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SOLUBILITY ISOTHERM AND THERMAL ANALYSIS OF THE SELENITES OF THE THREE-COMPONENT SYSTEM La_2O_3–SeO_2–H_2O AT 100°C

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Abstract

The solubility isotherm of the system La_2O_3–SeO_2–H_2O at 100°C was studied. The compounds of the three-component system were identified by the Schreinemakers method as well as by chemical and X-ray phase analyses. Simultaneous TG and DTA analyses of all compounds of the system were made by using a derivatograph. The mechanism of thermal decomposition was described.

Keywords: isotherm, lanthanum selenites, phase transformations, reaction mechanisms, selenites, solubility, X-ray structure determination

Introduction

In 1875 Nilson [1] first obtained intermediate and acid selenites of lanthanum. Later, Espil [2] obtained anhydrous $La_2(SeO_3)_3$. The solubility of lanthanum selenites was studied [3]. Some data concerning the thermal decomposition of the rare earth selenites including those lanthanum are also available [4]. Other authors [5] described the synthesis of lanthanum selenites by mixing aqueous solutions of H_2SeO_3 with solutions of lanthanum acetate or chloride. Synthesis was carried out using different excess of selenious acid in the temperature range from room temperature to 60°C and also under static conditions by mixing the solutions. The thermodynamic properties of lanthanum selenites were studied [6, 7]. The heat of formation of lanthanum selenites in hydrochloric acid was determined in a calorimeter under non-isothermal conditions. Crystallographic characteristics of $LaH(SeO_3)_2$ were also given [8]. Nowadays de Pedro *et al.* [9] synthesizes anhydrous selenites of lanthanum under the method of solid phase synthesis defining the parameters of the crystal lattice of $La_2Se_3O_9$ and La_2SeO_5 [10].

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Experimental

25 samples were prepared to study the system. For that purpose, $La_2(SeO_3)_3$ was obtained from high-purity lanthanum chloride and sodium selenites. Razotherm glass ampoules were used and each was filled with 2 g of $La_2(SeO_3)_3$ and with H_2SeO_3 in various concentrations (from 0 to 80 mass%). The ampoules were sealed and placed in an air thermostat at 100±0.5°C. They were periodically shaken. After chemical and X-ray phase equilibrium was reached, which was proved by chemical and X-ray phase analyses by using a method described in reference [11], the system was studied. For that purpose, the ampoules were opened, the liquid and solid phases were separated at the experimental temperature and were subjected to chemical analysis. La_2O_3 was analysed by compleximetric titration with 0.05 M solution of complexonIII using xylenolorange as an indicator [12]. The concentration of SeO_3^{2-} ions was iodometrically or gravimetrically determined as elementary selenium by the technique described in [13]. The concentration of La^{3+} ions in the liquid phase was spectrophotometrically determined with a Specol-11 apparatus (Carl Zeiss, Jena, Germany) using 8-hydroxyquinoline as an indicator. X-ray phase analysis was carried out with a URD-6 apparatus (Germany) using Cu anode for K_α-emission and a nickel filter for β-emission. An OD-102 derivatograph (MOM, Hungary) was used for simultaneous TG and DTA analyses. TG and DTA curves were obtained in the temperature range up to 1000°C at a heating rate of 5°C min^{-1} and sample mass 250 mg. Crystallooptical analysis was made with a Dokuval apparatus (Carl Zeiss, Jena, Germany).

