ТЕРМОДИНАМИЧЕСКОЕ ИССЛЕДОВАНИЕ ФАЗОВЫХ РАВНОВЕСИЙ И СИНТЕЗ ПРОМЕЖУТОЧНЫХ ФАЗ В СИСТЕМАХ $M\mathrm{Se}_{2-\delta}$–$M\mathrm{Se}_{1.5}$ (M = La–Nd, Y, Sm, Gd, Dy, Ho)

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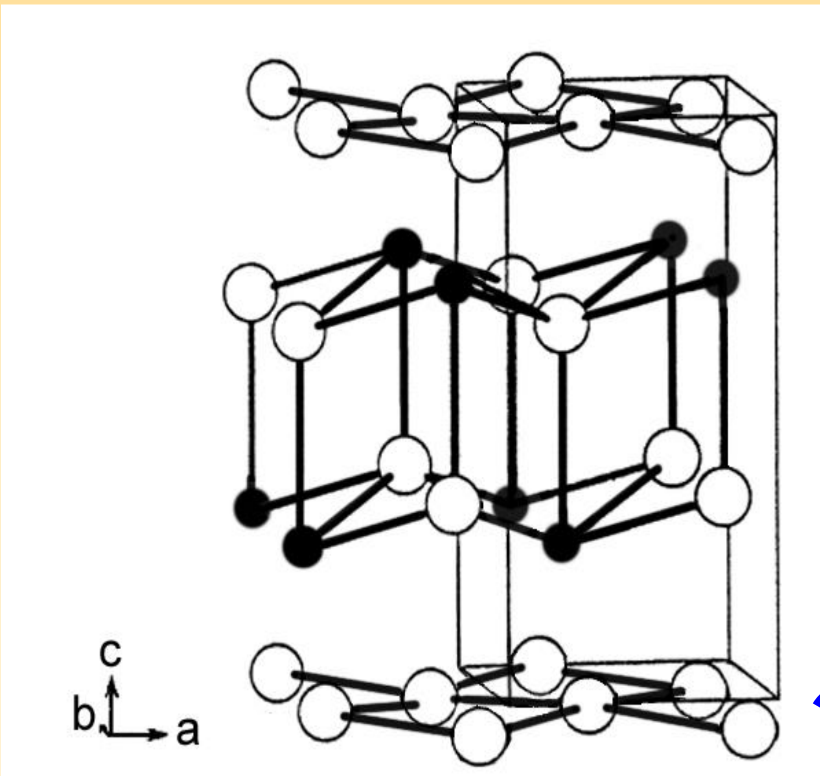
Структура MSe_2

$MSe_2 \rightarrow [M^{3+}Se^{2-}]_2[Se_2^{2-}]$

$CeSe_{1.9} \rightarrow Ce_{10}Se_{19}$



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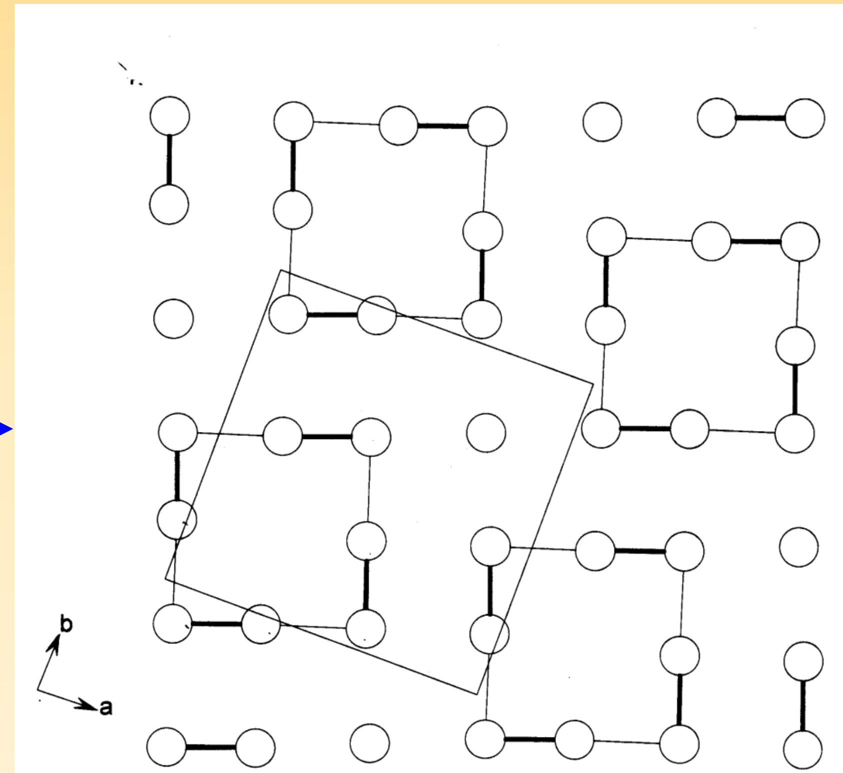


● - M ○ - Se

MSe_x, $1.5 \leq x \leq 2.0$

Литературные данные по составам твердых фаз

system	solid phases
$LaSe_2$-$LaSe_{1.5}$	$LaSe_2$; $LaSe_{1.9}$; $(LaSe_{1.82}$- $LaSe_{1.67})_{solid\ solution}$; $LaSe_{1.5}$
$CeSe_2$-$CeSe_{1.5}$	$CeSe_2$; $CeSe_{1.9}$; $(CeSe_{1.8}$- $CeSe_{1.6})_{solid\ solution}$; $CeSe_{1.5}$
$PrSe_2$-$PrSe_{1.5}$	$PrSe_2$; $PrSe_{1.9}$; $(PrSe_{1.8}$- $PrSe_{1.6})_{solid\ solution}$; $PrSe_{1.5}$
$NdSe_2$-$NdSe_{1.5}$	$NdSe_2$; $NdSe_{1.9}$; $(NdSe_{1.78}$- $NdSe_{1.67})_{solid\ solution}$; $NdSe_{1.5}$
$SmSe_{1.9}$-$SmSe_{1.5}$	$SmSe_{1.9}$; $(SmSe_{1.9}$- $SmSe_{1.7})_{solid\ solution}$; $SmSe_{1.5}$
$GdSe_{1.875}$-$GdSe_{1.5}$	$GdSe_{1.875}$; $(GdSe_{1.862}$- $GdSe_{1.775})_{solid\ solution}$; $GdSe_{1.5}$
$DySe_{1.875}$-$DySe_{1.5}$	$DySe_{1.875}$; $DySe_{1.84}$; $DySe_{1.5}$
$HoSe_{1.85}$-$HoSe_{1.5}$	$HoSe_{1.85}$; $HoSe_{1.50}$
$YSe_{1.85}$-$YSe_{1.5}$	$YSe_{1.85}$; $YSe_{1.80}$; $YSe_{1.50}$

Исходные соединения

Element	Provenance	Mass fraction purity
La	Chempur, Karlsruhe	0.999
Ce	Treibacher AG, Austria	0.999
Pr	Chempur, Karlsruhe	0.999
Nd	powder, Alfa	0.999
Sm	powder, Fluka	0.999
Gd	powder, Alfa	0.999
Dy	powder, Alfa	0.999
Ho	powder, Strem	0.999
Y	powder, Alfa	0.999
Se	powder, Strem	0.9999

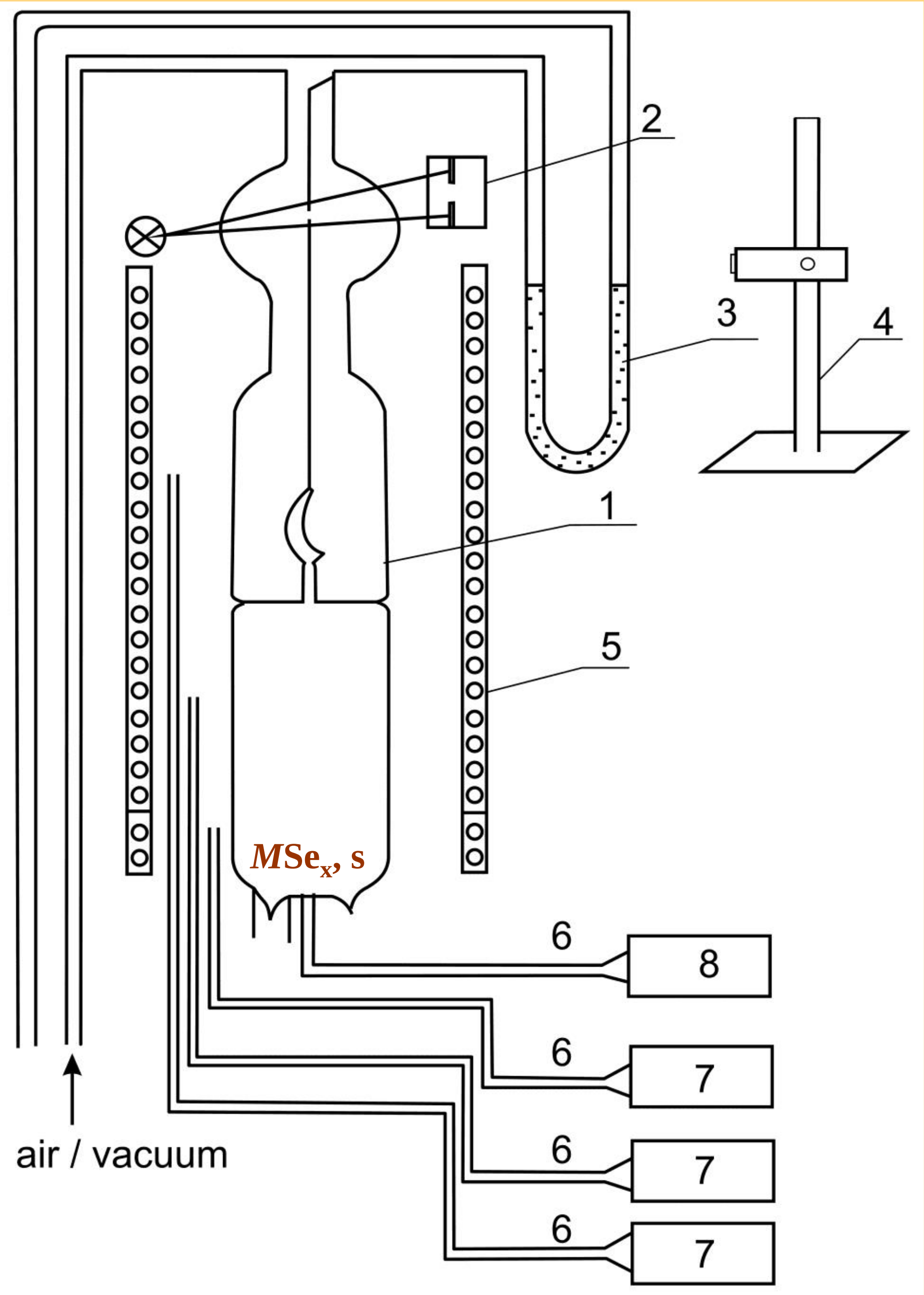
Th. Doert, E. Dashjav, B. P. T. Fokwa,
Z. anorg. allg. Chem., 633 (2007), 261.

