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THERMOCHEMICAL INVESTIGATION OF RE_2O_3–SeO_2 SYSTEMS
III. Yttrium selenium oxides in the pseudo-binary system

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Abstract

Ternary pure phases in the thermodynamical equilibrium $Y_2Se_xO_{3+2x}$ in the pseudo-binary Y_2O_3–SeO_2 system have been synthesized by solid state reactions and characterized by X-ray powder diffraction, IR spectroscopy and DSC measurements. A new phase $Y_2Se_{3.5}O_{10}$ was found besides the known phases $Y_2Se_4O_{11}$, $Y_2Se_3O_9$ and Y_2SeO_5. The thermal decomposition properties of the compounds have been determined by total pressure measurements and their thermodynamics data have been derived from their decomposition functions and C_p values. The phase diagram and the phase barogram have been established.

Keywords: C_p measurement, phase diagram, thermal decomposition, thermodynamic data, yttrium selenium oxides

Introduction

Rare earth selenoxides have attracted special interests due to their optical, magnetic and catalytical properties. In the earlier researches on the rare earth selenides four ternary compounds $Y_2Se_4O_{11}$, $Y_2Se_3O_9$, $Y_2Se_2O_7$ and Y_2SeO_5 have been reported in the binary system Y_2O_3–SeO_2 [1–3]. Pedro *et al*. [1] synthesized $Y_2Se_4O_{11}$ with solid state reaction and obtained $Y_2Se_3O_9$ and Y_2SeO_5 through decomposition of the former phase. The characterization of the compounds by X-ray and IR spectroscopy showed that they belong to different structure families. $RE_2Se_4O_{11}$ (where *RE*=rare earth elements) were found to crystallize in three structure types, in which $Y_2Se_4O_{11}$ was classified together with other $RE_2Se_4O_{11}$ (*RE*=Sm, Eu, Gd and Lu) into one group. Pedro *et al*. subdivided the $RE_2Se_3O_9$ phases in two types. $Y_2Se_3O_9$ and its analogous $RE_2Se_3O_9$ (*RE*=Gd, Dy, Ho, Er, Tm, Yb and Lu) were included in one group. All RE_2SeO_5 compounds (*RE*=Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) form only one type of structure.

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Castro *et al.* [2] described the TG and DTA of the $Y_2Se_xO_{3+2x}$ compounds and found that the decomposition of $Y_2Se_4O_{11}$ takes place in three steps. $Y_2Se_4O_{11}$ decomposes into $Y_2Se_3O_9$ and gaseous SeO_2 in the temperature region 700-800K $Y_2Se_3O_9$ further decomposes in the region 880–1080 K to Y_2SeO_5 and SeO_2. Y_2SeO_5 decomposes directly to Y_2O_3 and $SeO_{2,g}$ starting from 1128 K.

The fourth compound, $Y_2Se_2O_7$, was obtained by Niinistö *et al.* [3] by thermal decomposition of $Y(Se_2O_5)NO_3$.

This paper reports our research results on the Y_2O_3–SeO_2 system from which we confirm the existence of three known phases $Y_2Se_4O_{11}$, $Y_2Se_3O_9$, Y_2SeO_5 and a new phase $Y_2Se_{3.5}O_{10}$. The phase $Y_2Se_2O_7$, described by Niinistö *et al.* [3] was not confirmed in our work. A phase $Y_2Se_{1.5}O_6$ with 60 mol% SeO_2, as it exists on the line Nd_2O_3–SeO_2 [4] and Sm_2O_3–SeO_2 [5] does not exist in thermodynamic equilibrium in this system.

Synthesis and characterization of the ternary compounds

Syntheses

The ternary compounds in the Y_2O_3–SeO_2 system are synthesized by solid state reactions between corresponding stoichiometric amounts of Y_2O_3 (purity 99.9%, Riedel-de Haen AG) and SeO_2 in evacuated quartzglass tubes, as described previously [4, 5]. X-ray powder diffraction patterns and IR spectra of end-products show that all four phases $Y_2Se_4O_{11}$, $Y_2Se_{3.5}O_{10}$, $Y_2Se_3O_9$ and Y_2SeO_5 are pure. The optimal reaction temperature for preparation of $Y_2Se_4O_{11}$ is 300–350°C, and for $Y_2Se_{3.5}O_{10}$ is 400°C. Traces of $Y_2Se_3O_9$, detectable by X-ray, are found in $Y_2Se_{3.5}O_{10}$ product synthesized above 450°C. The phase pure $Y_2Se_3O_9$ can not be obtained until 700, while pure Y_2SeO_5 is obtained above 800°C. The SeO_2-rich products show white colour, while the SeO_2-poorer phases are rose.

Characterizations by X-ray diffraction

All synthesized phases and products are characterized by X-ray diffraction, shown in Figs 1 and 2, using a Siemens diffractometer D5000 with CuK_α radiation in 2θ range from 10 to 70°. From these figures we can detect the existence of four thermodynamically stable phases in the binary Y_2O_3–SeO_2, system: $Y_2Se_4O_{11}$, $Y_2Se_{3.5}O_{10}$, $Y_2Se_3O_9$ and Y_2SeO_5, containing 80, 77.8, 75 and 50 mol% SeO_2, respectively.

