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STUDY OF THE SYSTEM Pr_2O_3–SeO_2–H_2O AT 100°C AND THE PROPERTIES OF THE COMPOUNDS OBTAINED

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Abstract

The solubility of the system Pr_2O_3–SeO_2–H_2O at 100°C was studied. The fields of crystallization of $Pr_2(SeO_3)_3{\cdot}H_2O$, $PrH(SeO_3)_2$, $Pr(HSeO_3)_3$ were established. The compounds obtained were identified by means of chemical, X-ray and thermal analysis. The thermal decomposition of $Pr_2(SeO_3)_3{\cdot}H_2O$, $PrH(SeO_3)_2$, and $Pr(HSeO_3)_3$ was determined.

Keywords: praseodymium selenites, reaction mechanisms, solubility isotherm, X-ray pattern

Introduction

The selenites of the rare earths (praseodymium in particular) are used to synthesize selenides, which find application as semiconducting materials. They are also used as initial compounds in the production of luminophors, pigments, etc. The method of obtaining selenides by reduction of selenites of the rare-earth elements has the advantage of taking place quickly and at relatively low temperatures. The composition of the reduction products may vary depending on the composition of the reaction gas medium [1–3].The data concerning the selenites of praseodymium are rather scarce [4–11]. Authors reported about the synthesis of normal and acid selenites of praseodymium at fixed concentrations of the initial solutions. No studies were carried out for all concentration intervals. No answer was given to the question whether these compounds are the only possible ones in the three-component system Pr–Se–O.

Experimental

High-purity Pr_2O_3 (99.99 mass%) and SeO_2, obtained by the authors by oxidation of high-purity Se with nitric acid, were used to prepare the system Pr_2O_3–SeO_2–H_2O at 100°C. SeO_2 was subjected to additional triple sublimation to achieve better purifi-

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cation. According to spectral analysis data the product obtained has the purity of 99.999% (the calculation was made on the concentration of 10 impurities).

In order to study the system Pr_2O_3–SeO_2–H_2O at 100°C, 25 samples were prepared each containing 2 g of Pr_2O_3 and varying concentrations of selenious acid (from 0 to 85 mass%). The ampoules were sealed and thermostated in an air thermostat at 100±0.5°C, and were periodically shaken to ensure further precrystallization. To determine the necessary time for reaching chemical equilibrium, kinetic curves were obtained. For that purpose, more ampoules with the same composition were prepared and opened periodically. Equilibrium was reached when chemical analysis showed that the liquid and the solid phases did not change their composition. It was considered that crystallographic equilibrium was established when the peak intensities and the interplanar distances in the X-ray patterns no longer changed. After chemical and X-ray equilibrium was reached, the liquid and the solid phases were separated at the experimental temperature and subjected to chemical, thermal and X-ray phase analyses.

Chemical analysis was made complexonometrically [12] for Pr^{3+} as Pr_2O_3 using xylenol orange as an indicator, and iodometrically and gravimetrically [13] for selenite ions. The concentration of Pr^{3+} ions in the liquid phase was determined spectrophotometrically on a Specol-11 apparatus (Karl Zeiss, Germany) [14].

X-ray analysis was carried out on a URD-6 apparatus (Germany) at Cu anode for Kα-emission and a nickel filter for β-emission. An OD-102 derivatograph (MOM, Hungary) was used for thermal analysis by heating the phases from 25 to 1000°C at a rate of 5°C min^{-1} in metal ceramic crucibles; α-Al_2O_3 was used as a standard substance.

Results and discussion

The results from studying the system Pr_2O_3–SeO_2–H_2O are presented in Fig. 1 and Table 1. Three salts were formed in the system – one normal and two acid ones. In the concentration interval 0.52–3.24 mass% SeO_2 in the liquid phase, a normal salt is ob-