X-ray

EDXA

$\mathbf{LaSe_{2.0}}$
$\mathbf{CeSe_{2.0}}$
$\mathbf{PrSe_{2.0}}$
$\mathbf{NdSe_{2.0}}$
$\mathbf{SmSe_{1.9}}$
$\mathbf{GdSe_{1.875}}$
$\mathbf{DySe_{1.875}}$
$\mathbf{HoSe_{1.85}}$
$\mathbf{YSe_{1.80}}$

Схема тензиметрической установки



1 – quartz membrane-spoon manometer;
2 – optical registration system of manometer null-position;
3 – mercury barometer; 4 – cathetometer;
5 – furnace; 6 – thermocouples;
7 – heat-control units; 8 – voltmeter.

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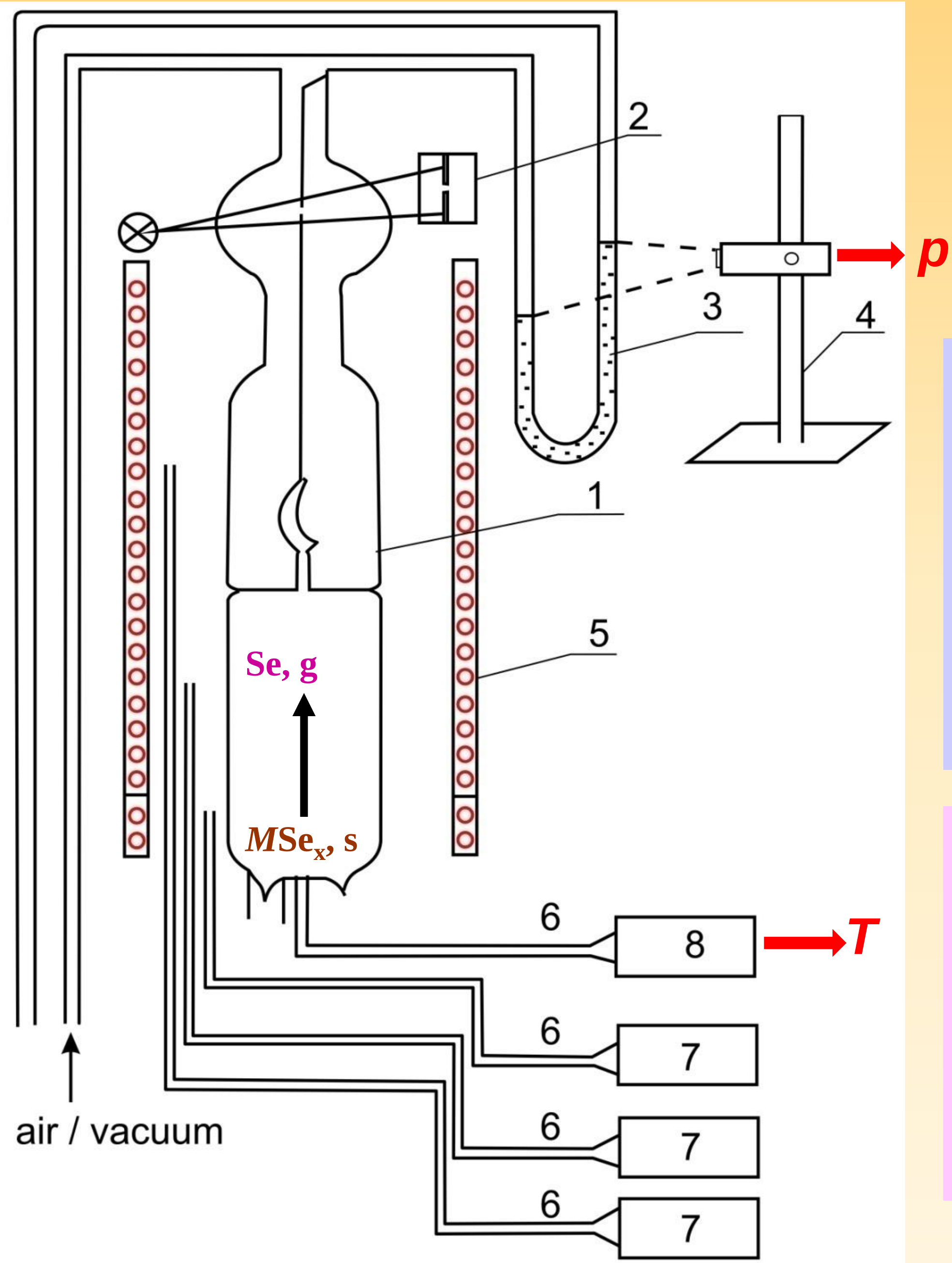

1 – quartz membrane-spoon manometer;
2 – optical registration system of manometer null-position;
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7 – heat-control units; 8 – voltmeter.

Δp = 0.5 Torr
ΔT = 0.5^0
Δx = 0.01 f. u.
400 ≤ T, C ≤ 1130
1 ≤ p, Torr ≤ 760
MSe$_x$, 1.5 ≤ x ≤ 2.0

The time of the three-phase equilibrium establishment:
~ 400 h. at T = 400 C
1 h. at T = 1130 C

Расчет состава твердых фаз

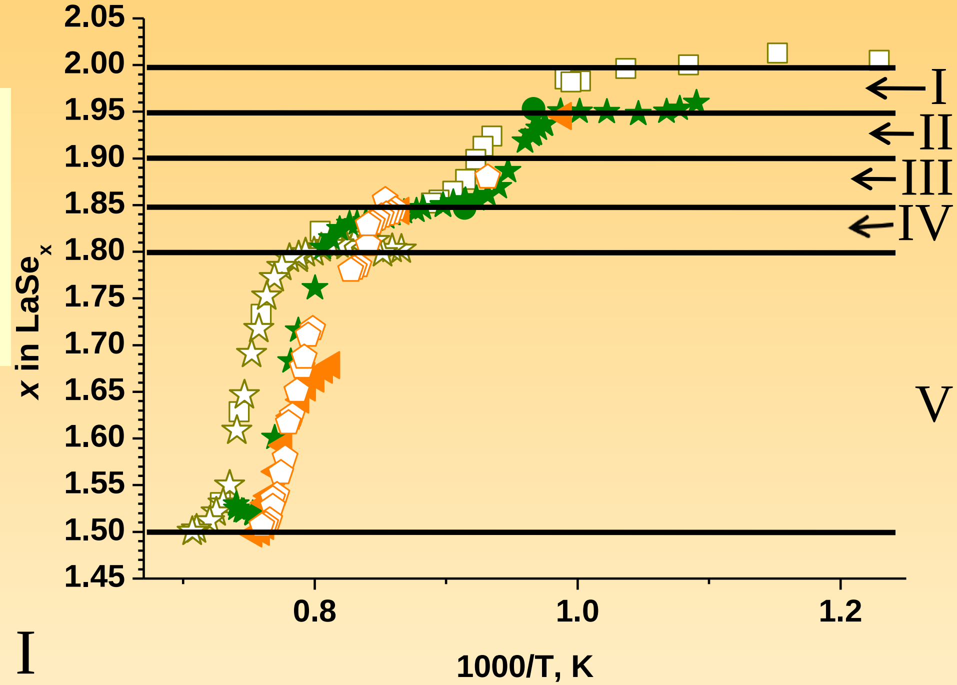
$$\mathbf{\mathit{M}Se_{x,}} \qquad x = \left(\frac{N_{Se}}{N_{Ln}}\right)_{ij} = \frac{N_{Se,\,j} - \sum_{n=1}^{8} n\left(\frac{p_{Se_n} V_j}{RT_{ij}}\right)}{m_j / M}$$

