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THERMAL BEHAVIOR OF SAMARIUM PHOSPHATE MONOHYDRATE IN THE SOLID STATE

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ABSTRACT

Some properties of samarium orthophosphate hydrate were determined by means of TG–DTA, infrared absorption spectra and X-ray diffraction measurements. The results are (1) samarium orthophosphate prepared by precipitation method was formulated as $SmPO_4 \cdot H_2O$, and (2) the salt readily lost its water of hydration at 57 and 183° C, and changed from the hexagonal to the monoclinic form at about 1000° C in an argon atmosphere.

INTRODUCTION

Considerable progress has been made in the chemistry of rare earth phosphates in recent years. First, the metal phosphates are suitable for further development of the chemistry of inorganic polymers. Second, they are of technical interest as starting materials (particularly the rare earth phosphates) for obtaining laser devices, because of their properties characterized by rather high luminescent quantum yield [1], and as catalysts for hydrolysis of monochlorbenzene to phenol [2], and for dehydration of butanol to butylene [3]. As a part of a general study of lanthanoid chelates in progress in this laboratory, we investigated the electrochemical properties of this class of compounds. Slightly soluble electrodes which are made of lanthanoid phosphates, particularly in samarium phosphate, reveal selectively in an activated form to phosphate ion. The thermal decomposition of metal phosphates has been widely investigated: Thilo [4], Griffith [5a], and Tananaev [5b] have reviewed the structural chemistry, and the physical and chemical properties of the condensed phosphates, respectively. Much work is being done on the thermal decomposition of metal phosphates in order to understand the nature of the decomposition products. However, there is no

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detailed report concerning the behavior on the thermal treatment of lanthanoid phosphates. In this study, the thermal properties of samarium phosphate were investigated by the techniques of TG (thermogravimetric analysis), DTA (differential thermal analysis), infrared absorption spectra, and X-ray diffraction.

EXPERIMENTAL

Materials

Samarium phosphate was precipitated by two different processes. In the first method, a dilute solution (0.6 mol) of potassium dihydrogen phosphate, KH_2PO_4, was added slowly to an aqueous solution of samarium nitrate (0.1 mol) at room temperature, until there was a slight excess of KH_2PO_4. The precipitate so formed was allowed to stand overnight, and then was washed about 20 times with dilute phosphoric acid (pH 3.5) to prevent the formation of samarium hydroxide, until the quantities of potassium ion in the filtrate did not exceed 0.5 ppm. The formation of samarium hydroxide was prevented by keeping the pH below 5, on the basis of the titration curve against a suspension of samarium oxide with a solution of hydrochloric acid (as shown in Fig. 1). Therefore, the precipitate obtained was washed with a solution of dilute phosphoric acid of pH 3.5. In the second method, samarium phosphate was prepared by dissolving a suspension of samarium oxide with double the molar quantity of the phosphoric acid (1:1 mol). The

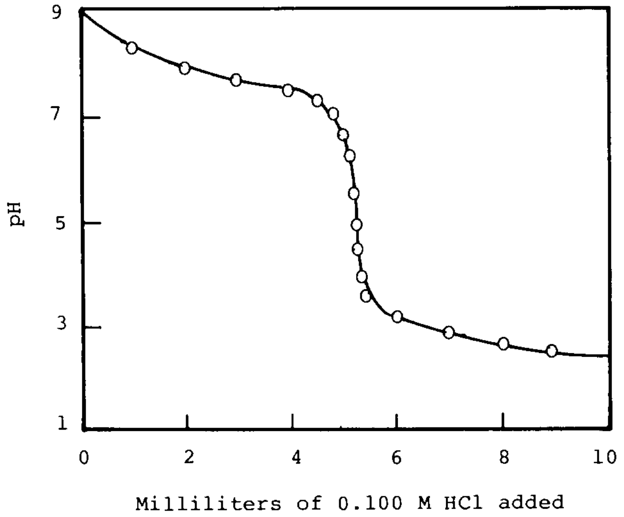

Fig. 1. Curve for titration of a suspension of Sm_2O_3 by 0.100 M HCl.

precipitate was then washed with dilute phosphoric acid until the filtrate became pH 3.5. The precipitates prepared by the different method were centrifuged and then dried in a vacuum desiccator for several days.

