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A New Synthetic Route for the Layered Phosphate: Solid-State Reaction and Characterization of α-Sn(HPO$_4$)$_2$ · H$_2$O

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A new synthetic route for the layered phosphate α-Sn(HPO$_4$)$_2$ · H$_2$O, obtained from solid-state reaction of SnCl$_4$ · 5H$_2$O and P$_2$O$_5$ at a lower heating temperature, is reported. The final product was characterized by ICP, TGA–DTA, FT–IR, ^{31}P MAS NMR, and XRD. The BET measurement showed that the surface area of the product is 27.6 m^2/g. The X-ray powder diffraction pattern matched the calculated powder pattern. Twenty lines ($5^\circ < 2\theta < 100^\circ$) were indexed to give the unit cell parameters $a = 8.6185(3)$ Å, $b = 4.9743(5)$ Å, $c = 15.6165(4)$ Å, $\beta = 100.42(1)^\circ$ which agree well with the structural parameters previously determined by S. Bruque *et al.* © 2001 Academic Press

Key Words: **solid-state reaction; layered phosphate; α-Sn(HPO$_4$)$_2$ · H$_2$O; Sn$_2$P$_2$O$_7$.**

INTRODUCTION

Great interest has been directed toward the search for new layered phosphates of tetravalent metals since the 1960s due to their potential applications as ion exchangers, proton conductors, sensors, and catalysts for heterogeneous acid-catalyzed reactions (1–7). It has been found that these layered phosphates usually contain layers of tetravalent metal atoms bridged by singly protonated phosphate groups. The P–OH groups point toward the interlayer spaces and are arranged alternatively above and below the layer plane. Preparation of these compounds is often conducted by the conventional hydrothermal reaction method. It must be noted, however, that the hydrothermal reaction has a few limitations such as relatively low yield, a very consuming time, and contaminated product under hydrothermal conditions.

Our interest in solid-state chemistry has promoted us to develop a new approach to synthesize the layered phosphates of tetravalent metals, namely the solid-state reaction at the lower heating temperature. This new approach has several distinguishing features from both the solid-state reaction at high temperature and the solution reaction. It has been employed by us recently in making other synthetic studies. For example, some Mo(W)–Cu(Ag)–S cluster compounds with different structural modes and excellent third-order nonlinear optical properties have been successfully prepared (8). Some complexes, which are difficult to obtain in solution reaction because of their decomposition in solvents, may be synthesized through solid-state reactions at lower heating temperature (9). Some nanometric materials have also been prepared by this synthetic method in a very high yield (10).

Herein, we report the new approach for the preparation of a layered tin phosphate α-Sn(HPO$_4$)$_2$ · H$_2$O by the following reaction in the solid-state at a lower heating temperature (413 K)

$$\mathrm{SnCl_4 \cdot 5H_2O(s) + P_2O_5(s) = Sn(HPO_4)_2 \cdot H_2O(s) + 4HCl(g) + H_2O(g).}$$

Compared with the hydrothermal method, the present method has three main advantages: (i) it is simple and convenient, (ii) it involves less solvent and reduces contamination, and (iii) it gives a high yield product.

EXPERIMENTAL

Materials and Methods

The starting materials were reagent grade used as purchased. Tin and phosphorus contents were determined by ICP spectrometer (Perkin–Elmer, Plasma 400). The thermal stability of α-Sn(HPO$_4$)$_2$ · H$_2$O was preformed on a TA Inst 2100 TGA–DTA apparatus. The sample was heated under a nitrogen flow (100 mL/min) at a heating rate of 10 K/min in the range of room temperature to 1273 K. α-alumina

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(α-Al_2O_3) was used as a reference. The surface area of the compound was measured by the BET method, with nitrogen as an absorbent. X-ray powder diffraction studies were carried out on a Rigaku D/-max 2500 diffractometer (λ (Cu$K\alpha$) = 1.54059 Å). Indexing of the X-ray powder diffraction pattern was performed using the program TREOR 90. The IR spectrum of α-$Sn(HPO_4)_2 \cdot H_2O$ was recorded on a Nicolet 170sx FT–IR using a dry KBr pellet containing 2% of the sample. The ^{31}P NMR results were obtained with a Varian INOVA 400 spectrometer. ^{31}P nucleus resonates at 161.8 MHz. Chemical shifts are reported with relative to 85% H_3PO_4. The number of transitions was 16 with a relaxation delay of 40 s. The 90 degree pulse (4.3 μs) of ^{31}P was used in conjunction with magic angle spinning and high-power proton decoupling. The sample spinning rate was 10.1 KHz. Line broadening at 20 Hz was used in processing data.