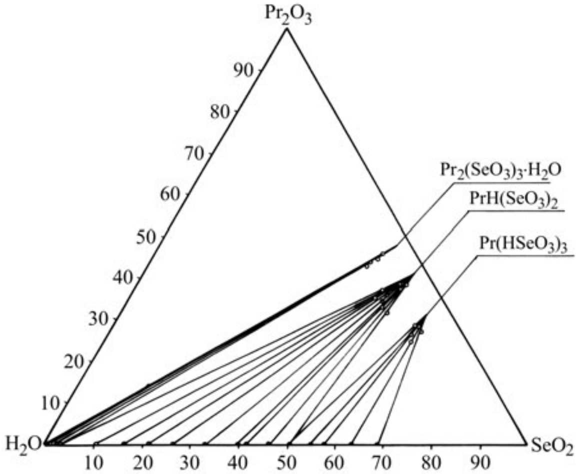

Fig. 1 Solubility isotherm of the system Pr_2O_3–SeO_2–H_2O at 100°C

tained with composition $Pr_2(SeO_3)_3 \cdot H_2O$. In the interval 3.24–50.48 mass% SeO_2 in the liquid phase, the acid salt $PrH(SeO_3)_2$, $[Pr(SeO_3)(HSeO_3)]$ is formed, and at 50.48–68.74 mass% SeO_2, the salt $Pr(HSeO_3)_3$ is formed. The phases obtained were identified by the Schreinemakers' method and also by chemical and X-ray phase analyses after isolating them in the pure state.

Table 1 Solubility isotherm of the system Pr_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase, mass%		Solid phase, mass%		Formula composition
	Pr_2O_3	SeO_2	Pr_2O_3	SeO_2	
1.	$5.2 \cdot 10^{-3}$	0.52	46.20	46.50	$Pr_2(SeO_3)_3 \cdot H_2O$
2.	$6.0 \cdot 10^{-3}$	1.08	44.05	45.48	$Pr_2(SeO_3)_3 \cdot H_2O$
3.	$6.4 \cdot 10^{-3}$	2.50	46.35	45.00	$Pr_2(SeO_3)_3 \cdot H_2O$
4.	$7.0 \cdot 10^{-3}$	3.24	45.06	46.40	$Pr_2(SeO_3)_3 \cdot H_2O$
5.	$8.1 \cdot 10^{-3}$	3.24	38.10	50.52	$PrH(SeO_3)_2$
6.	$8.7 \cdot 10^{-3}$	10.34	33.89	47.60	$PrH(SeO_3)_2$
7.	$8.9 \cdot 10^{-3}$	16.10	35.90	50.20	$PrH(SeO_3)_2$
8.	$9.3 \cdot 10^{-3}$	22.26	38.47	54.06	$PrH(SeO_3)_2$
9.	$9.4 \cdot 10^{-3}$	26.50	35.55	52.20	$PrH(SeO_3)_2$
10.	$9.8 \cdot 10^{-3}$	33.70	34.60	53.70	$PrH(SeO_3)_2$
11.	$1.2 \cdot 10^{-2}$	39.60	37.55	55.08	$PrH(SeO_3)_2$
12.	$1.8 \cdot 10^{-2}$	41.42	32.60	53.00	$PrH(SeO_3)_2$
13.	$2.5 \cdot 10^{-2}$	46.20	38.25	55.56	$PrH(SeO_3)_2$
14.	$3.0 \cdot 10^{-2}$	50.48	32.05	55.06	$PrH(SeO_3)_2$
15.	$4.6 \cdot 10^{-2}$	50.48	29.10	60.14	$Pr(HSeO_3)_3$
16.	$4.8 \cdot 10^{-2}$	55.00	27.15	62.51	$Pr(HSeO_3)_3$
17.	$5.2 \cdot 10^{-2}$	57.71	28.62	63.05	$Pr(HSeO_3)_3$
18.	$5.8 \cdot 10^{-2}$	63.48	25.48	63.54	$Pr(HSeO_3)_3$
19.	$6.4 \cdot 10^{-2}$	68.74	27.63	64.08	$Pr(HSeO_3)_3$

Well-formed crystals of $PrH(SeO_3)_2$ were identified by determining their crystallographic parameters: a=7.049, b=8.354, c=19.012 Å, Dx=4.697 g cm^{-3}. The compound crystallizes in an orthorhombic system with a space group *Pbc*21.