The samarium contents of both phosphates described above were determined by complexometric titrations with EDTA using BT indicator. The phosphorus contents and the numbers of molecules of water of hydration in one samarium phosphate molecule were determined using a colorimetric method and TG measurements, respectively. The results of the elemental analysis agreed with those calculated, and the formula may be represented by $SmPO_4 \cdot H_2O$. Since the samples prepared by the first and the second methods follow the same thermal behavior, the former sample was hereafter used for this study.

Measurements

The TG and DTA curves were simultaneously recorded with a Shinku Riko TGD-3000RH differential thermal microbalance at a heating rate of $5\,^{\circ}C\ min^{-1}$ in an atmosphere of argon flowing at $50\ ml\ min^{-1}$. Samples about 10 mg were weighed into a platinum crucible and measured, using α-alumina as a reference material. Infrared absorption spectra were measured from 4000 to $650\ cm^{-1}$ by the KBr disk method with a Hitachi 215 spectrophotometer. The powder X-ray diffractograms were obtained with a Rigaku Denki DS X-ray diffractometer using nickel-filtered Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION

Thermal decomposition process

The TG and DTA curves of samarium phosphate monohydrate ($SmPO_4 \cdot H_2O$) in a flowing argon atmosphere are shown in Fig. 2. The number of dehydration stages n', the initial dehydration temperature t_i, the DTA peak temperature t_m, the weight loss at each dehydration step ΔW, and the moles of water molecules lost N are listed in Table 1. The dehydration reaction proceeded in two steps with DTA endothermic peaks at 57 and at 183 °C. The weight loss associated with the first dehydration step (2.74%) was somewhat less than that expected (3.42%) for the step of $SmPO_4 \cdot H_2O$ to $SmPO_4 \cdot \frac{1}{2}\ H_2O$, and the weight loss in the second dehydration step (3.98%) was somewhat more than the expected value. It may be suggested that the two steps overlap. Water molecules in hydrates can be classified for convenience into two types: (1) the relatively loose bound water, that is, physically bound water (adsorbed water) that is released at a relatively low temperature, and (2) chemically bound water (water of crystallization, constitutional

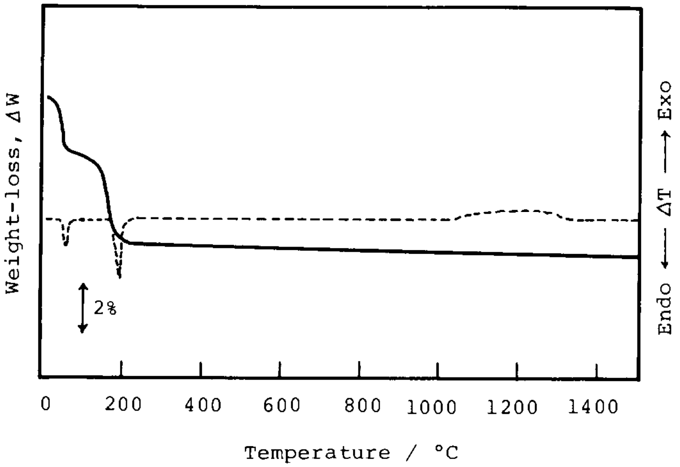

Fig. 2. TG–DTA curves of samarium phosphate hydrate in a flowing argon atmosphere. Heating rate of furnace, 10 °C min^{-1}; ———, TG; — — —, DTA.

water, coordinated water, lattice water, and hydrogen-bond water) that is released at a higher temperature [6]. The thermal dehydration and decomposition of solids are in general very complex processes, which take place with a breaking of bonds and a destruction of the crystal lattice, followed by the formation of a new solid product, along with the appearance of crystallization centers, the growth of these centers, adsorption–desorption gaseous products, and diffusion of gaseous products [7].