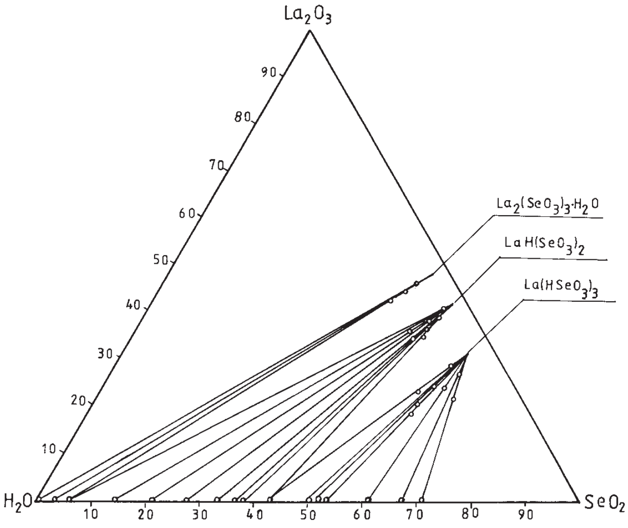

Fig. 1 Solubility isotherm of the system La_2O_3–SeO_2–H_2O at 100°C

Results and discussion

The results of studying the system La_2O_3–SeO_2–H_2O at 100°C are presented in Table 1 and Fig. 1. In this system, one normal and two acid salts were formed. The normal salt was obtained in the concentration range from 0 to 6.50 mass% SeO_2 in the liquid phase. In the interval of 6.66–42.90 mass% SeO_2 in the liquid phase, an acid salt with composition $LaH(SeO_3)_2$ was formed. At a higher concentration, an acid salt with composition $La(HSeO_3)_3$ was obtained. The eutonic point of those two salts is at 42.90 mass% SeO_2 and $4.5\cdot10^{-3}$ mass% La_2O_3. The above conclusions concerning the number and the type of the salts in the system were made on the basis of the Schreinemakers method (the solubility isotherm) and also by chemical and X-ray phase analyses of the solid phases.

A new acid salt, $La_2(SeO_3)_3\cdot3H_2SeO_3$, not described in literature so far, was formed. Therefore, the volumes of the complexing agent and the addenda make it possible, at the corresponding high temperature, to increase the coordination number and the addition of a greater number of addenda, so that a second acid salt was obtained.

Table 1 Solubility isotherm of the system La_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition
	La_2O_3	SeO_2	La_2O_3	SeO_2	
1	$2.1\cdot10^{-2}$	0.85	4.02	46.60	$La_2(SeO_3)_3\cdot H_2O$
2	$2.7\cdot10^{-2}$	3.50	45.05	45.40	$La_2(SeO_3)_3\cdot H_2O$
3	$2.8\cdot10^{-2}$	6.66	41.67	43.85	$La_2(SeO_3)_3\cdot H_2O$
4	$3.7\cdot10^{-2}$	6.66	40.50	54.48	$LaH(SeO_3)_2$
5	$3.2\cdot10^{-2}$	14.26	35.38	50.12	$LaH(SeO_3)_2$
6	$3.5\cdot10^{-2}$	21.49	38.62	52.63	$LaH(SeO_3)_2$
7	$2.0\cdot10^{-2}$	27.69	39.42	55.01	$LaH(SeO_3)_2$
8	$2.1\cdot10^{-2}$	33.30	34.38	51.52	$LaH(SeO_3)_2$
9	$2.0\cdot10^{-2}$	36.70	37.00	52.48	$LaH(SeO_3)_2$
10	$1.9\cdot10^{-2}$	38.17	39.10	55.08	$LaH(SeO_3)_2$
11	$1.9\cdot10^{-2}$	42.90	34.60	54.10	$LaH(SeO_3)_2$
12	$1.5\cdot10^{-2}$	42.90	28.54	61.58	$LaH(SeO_3)_3$
13	$1.1\cdot10^{-2}$	50.03	25.94	61.50	$LaH(SeO_3)_3$
14	$9.0\cdot10^{-1}$	52.03	20.46	59.50	$LaH(SeO_3)_3$
15	$8.2\cdot10^{-1}$	53.72	18.24	62.79	$LaH(SeO_3)_3$
16	$8.0\cdot10^{-1}$	61.13	25.30	63.46	$LaH(SeO_3)_3$
17	$7.8\cdot10^{-1}$	67.50	26.82	64.80	$LaH(SeO_3)_3$
18	$6.5\cdot10^{-1}$	71.18	21.20	65.69	$LaH(SeO_3)_3$

