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THERMAL ANALYSIS OF THE SELENITES OF THE TERNARY SYSTEM Nd_2O_3–SeO_2–H_2O AT 100°C

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Abstract

The solubility isotherm of the system Nd_2O_3–SeO_2–H_2O at 100°C was studied and drawn. All possible selenites of neodymium were obtained and characterized. Thermal decomposition of all phases in the system was studied and its mechanism was described.

Keywords: Nd_2O_3–SeO_2–H_2O, selenites of neodymium, ternary system

Introduction

The selenites of neodymium and other rare-earths have been attracting attention recently since their reduction in the corresponding gas medium is one of the ways of obtaining selenides. They possess valuable technical properties. The data concerning the conditions of obtaining neodymium selenites, their composition and properties are scarce.

The results of a study of the interaction between solutions of $NdCl_3$ with Na_2SeO_3 and H_2SeO_3 as well as the solubility of the system Nd_2O_3–SeO_2–H_2O at 25°C were reported in [1]. A normal salt $Nd_2(SeO_3)_3$ and two acid salts, $Nd_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 3H_2O$ and $Nd(HSeO_3)3 \cdot H_2O$, were obtained.

A procedure for obtaining anhydrous selenites of neodymium by mixing a slightly acidic solution of $NdCl_3$ and a solution of Na_2SeO_3 used in equimolar ratios was suggested in [2].

An acid salt with composition $Nd(HSeO_3)_3 \cdot 2.5H_2O$ was described in [3]. Crystalline acid selenite was synthesized by mixing solutions of $NdCl_3$ (containing NH_3) and H_2SeO_3.

In [4], $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ was synthesized and its X-ray parameters were determined.

Experimental

In order to study the solubility isotherm of the system Nd_2O_3–SeO_2–H_2O at 100°C, 20 samples were prepared by adding 2 g of neodymium selenite to 50 g of H_2SeO_3 with

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different concentrations. The samples were thermostated at 100°C by continuous stirring for 24 h. The samples were then sealed in glass ampules which were placed in air thermostat at 100+0.5°C. The ampules were periodically shaken. In order to determine the time needed to reach equilibrium, the kinetic curves of the equilibrium were obtained. Further samples with the same chemical composition were prepared. Every 10 days, the samples with the same composition were opened periodically and the solid and the liquid phases were subjected to chemical analysis. It was shown that after 30 days the composition of the solid and the liquid phases no longer changed, in other words, chemical equilibrium was reached. Crystallographic equilibrium (proved by studying the changes in the peaks lines on the X-ray patterns) was reached for 3 months. After equilibrium was reached, the samples were taken out of the ampules at the experimental temperature and were filtered through a G4 filter. Both phases were subjected to chemical analysis, and results were used to draw the solubility isotherm of the system by the Gibbs-Rosebom method. The compounds obtained were identified by Schreinemakers' method, chemical analysis and X-ray phase analysis.

The Schreinemakers' method involves graphic measurement of the percentage of the metal oxide and selenium dioxide at the intersection point of the conodes connecting the equilibrium liquid and solid phases in a particular crystallization field. The intersection point gives the percentage of the metal oxide, SeO_2 and H_2O in the ideally dried solid phase. Before chemical analysis, the solid phase was washed with alcohol and ether in a ratio 1:1. Then it was dried at a room temperature for 4 or 5 h and subjected to chemical analysis.

X-ray analyses of 5 samples of the solid phase from each crystallization field of the metal selenite showed that the products from a given crystallization field are identical.

Chemical analysis was carried out by reverse complexometric titration using xylenol orange as an indicator [5], and SeO_3^{2-} ions were analyzed iodometrically and gravimetrically [6]. The concentration of Nd^{3+} in the liquid phase was determined spectrophotometrically on a Spekol-11 apparatus (Germany) using pyrocatechol-violet as an indicator.

X-ray phase analysis was carried out on a URD-6 apparatus (Germany) at Cu anode for K_α-radiation and a nickel filter for β-emission. An OD-102 derivatograph (MOM, Hungary) was used for thermal analyses. The operating conditions were as follows: sample mass 250 mg, placed in metalloceramic crucible; temperature range up to 1200°C; heating rate 10°C min^{-1}; standard substance α-Al_2O_3; chemically pure nitrogen as a medium.

Results and discussion

The results from studying the system Nd_2O_3–SeO_2–H_2O at 100°C are presented in Table 1, and the solubility isotherm is shown in Fig. 1.