In order to determine the amount of physically adsorbed water in $SmPO_4 \cdot H_2O$, the weight increase of the sample heated for 2 h at 120 °C was measured as a function of time under the saturated vapor pressure of water at 20 °C. It required 20 h to reach a constant weight (Fig. 3) and, within experimental error, the final weight was equal to the weight of the original sample, $SmPO_4 \cdot H_2O$.

The infrared spectra of the heated samples at various temperatures are shown in Fig. 4. The adsorption bands around 3400 and around 1650 cm^{-1} are known for the stretching modes of hydroxyl group and the deformation

TABLE 1

Thermal dehydration of samarium phosphate hydrate in a flowing argon atmosphere. The number of dehydration stages n'; initial dehydration temperature t_i; DTA peak temperature t_m; weight loss ΔW; moles of water molecules lost N

Phosphate	Atmosphere	n'	Dehydration				
			t_i (°C)	t_m (°C)	ΔW_{obsd} (%)	ΔW_{calcd} (%)	N
$SmPO_4 \cdot H_2O$	Ar	1	48	57	2.74	3.42	$0.5H_2O$
		1	136	183	3.98	3.42	$0.5H_2O$

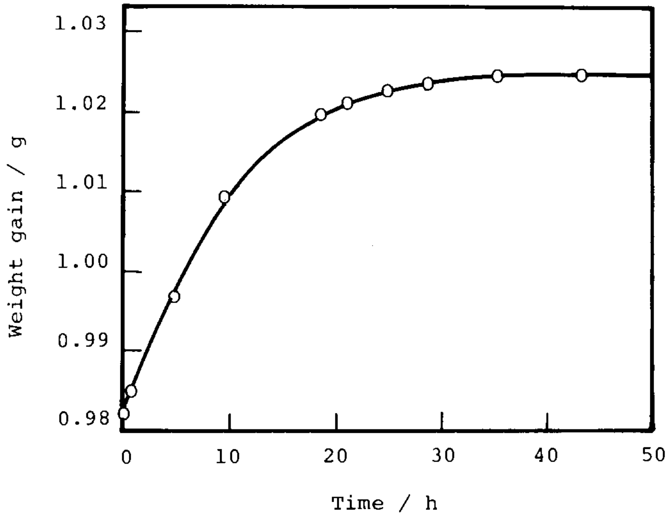

Fig. 3. Rehydration curve of $SmPO_4 \cdot 0.5H_2O$ obtained by dehydration for 2 h at 120 °C.

modes of water, respectively [8]. In these samples, the deformation appeared as a broad band with a maximum at 1640–1620 cm^{-1}. Even when the hydrated phosphate is heated at 1000 °C, the infrared spectrum still shows a small amount of water (spectrum e in Fig. 4). However, spectrum f in Fig. 4 (sample heated at 1500 °C) shows no peaks for water. Water molecules in hydrates are known to be released below 300 °C. The samples obtained by heating below 1000 °C may very rapidly adsorb water in the air before the infrared measurements, whereas the sample obtained beyond 1000 °C may hardly adsorb water. The assignment of the phosphate frequencies was made according to the literature [9]. The samples heated at 1000 and 1500 °C gave finely splitting infrared bands in the range 1110–950 cm^{-1}. The splitting may be due to the presence of the polymer chain of the combined PO_4 groups [10] and of two structurally non-equivalent PO_4 groups [11].