The phase $Y_2Se_4O_{11}$ is characterized by a group of intensive lines in the 2θ range between 24 and 34° with the strongest reflection at 28.5°. $Y_2Se_{3.5}O_{10}$, is characterized by two strong lines at 13.5 and 14.7°, which clearly differentiate it from other phases. The diffraction pattern of $Y_2Se_3O_9$ has only two strong main reflections at 25 and 25.5°, it is similar to that of $Dy_2Se_3O_9$, shown by Pedro *et al.* [1]. Comparing with the pattern of Dy_2SeO_5, which was given by Pedro *et al.* [1], the two stronger reflections at 28 and 28.3° are also characteristic of Y_2SeO_5 besides the strongest main reflection at 29°. Therefore the statement of Pedro *et al.* [1], that all RE_2SeO_5 must have the same structure, cannot be confirmed.

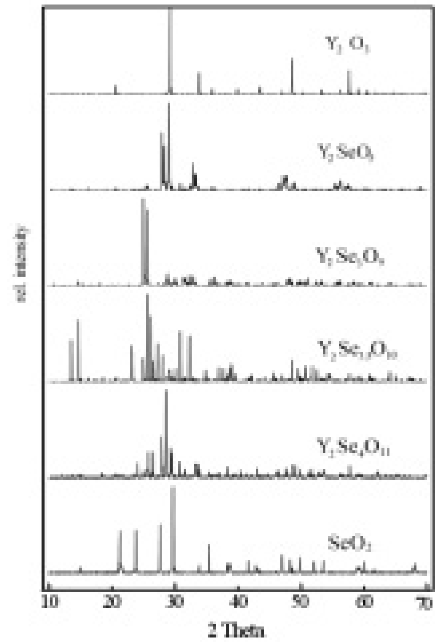

Fig. 1 Powder diffraction patterns of yttrium selenium oxides and of the initial compounds Y_2O_3 and SeO_2

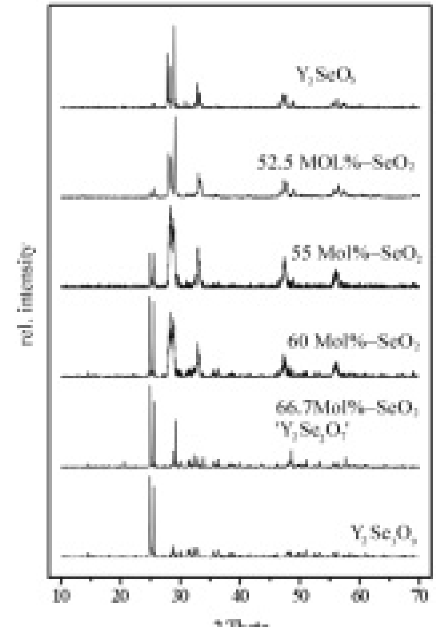

Fig. 2 Powder diffraction patterns of tempered composition of 66.7 and 50–60 mol% SeO_2 in correlation with Y_2SeO_5 and $Y_2Se_3O_9$

Figure 2 depicts the X-ray patterns of samples with the composition between 50–60 mol% SeO_2 and of 66.7 mol% SeO_2 (‘$Y_2Se_2O_7$’) in correlation to that of the 50 and 75 mol% SeO_2 phases. The figure shows that all samples are mixtures of the 50 and 75 mol% SeO_2 phases. So it follows, that neither a 60 nor a 66.7 mol% SeO_2 phase exist in this system. The phase $Y_2Se_2O_7$, described by Niinistö *et al.* [3] may not be a thermodynamically stable phase. These conclusions are also confirmed by the total pressure measurements.

If $Y_2Se_4O_{11}$ samples, annealed in small ampoules at different temperatures, are quickly quenched, it follows from the X-ray patterns (Fig. 3) that more reflections of $Y_2Se_{3.5}O_{10}$ will be shown in the patterns with increasing temperatures. The sample, quenched at 700 K, mainly contains $Y_2Se_{3.5}O_{11}$. So it is obvious from this that there is a typical peritectic of $Y_2Se_4O_{11}$ near 700 K, which is in agreement with DTA investigations.

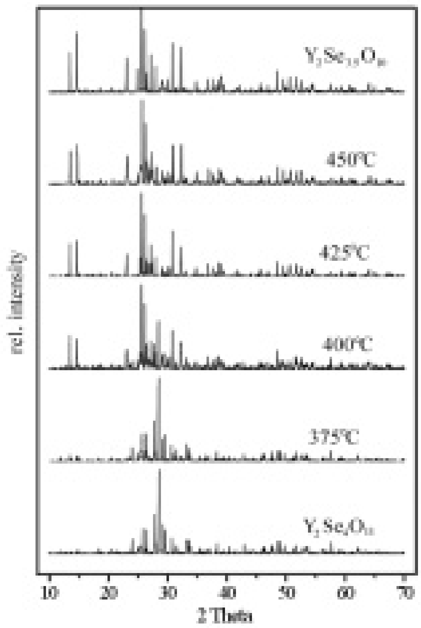

Fig. 3 Powder diffraction patterns of $Y_2Se_4O_{11}$ after tempering and quenching at different temperatures, 1*d* in correlation with $Y_2Se_{3.5}O_{10}$

$Y_2Se_{3.5}O_{10}$ samples are also annealed at different temperatures. The X-ray patterns are demonstrated in Fig. 4, showing the peritectic decomposition of $Y_2Se_{3.5}O_{10}$ near 775 K. The pattern near 13.5° (2θ) at 500°C allows the assumption of a α–β transition of the $Y_2Se_{3.5}O_{10}$ phase, which is also found in DTA.