In this system four selenites crystallize: $Nd_2(SeO_3)_3 \cdot 4H_2O$, $NdH(SeO_3)_2 \cdot 2H_2O$, $Nd2(SeO_3)_3 \cdot 3H_2SeO_3$ and $Nd_2(Se_2O_5)_3 \cdot H_2SeO_3 \cdot 2H_2O$.

Table 1 Solubility isotherm of the system Nd_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition
	Nd_2O_3	SeO_2	Nd_2O_3	SeO_2	
1	$5.3\cdot10^{-3}$	0.08	42.80	39.02	$Nd_2(SeO_3)_3\cdot4H_2O$
2	$5.2\cdot10^{-3}$	0.87	38.89	37.25	$Nd_2(SeO_3)_2\cdot4H_2O$
3	$7.5\cdot10^{-3}$	0.87	36.88	47.38	$NdH(SeO_3)_2\cdot2H_2O$
4	$8.1\cdot10^{-3}$	5.22	29.50	40.41	$NdH(SeO_3)_2\cdot2H_2O$
5	$8.4\cdot10^{-3}$	7.31	30.19	42.10	$NdH(SeO_3)_2\cdot2H_2O$
6	$8.7\cdot10^{-3}$	15.20	32.90	45.38	$NdH(SeO_3)_2\cdot2H_2O$
7	$8.6\cdot10^{-3}$	24.30	36.10	49.12	$NdH(SeO_3)_2\cdot2H_2O$
8	$9.0\cdot10^{-3}$	29.51	36.52	49.76	$NdH(SeO_3)_2\cdot2H_2O$
9	$1.0\cdot10^{-2}$	39.16	32.12	48.22	$NdH(SeO_3)_2\cdot2H_2O$
10	$1.2\cdot10^{-2}$	42.27	26.30	47.57	$NdH(SeO_3)_2\cdot2H_2O$
11	$2.2\cdot10^{-2}$	47.87	30.85	50.08	$NdH(SeO_3)_2\cdot2H_2O$
12	$2.4\cdot10^{-2}$	49.08	26.03	50.63	$NdH(SeO_3)_2\cdot2H_2O$
13	$2.5\cdot10^{-2}$	50.63	32.78	50.31	$NdH(SeO_3)_2\cdot2H_2O$
14	$2.4\cdot10^{-2}$	50.63	27.50	61.60	$Nd(HSeO_3)_3$
15	$2.6\cdot10^{-2}$	52.12	29.65	58.90	$Nd(HSeO_3)_3$
16	$3.5\cdot10^{-2}$	56.65	26.09	62.79	$Nd(HSeO_3)_3$
17	$3.0\cdot10^{-2}$	60.17	23.17	63.05	$Nd(HSeO_3)_3$
18	$2.7\cdot10^{-2}$	60.17	26.62	65.90	$Nd_2(Se_2O_5)_3\cdot H_2SeO_3\cdot2H_2O$
19	$2.4\cdot10^{-2}$	63.55	20.62	65.51	$Nd_2(Se_2O_5)_3\cdot H_2SeO_3\cdot2H_2O$
20	$2.4\cdot10^{-2}$	69.15	24.48	67.00	$Nd_2(Se_2O_5)_3\cdot H_2SeO_3\cdot2H_2O$
21	$2.6\cdot10^{-2}$	73.20	23.02	68.10	$Nd_2(Se_2O_5)_3\cdot H_2SeO_3\cdot2H_2O$
22	$2.9\cdot10^{-2}$	76.86	25.04	68.54	$Nd_2(Se_2O_5)_3\cdot H_2SeO_3\cdot2H_2O$

The eutonic points have coordinates as follows:

The eutonic point between $Nd_2(SeO_3)_3\cdot4H_2O$ and $NdH(SeO_3)_2\cdot2H_2O$ is at $5.5\cdot10^{-3}$ mass% of Nd_2O_3 and 0.87 mass% of SeO_2. The second eutonic point between $NdH(SeO_3)_2\cdot2H_2O$ and $Nd_2(SeO_3)_3\cdot3H_2SeO_3$ is at $7.8\cdot10^{-2}$ mass% of Nd_2O_3 and 50.63 mass% of SeO_2. The eutonic point between $Nd_2(SeO_3)_3\cdot3H_2SeO_3$ and $Nd_2(Se_2O_5)_3\cdot H_2SeO_3\cdot2H_2O$ is at $9.3\cdot10^{-2}$ mass% of Nd_2O_3 and 60.17 mass% of SeO_2.