The crystal structures of lanthanoid orthophosphates have been studied for Ce [12], Tb, Dy, and Ho [13a], and Er, Tm, and Yb [13b]. Palkina [14a] presented a detailed review on the structures of phosphates and divided them into three groups: (1) the monoclinic modification (La–Dy), space group $P2_1/a$ (monazite type), (2) the tetragonal modification (Gd–Lu), space group $I4_1/amd$ (xenotime type), and (3) the hexagonal modification (La–Gd), space group $P6_222$. While Hikichi [14b] has recently proposed that the structures of rare earth orthophosphates are classified into five types, namely, (1) the monazite type RPO_4 (R = La–Gd, monoclinic form), (2) the xenotime type RPO_4 (R = Y, Dy–Yb, tetragonal), (3) the rhabdophane type $RPO_4 \cdot (0.5–1)H_2O$ (R = La–Gd, hexagonal), (4) the weinschenkite type $RPO_4 \cdot 2H_2O$ (R = Y, Dy–Yb, monoclinic), and (5) the orthorhombic form $DyPO_4 \cdot 1.5H_2O$. The X-ray diffraction patterns of sam-

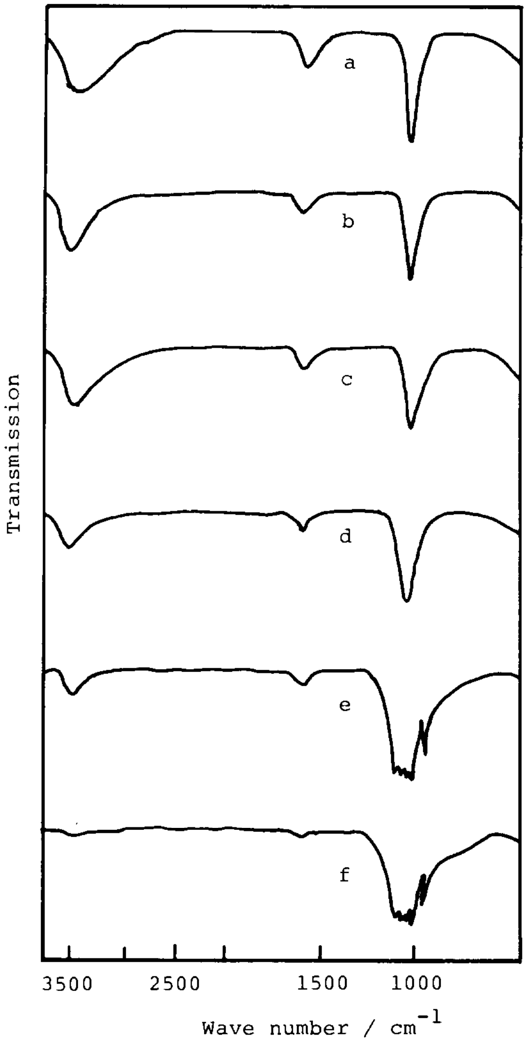

Fig. 4. Infrared spectra of the heating products of $SmPO_4 \cdot H_2O$. (a) $SmPO_4 \cdot H_2O$ and its products at (b) 120, (c) 350, (d) 800, (e) 1000, and (f) 1500 ° C in a flowing argon atmosphere.

ples which were obtained by heating at 120 and at 200 ° C, respectively, were the same: the structure was unchanged by the dehydration. As shown in Fig. 5, the X-ray diffraction patterns of $SmPO_4 \cdot H_2O$ heated in the range 120–600 ° C were found to belong to the hexagonal system with axial ratio 1.82 by using the Hull-Davey chart [15], and its lattice calculated constants were $a_0 = 7.0$ and $c_0 = 12.8$ Å from the knowledge of crystal geometry. The structure of samarium phosphate heated at 800 and 1000 ° C is monoclinic, in agreement with the values reported in ASTM card No. 32-983. The structural change of samarium phosphate in the range 600 °–800 ° C could be characterized by the transition hexagonal–monoclinic from the change of