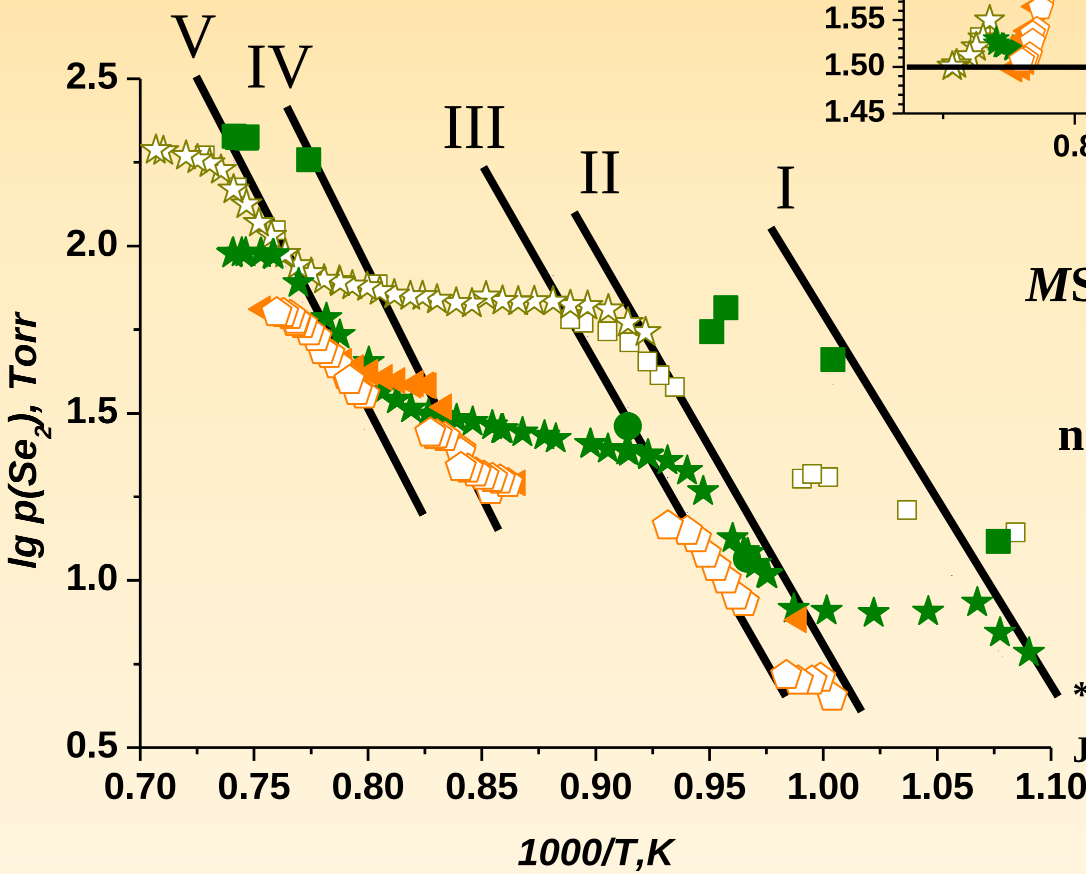
$$Se_n\ (g) = nSe\ (g)$$

$$x = f(p, T)$$

$LaSe_2$-$LaSe_{1.5}$

I. $40LaSe_{2.0}(s) = 40LaSe_{1.95}(s) + Se_2(g)$
II. $40LaSe_{1.95}(s) = 40LaSe_{1.90}(s) + Se_2(g)$
III. $40LaSe_{1.90}(s) = 40LaSe_{1.85}(s) + Se_2(g)$
IV. $40LaSe_{1.85}(s) = 40LaSe_{1.80}(s) + Se_2(g)$
V. $6.67LaSe_{1.80}(s) = 6.67LaSe_{1.50}(s) + Se_2(g)$





MSe_2 – $MSe_{1.5}$ (M = La, Ce, Pr, Nd)*

M_nSe_{2n-1}

n = 5, 7, 10, 20,

$5 \downarrow MSe_{1.8} \downarrow M_5Se_9$

$7 \downarrow MSe_{1.85} \downarrow M_7Se_{13}$

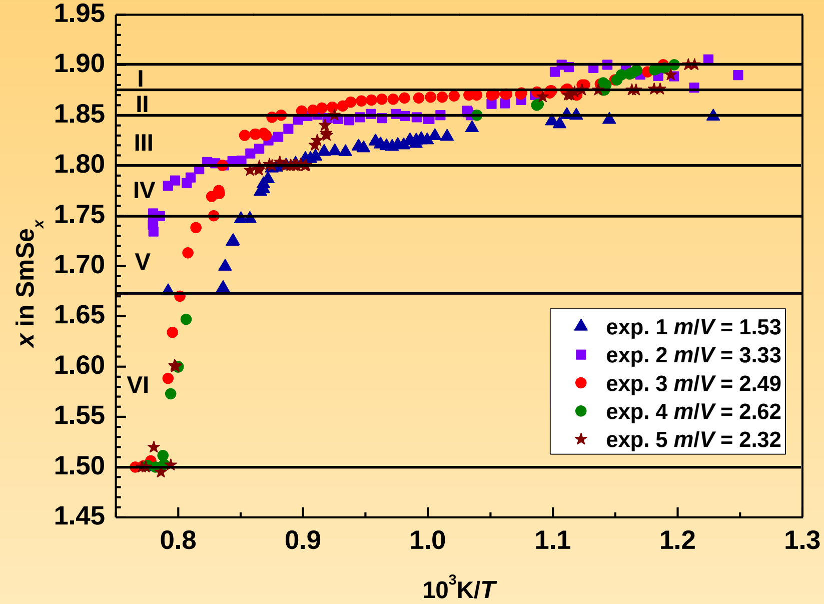
$10 \downarrow MSe_{1.9} \downarrow M_{10}Se_{19}$

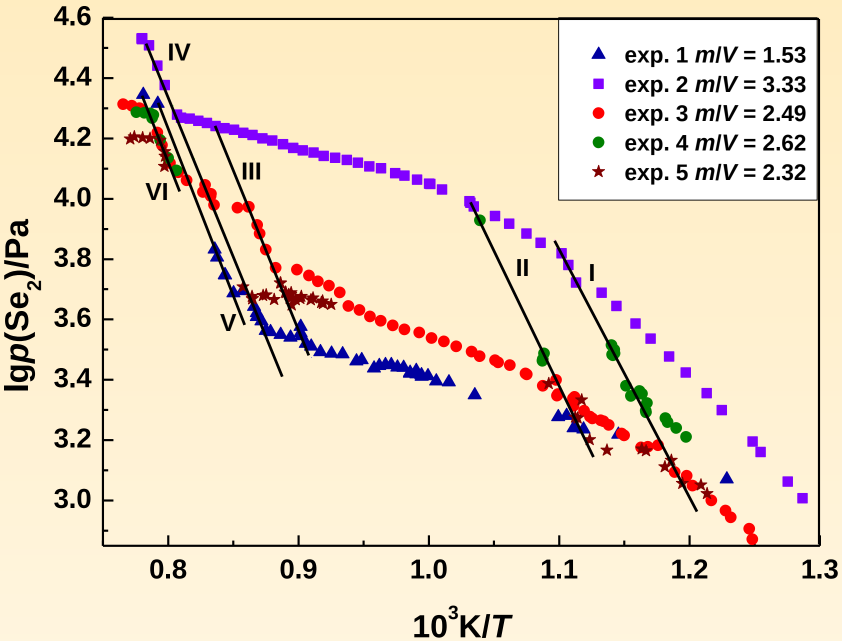
$20 \downarrow MSe_{1.95} \downarrow M_{20}Se_{39}$

*L.N. Zelenina, T.P. Chusova, I.G. Vasilyeva, J. Chem. Therm. 57 (2013) 101-107.

$SmSe_{1.9}$-$SmSe_{1.5}$

I. $80SmSe_{1.90}(s)=80SmSe_{1.875}(s) + Se_2(g)$
II. $80SmSe_{1.875}(s)=80SmSe_{1.85}(s) + Se_2(g)$
III. $40SmSe_{1.85}(s)=40SmSe_{1.80}(s) + Se_2(g)$
IV. $40SmSe_{1.80}(s)=40SmSe_{1.75}(s) + Se_2(g)$
V. $25SmSe_{1.75}(s)=25SmSe_{1.67}(s) + Se_2(g)$
VI. $11.76SmSe_{1.67}(s)=11.76SmSe_{1.50}(s) + Se_2(g)$





Sm_nSe_{2n-1}*

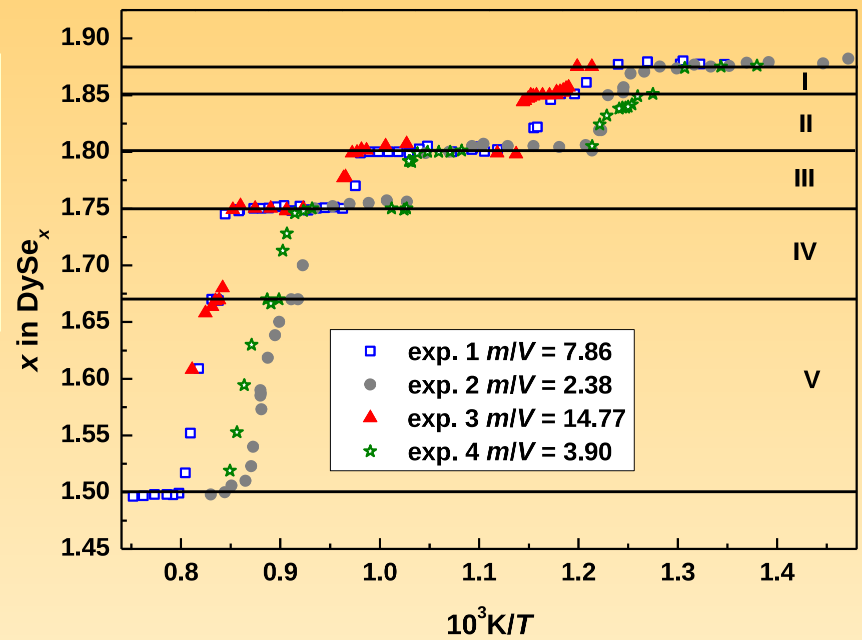
n= 3, 4, 5, 7, 8

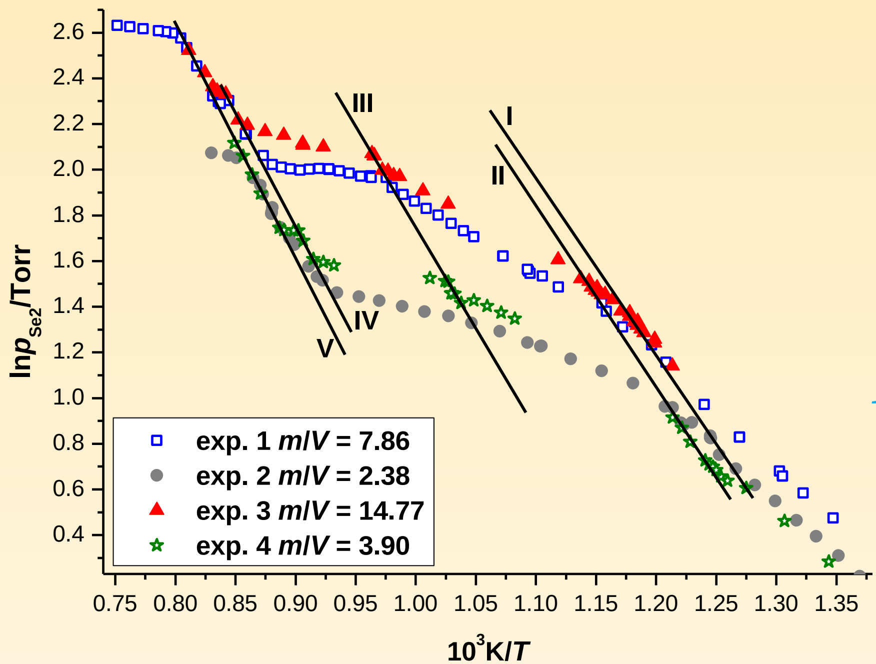
$MSe_{1.67} \downarrow M_3Se_5$ | $MSe_{1.75} \downarrow M_4Se_7$ | $MSe_{1.8} \downarrow M_5Se_9$ | $MSe_{1.85} \downarrow M_7Se_{13}$ | $MSe_{1.875} \downarrow M_8Se_{15}$