Synthesis of α-$Sn(HPO_4)_2 \cdot H_2O$

The mixed solid reactants $SnCl_4 \cdot 5H_2O$ (3.51 g, 0.01 mol) and P_2O_5 (1.42 g, 0.01 mol) were ground for 30 min in air to get the possible homogeneity. The mixture was then heated for 4 h at 413 K, at meantime some irritant gas and vapor was released. The vast product was resuspended in distilled water and dispersed by ultrasound for 10 min, and then centrifuged for 10 min (8000 rpm). The procedure was repeated until the pH of the washing liquid solution was close to 4.0. The resulting product was again washed twice with 50 mL of ethanol, then followed by drying in vacuum to yield white powder. Yield: 3.21 g (98%). IR(KBr, cm^{-1}): 3558.8(s), 3492.3(m), 3352.0(m), 3072.0(m), 1623.7(m), 1088.3(s), 680.2(s), 615.5(w), 525.4(m), 446.7(m), 407.6(w).

ICP analysis indicated that the white powder contains Sn and P in an approximately 1:2 molar ratio. The compound was further identified as α-$Sn(HPO_4)_2 \cdot H_2O$, judged by the characteristic powder X-ray diffraction pattern. The surface area of the compound was measured to be 27.6 m^2/g.

RESULTS AND DISCUSSION

1. *Synthetic Reaction*

It takes 7 days to prepare α-$Sn(HPO_4)_2 \cdot H_2O$ under hydrothermal conditions at 423 K (2). In comparison, about 4 h is needed to give the same product by using the new synthetic route of solid-state reaction at lower heating temperature.

Powder X-ray diffraction was used to investigate the formation of the crystalline solids α-$Sn(HPO_4)_2 \cdot H_2O$ in real time. Initially the two reactants, $SnCl_4 \cdot 5H_2O$ and P_2O_5, were mixed and then ground at room temperature for 30 min. The XRD pattern showed that the characteristic peaks of $SnCl_4 \cdot 5H_2O$ and P_2O_5 were vanishing quickly. In the meantime, no new peaks corresponding to the product α-$Sn(HPO_4)_2 \cdot H_2O$ appear. After heating the mixture at 413 K for 2 h several broad peaks appeared. After heating for 3 h, the peaks of the product α-$Sn(HPO_4)_2 \cdot H_2O$ grow from these widened peaks, which remained unchanged on further heating for one more hour.

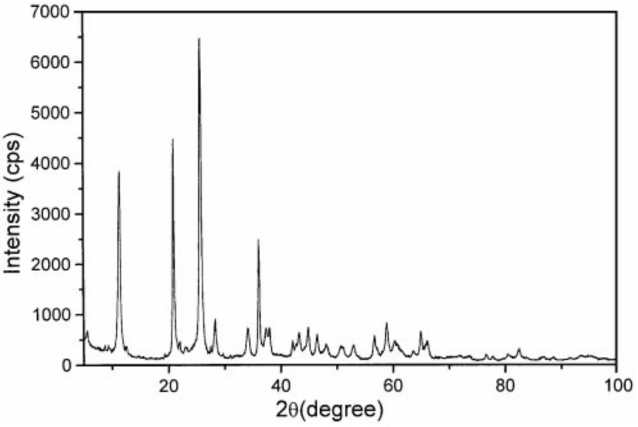

FIG. 1. XRD pattern of α-$Sn(HPO_4)_2 \cdot H_2O$.

The X-ray powder diffraction pattern of α-$Sn(HPO_4)_2 \cdot H_2O$ (Fig. 1) was directly indexed using the program TREOR90 and was then refined using the program PIRUM930101. The unit cell parameters were calculated to be $a = 8.6185(3)$ Å, $b = 4.9743(5)$ Å, $c = 15.6165(4)$ Å, and $\beta = 100.42(1)°$. The figures of merit were $M_{20} = 33$ and $F_{20} = 21$ (0.00795,47). These cell parameters are similar to those previously reported (2). Since the structure of α-$Sn(HPO_4)_2 \cdot H_2O$ has been reported, further Rietveld refinement on the present data is unnecessary.