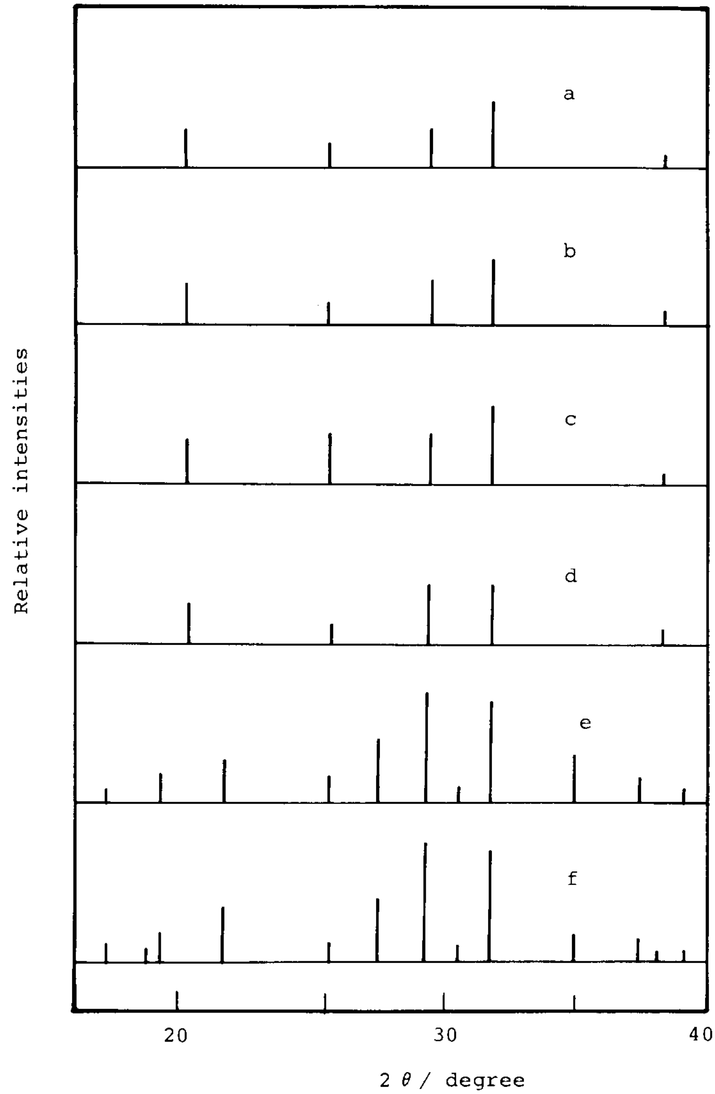

Fig. 5. X-ray patterns of (a) $SmPO_4 \cdot H_2O$ and its products at (b) 120, (c) 200, (d) 600, (e) 800, and (f) 1000 °C in a flowing argon atmosphere.

the infrared and the X-ray diffraction spectra, although the corresponding DTA change could not be observed.

Kinetics

Using the TG data, the kinetic parameters i.e. reaction order n, activation energy E_a, and frequency factor A, were calculated by the integral method according to the Coats–Redfern equation, which is one of the widely employed approximations and a reliable method [16]. The equations are f(α) functions of the type f(α) = $(1-\alpha)^n$.

$$\log\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right) = \log\left(\frac{AR}{\Phi E_a}\right)\left(1-\frac{2RT}{E_a}\right) - \left(\frac{E_a}{2.3RT}\right) \qquad \text{for } n \neq 1$$

and

$$\log\left(-\log\left(\frac{(1-\alpha)}{T^2}\right)\right) = \log\left(\frac{AR}{\Phi E_a}\right)\left(1-\frac{2RT}{E_a}\right) - \left(\frac{E_a}{2.3RT}\right) \qquad \text{for } n = 1$$

where f(α) = $(1-\alpha)^n$ is a function depending on the reaction mechanism, α the fraction reacted at time t, and Φ the linear heating rate. Thus a plot of