*L.N. Zelenina, T.P. Chusova, I.G. Vasilyeva, J. Chem. Therm. 90 (2015) 122-128.

$DySe_{1.875}$-$DySe_{1.5}$

I. $80DySe_{1.875}(s) = 80DySe_{1.85}(s) + Se_2(g)$
II. $40DySe_{1.85}(s) = 40DySe_{1.80}(s) + Se_2(g)$
III. $40DySe_{1.80}(s) = 40DySe_{1.75}(s) + Se_2(g)$
IV. $25DySe_{1.75}(s) = 25DySe_{1.67}(s) + Se_2(g)$
V. $11.8DySe_{1.67}(s) = 11.8DySe_{1.50}(s) + Se_2(g)$





M_nSe_{2n-1} (M = Gd, Dy)*

n= 3 → $MSe_{1.67}$ → M_3Se_5

4 → $MSe_{1.75}$ → M_4Se_7

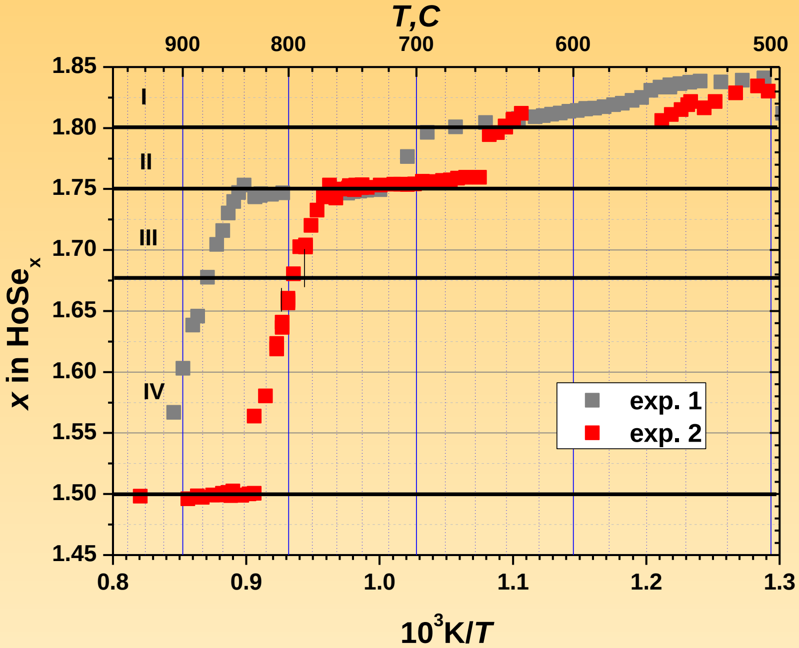
5, → $MSe_{1.8}$ → M_5Se_9

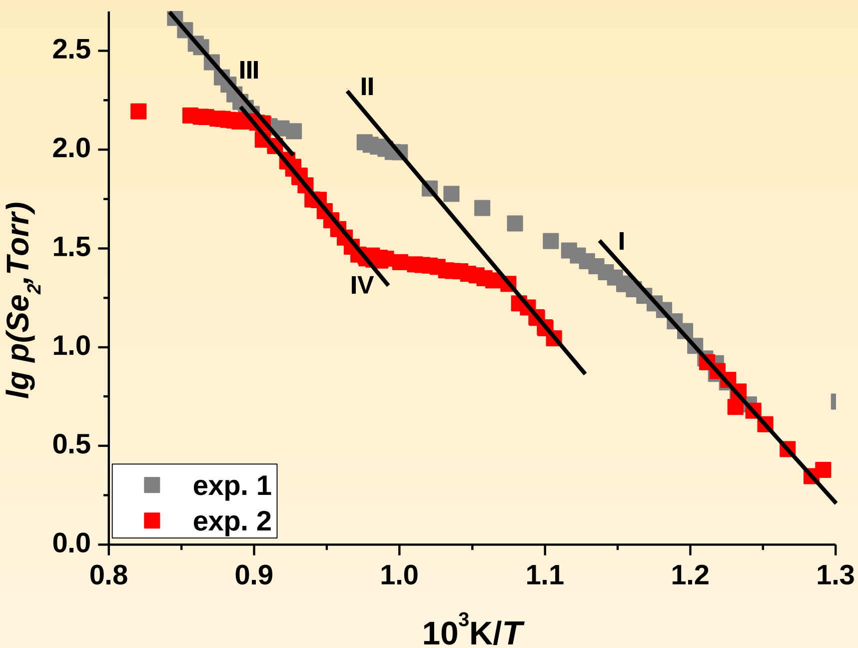
7 → $MSe_{1.85}$ → M_7Se_{13}

*L.N. Zelenina, T.P. Chusova, A.V. Isakov, J. Chem. Therm. 102 (2016) 89-94.

$HoSe_{1.85}$-$HoSe_{1.5}$

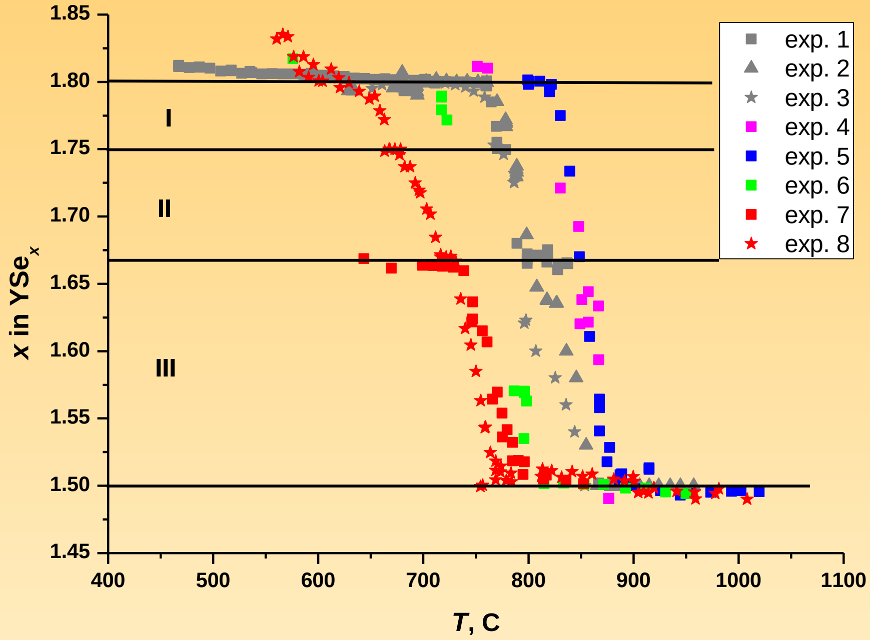
I. $40HoSe_{1.85}(s) = 40HoSe_{1.80}(s) + Se_2(g)$
II. $40HoSe_{1.80}(s) = 40HoSe_{1.75}(s) + Se_2(g)$
III. $25HoSe_{1.75}(s) = 25HoSe_{1.67}(s) + Se_2(g)$
IV. $11.8HoSe_{1.67}(s) = 11.8HoSe_{1.50}(s) + Se_2(g)$

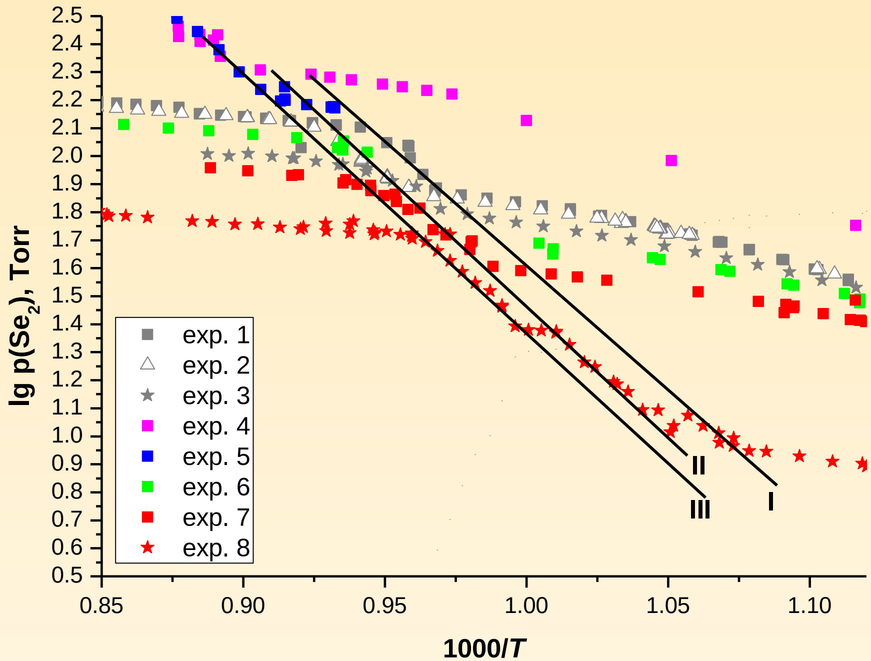




$YSe_{1.80}$-$YSe_{1.5}$

I. $40YSe_{1.80}(s) = 40YSe_{1.75}(s) + Se_2(g)$
II. $25YSe_{1.75}(s) = 25YSe_{1.67}(s) + Se_2(g)$
III. $11.8YSe_{1.67}(s) = 11.8YSe_{1.50}(s) + Se_2(g)$