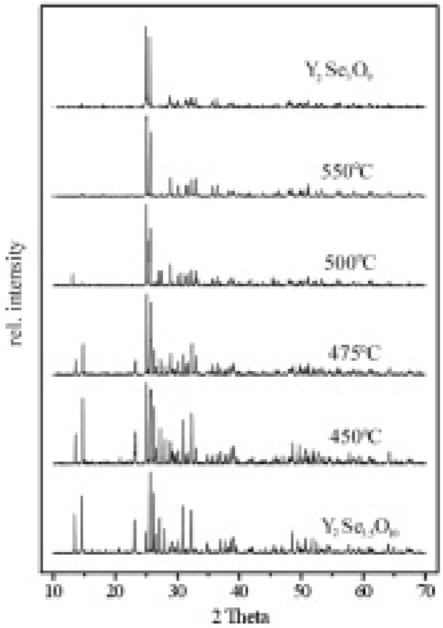

Fig. 4 Powder diffraction patterns of $Y_2Se_{3.5}O_{10}$ after tempering and quenching at different temperatures, 1*d* in correlation with $Y_2Se_3O_9$

Characterization by IR spectroscopy

IR spectroscopy was used as a second method for characterization of the $Y_2Se_xO_{3+2x}$ phases. The samples were measured in KBr-pressed pellets on a Spekord M80.

The IR spectra of synthesized compounds are depicted in Fig. 5. The phases shown in their spectra are distinguishable one from each other. The region between 300–900 cm^{-1} show the most characteristic Se–O bond vibrations, as is observed in a large number of selenites and selenites in the reported literature [6].

Total pressure measurements

The decomposition behaviour of the yttrium selenium oxides was investigated by total pressure measurements on pure phase powder products in glass- or quartzglass-membrane manometers, as otherwise described [5–10].

For the determination of the decomposition pressure at various temperatures we measured the pressure step by step in intervals of 25 or 50 degree. The achievement of the equilibrium at one temperature is very slow. Therefore, we evaluated only the series by increasing the temperature. The total pressure functions of the phases obtained in coexistence with SeO_2-pure neighbour phases are shown in Fig. 6. Every function was obtained from more experiment cycles by increasing temperature. All phases decompose into the next SeO_2-poorer coexistent solid phase and gaseous SeO_2. Since the partial or sublimation pressure of the solid phases are negligible, the total pressure was equal to the SeO_2-decomposition pressure.

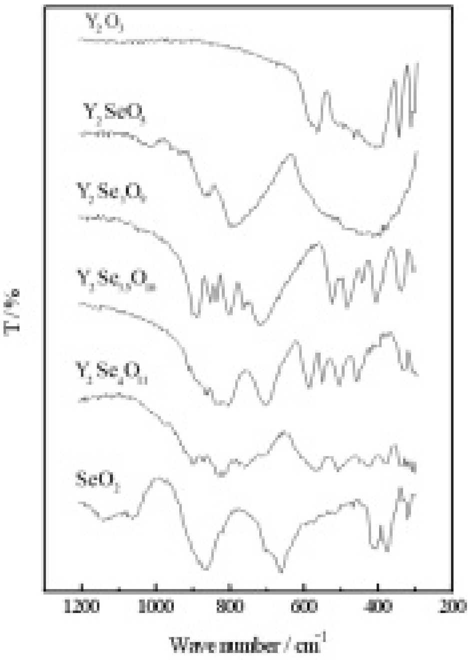

Fig. 5 IR spectra of the yttrium selenium oxides and the initial compounds Y_2O_3 and SeO_2

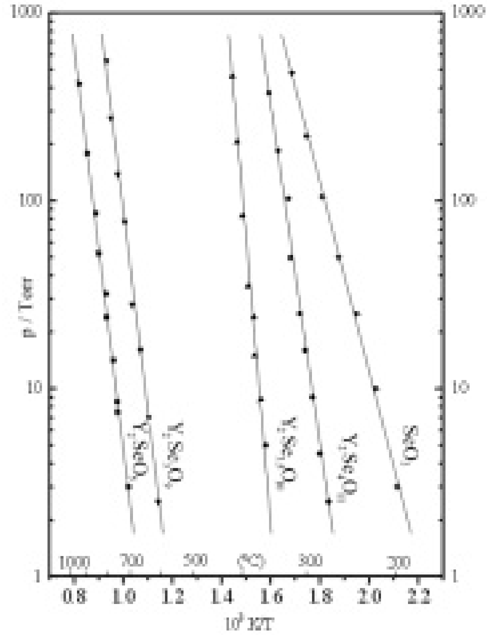

Fig. 6 Total pressure functions of SeO_2, $Y_2Se_4O_{11}$, $Y_2Se_{3.5}O_{10}$, $Y_2Se_3O_9$ and Y_2SeO_5