Figure 2 shows the simultaneous TG and DTA curves of $La_2(SeO_3)_3\cdot H_2O$. The compound is thermally stable from room temperature to 300°C. At 320–380°C crystal water is liberated and the salt is transformed into anhydrous $La_2(SeO_3)_3$. The mass loss is 3.40 mass% (theoretical calculation is 2.60 mass%). Chemical analysis gave the concentration of La_2O_3 as 49.55 and that of SeO_2 as 50.48 mass% (theoretical calculations were 49.46 and 50.54 mass%, respectively). $La_2(SeO_3)_3$ is thermally stable at 400°C. At 540–600°C one mole of SeO_2 is liberated, and $La_2(SeO_3)_3$ is transformed into oxyselenite $La_2O(SeO_3)_2$. The mass loss is 19.56 mass% (theoretical calculation is 19.06 mass%). Chemical analysis of the product obtained in that transformation gave the concentration of La_2O_3 as 59.58 and that of SeO_2 as 40.63 mass% (theoretical calculations are 59.49 and 40.52 mass%, respectively). The phase obtained is thermally stable at 840°C. At 900–960°C another mole of SeO_2 is liberated and $La_2O(SeO_3)_2$ is transformed into oxyselenite $(LaO)_2SeO_3$. The mass loss corresponding to that transformation is 35.90 mass% (theoretical calculation is 35.45 mass%). Chemical analysis of a product obtained at 950°C gave the concentration of La_2O_3 as 74.77 and that of SeO_2 as 25.33 mass% (theoretical calculations are 74.60 and 25.40 mass%, respectively). The endothermal peak in the temperature range