Обработка экспериментальных данных

$$L = (2\pi)^{-\frac{N}{2}} e^{-\frac{1}{2}\Psi}$$

$$\Psi = \sum_{j=1}^{N} \sum_{i=1}^{nj} \frac{\left(p_{ij(\exp)} - p_{ij(calc)}\right)^2}{\left(\Delta p_{ij}\right)^2 + \left(\Delta T_{ij}\right)^2 \left(\frac{dp}{dT}\right)_{ij}^2}$$

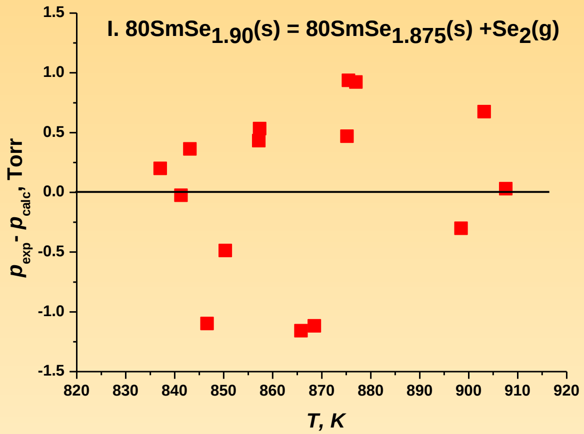
where $p_{\exp}$ is experimental pressure,
p_c is the pressure calculated by equation:
$p_{calc} = p°exp[-\Delta_r H_T/RT + \Delta_r S°_T/R + \varphi(\Delta_r C°_p, T)]$
here $p°$ is the standard pressure of 101.325 kPa,
$\Delta_r H_{298}$, $\Delta_r S°_{298}$ are the enthalpy and the entropy of the process, $\varphi(\Delta_r C°_p, T)$ is heat capacity change in the process studied
Δp and ΔT are the errors in the measurements of the pressure and temperature, respectively.

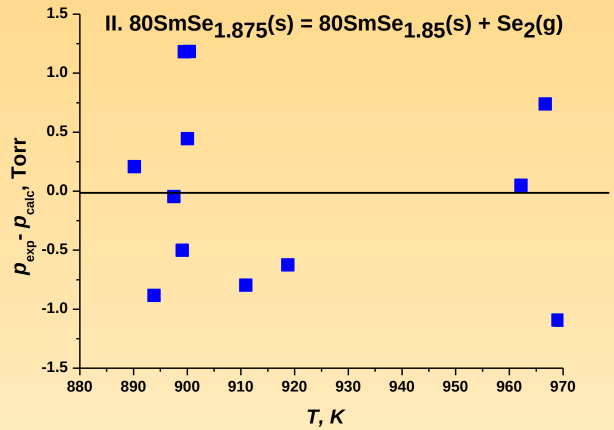
$\Delta_r H_T$, $\Delta_r S_T$
$\ln(p/p°) \pm 2\sigma = A - B/T - C\ln(T)$
$\sigma^2 = a/T^2 - b/T + c$
$\Delta_r H_T \pm t\sqrt{a}$, $\Delta_r S_T \pm t\sqrt{c}$

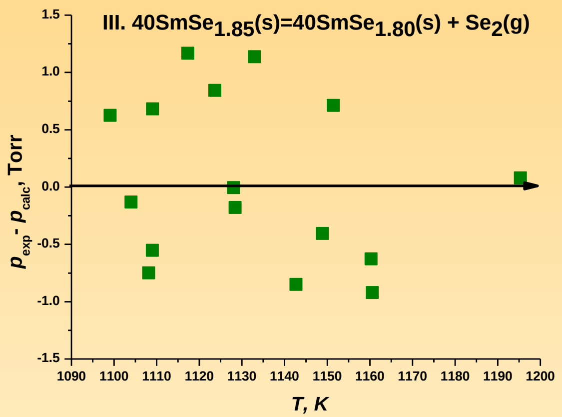
Термодинамические параметры реакций для системы $SmSe_{1.9}$-$SmSe_{1.5}$

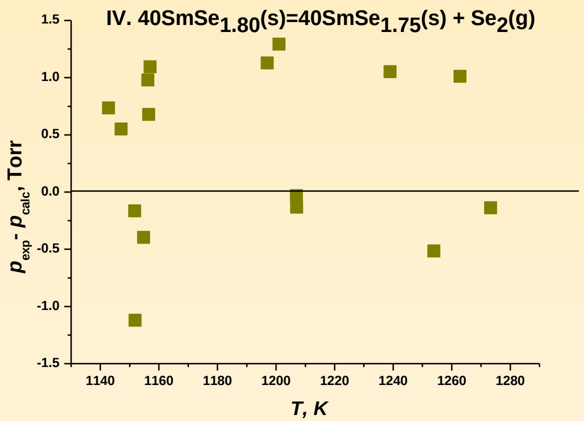
$x_1 \rightarrow x_2$	A	B	C	$\Delta_r H^o_{298}$ $kJ \cdot mol^{-1}$		$\Delta_r S^\circ_{298}$ $J \cdot mol^{-1} K^{-1}$	
				II-law	III-law	II-law	III-law
$SmSe_x$	$\ln p(Se_2)/(atm) = A - B/T - C\ln(T)$						
1.90→875	26.195	20055.0	1.00294	164.2±2.6	165±2.6	161.9±3.0	163±3
1.875→1.85	26.273	21039.7	1.00314	172.4±2.4	172±2.4	162.6±2.5	163±3
1.85→1.80	26.419	25152.3	100474	206.6±0.7	206±0.7	163.5±0.6	163±3
1.80→1.75	26.359	25894.4	1.00294	212.8±2.2	212±2.2	163.3±1.8	163±3
1.75→1.67	26.321	28188.2	1.00742	215.2±1.6	215±1.6	162.7±1.4	163±3
1.67→1.50	26.272	26393.3	1.00546	217.0±4.9	217±4.9	162.4±3.9	163±3

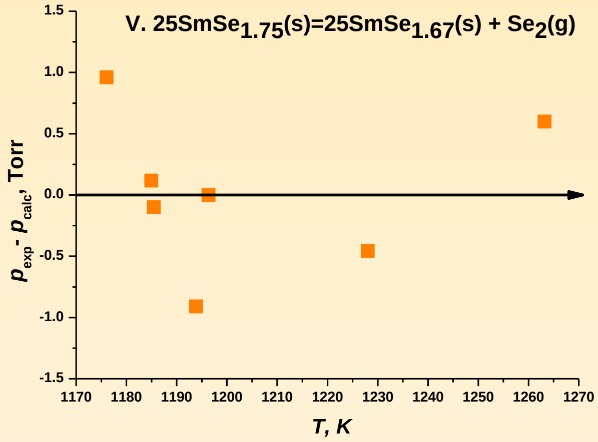
Разница между величинами экспериментального (p_{exp}) и рассчитанного (p_{calc}) давления

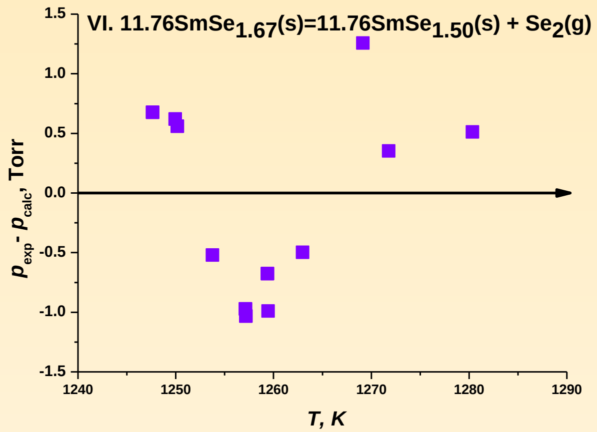












Термодинамические характеристики $LaSe_x$ and $CeSe_x$

Phase (s)	$-\Delta_f H^o_{298}$ kJ · mol^{-1}	$S°_{298}$ J · mol^{-1}K^{-1}	$C°_{p,298}$* J · mol^{-1}K^{-1}	$S°_{298}$* J·mol^{-1}K^{-1}
$LaSe_2$	485.9	122.5±1.0	75.3	122
$LaSe_{1.95}$	484.9	120.3±1.0	74.0	120
$LaSe_{1.90}$	483.4	118.2±1.0	72.8	118
$LaSe_{1.85}$	481.5	116.1±1.0	71.5	116
$LaSe_{1.80}$	479.5	114.1±0.4	70.3	114
$LaSe_{1.50}$	466.5±11[lit]	101.1±0.3[lit]	68.78±0.2[lit]	-
$CeSe_2$	484	131.9±4.0	82.7	132
$CeSe_{1.95}$	483	129.7±4.0	81.4	130
$CeSe_{1.90}$	482	127.6±4.0	80.2	128
$CeSe_{1.85}$	480	125.5±4.0	78.9	126
$CeSe_{1.80}$	478	123.4±4.0	77.7	124
$CeSe_{1.50}$	466±63 [lit]	110.9±4.0 [lit]	70.2±3.5 [lit]	-