2. *Thermal Analysis*

Figure 2 shows that the final product decomposes in two steps. The first step occurs between 343 and 493 K with an

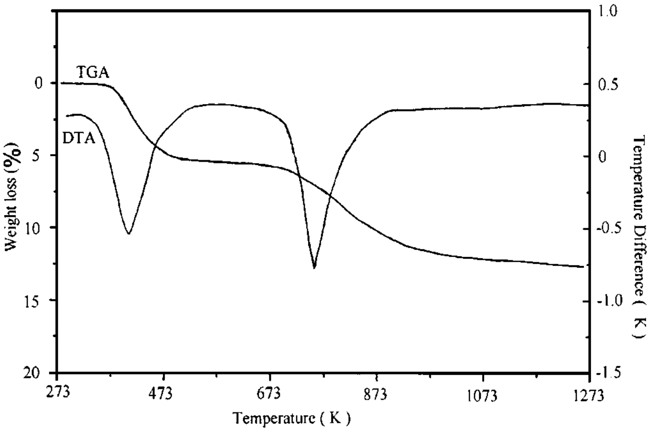

FIG. 2. TGA–DTA curves of α-$Sn(HPO_4)_2 \cdot H_2O$: TGA (upper left) and DTA (lower left).

endothermic peak in the DTA curve. The weight loss in this step is 5.2%, which corresponds to the dehydration of α-$Sn(HPO_4)_2 \cdot H_2O$ (calc. 5.5%), thus resulting in the anhydrous acid phosphate $Sn(HPO_4)_2$. In the second step, a condensation process occurs and, subsequently, one more water molecule is released above 733 K with the formation of a layered pyrophosphate SnP_2O_7 (1). Finally, cubic SnP_2O_7 can be formed on heating up to 1173 K, which was proved by the X-ray powder diffraction. The FT–IR, and ^{31}P MAS NMR spectra confirm these results.

3. *Infrared Spectra*

The IR spectra of the product were measured at 298 and 873 K. At room temperature, a strong absorption band is observed at about 3500 cm^{-1} corresponding to the O–H asymmetric stretching vibration. The absorption band at 1623.7 cm^{-1} may be assigned to the bending vibration of water. The band at about 3072 cm^{-1} is attributed to hydrogen-bond interactions from the OH groups of the water molecule and the P–OH groups. The bands at 1088.3 and 700–500 cm^{-1} are attributed to the P–O band stretches and deformations, respectively. When the title compound was heated up to 873 K, a weak absorption band was found at 725 cm^{-1}, which belongs to the vibrations of the P–O–P bridge, indicating the formation of the pyrophosphate compound SnP_2O_7.

4. *^{31}P MAS NMR Spectra*

The ^{31}P MAS NMR spectra of α-$Sn(HPO_4)_2 \cdot H_2O$ were determined at 298, 873, and 1173 K, respectively. As shown in Fig. 3, one resonance at $\delta = -20.5$ ppm is observed in ^{31}P NMR spectrum of the α-$Sn(HPO_4)_2 \cdot H_2O$. Spinning