$Y_2Se_4O_{11}$

The decomposition pressure of $Y_2Se_4O_{11}$ is 0.133 kPa at 275°C (548 K), and it reaches 101.3 kPa at temperature near 375°C (648 K). The decomposition normalised to 1 mol gaseous SeO_2 is:

$$2Y_2Se_4O_{11,s}=2Y_2Se_{3.5}O_{10,s}+SeO_{2,g}$$

The decomposition pressure of $Y_2Se_4O_{11}$ at the peritectic temperature near 425°C (798K) is not measurable with our method.

$Y_2Se_{3.5}O_{10}$

The measured decomposition temperature of $Y_2Se_{3.5}O_{10}$ with 0.133 kPa pressure is 327°C (600 K) and the pressure arrives 101.3 kPa near 425°C (698 K). The transition temperature of this phase lies outside the measurable *p–T* region. The decomposition can be described by:

$$2Y_2Se_{3.5}O_{10,s}=2Y_2Se_3O_{9,s}+SeO_{2,g}$$

$Y_2Se_3O_9$

This phase decomposes above 600°C (873 K) and the total pressure reaches 101.3 kPa near 825°C (1100 K). Therefore, the phase transformation at 827°C

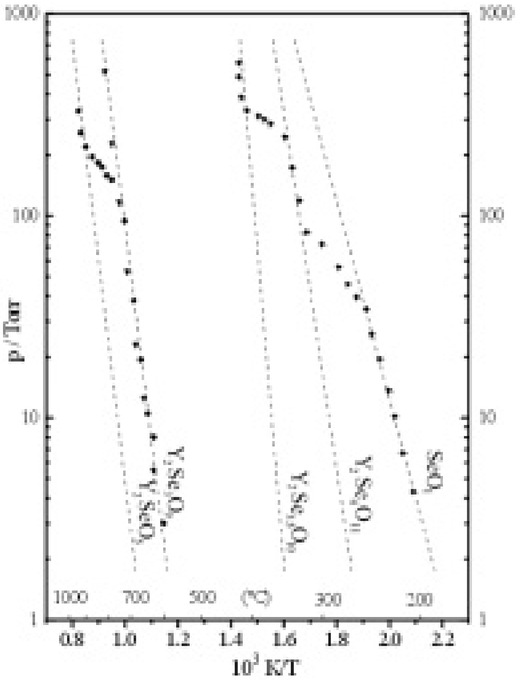

Fig. 7 Total pressure measurements in- and outside and saturation of the SeO_2-rich phase

(1100 K) and peritectic reaction at 1125°C (1398 K) can not be observed. The decomposition reaction can be formulated as follows:

$$0.5Y_2Se_3O_{9,s}=0.5Y_2SeO_{5,s}+SeO_{2,g}$$

Y_2SeO_5

This Y_2O_3-richest phase shows a measurable decomposition pressure at a temperature higher than 700°C (973 K). The decomposition function lies parallel and close to that of the $Y_2Se_3O_9$ phase. The decomposition can be described by:

$$Y_2Se_3O_{5,s}=Y_2O_{3,s}+SeO_{2,g}$$

If we measure the total pressure of composition from a mixture of $Y_2Se_4O_{11}$ and SeO_2 out of the saturation, we obtain the function, as it is demonstrated in Fig. 7 (marked with ♦). The pressure increases first step by step along the SeO_2-saturation-function, arrives at a divariant region and the goes along the $Y_2Se_4O_{11}$-decomposition line, arrives again at a divariant region and increases along the decomposition line of $Y_2Se_{3.5}O_{10}$. So we may conclude that there are no more phases in equilibrium besides SeO_2, $Y_2Se_4O_{11}$ and $Y_2Se_{3.5}O_{10}$ in the region from 77.8 mol% SeO_2 to the binary phase SeO_2. A composition between 50 to 75 mol% SeO_2 (see ▼ curve in Fig. 7) shows the increasing of the pressure first along the decomposition function of $Y_2Se_3O_9$ and after a divariant period along the function of Y_2SeO_5. So we obtain from the total pressure measurements the same information as we obtained by X-ray and IR spectroscopy. Between the 50 and 75 mol% SeO_2 phase there exist no more phases, neither a 60 mol% SeO_2 phase, obtained in the Nd_2O_3–SeO_2 and Sm_2O_3–SeO_2 systems [4, 5], nor a 66.7 mol% SeO_2 phase, reported by Niinistö *et al*. [3].