The DTA and TG curves of $Nd_2(SeO_3)_3\cdot4H_2O$ in Fig. 2 show that decomposition takes place in stages.

Dehydration of the crystal hydrate starts at 100°C with a minimum at 130°C and takes place in two stages. Anhydrous $Nd_2(SeO_3)_3$ is thermally stable at 810°C. At 600–670°C there is an endothermal peak which is not connected with a mass change in $Nd_2(SeO_3)_3$. The exothermal peak at T=690°C is not associated with a change in the mass of the anhydrous selenite either, but is connected with a change in the size of

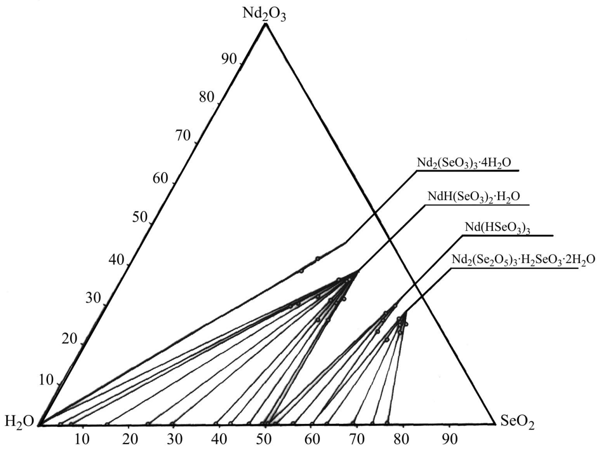

Fig. 1 Solubility isotherm of the system Nd_2O_3–SeO_2–H_2O at 100°C

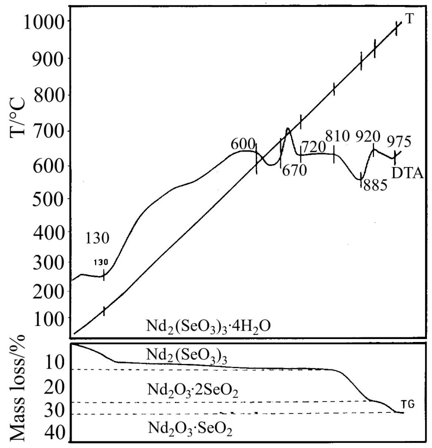

Fig. 2 DTA and TG curves of $Nd_2(SeO_3)_3\cdot 4H_2O$

the peaks in the X-ray pattern. The X-ray data show a change in the crystal lattice of the selenite indicating that a new polymorphous compound results at that temperature. It is stable at 810°C. The endothermal peak at 885°C is associated with the decomposition of the high temperature modification of $Nd_2(SeO_3)_3$ and the formation of oxiselenite by the following scheme:

$$Nd_2(SeO_3)_3 = Nd_2O_3.2SeO_2 + SeO_2$$

At 975–1000°C another mole of SeO_2 is liberated and $Nd_2O_3\cdot SeO_2$ is formed. Pure Nd_2O_3 is obtained at a temperature higher than 1100–1200°C. These transformations were also proved by chemical and X-ray phase analyses.

Figure 3 shows the DTA and TG curves of $NdH(SeO_3)_2 \cdot 2H_2O$. At 130°C the crystal hydrate loses 4 moles of crystallization water and turns into anhydrous hydrogen selenite $Nd_2(SeO_3)_3 \cdot H_2SeO_3$. Mass loss is 8.17 mass% (theoretical calculation is 8.27 mass%). The constitutional water of hydrogen selenite is liberated at 280°C to form tetraselenite $Nd_2(SeO_3)_3 \cdot SeO_2$ (or $Nd_2Se_4O_{11}$). Mass loss is 11.15 mass% (theoretical calculation is 10.84 mass%). Tetraselenite is stable up to 280°C but above this temperature 1 mole of SeO_2 is liberated and normal $Nd_2(SeO_3)_3$ is formed. At 438°C, pyrolysis of the normal salt obtained results in $Nd_2O_3 \cdot 2SeO_2$. Further decomposition of $Nd_2O_3 \cdot 2SeO_2$ takes place at 698°C yielding a stable base salt $Nd_2O_3 \cdot SeO_2$ or $(NdO)_2SeO_3$. This salt is stable up to 1100°C. At 1100–1200°C it loses its last mole of SeO_2 and turns into Nd_2O_3. The scheme of thermal decomposition was also proved by chemical analyses of $NdH(SeO_3)_2 \cdot 2H_2O$ and the phases obtained by modelling the conditions of thermal decomposition as well as by X-ray phase analysis comparing the X-ray data of the phases.