* Оценка по уравнению: $MSe_x = MSe_{1.50} + (x\text{-}1.5)Se$

Термодинамические характеристики $PrSe_x$ and $NdSe_x$

Phase (s)	$-\Delta_f H^o_{298}$ kJ · mol^{-1}	$S°_{298}$ J · mol^{-1}K^{-1}	$C°_{p,298}$ * J · mol^{-1}K^{-1}	$S°_{298}$ * J·mol^{-1}K^{-1}
$PrSe_2$	488	134.0±2.0	76.7*	136.7
$PrSe_{1.95}$	487	132.0±2.0	75.4*	134.6
$PrSe_{1.90}$	486	129.9±1.0	74.2*	132.5
$PrSe_{1.85}$	485	127.8±1.0	72.9*	130.3
$PrSe_{1.80}$	483	125.7±1.0	71.7*	128.2
$PrSe_{1.50}$	471±42[lit]	115.5±0.9[lit]	64.2±0.5 [lit]	-
$NdSe_2$	486	132.6±2.4	77.6*	132
$NdSe_{1.95}$	485	130.4±2.4	76.4*	130
$NdSe_{1.90}$	484	128.3±2.4	75.1*	128
$NdSe_{1.85}$	483	126.2±2.4	73.9*	126
$NdSe_{1.80}$	482	124.1±2.3	72.6*	124
$NdSe_{1.50}$	471 ±63[lit]	111.3±2.2[lit]	65.1±1.3 [lit]	-

*Оценка по уравнению: $MSe_x = MSe_{1.50} + (x\text{-}1.5)Se$

Термодинамические характеристики $SmSe_x$

Phase (s)	$-\Delta_f H^o_{298}$ kJ · mol^{-1}	$S°_{298}$ J · mol^{-1}K^{-1}	$C°_{p,298}$ * J · mol^{-1}K^{-1}	$S°_{298}$ * J·mol^{-1}K^{-1}
$SmSe_{1.9}$	452.3	127.5±1.5	74.1	127.5
$SmSe_{1.875}$	452.0	126.4±1.4	73.5	126.4
$SmSe_{1.85}$	451.7	125.4±1.4	72.9	125.4
$SmSe_{1.80}$	450.1	123.3±1.4	71.6	123.3
$SmSe_{1.75}$	448.3	121.2±1.3	70.4	121.2
$SmSe_{1.67}$	445.5	117.8±1.3	69.1	119.0
$SmSe_{1.50}$	439±42[lit]	110.6±0.9[lit]	64.1±0.2 [lit]	-

*Оценка по уравнению: $M\text{Se}_x = M\text{Se}_{1.50} + (x\text{-}1.5)\text{Se}$

Термодинамические характеристики $GdSe_x$ and $DySe_x$

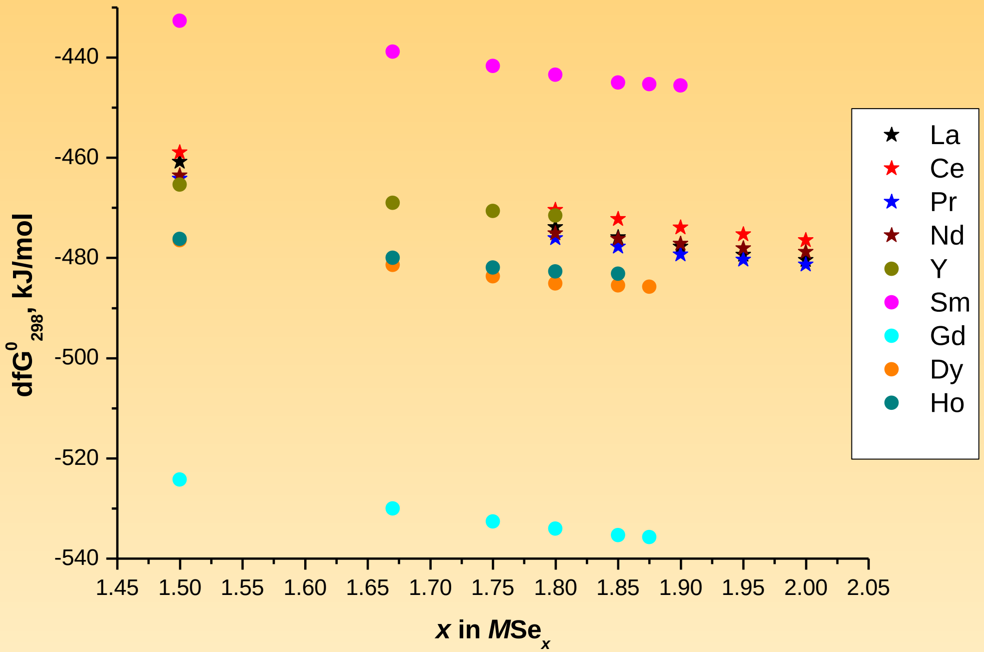
Phase (s)	$-\Delta_f H^o_{298}$ kJ · mol^{-1}	$S°_{298}$ J · mol^{-1}K^{-1}	$C°_{p,298}$ * J · mol^{-1}K^{-1}	$S°_{298}$ * J·mol^{-1}K^{-1}
$GdSe_{1.875}$	545.5	114.4±1.4	72.40	114 .1
$GdSe_{1.85}$	545.1	113.4±1.4	71.78	113.0
$GdSe_{180}$	543.8	111.3±1.4	70.52	110.9
$GdSe_{1.75}$	542.4	109.1±1.3	69.27	108.8
$GdSe_{1.67}$	539.7	105.7±1.3	67.27	105.4
$GdSe_{1.50}$	534±17[lit]	98.25±0.8[lit]	63.01±0.2[lit]	-
$DySe_{1.875}$	491.2	136.3	74.1	136.1
$DySe_{1.85}$	491.0	135.2	73.5	135.1
$DySe_{180}$	490.6	133.1	72.3	133.0
$DySe_{1.75}$	489.2	130.9	71.0	130.9
$DySe_{1.67}$	486.9	127.5	69.0	127.5
$DySe_{1.50}$	482±16[lit]	120.3±10.5	64.7±2.5	-

*Оценка по уравнению: $MSe_x = MSe_{1.50} + (x-1.5)Se$

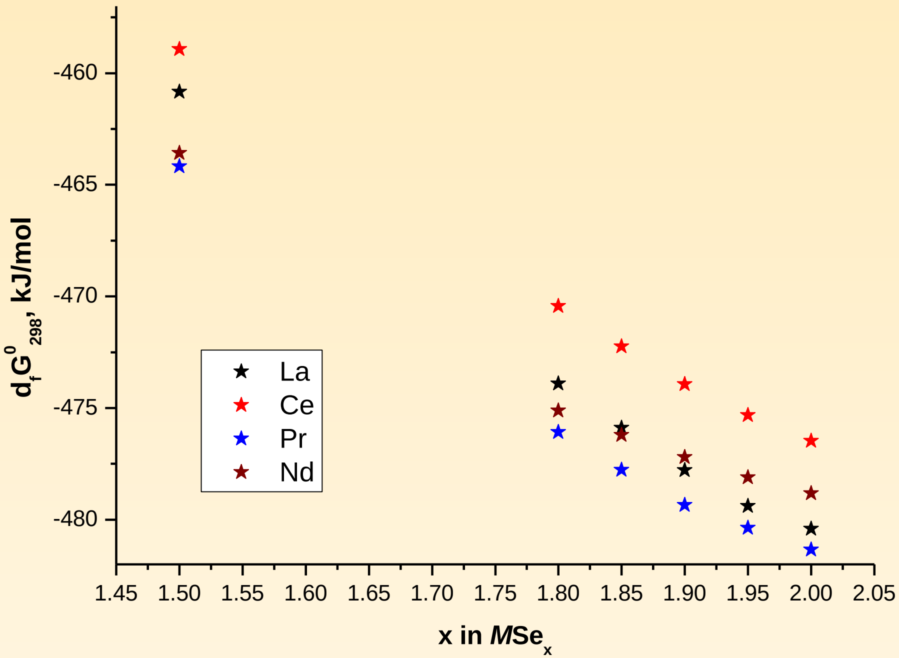
Термодинамические характеристики $HoSe_x$ and YSe_x

Phase (s)	$-\Delta_f H^o_{298}$ kJ · mol^{-1}	$S°_{298}$ J · mol^{-1}K^{-1}	$C°_{p,298}$ * J · mol^{-1}K^{-1}	$S°_{298}$ * J·mol^{-1}K^{-1}
$HoSe_{1.85}$	488	137.4	72.5	137.2
$HoSe_{1.80}$	488	135.2	71.3	135.1
$HoSe_{1.75}$	487	133.1	70.0	132.9
$HoSe_{1.67}$	485	129.8	68.0	129.6
$HoSe_{1.50}$	481±63[lit]	122.4±10[lit]	63.7±10[lit]	122.4
$YSe_{1.80}$	477	102.9	69.7	102.6
$YSe_{1.75}$	476	100.7	68.3	100.5
$YSe_{1.67}$	474	97.3	66.2	97.1
$YSe_{1.50}$	471±83[lit]	90.0±10.5[lit]	61.6±10[lit]	-

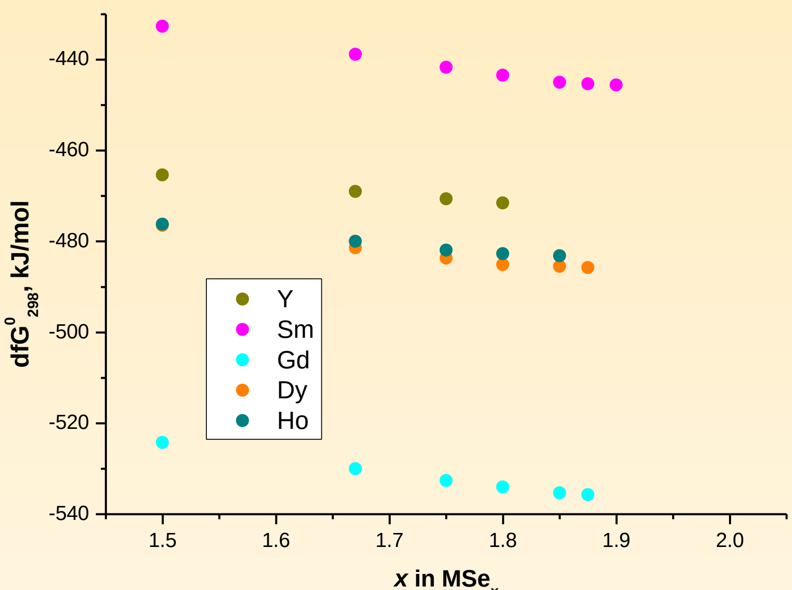
*Оценка по уравнению: $M\text{Se}_x = M\text{Se}_{1.50} + (x\text{-}1.5)\text{Se}$



dfG$^0_{298}$, kJ/mol
-440
-460
-480
-500
-520
-540
1.45 1.50 1.55 1.60 1.65 1.70 1.75 1.80 1.85 1.90 1.95 2.00 2.05
x in *M*Se$_x$
La
Ce
Pr
Nd
Y
Sm
Gd
Dy
Ho