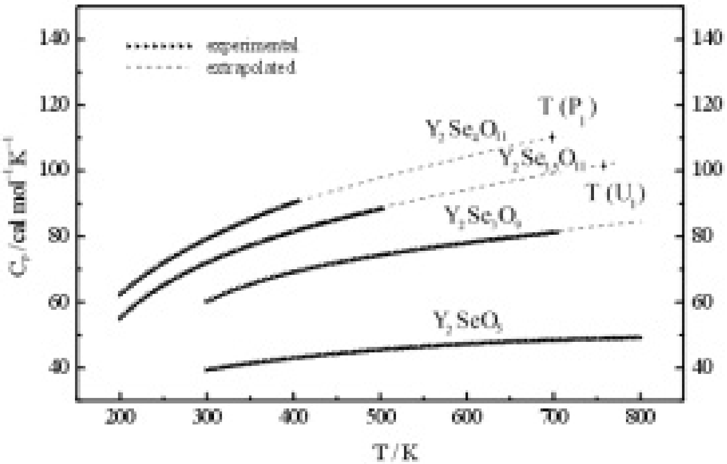

Fig. 8 C_p functions of yttrium selen oxides

Table 2 Experimental and estimated* C_p values (J mol^{-1} K^{-1}) for $Y_2Se_xO_{3+2x}$ compounds

T/K	$YSeO_5$		$Y_2Se_3O_9$		$Y_2Se_{3.5}O_{10}$		$Y_2Se_4O_{11}$	
	exp.	NK	exp.	NK	exp.	NK	exp.	NK
298	164.3±2.5	160.5±10.9	250.4±4.2	276.7±15.0	299.7±6.3	306.0±15.9	329.1±6.3	334.8±17.1
400	179.7±2.5	178.9±12.5	288.8±4.2	311.0±16.7	340.7±6.3	344.0±18.0	377.5±6.3	377.0±18.8
500	190.2±2.5	190.6±12.5	310.6±4.2	336.1±16.7	369.1±6.3	372.4±18.0	411.7±6.3	408.8±18.8
600	197.7±2.5	200.2±12.5	326.0±4.2	358.2±16.7	391.2±6.3	397.9±18.0	436.4±6.3	437.2±18.8
700	202.7±2.5	–	339.4±4.2	–	408.8±6.3	–	452.7±6.3	–

*Estimated by Neumann–Kopp rule (NK) from tabulated data [11]

Heat capacities of $Y_2Se_xO_{3+2x}$

The heat capacities of Y_2SeO_5 and $Y_2Se_3O_9$ were determined by DSC measurements with a DSC 404 (Netzsch) from 323 to 773 K. Since the another two phase $Y_2Se_4O_{11}$ and $Y_2Se_{3.5}O_{10}$ decompose above 400 and 500 K [4], we used a DSC 111 (Setaram) in lower temperature region from 150 to 473 K. The curves, which are presented in Fig. 8, are obtained from average values of several single determinations. The coefficients of the fit-function $C_p=a+bT+cT^{-2}+dT^3$ are listed in Table 1. In Table 2 the experimental values are compared with the data, obtained by the Neumann–Kopp rule. The agreement between the experimental and estimated values are good at lower temperatures, while the differences increase with increasing temperature.

Table 1 Coefficient of the C_p functions of Y_2SeO_{3+2x} ($C_p=a+bT+cT^2+dT^3$)

Phase	a/ J mol^{-1} K^{-1}	$b\cdot 10^3$/ J mol^{-1} K^{-2}	$c\cdot 10^{-5}$/ J mol^{-1} K^{-3}	$d\cdot 10^6$/ J mol^{-1} K^{-4}	T region/ K	Error/ J mol^{-1} K^{-1}
Y_2SeO_5	140.51	150.81	–12.25	–83.60	323–773	±2.5
$Y_2Se_3O_9$	308.60	37.20	–64.48	–36.44	323–673	±4.2
$Y_2Se_{3.5}O_{10}$	238.69	368.84	–30.12	–167.20	153–473	±6.3
$Y_2Se_4O_{11}$	193.59	638.70	–18.24	–376.20	153–373	±6.3

Evaluation of the total pressure measurements

The enthalpy of formation and standard entropy of phases Y_2SeO_5, $Y_2Se_3O_9$ and $Y_2Se_4O_{11}$ were obtained by evaluation of the total pressure measurements with the determined C_p functions via the second law.

The obtained functions for the decomposition reactions of the phases (Fig. 6) correspond to the decomposition pressure p_{SeO_2} in the form:

$$\lg p(\mathrm{atm})=A+\frac{B}{T}$$

and give through the combination with the Gibbs–Helmholtz equation and Van't-Hoff equation the decomposition enthalpy ΔH^0_{ZT} and entropy ΔS^0_{ZT} at the middle temperature T:

$$\lg p=\frac{\Delta S^0_{Z,T}}{4.575}-\frac{\Delta H^0_{Z,T}}{4.575T}$$

From this we can derive the enthalpy of formation and the standard entropy.