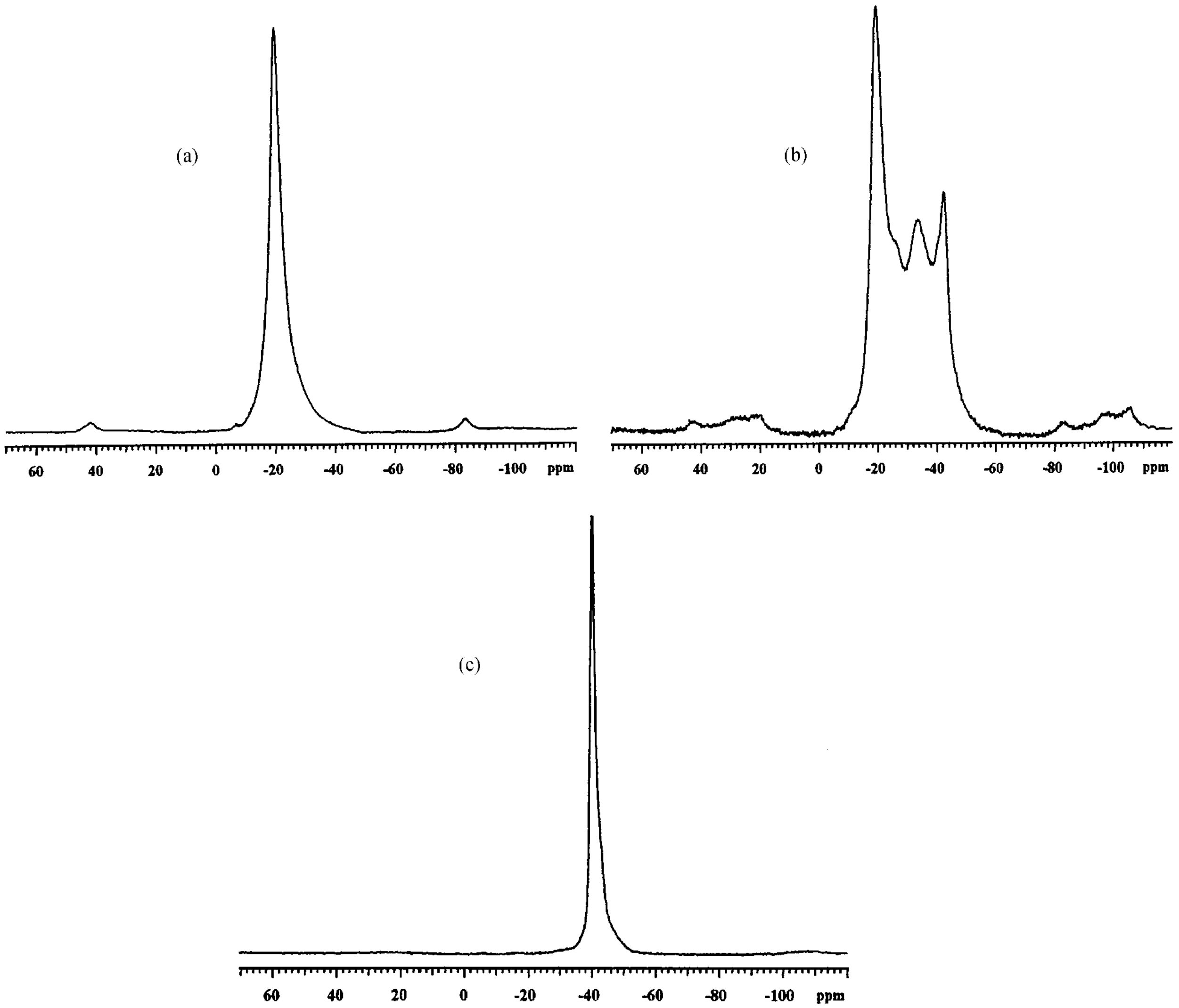

FIG. 3. ^{31}P NMR spectra of α-$Sn(HPO_4)_2 \cdot H_2O$ at (a) 298 K, (b) 873 K, and (c) 1173 K.

sidebands are located in either side of the isotropic resonance. Their weak intensity implies that the electronic environments of the phosphorus nuclei are similar. When α-$Sn(HPO_4)_2 \cdot H_2O$ was heated up to 873 K, three resonances were found. The resonance at $\delta = -20.5$ ppm is due to the ^{31}P nuclei resonance in $Sn(HPO_4)_2$. As can be seen from Figs. 3a and 3b the ^{31}P NMR spectra show that the chemical shift remains constant during the transition α-$Sn(HPO_4)_2 \cdot H_2O \rightarrow Sn(HPO_4)_2$. The resonance at $\delta = -34.0$ and -40 ppm are attributed to ^{31}P nuclei resonance in the layered SnP_2O_7 and cubic SnP_2O_7, respectively. The above results indicate that three phases, e.g., $Sn(HPO_4)_2$, layered and cubic SnP_2O_7 coexist at 873 K. When the sample was heated to 1173 K, only the resonance $\delta = -40$ ppm was observed in the ^{31}P MAS NMR spectrum, which infers that the pure cubic SnP_2O_7 was formed.

SUMMARY

α-$Sn(HPO_4)_2 \cdot H_2O$ was synthesized by a simple and convenient solid-state reaction at a lower heating temperature. The ICP, TGA–DTA, FT–IR, ^{31}P MAS NMR, and XRD analyses indicated that the obtained product is very similar to that synthesized under hydrothermal conditions. Its thermal behavior with the phase changes observed between 298 and 1273 K is reported. Two SnP_2O_7 phases are characterized by ^{31}P MAS NMR. The same method can also be used for the preparation of some other phosphates The solid-state reactions at lower heating temperature, which consume less energy, are environmentally benign and economically advantageous, thus providing a good route in synthetic chemistry.

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