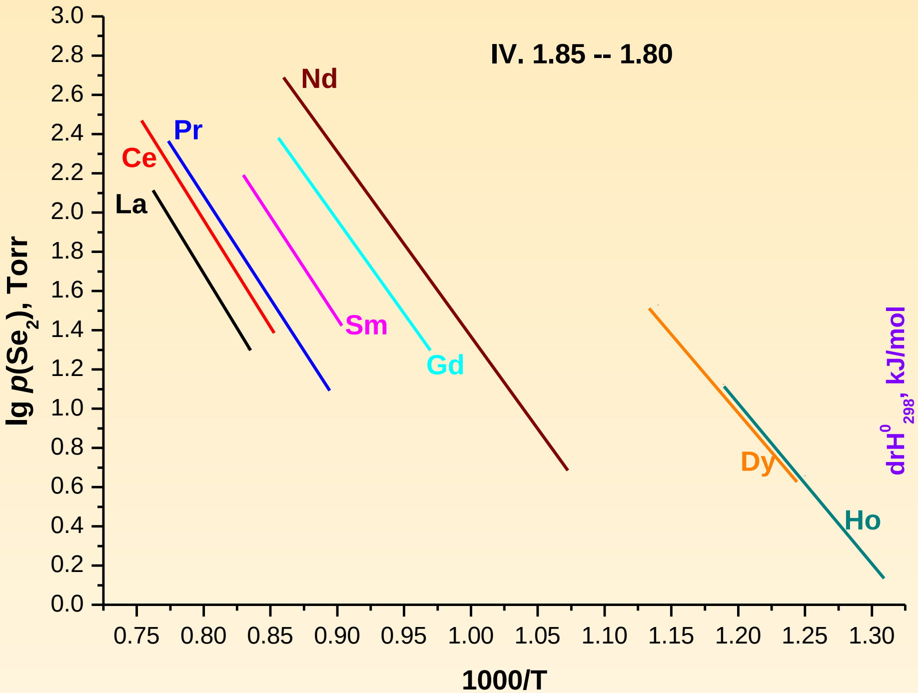


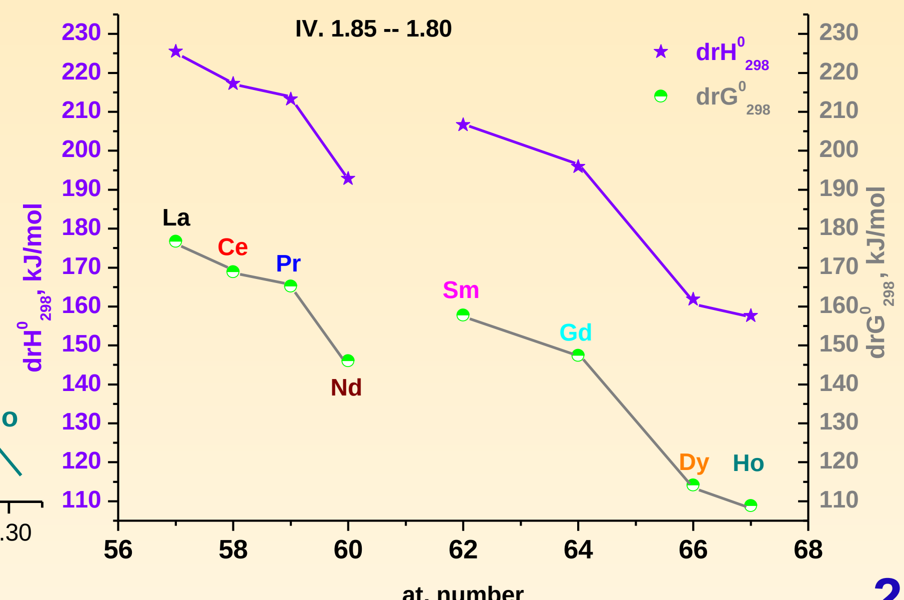
d$_f$G$^0_{298}$, kJ/mol
-460
-465
-470
-475
-480
1.45 1.50 1.55 1.60 1.65 1.70 1.75 1.80 1.85 1.90 1.95 2.00 2.05
x in *M*Se$_x$
La
Ce
Pr
Nd



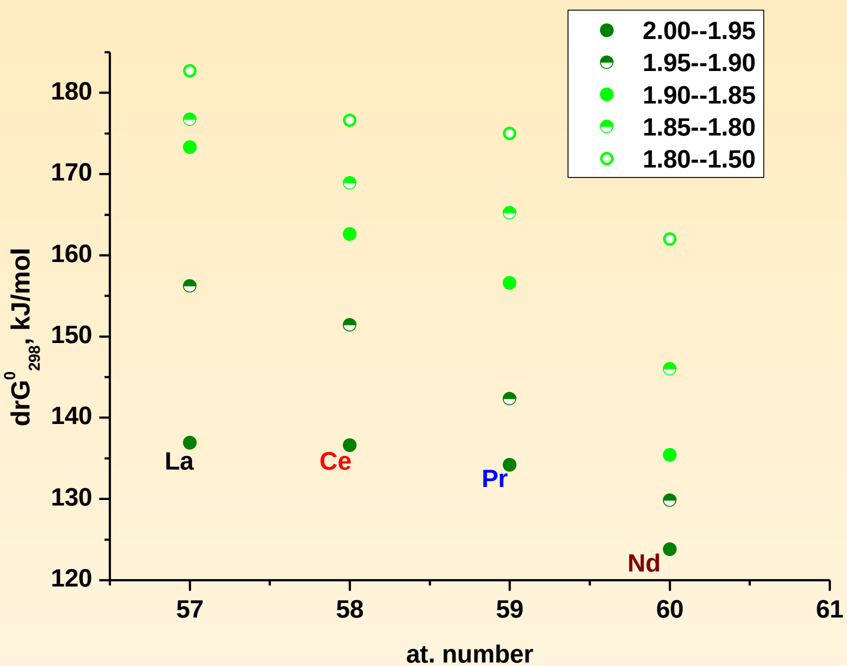
dfG$^0_{298}$, kJ/mol
-440
-460
-480
-500
-520
-540
1.5 1.6 1.7 1.8 1.9 2.0
x in MSe$_x$
Y
Sm
Gd
Dy
Ho

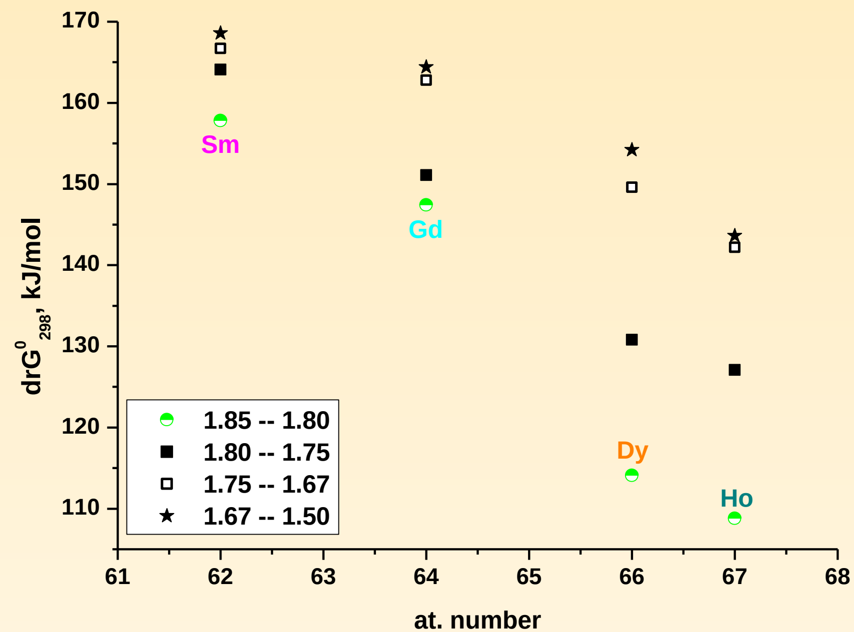
№	La, Ce, Pr, Nd	Sm	Gd, Dy	Ho	Y
I	2.0 → 1.95				
II	1.95 →1.90				
III	1.90 → 1.85	1.90 → 1.875			
		1.875 →1.85	1.875 →1.85		
IV	1.85 → 1.80	1.85 → 1.80	1.85 → 1.80	1.85 → 1.80	
V	1.80 →1.50	1.80 → 1.75	1.80 → 1.75	1.80 → 1.75	1.80 → 1.75
		1.75 → 1.67	1.75 → 1.67	1.75 → 1.67	1.75 → 1.67
		1.67 → 1.50	1.67 → 1.50	1.67 → 1.50	1.67 → 1.50