Figure 2 shows the derivatogram of $Pr_2(SeO_3)_3 \cdot H_2O$. The compound is thermally stable at 250°C. At 390°C crystallization water is liberated, and anhydrous praseodymium selenite is formed. The mass loss indicated by the TG curve is 2.50 mass% (theoretical calculation for this transition is 2.64 mass%). Chemical analysis gave the composition of Pr_2O_3 as 49.66 mass%, and that of SeO_2 as 50.23 mass% (theoretical calculations for Pr_2O_3 and SeO_2 are 49.47 and 50.33 mass%, respectively). In the temperature interval 600–640°C, $Pr_2(SeO_3)_3$ decomposes, 1 mole of SeO_2 is liberated

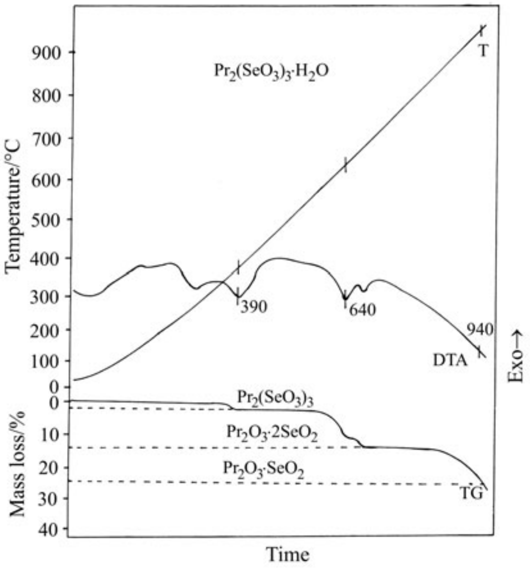

Fig. 2 Thermoanalytical curves of $Pr_2(SeO_3)_3 \cdot H_2O$

and oxoselenite $Pr_2O_3 \cdot 2SeO_2$ is obtained. The mass loss resulting from this transition is 17.99 mass% (theoretical calculation is 18.94 mass%). Chemical analysis gave the composition of Pr_2O_3 as 59.82 mass% and that of SeO_2 as 40.33 mass% (theoretical calculations for Pr_2O_3 is 59.78 mass% and that for SeO_2 is 40.22 mass%). The endothermal peak at 700°C corresponds to liberation of another mole of SeO_2 and transformation of the compound into oxoselenite with composition $Pr_2O_3 \cdot SeO_2$. However, at 940°C, which is the temperature at which the sample was heated for derivatograph analysis, the mass loss due to thermal decomposition is 25.00 mass%, while the theoretically calculated mass loss is 35.25 mass%, which shows that the process is incompleted. SeO_2 was completely liberated and a pure phase of Pr_2O_3 was obtained in the temperature interval 1000–1200°C.

Figure 3 shows the TG, DTA, T curves of $PrH(SeO_3)_2$. This compound is thermally stable at 150°C. In the temperature interval 180–250°C adsorbed and constitutionally bounb water is liberated and $PrH(SeO_3)_2$ turns into tetraselenite $Pr_2Se_4O_{11}$. The mass loss due to this transition is 3.33 mass% (theoretical calculation is 2.27 mass%). Chemical analysis gave the composition of Pr_2O_3 as 42.59 mass%, and that of SeO_2 as 57.40 mass% (theoretical calculation for Pr_2O_3 is 42.63 mass%, and that for SeO_2 is 57.37 mass%). In the temperature interval 395–440°C, 1 mole of SeO_2 is liberated, and tetraselenite is transformed into a normal salt $Pr_2(SeO_3)_3$. The total mass loss due to these transitions is 22.33 mass% (theoretical calculation is 16.29 mass%). The difference between the experimental mass loss and the theoretical one is due to presence of small amount of adsorption water. At 450°C another mole of SeO_2 is liberated and the basic salt $Pr_2O_3 \cdot 2SeO_2$ is formed. The mass loss according to the data from TG curve is 33.33 mass% (theoretical calculation is 33.47 mass%). Chemical analysis gave the composition of Pr_2O_3 as 59.82 mass% and that of SeO_2 as 40.28 mass% (theoretical cal-

