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PREPARATION, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SAMARIUM(III) CYCLOTRIPHOSPHATE(V), $SmP_3O_9 \cdot 5H_2O$

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Abstract

A new samarium cyclotriphosphate pentahydrate powder, $SmP_3O_9 \cdot 5H_2O$, has been prepared using a classical chemistry method and characterized by X-ray diffraction (XRD), thermogravimetric analysis (TG) and infrared spectroscopy. The IR spectrum shows the characteristic bands of cyclotriphosphates as the triplet in the range 1330–1250 cm^{-1}. The results of differential thermal analysis, X-ray powder diffraction and IR spectra of the compound heated at different temperatures showed that, after dehydration, $SmP_3O_9 \cdot 5H_2O$ decomposes to form an amorphous compound, which, then crystallises at 873 K and give the polyphosphate $Sm(PO_3)_3$.

Keywords: cyclotriphosphate of samarium, $SmP_3O_9 \cdot 5H_2O$, thermal analysis, X-ray diffraction

Introduction

The cyclotriphosphates of the monovalent or bivalent cations such as $M^{II}(NH_4)_4(P_3O_9)_2 \cdot 4H_2O$ [1] and $NiNa_4(P_3O_9)_2 \cdot 6H_2O$ [2] are largely studied. Trivalent rare earth cyclotriphosphates are worth studying. Nevertheless, they are poorly investigated owing to the fact that only a few of them have been well characterized. Up to now, in the rare-earth cyclotriphosphate field three rare-earth salts of general formula $LnP_3O_9 \cdot 3H_2O$ with *Ln*=La, Ce and Nd were first described by Serra and Giesbrecht [3]. Then, the chemical preparation and thermal behaviour (DTA/TG curves) for $PrP_3O_9 \cdot 4H_2O$, $LaP_3O_9 \cdot 4H_2O$ and $ErP_3O_9 \cdot 4H_2O$ were studied by Birke and Kempe [4]. Next, Bagieu-Beucher and Durif [5] focused on a series of three $LnP_3O_9 \cdot 3H_2O$ compounds, with *Ln*=La, Ce and Pr and in order to determine their crystal data, in fact the cerium salt's crystal structure was identified by Bagieu-Beucher *et al.* The structure is solved in the space group P-6 with the following parameters a=6.770(3), C=6.079(3) Å

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[6]. The thermal behaviour of $LaP_3O_9\cdot 3H_2O$, $CeP_3O_9\cdot 3H_2O$ and $PrP_3O_9\cdot 3H_2O$ was carefully investigated by Gobled [7]. These compounds are unstable in air and decompose irreversibly according to the following scheme [8]:

$$LnP_3O_9\cdot 3H_2O\rightarrow LnPO_4+P_2O_5+3H_2O$$

Owing to its high stability exceeding a year the lanthanum salt was chosen for this investigation. In addition to the compounds listed above, Bagieu gave only the X-ray diagrams of rare earth cyclotriphosphates, $NdP_3O_9\cdot 5H_2O$ and $SmP_3O_9\cdot 5H_2O$ [9]. Horchani *et al*. [10, 11] have prepared and characterized, by X-ray diffraction, IR spectroscopy and thermal behaviour, two cyclotriphosphates $NdP_3O_9\cdot 4H_2O$ and $Na_3Nd_3(P_3O_9)_4\cdot 13H_2O$.

Our aim is research new condensed rare earth phosphates being able to present powerful optical properties. The present work deals with the synthesis and characterization of $SmP_3O_9\cdot 5H_2O$.

Experimental

Conductivity measurements

The conductivity measurements were performed using a Consort conductometer (Consort C 832 provided with a coductimetric cell; K=1.11). The concentration of titrating agent ($Na_3P_3O_9$) and the titrated ($SmCl_3\cdot 6H_2O$) solutions were always maintained at 0.027 and 0.01 M, respectively [3]. 40 mL of the titrated solution were always placed in a thermostated jacketed glass reactor.