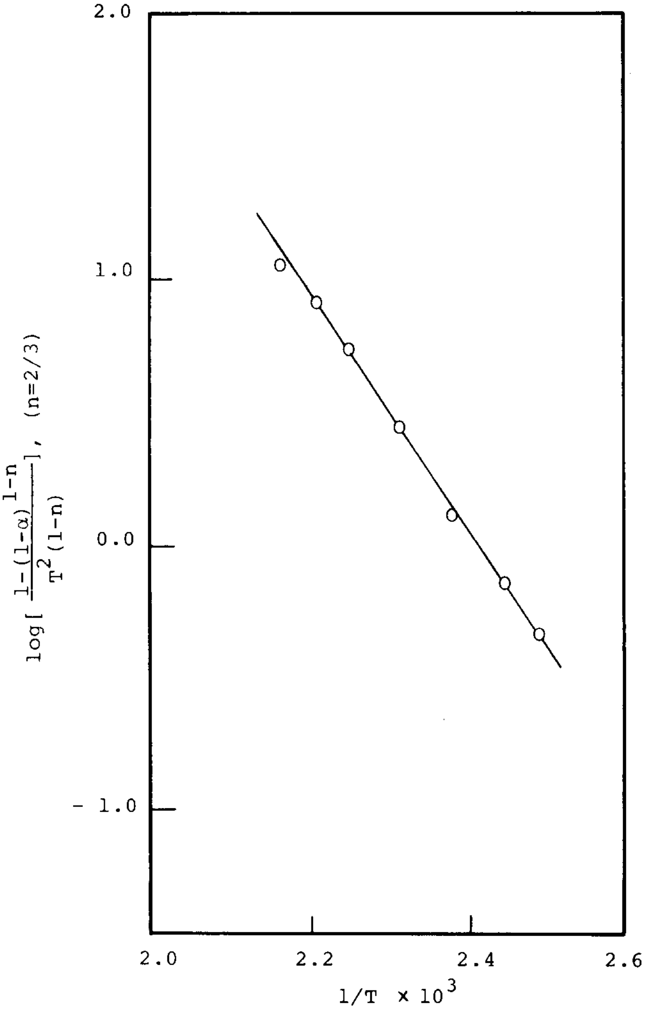

Fig. 6. Plots by the Coats–Redfern method in the second dehydration step of $SmPO_4 \cdot H_2O$.

TABLE 2

Reaction order n, activation energy E_a, and frequency factor A for the dehydration of samarium phosphate monohydrate in a flowing argon atmosphere

Phosphate	Dehydration			
	Stage	n	E_a (kcal mol^{-1})	A (s^{-1})
$SmPO_4 \cdot H_2O$	1st	2/3	8.1	1.4×10^6
	2nd	2/3	21.3	1.3×10^{11}

either $\log(1-(1-\alpha)^{1-n}/T^2(1-n))$ against $1/T$ for $n \neq 1$ or $\log(-\log(1-\alpha)/T^2)$ against $1/T$ for $n=1$ should produce a straight line of slope $-E_a/(2.3R)$ for the correct value of n. A computer program tests the values of n from 0 to 2 (0.0, 0.5, 0.66, 1.00, 1.5, and 2.0). All calculations were performed on an OKITAK 50 digital computer using a FORTRAN IV program. Figure 6 shows the Coats–Redfern plots for the second dehydration step of samarium phosphate semihydrate. When n was assumed to be 2/3, which indicated that the mechanism of the dehydration was a phase boundary-controlled reaction, the plots for the first and the second dehydration steps gave a straight line to yield the values of activation energy, 8.1 and 21.3 kcal mol^{-1}, respectively (Table 2). The values of the activation energies determined may support the proposal that the starting sample $SmPO_4 \cdot H_2O$ includes both types of water (physically bound water and chemically bound water): this is also suggested by the values of the dehydration temperatures on the TG and DTA curves. Consequently, the deaquations in the first and the second dehydration processes of samarium phosphate monohydrate are assumed to be the physically and the chemically bound water, respectively.

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