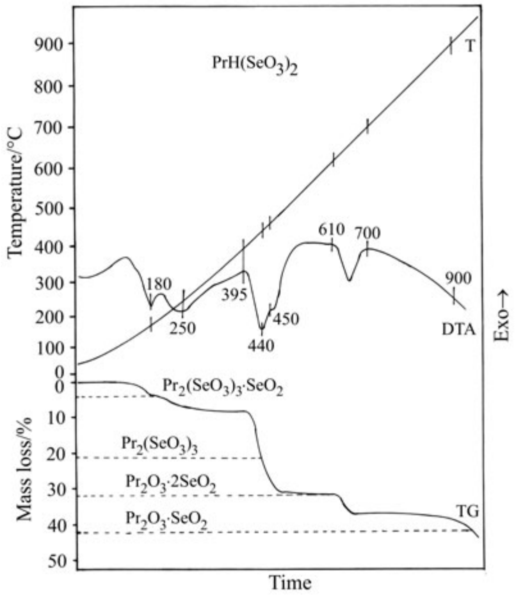

Fig. 3 TG, DTA, T curves of $PrH(SeO_3)_2$

culation for Pr_2O_3 is 59.78 mass% and that for SeO_2 is 40.22 mass%). In the temperature interval 610–700°C yet another mole of SeO_2 is liberated, and a second basic salt $Pr_2O_3{\cdot}SeO_2$ is obtained. The total mass loss due to all decomposition reactions so far is 42.00 mass% (theoretical calculation is 44.33 mass%). X-ray phase analysis data show that the main phase obtained in this transformation is $Pr_2O_3{\cdot}SeO_2$. Insignificant amount of $Pr_2O_3{\cdot}2SeO_2$ is also present. Complete liberation of SeO_2 takes place at 1100–1200°C, and Pr_2O_3 and insignificant quantities of Pr_6O_{11} are obtained.

The compound $Pr(HSeO_3)_3$ is thermally stable at 300°C. Dehydration with liberation of constitutional water takes place at higher temperatures. The mass loss due to this transformation is 5.17 mass% (theoretical calculation is 5.14 mass%). Chemical analysis gave the composition of Pr_2O_3 as 33.20 mass% and that of SeO_2 as 66.73 mass% (theoretical calculation is 33.13 mass% for Pr_2O_3, and 66.87 mass% for SeO_2). At 460°C two moles of SeO_2 are liberated and the initial selenite turns into $Pr_2(SeO_3)_3{\cdot}SeO_2$. The mass loss due to this transformation is 26.34 mass% (theoretical calculation is 26.28 mass%). At 600°C yet another mole of SeO_2 is liberated and the compound is transformed into a normal salt $Pr_2(SeO_3)_3$. The mass loss in this transformation is 36.90 mass% (theoretical calculation is 36.86 mass%). Chemical analysis gave the composition of Pr_2O_3 as 49.83 mass%, and that of SeO_2 as 50.25 mass% (theoretical calculation for Pr_2O_3 is 49.77 mass% and that for SeO_2 is 50.23 mass%). The selenite obtained has stoichiometric composition.

Further decomposition of $Pr_2(SeO_3)_3$ takes place by the scheme of the normal salt described by us. The suggested mechanism of thermal decomposition of $Pr(HSeO_3)_3$ is in good agreement with the one described in [15, 16].

Identification of the intermediate phases obtained in the course of thermal decomposition of the three salts was confirmed by chemical and X-ray phase analyses of these products by modeling the conditions of thermal analysis. This paper represents continuation of our investigation on the three-component systems of the type Ln_2O_3–SeO_2–H_2O [17–21].

Conclusions

- The solubility isotherm of the system Pr_2O_3–SeO_2–H_2O at 100°C was studied. It was proved that three salts are formed in the system, namely: $Pr_2(SeO_3)_3{\cdot}H_2O$, $PrH(SeO_3)_2$ and $Pr(HSeO_3)_3$.
- The parameters of the crystal lattice of $PrH(SeO_3)_2$ were determined.
- Complex thermal analysis by means of the derivatograph of the compounds obtained was made. Furthermore, the intermediate phases and the mechanism of the decomposition were studied.

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