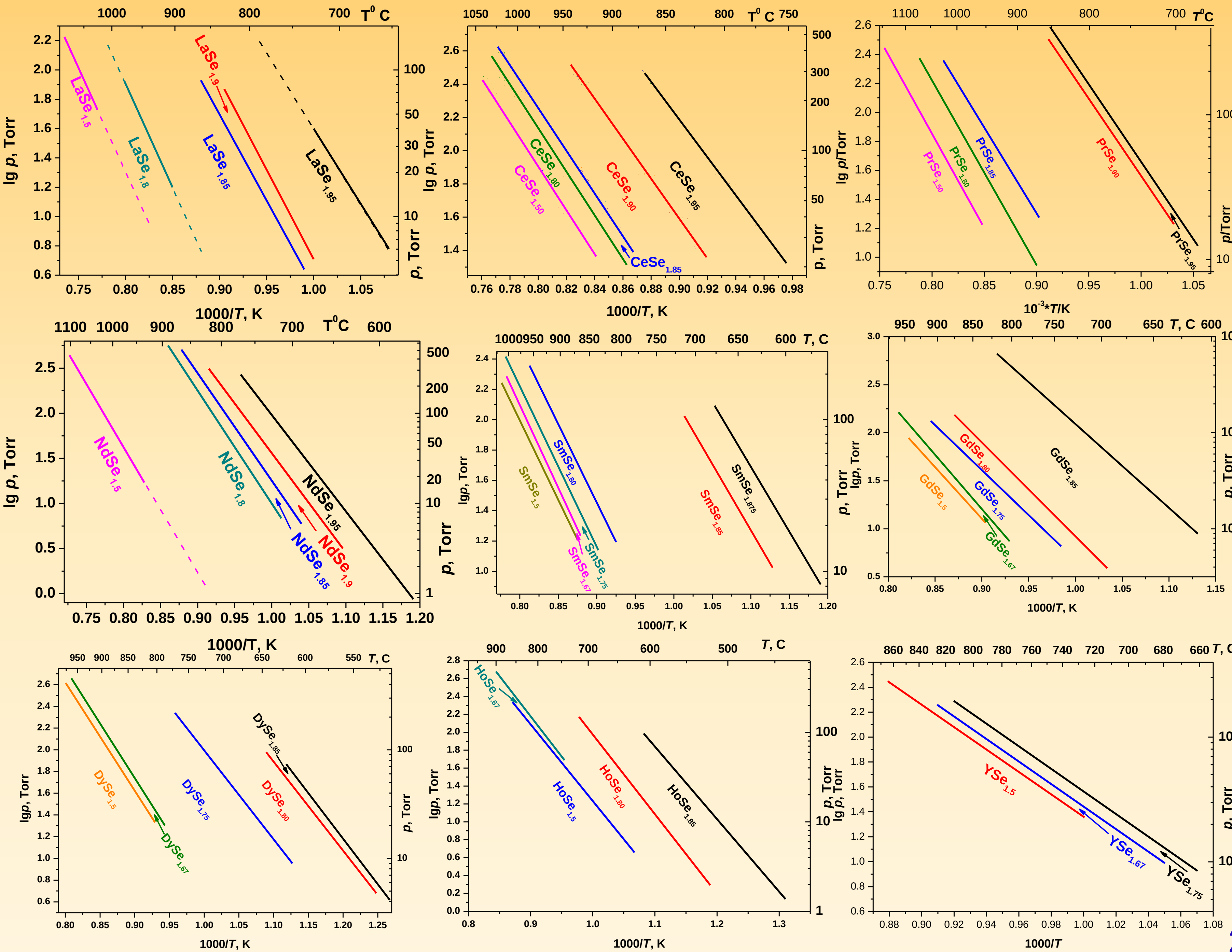




№	La, Ce, Pr, Nd	Sm	Gd, Dy	Ho	Y
I	2.0 → 1.95				
II	1.95 →1.90				
III	1.90 → 1.85	1.90 → 1.875			
		1.875 →1.85	1.875 →1.85		
IV	1.85 → 1.80	1.85 → 1.80	1.85 → 1.80	1.85 → 1.80	
V	1.80 →1.50	1.80 → 1.75	1.80 → 1.75	1.80 → 1.75	1.80 → 1.75
		1.75 → 1.67	1.75 → 1.67	1.75 → 1.67	1.75 → 1.67
		1.67 → 1.50	1.67 → 1.50	1.67 → 1.50	1.67 → 1.50






T⁰ C
lg p, Torr
p, Torr
1000/T, K
LaSe1.5
LaSe1.8
LaSe1.85
LaSe1.9
LaSe1.95
lg p, Torr
p, Torr
CeSe1.50
CeSe1.80
CeSe1.85
CeSe1.90
CeSe1.95
lg p/Torr
p/Torr
10⁻³*T/K
PrSe1.50
PrSe1.80
PrSe1.85
PrSe1.90
PrSe1.95
lg p, Torr
p, Torr
1000/T, K
NdSe1.5
NdSe1.8
NdSe1.85
NdSe1.9
NdSe1.95
T, C
lgp, Torr
p, Torr
1000/T, K
SmSe1.5
SmSe1.67
SmSe1.75
SmSe1.80
SmSe1.85
SmSe1.875
T, C
lgp, Torr
p, Torr
1000/T, K
GdSe1.5
GdSe1.67
GdSe1.75
GdSe1.80
GdSe1.85
T, C
lgp, Torr
p, Torr
1000/T, K
DySe1.5
DySe1.67
DySe1.75
DySe1.80
DySe1.85
T, C
lgp, Torr
p, Torr
1000/T, K
HoSe1.67
HoSe1.5
HoSe1.80
HoSe1.85
T, C
p, Torr
1000/T
YSe1.5
YSe1.67
YSe1.75

Термодинамическое моделирование

I-*M*-Se-Si-O

$$\Delta_f G\,(T) = \sum n_i\, \Delta_f G^o{}_{icond}(T) + \sum n_i\, \Delta_f G^o{}_{igas}(T) + \sum p_i \mathrm{R} T \ln p_i$$

$$\Delta_f G^o{}_{icond}\,(T) = \Delta_f H^o{}_i(T_0) + \int_{T_0}^{T} \Delta C_p(T) dT - T\Delta S^o{}_i(T_0) - T\int_{T_0}^{T} \Delta C_p(T)/T dT$$

conditions used :

$p = 1.013\ 10^5$ Pa,

$873 \le T/\mathrm{K} \le 1273$

~50 cond. phases and gas. species

information used :

$\Delta_f H^o{}_{298}$, $S^o{}_{298}$, $C^o p = f(T)$

condensed phases

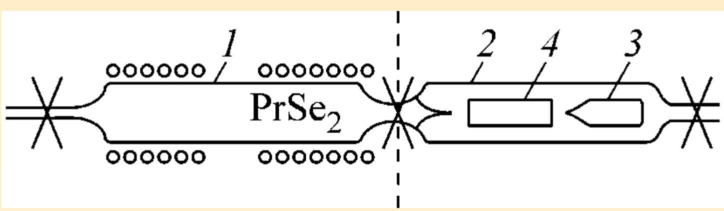
Se, MSe$_x$, I_2, SiO, SiO_2, SeO_2, M_2O_3, MI_2, MI_3,

gaseous species

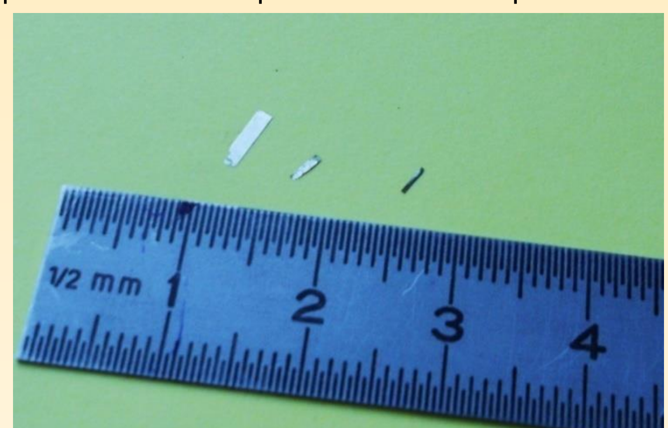
Ar, O, O_2, Se, Se_2, Se_3, Se_4, Se_5, Se_6, Se_7, Se_8, SiO, SiO_2, SeO_2, SeO, MO, SiI_4, SiI_3, SiI_2, SiI, MI_2, MI_3, IO, I_2, I

Результаты моделирования процесса роста кристаллов $PrSe_{1.95}$

Atomic concentrations of elements *n*, g-atom				Total pressure *p* = 1 atm		
					Condensed phases formed	
Ar	I	Se	Pr	*T*, °C	Composition (*x* in $PrSe_x$)	Yield (mol % $PrSe_x$)
1	0.01	1.95	1	607—613	1.95	99.7
1	0.1	1.95	1	697—702	1.95	96.1
1	0.09	2.0	1	721—723	1.95	97.0
				724—726	1.95	85.5
					1.90	11.5
1	**0.1**	**2.0**	1	**721—726**	**1.95**	**96.7**



Scheme of the reactor for the crystal synthesis:
1 reactor, *2* system for iodine addition,
3 glass capillary with iodine, *4* magnetic sticker,
the circles denote a two-zone furnace.



L.N. Zelenina., T.P. Chusova, N.V. Podberezskaya, D.A. Piryazev, I.V. Korolkov. J. Struct. Chem. 56 (2015) 721-727

Выводы

– Детальное термодинамическое исследование показало, что в изученном интервале составов существуют не твердые растворы, а дискретные соединения, которые можно описать общей формулой M_nSe_{2n-1} (n = 3, 4, 5, 7, 8, 10, 20)

– По экспериментальным данным рассчитаны термодинамические характеристики взаимных превращений твердых фаз в изученных системах. ($\Delta_r H°_T$, $\Delta_r S°_T$)

– С привлечением литературных данных оценены стандартные термодинамические характеристики ($\Delta_f H°_T$, $S°_T$, $\Delta_f G°_T$) исследуемых соединений.

– Найдены термодинамические параметры (p_{Se} и T), определяющие поля стабильности и условия роста однородных фаз полиселенидов La–Nd, Y, Sm, Gd и Ho заданного состава

– Проведено термодинамическое моделирование процессов роста кристаллов методом химических транспортных реакций на I_2 и получены кристаллы промежуточных полиселенидов в исследованных системах

Спасибо

за

внимание!