Synthesis of samarium cyclotriphosphate pentahydrate powder

$SmP_3O_9\cdot 5H_2O$ was prepared at ambient temperature by adding, drop by drop, during a night, in the proper ratio, an aqueous solution of 0.1 M $Na_3P_3O_9$ to an aqueous, magnetically stirred, 0.1 M solution of $SmCl_3\cdot 6H_2O$ of the same concentration. The resulting product, insoluble in water, has a white colour. It was separated from the liquid phase by filtration and air dried. The reaction is as follows:

$$Na_3P_3O_9+SmCl_3\cdot 6H_2O\rightarrow SmP_3O_9\cdot 5H_2O+3NaCl+H_2O$$

Methods of characterization

Powder X-ray diffraction (XRD) data of $SmP_3O_9\cdot 5H_2O$ were recorded on a Philips PW 1730 with CuK_{α_1} radiation (λ=1.54056 Å).

The infrared absorption spectra of a KBr pressed pellet of the powdered sample was studied in the range 4000–400 cm^{-1} using a Perkin Elmer 783 spectrometer.

Thermogravimetric analysis (TG) was carried out with a thermobalance of Setaram 2400. The powdered sample was heated from 298 to 600 K at a rate of 10 K min^{-1}, with an initial mass of 30 mg. Rigaku differential thermal analyser with a platinum crucible was used for the DTA measurements. Due to the fact that the maximum temperature reached in the DTA was 1000 K, a calcination study (until 1500 K) of the starting samples was also carried out in the furnace.

Results and discussion

The conductometric titration of samarium chloride solutions with sodium cyclotriphosphate solutions (Fig. 1) always showed the formation of two stable 1/1 and 1/2 complexes, having the following formula $SmP_3O_9{\cdot}5H_2O$ and $Na_3Sm(P_3O_9)_2{\cdot}9H_2O$, respectively. This conductometric titration was carried out at three different temperatures (298, 308 and 318 K). It was shown that the formed complexes were stable at these studied temperatures.

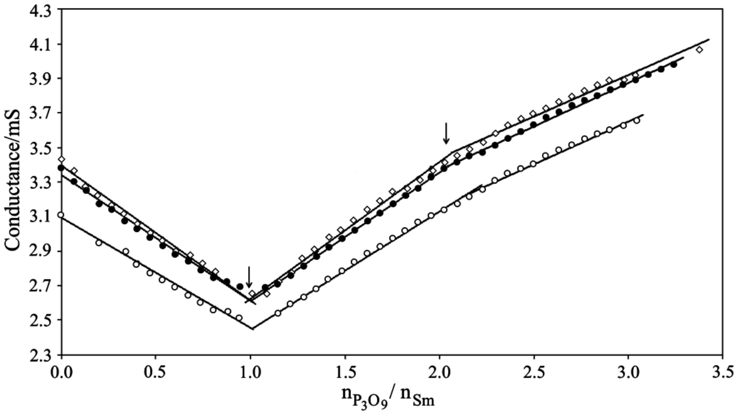

Fig. 1 The curves of conductimetric titration of a 0.01 M $SmCl_3{\cdot}6H_2O$ with 0.0027 M $Na_3P_3O_9$ solution

The XRD pattern shows that $SmP_3O_9{\cdot}5H_2O$ is well crystallized. The observed inter-reticular distances as well as the relative intensities of $SmP_3O_9{\cdot}5H_2O$ are given in Table 1.

The results of the IR spectrum are presented in Table 2. Figure 2 shows the characteristic spectrum of the samarium cyclotriphosphate pentahydrate. The water of crystallization of $SmP_3O_9{\cdot}5H_2O$ absorbs in the 3580 and 1640 cm^{-1} regions, which presumably correspond to O–H stretching and O–H bending vibrations, respectively. One of the most noteworthy features being the appearance of very strong absorption band, usually a triplet, in the 1330–1250 cm^{-1} area is assigned to the $\nu_{as}(PO_2)$ stretching modes. The two bands of doublet and triplet observed at 1185 and 1175 and at 1125, 1100 and 1015 cm^{-1} can be assigned to the stretching modes of the $\nu_s(PO_2)$ and $\nu_{as}(POP)$, respectively. The bending modes for the $\delta(POP)$ and $\delta(PO_2)$ have two absorption bands of triplets observed at 770, 670 and 650 and 590, 550 and 510 cm^{-1}, respectively.