Y_2SeO_5

The evaluated pressure function for the decomposition:

$$Y_2SeO_{5,s}=Y_2O_{3,s}+SeO_{2,g}$$

is given by

$$\lg p(\text{atm})=(8.67\pm0.22)-(10850\pm250)/T$$

from which it follows that

$$\Delta H^0_{Z,1200}=207.5\pm4.2\ \text{kJ mol}^{-1}$$
$$\Delta S^0_{Z,1200}=166.1\pm4.2\ \text{J mol}^{-1}\ \text{K}^{-1}$$

So we obtain the enthalpy H^0($Y_2SeO_{5,s}$, 1200) and entropy S^0($Y_2SeO_{5,s}$, 1200) via the Hess law:

$$H^0(Y_2SeO_{5,s},\ 1200)=H^0(Y_2O_{3,s},\ 1200)+H^0(SeO_{2,g},\ 1200)-\Delta H^0_{Z,1200}$$
$$S^0(Y_2SeO_{5,s},\ 1200)=S^0(Y_2O_{3,s},\ 1200)+S^0(SeO_{2,g},\ 1200)-\Delta S^0_{Z,1200}\ .$$

and with the data in Table 3 to:

$$H^0(Y_2SeO_{5,s},\ 1200)=-2065.2\pm12.5\ \text{kJ mol}^{-1}$$
$$S^0(Y_2SeO_{5,s},\ 1200)=433.0\pm12.5\ \text{J mol}^{-1}\ \text{K}^{-1}$$

The values at T are converted to 298 K with the determined value C_p ($Y_2SeO_{5,s}$,700)=202.7±2.5 J mol^{-1} K^{-1} and Kirchoff's law:

$$\Delta H^0_B(Y_2SeO_{5,l},\ 298)=-2248.1\pm16.7\ \text{kJ mol}^{-1}$$
$$S^0(Y_2SeO_{5,l},\ 298)=150.2\pm18.4\ \text{J mol}^{-1}\ \text{K}^{-1}$$

$Y_2Se_3O_9$

The p–T function for the decomposition

$$0.5Y_2Se_3O_{9,s}=0.5Y_2SeO_{5,s}+SeO_{2,g}$$

can be given in the temperature region from 873 to 1098 K with

$$\lg p(\text{atm})=(9.81\pm0.30)-(10750\pm300)/T$$

The enthalpy and entropy of decomposition at middle temperature 1000 K are the following:

$$\Delta H^0_{Z,1200}=205.4\pm6.3\ \text{kJ mol}^{-1}$$
$$\Delta S^0_{Z,1200}=187.9\pm6.3\ \text{J mol}^{-1}\ \text{K}^{-1}$$

The enthalpy and entropy are then obtained via the Hess law at 1000 K:

$$H^0(Y_2Se_3O_{9,s},\ 1000)=H^0(Y_2SeO_{5,s},\ 1000)+2H^0(SeO_{2,g},\ 1000)-2\Delta H^0_{Z,1000}$$

$$S^0(Y_2Se_3O_{9,s},\ 1000)=S^0(Y_2SeO_{5,s},\ 1000)+2S^0(SeO_{2,g},\ 1000)-2\Delta S^0_{Z,1000}$$

With the derivated data of Y_2SeO_5 at 1000 K

$$H^0(Y_2SeO_{5,s},\ 1000)=-2105.8\pm20.9\ \text{kJ mol}^{-1}$$
$$S^0(Y_2SeO_{5,s},\ 1000)=395.8\pm23.0\ \text{J mol}^{-1}\ \text{K}^{-1}$$

to

$$H^0(Y_2Se_3O_{9,l},\ 1000)=-2663.9\pm41.8\ \text{kJ mol}^{-1}$$
$$S^0(Y_2Se_3O_{9,l},\ 1000)=666.9\pm43.9\ \text{J mol}^{-1}\ \text{K}^{-1}$$

These data converted with the determined data $C_p(Y_2Se_3O_{9,l},600)=326.4\pm 4.18$ J mol^{-1} K^{-1} to the standard data at 298 K:

$$\Delta H_B^0(Y_2Se_3O_{9,s},\ 298)=-2892.8\pm50.2\ \text{kJ mol}^{-1}$$
$$S^0(Y_2Se_3O_{9,s},\ 298)=271.5\pm58.5\ \text{J mol}^{-1}\ \text{K}^{-1}$$

$Y_2Se_{3.5}O_{10}$

The enthalpy of formation and standard entropy of $Y_2Se_{3.5}O_{10}$ are obtained via the third law. The pressure functions show (Fig. 6) an overlapping for $Y_2Se_3O_9$ and $Y_2Se_{3.5}O_{10}$ near 400°C (673 K). This would lead to an instability of the $Y_2Se_3O_9$ phase at 400°C, which we cannot detect from DSC measurement. So we assume, that the adjustment of the equilibrium is too slow at low temperature and the obtained slopes of functions (Fig. 6) are too steep.

From the decomposition pressure $p_{SeO_2}=-2.026$ kPa for the reaction:

$$2Y_2Se_{3.5}O_{10,s}=2Y_2Se_3O_{9,s}+SeO_{2,g}$$

at 600 K (Fig. 6) we can obtain the free reaction enthalpy

$$\Delta G_{Z,650}^0=20.7\pm4.2\ \text{kJ mol}^{-1}$$

The standard entropy for $Y_2Se_{3.5}O_{10}$ follows via the solid state reaction

$$Y_2O_{3,s}+3.5SeO_{2,s}=Y_2Se_{3.5}O_{10,s}$$

with the tabulated data (Tab. 5) as

$$S^0(Y_2Se_{3.5}O_{10,s},\ 298)=332.6\pm8.4\ \text{J mol}^{-1}\ \text{K}^{-1}$$

with the determined value $C_p(Y_2Se_{3.5}O_{10},\ 450)=356.4\pm41.8$ J mol^{-1} K^{-1} we obtain the entropy at 650 K via Kirchhoff's law:

$$S^0(\ Y_2Se_{3.5}O_{10,l},\ 650)=-610.9\pm12.5\ \text{J mol}^{-1}\ \text{K}^{-1}$$