The second acid salt $Nd_2(SeO_3)_3 \cdot 3H_2SeO_3$ decomposes within the acceptable thermal analysis error by a scheme described in detail in [1]. The temperatures after liberation of crystallization water differ from the temperatures reported by Savchenco *et al.* [1] by no more than 100°C.

Figure 4 shows the DTA and TG curves of the acid salt $Nd_2(Se_2O_5)_3 \cdot H_2SeO_3 \cdot 2H_2O$. This salt is stable at 120°C. First, 2 moles of crystallization water are liberated and anhydrous salt is formed at 200°C. Mass loss is 4.50 mass% (theoretical calculation is

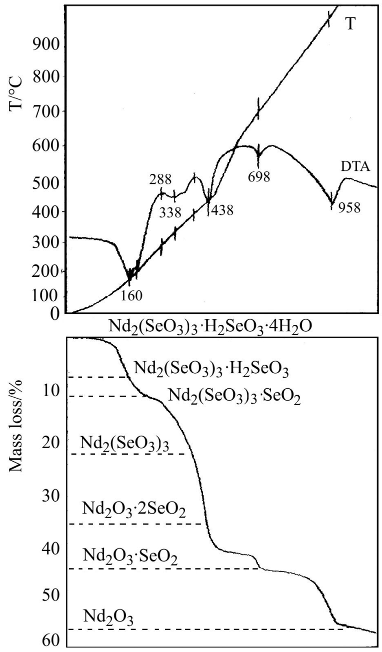

Fig. 3 DTA and TG curves of $NdH(SeO_3)_2 \cdot 2H_2O$

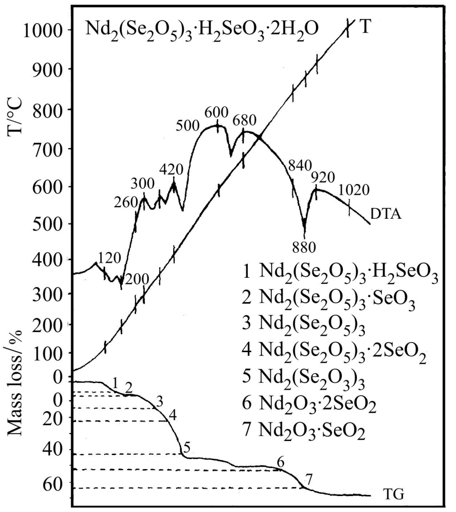

Fig. 4 DTA and TG curves of $Nd_2(Se_2O_5)_3 \cdot H_2SeO_3 \cdot 2H_2O$

3.08 mass %). This difference may be explained by the fact that the acid salt obtained has a very well developed surface and because of that it contains adsorbed water. At 200–260°C the acid salt liberates the constitutional water and turns into heptaselenite with composition $Nd_2(Se_2O_5)_3 \cdot SeO_2$. At 300–360°C the mass loss corresponds to the liberation of 1 mole of SeO_2 resulting in hexaselenite with composition $Nd_2(Se_2O_5)_3$. At 400°C the next mole of SeO_2 is liberated and pentaselenite with composition $Nd_2(SeO_3)_3 \cdot 2SeO_2$ is obtained. The mass loss is 22.20 mass% (theoretical calculation is 23.63 mass%). At 420–500°C more SeO_2 is liberated and the mass loss is 43.00 mass%. This transformation corresponds to the formation of normal salt $Nd_2(SeO_3)_3$. At 800–840°C 1 mole of SeO_2 is liberated and oxiselenite with composition $Nd_2O_3 \cdot 2SeO_2$ is formed. In the temperature interval 880–920°C another mole of SeO_2 is liberated and the other oxiselenite with composition $Nd_2O_3 \cdot SeO_2$ is obtained. The sample was heated up to 1020°C but complete liberation of selenium dioxide did not take place. Mass loss is 70.70 mass% (71.17 mass% is the mass loss for the complete liberation of SeO_2 and the formation of a pure phase Nd_2O_3).

For the three compounds, all intermediate phases from the thermolysis were subjected to chemical and X-ray phase analyses after they were isolated in the pure state, and the data obtained confirmed the identity of the separate phases.

Conclusions

The solubility isotherm of the system Nb_2O_3–SeO_2–H_2O at 100°C was studied. The equilibrium phases of the system were identified by the Scheinemakers' method and by chemical and X-ray analysis after they were isolated in the pure state. All compounds of this system were subjected to derivatograph analysis and mechanism of their decomposition was described.

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