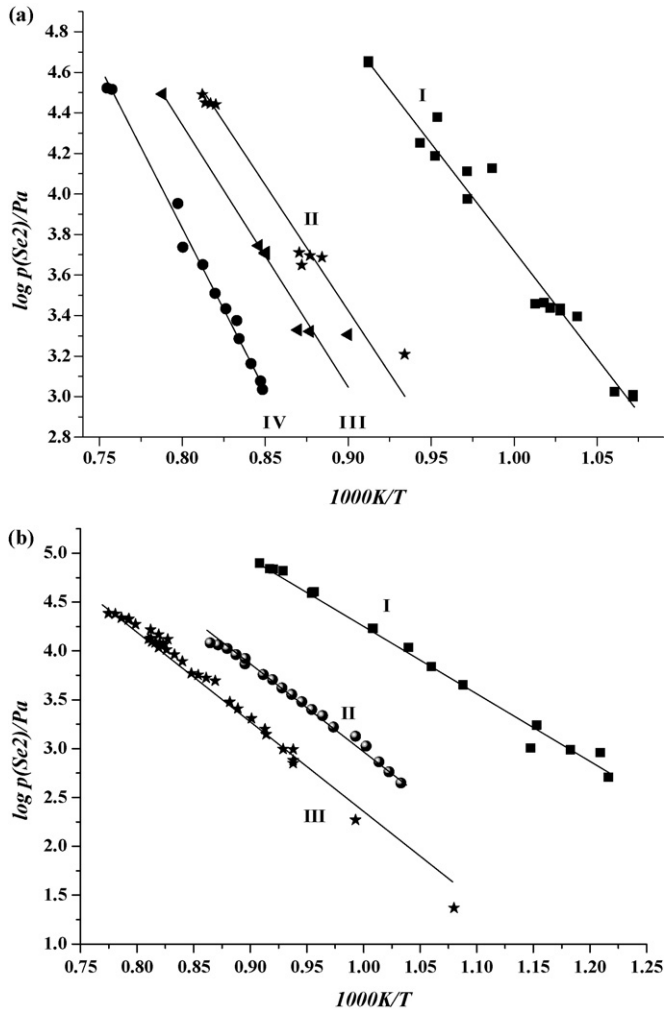


Fig. 3. The three-phase lines in the coordinates $\log p(\text{Se}_2) = f(1/T)$ of the systems $\text{PrS}_{2.00}\text{--PrS}_{1.50}$ (a) and $\text{GdSe}_{1.875}\text{--GdSe}_{1.50}$ (b).

In order to calculate the enthalpies and the entropies of these reactions the vapour pressure Se was plotted as $\log p(\text{Se}_2)$ versus the inverse temperature $1/T$. The points located on the three-phase lines (see I–IV in Fig. 3a and I–III in Fig. 3b) are used for the calculation.

For these processes, the partial pressure of Se_2 is expressed by equation:

$$p = p_{\text{st}} \exp \left[\frac{-\Delta H_{T_0}^\circ}{RT} + \frac{-\Delta S_{T_0}^\circ}{R} + \varphi(\Delta C_p^\circ, T) \right] \quad (2)$$

where p_{st} is the standard pressure of 101.325 kPa, $\Delta H_{T_0}^\circ$, $\Delta S_{T_0}^\circ$ are the enthalpy and the entropy of the process, respectively, at a definite fixed temperature T_0 . $\varphi(\Delta C_p^\circ, T)$ 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 on the basis of the second and third law of thermodynamics [12]. It means that in the first case, 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. Experimental [14] and approximative values (Neumann–Kopp rule) of standard entropies and heat capacities, which were necessary for calculations, are shown in Table 3. The results of the calculation are presented in Table 2.

It follows from Table 2 that, within the indicated error limits, a good agreement between the results of the treatment according to the second and third laws of thermodynamics is observed. This circumstance confirms the absence of substantial systematic errors both in the experimental data and in the calculations of absolute entropies.

Though the existence of the $\text{GdSe}_{1.80}$ phase was established unambiguously on the basis of analysis of $x\text{--}1/T$ diagrams (see Fig. 2b), our experimental data on $\log p(\text{Se}_2)\text{--}1/T$ are insufficient yet to calculate its thermodynamic parameters.

The thermodynamic characteristics of the dissociation processes ($\Delta_f H_{298}^\circ$, $\Delta_f S_{298}^\circ$) presented in Table 2 were used to calculate the standard enthalpies of formation and the absolute entropies of praseodymium and gadolinium polyselenides (Table 3). One can see from Table 3 that the $\Delta_f H^\circ$ and S° values undergo insignificant changes in the polyselenide series of Pr and Gd. This means that the bonding character and the extent of ordering are the same in these series.

According to the results obtained in our experimental investigation, all the polyselenide phases dissolve very small amounts of selenium, and the regions of homogeneity of these phases practically do not exist within the entire temperature range investigated. This means that Se-vacancies of non-stoichiometric

Table 3

Standard enthalpies of formation $\Delta_f H^\circ$, absolute entropies S° and heat capacities ΔC_p° of praseodymium and gadolinium polyselenides at 298 K

Solid phase	$\Delta_f H^\circ$ (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	ΔC_p° (J mol ⁻¹ K ⁻¹)	S° (J mol ⁻¹ K ⁻¹)
PrSe ₂	555	126 ± 8	70.2 ± 0.5 ^a	125 ^a
PrSe _{1.90}	538	122 ± 8	68.1 ± 0.5 ^a	122 ^a
PrSe _{1.85}	529	120.7 ± 7	67.1 ± 0.5 ^a	121 ^a
PrSe _{1.80}	539	119 ± 5.6	66.1 ± 0.5 ^a	119 ^a
PrSe _{1.50}	471 ± 42 [15]	115.5 ± 0.9 [14]	59.94 ± 0.5 [14]	–
GdSe _{1.875}	595	113.9 ± 2.9	76.40 ^a	114 ^a
GdSe _{1.85}	592	112.8 ± 2.7	75.51 ^a	113 ^a
GdSe _{1.71}	570	106.9 ± 3.2	70.51 ^a	107 ^a
GdSe _{1.50}	534 ± 170 [15]	98.25 ± 0.8 [14]	63.015 ± 0.25 [14]	–

^a Neumann–Kopp.

phases found in this thermodynamic study should be ordered in superstructures. The general structure theory of the Se/Ln (Ln = La–Lu) polyselenides based on the type of ordering for some Gd-, Pr- and Ce-polyselenides was formulated in ref. [16]. The theory will be developed on the basis of the new structural data. The appearance of these data is facilitated when definite Se/Ln ratios result from the thermodynamic study.

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