By using the calculated value $S°(Y_2Se_3O_{9,l},\ 650)=526.3\pm43.9$ J mol^{-1} K^{-1} and the data in Table 3 the decomposition entropy can be obtained according to the following equation

$$\Delta S_{Z,650}^0=2S^0(Y_2Se_3O_{9,l},\ 650)+S^0(SeO_{2,g},\ 650)-2S^0(Y_2Se_{3.5}O_{10,l})$$

as:

$$\Delta S^0_{Z,650}=131.3\pm108.7\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

The Gibbs–Helmholtz equation leads to

$$\Delta H^0_{Z,650}=106.2\pm117.0\ \mathrm{kJ\ mol^{-1}}$$

So the enthalpy $H^0(Y_2Se_{3.5}O_{10,l}, 650)$ can be followed by using the Hess law via

$$H^0(Y_2Se_{3.5}O_{10,l}, 650) = H^0(Y_2Se_3O_{9,l}, 650) + 0.5H^0(SeO_{2,g}, 650) - 0.5\Delta H^0_{Z,650}$$

to

$$H^0(Y_2Se_{3.5}O_{10,l}, 650)= -2877.3\pm56.4\ \mathrm{kJ\ mol^{-1}}$$

At last we obtain, with the quoted C_p, the standard enthalpy:

$$\Delta H^0_B(Y_2Se_{3.5}O_{10,l}, 298)= -3002.0\pm58.5\ \mathrm{kJ\ mol^{-1}}$$

Table 3 Thermodynamic data* for SeO_2 and Y_2O_3 [11]

Compound		$SeO_{2,g}$	$SeO_{2,s}$	$Y_2O_{3,s}$
H^0_{1200}	kJ mol^{-1}	–62.3±4.2		–1793.4±4.2
H^0_{1000}		–73.6±4.2		–1812.1±4.2
H^0_{700}		–89.5±4.2		–1856.8±4.2
H^0_{600}		–94.9±4.2		–1868.9±4.2
ΔH^0_{298}		–126.7±4.6 [12]	–224.5±0.6 [14]	–1903.2±4.2 [13]
S^0_{1200}	J mol^{-1} K^{-1}	333.6±4.2		265.0±4.2
S^0_{1000}		323.1±4.2		241.6±4.2
S^0_{700}		303.9±4.2		197.3±4.2
S^0_{600}		295.9±4.2		178.5±4.2
S^0_{298}		264.6±0.4 [12]	66.6±0.4 [12]	99.1±0.3 [12]

*Converted to T analoque Barin [11] on the basis of the data tabulated by Gluschko [12, 13] for 298 K. We assume error ±4.2 kJ mol^{-1} respective ±4.2 J mol^{-1} K^{-1}

$Y_2Se_4O_{11}$

We obtain the data of $Y_2Se_4O_{11}$ by the second law in using the above obtained data of $Y_2Se_4O_{11}$. The thermal decomposition

$$2Y_2Se_4O_{11,s}=2Y_2Se_{3.5}O_{10,s}+SeO_{2,g}$$

is described by the total pressure function

$$\lg p(\mathrm{atm}) = (14.36\pm0.60) - (9200\pm400)/T$$

We obtain with $\Delta H^0_{Z,600}=176.0\pm8.4$ kJ mol^{-1} and $\Delta S^0_{Z,600}=274.9\pm12.5$ J mol^{-1} K^{-1}

$$H^0(Y_2Se_4O_{11,s}, 600)=H^0(Y_2Se_{3.5}O_{10,s}, 600)+0.5\mathrm{H}^0(SeO_{2,g}, 600)-0.5\Delta H^0_{Z,600}$$ and

$$S^0(Y_2Se_4O_{11,s}, 600)=S^0(Y_2Se_{3.5}O_{10,s}, 600)+0.5S^0(SeO_{2,g}, 600)–0.5\Delta S^0_{Z,600}$$

with the tabulated data (Table 3) and with $\Delta H^0(Y_2Se_{3.5}O_{10,s}, 298)= –2958.1\pm 7.9$ kJ mol^{-1} (determined by solution calorimetry, [15]) and $H^0(Y_2Se_{3.5}O_{10,s},600)= –2853.5\pm10.0$ J mol^{-1} as well as $S^0(Y_2Se_{3.5}O_{10,s},600)= 538.9\pm70.2$ J mol^{-1} K^{-1} will be the enthalpy of formation and entropy of $Y_2Se_4O_{11}$ at 600°C derived:

$$H^0(Y_2Se_4O_{11,s}, 600)= –2990.3\pm66.9 \text{ kJ mol}^{-1}$$

$$S^0(Y_2Se_4O_{11,s}, 600)=549.8\pm78.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

Via the Kirchoff's law and with the determined $C_p(Y_2Se_4O_{11,l},400)= 377.8\pm6.3$ J mol^{-1} K^{-1} at 298 K the enthalpy of formation

$$\Delta H^0_B(Y_2Se_4O_{11,s}, 298)= –3104.5\pm69.0 \text{ kJ mol}^{-1}$$

and standard entropy

$$S^0(Y_2Se_4O_{11,s}, 298)=285.3\pm83.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

are obtained.