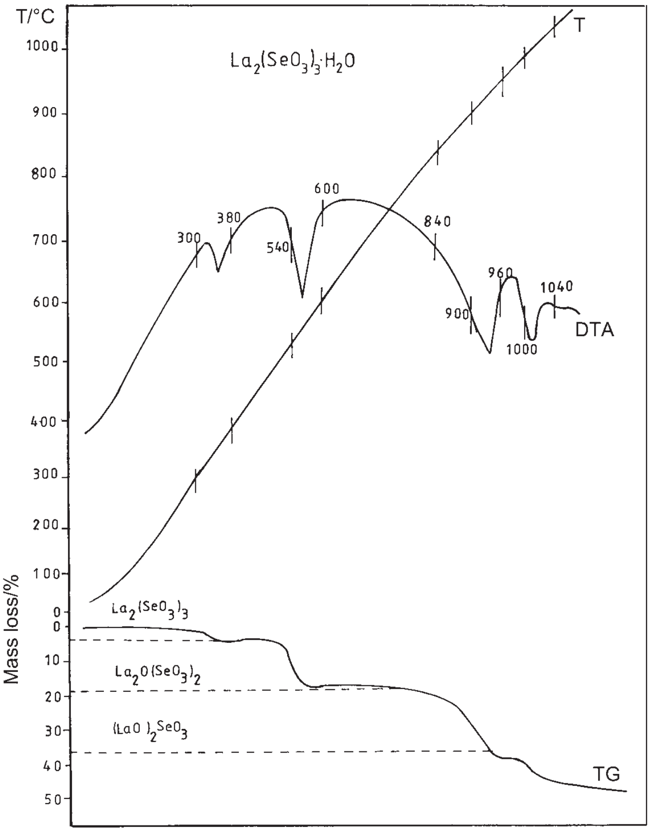

Fig. 2 Simultaneous TG and DTA curves of $La_2(SeO_3)_3 \cdot H_2O$

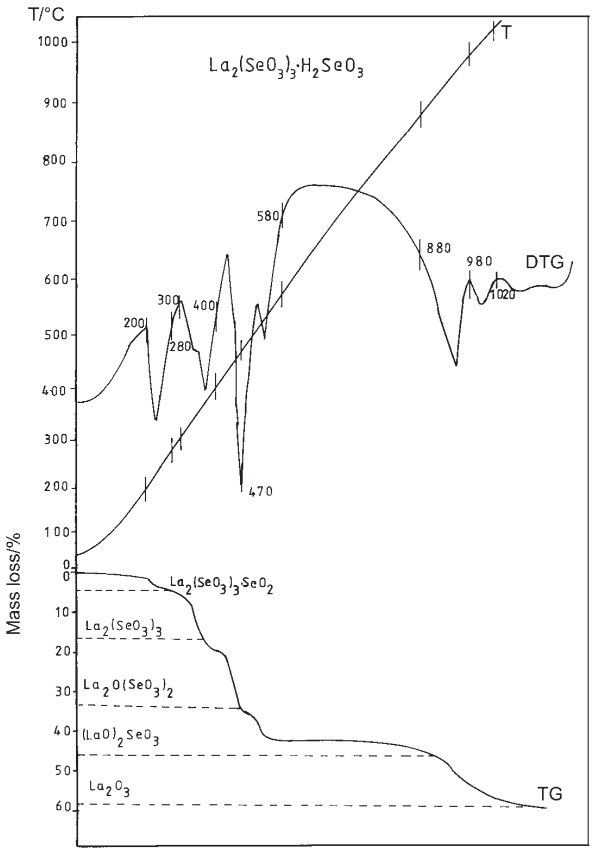

Fig. 3 Simultaneous TG and DTA curves of $LaH(SeO_3)_2$

1000–1040°C corresponds to the liberation of the last mole of SeO_2 and the formation of La_2O_3. At 1100°C, the SeO_2 was not liberated completely and a pure phase La_2O_3 was not obtained. The mass loss during that transformation is 48.50 mass% (theoretical calculation is 51.85 mass%). X-ray phase analysis shows that the final product is a mechanical mixture in which La_2O_3 is the prevailing phase.

Figure 3 gives simultaneous TG and DTA curves of $La_2(SeO_3)_3{\cdot}H_2SeO_3$, (or $LaH(SeO_3)_2$). The compound is thermally stable from room temperature to 200°C. At 200–280°C it loses adsorption water and turns into tetraselenite $La_2(SeO_3)_3{\cdot}SeO_2$ (or $La_2Se_4O_{11}$). The mass loss is 3.20 mass% (theoretical calculation is 2.28 mass%). From 300 to 400°C a two-stage liberation of one mole of SeO_2 takes place, and $La_2(SeO_3)_3$ is obtained. The mass loss in that transformation is 17.70 mass% (theoretical calculation is 16.37 mass%). The chemical analysis gave the concentration of La_2O_3 as 49.36 and that of SeO_2 as 50.59 mass%. At 470–570°C another mole of SeO_2 is liberated and $La_2O(SeO_3)_2$ is obtained. The chemical analysis gave the concentration of La_2O_3 is 59.53 and that of SeO_2 as 40.38 mass% (theoretical calculation is 59.46 and 40.38 mass% respectively). This oxyselenite is thermally stable until 880°C. At higher temperature (880–980°C) one mole of SeO_2 is liberated, and the compound is transformed into $(LaO)_2SeO_3$. The mass loss is 46.12 mass% (theoretical calculation is 44.54 mass%). The chemical analysis gave the concentration of La_2O_3 as 74.72 and that of SeO_2 as 25.34 mass% (theoretical calculation is 74.60 and 25.40 mass%, respectively), which theoretically corresponds to that transition. At 980–1020°C the mass loss is 58.02 mass% (theoretical calculation is 58.46 mass%). The analysis of the final product gave the concentration of La_2O_3 as 99.27 mass%.

The third compound $La_2(SeO_3)_3\cdot 3H_2SeO_3$ {or $La(HSeO_3)_3$}, decomposes at 250–280°C liberating 3 moles of constitutional water and turns into hexaselenite $La_2(SeO_3)_3\cdot 3SeO_2$ (or $La_2Se_6O_{15}$). At 380–420°C two moles of SeO_2 are liberated, and tetraselenite $La_2(SeO_3)_3\cdot SeO_2$ (or $La_2Se_4O_{11}$) is obtained. One mole of SeO_2 is liberated and selenites is formed at 510°C. Within thermal analysis accuracy, the temperatures and the mechanism of thermal decomposition of $La_2(SeO_3)_3\cdot 3H_2SeO_3$ suggested here are in good agreement with those described in references [14, 15].

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

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