Figure 3 shows the DTG–TG curves of the compound, showing four peaks with 18.46% mass loss due to the dehydration of water of crystallization between 318 and 553 K. These peaks correspond to the loss of five moles of H_2O per formula unit.

Table 1 The observed inter-reticular distances and the relative intensities of powder X-ray diffraction of $SmP_3O_9 \cdot 5H_2O$

d_{obs}	I_{obs}	d_{obs}	I_{obs}
6.81	92	2.80	11
6.21	13	2.75	27
5.94	13	2.72	57
5.32	96	2.67	61
4.46	80	2.56	27
4.24	54	2.48	19
4.13	15	2.44	15
3.97	100	2.39	23
3.74	15	2.33	20
3.52	7	2.22	18
3.43	31	2.15	38
3.33	35	2.07	15
3.27	23	2.04	16
3.13	15	1.99	38
3.07	27	1.95	36
2.98	35		

Table 2 IR spectrum of $SmP_3O_9 \cdot 5H_2O$

Assignment	Frequencies/cm^{-1}
ν_1 and $\nu_3 H_2O$	3580–3500–3360–3240
$\nu_2 H_2O$	1640
$\nu_{as}(PO_2)$	1330–1280–1250
$\nu_s(PO_2)$	1185–1175
ν_{as}(P–O–P)	1125–1100–1015
ν_s(P–O–P)	770–670–650
$\delta(PO_2)$	590–550–510

During the dehydration process of the compound the water molecules lost in approximately 4 steps (DTA curve) very brought closer and difficult to separate.

While heating $SmP_3O_9 \cdot 5H_2O$, the bands of water vibration in the IR spectra (Fig. 4) disappear at 523 K and the compound becomes amorphous. At 873 K, the characteristic bands of samarium polyphosphate $Sm(PO_3)_3$ appear. A proposed decomposition pathway is indicated in the equation below:

$$SmP_3O_9 \cdot 5H_2O \rightarrow Sm(PO_3)_3 + 5H_2O$$

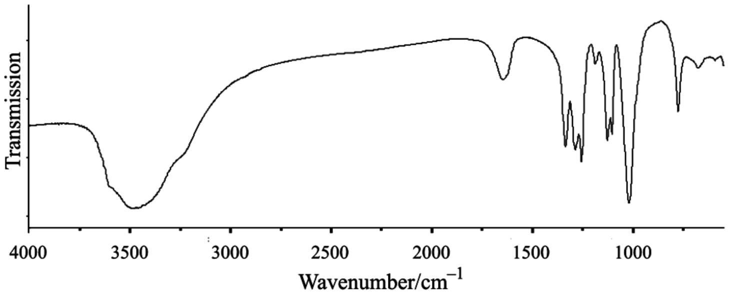

Fig. 2 IR spectrum of $SmP_3O_9 \cdot 5H_2O$

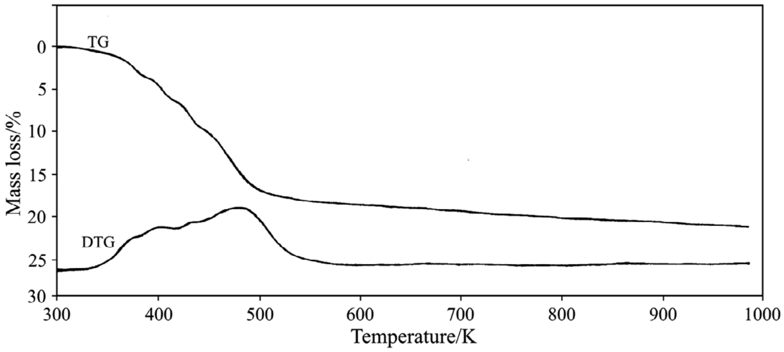

Fig. 3 DTG-TG curves of $SmP_3O_9 \cdot 5H_2O$

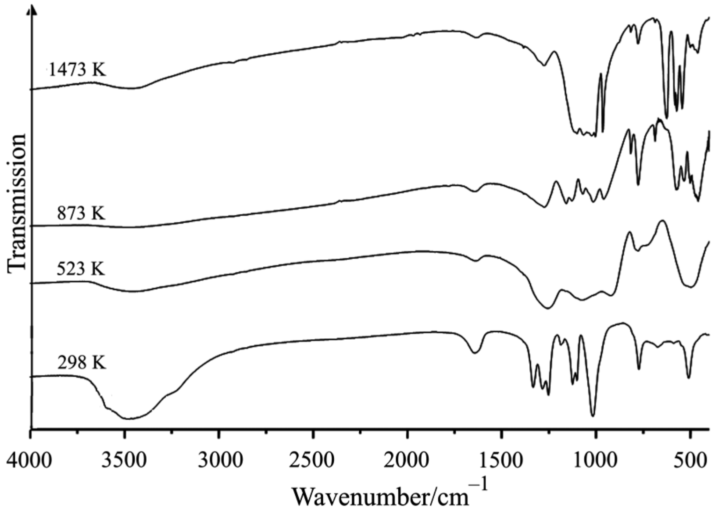

Fig. 4 IR spectra of $SmP_3O_9 \cdot 5H_2O$ heated at various temperatures

At 1473 K the absorption bands of $Sm(PO_3)_3$ disappear and we note the appearance of those of the samarium phosphate $SmPO_4$.

The X-ray diffraction pattern of the compound heated at various temperatures (Fig. 5) confirms the results observed in the spectra, so we have the amorphous phase at 523 K, then the polyphosphate of samarium, $Sm(PO_3)_3$, is formed at 873 K.

All the collected data allow to present the interpretation of the DTA curve (Fig. 6), which first shows four endothermic peaks of dehydratation at 327, 363, 389 and 418 K, then a constant period and finally an exothermic peak at 946 K assigned to the crystallization of $Sm(PO_3)_3$.

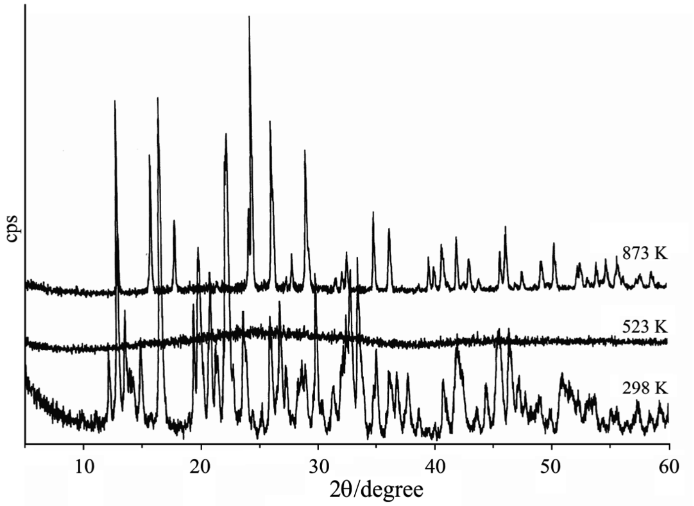

Fig. 5 Powder X-ray diffraction patterns of $SmP_3O_9 \cdot 5H_2O$ heated at various temperatures

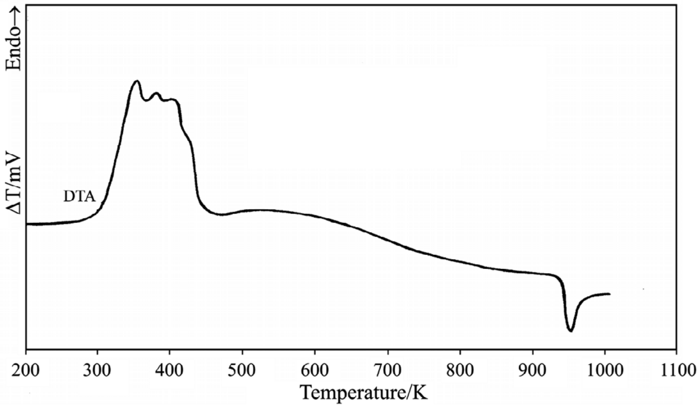

Fig. 6 DTA curve of $SmP_3O_9 \cdot 5H_2O$

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