DTA and phase diagram of the system Y_2O_3–SeO_2

Different thermoanalytical investigations are used besides the total pressure measurements for the construction of the phase diagram of the Y_2O_3–SeO_2 system. A

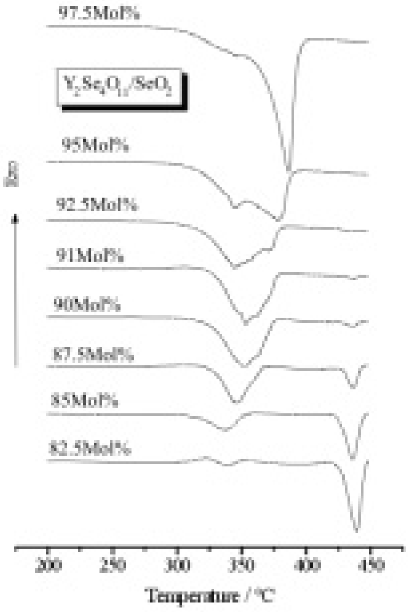

Fig. 9 DSC curves of compositions from $Y_2Se_4O_{11}$ and SeO_2

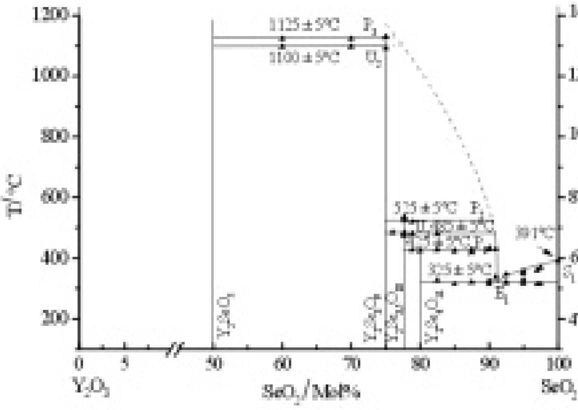

Fig. 10 Phase diagram of the pseudo-binary Y_2O_3–SeO_2 system

Labsys TM DSC 12 equipment was used for the measurements. The ternary phases, compositions of the ternary phases of Y_2O_3 and SeO_2 are filled in DSC quartzglass ampoules, evacuated and sealed. The samples are heated with a rate of 10 K min^{-1} in reference to Al_2O_3. The 'onset-temperatures' of effects for the corresponding compositions are given in Fig. 10, from which we may obtain the following conclusions:

1. There exist four thermodynamically stable phases: $Y_2Se_4O_{11}$, $Y_2Se_{3.5}O_{10}$, $Y_2Se_3O_9$ and Y_2SeO_5 in the pseudo-binary Y_2O_3–SeO_2 system. There are no thermal signals between 0–50 mol% SeO_2.

2. $Y_2Se_4O_{11}$ melts peritectically at 425±5°C (698°K) and results to solid $Y_2Se_{3.5}O_{10}$ and SeO_2-rich melt. This finding is in good agreement with X-ray and IR spectroscopy results.

3. Investigations of compositions from $Y_2Se_4O_{11}$ to SeO_2 between 82.5 and 91 mol% SeO_2 show two endothermic signals. One signal is at 325±5°C (598 K), its intensity increases with increasing SeO_2 concentration. The other signal is at 425±5°C (698 K), its intensity decreases with growing SeO_2 concentration. Compositions between 92.5 and 97.5 mol% SeO_2 show also two endothermic effects, for 92.5 mol% SeO_2 at 320°C (593 K) and 347°C (620 K), for 95 mol% SeO_2 at 329°C (602 K) and 357°C (630 K) and for 97.5 mol% SeO_2 at 325°C (598 K) and 369°C (642 K). With increasing of the SeO_2 concentration the intensity of the first effect decreases and the second increases (Fig. 9). These lead to an obvious eutectic reaction between $Y_2Se_4O_{11}$ and SeO_2 at 325°C (598 K) with eutectic point (E_1) at 91.5±5 mol% SeO_2.

4. $Y_2Se_{3.5}O_{10}$ melts peritectically at 525±5°C (798 K) (P_2). This value is also in good agreement with the results, obtained by annealing. The phase shows an endothermic transition (U_1), with a small effect at 485±5°C (758 K).

5. $Y_2Se_3O_9$ melts peritectically at 1125±5°C (1398 K) (P_3) and shows a kind of transition (U_2) at 1100°C (1373 K).

6. The SeO_2-poorest phase Y_2SeO_5 in the pseudo-binary Y_2O_3–SeO_2 system is thermodynamically stable over the whole temperature region up to 1200°C (1473 K).

7. The melting temperature of SeO_2 (S_1) is determined as 391±2°C (664 K) in agreement with earlier results [10].

* * *

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