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BRIEF COMMUNICATION

Hydrothermal Synthesis and Characterization of $NH_4Sn_2(PO_4)_3$

Yaohua Xu, Shouhua Feng, and Wenqin Pang

Key Laboratory of Inorganic Hydrothermal Synthesis, Department of Chemistry, Jilin University, Changchun 130023, The People's Republic of China

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$NH_4Sn_2(PO_4)_3$ has been synthesized hydrothermally from the NH_3–SnO_2–P_2O_5–H_2O system, and characterized by X-ray powder diffraction, differential thermal analysis–thermogravimetric analysis, and Raman and IR spectroscopy. © 1995 Academic Press, Inc.

$MSn_2(PO_4)_3$ (M = Li, Na, K, Tl, Ag, Rb), which has a NASICON-type structure (space group $R3C$) with a three-dimensional network of PO_4 tetrahedra corner-shaped with SnO_6 octahedra, has been prepared previously by solid-state reactions (1). However, there have been no reports of a hydrothermal synthesis of $NH_4SN_2(PO_4)_3$ so far. Here we report a novel synthesis method, hydrothermal crystallization for the synthesis of $NH_4Sn_2(PO_4)_3$.

Hydrothermal crystallization of $NH_2Sn_2(PO_4)_3$ was carried out in a stainless steel autoclave with a Teflon liner under autogenous pressure. SnO_2(AR), 85% orthophosphoric acid, and $(NH_4)_3PO_4$, and water were mixed in the molar ratio $0.8H_3PO_4 : 1.6SnO_2 : 3(NH_4)_3PO_4$ in the Teflon liner. The autoclave was sealed and heated in an oven at 250°C for 5–7 days. After cooling, the product was filtered, washed with distilled water, and dried at ambient temperature.

The crystalline product was identified by means of X-ray powder diffraction pattern of the product (Fig. 1) recorded with a Rigaku D/max-IIIA diffractometer using Cu$K\alpha$(λ = 1.5418) radiation, which is similar to that of $NaSn_2(PO_4)_3$ (2). The product is free of impurities. It could be indexed on the basis of a hexagonal unit cell with a = 8.330(1) Å and c = 23.90(5) Å. The indexed data are shown in Table 1. The Raman spectrum (see Fig. 2) was recorded on a Ramanor SPEX 1403 double spectrometer with an argon-ion laser (488.0-nm line, 100 mW). The spectrum is unique and quite characteristic of $NH_4Sn_2(PO_4)_3$ with three groups of absorption bands at 50–400 cm^{-1}, 400–700 cm^{-1}, and 900–1100 cm^{-1}, which are attributed to external vibrations, PO_4 bending, and stretching vibrations (3). The IR spectrum (Fig. 3) shows absorption bands at 400–700 cm^{-1} and 900–1250 cm^{-1}, which are attributed to PO_4 bending and stretching vibrations, and absorption bands at 1430 cm^{-1} and 3100–3300 cm^{-1}, which are attributed to NH_4 bending and stretching vibrations (4, 5). DTA–TGA (differential thermal analysis–thermogravimetric analysis) shows that $NH_4Sn_2(PO_4)_3$ synthesized hydrothermally was different from $NaSn_2(PO_4)_3$, which was stable at 1200°C (Fig. 4). $NH_4Sn_2(PO_4)_3$ gives off NH_3 at 769°C. After being calcined for 3 hr at 800°C, the XRD pattern shows that the product

TABLE 1
Indexed X-Ray Powder Diffraction Data of Rhombohedral $NH_4Sn_2(PO_4)_3$

h	k	l	d_{obs} (Å)	d_{cal} (Å)	I/I_0
0	1	2	6.177	6.176	52
1	0	4	4.602	4.602	71
1	1	0	4.165	4.165	94
1	1	3	3.680	3.691	51
0	2	4	3.088	3.088	54
1	1	6	2.878	2.879	100
1	0	8	2.738	2.760	4
2	1	4	2.480	2.481	17
0	3	0	2.404	2.405	27
3	0	2	2.338	2.357	4
3	0	3	2.304	2.302	4
2	0	8	2.276	2.301	3
2	1	7	2.108	2.131	2
2	2	0	2.082	2.083	10
0	3	6	2.058	2.059	19
0	2	10	1.992	1.992	16
3	1	2	1.987	1.987	6
1	3	4	1.896	1.897	13
2	2	6	1.845	1.846	26
2	1	10	1.800	1.797	26
3	0	9	1.744	1.783	2
3	1	8	1.670	1.662	5
2	2	9	1.630	1.638	10
4	1	0	1.582	1.574	17

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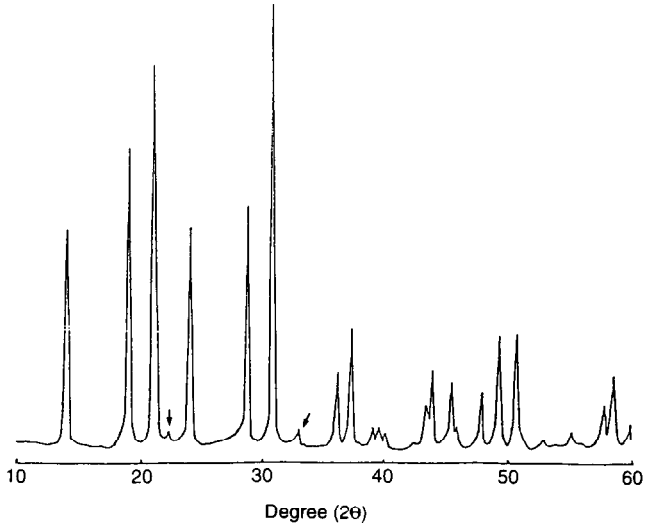

FIG. 1. X-ray powder diffraction pattern of the product.

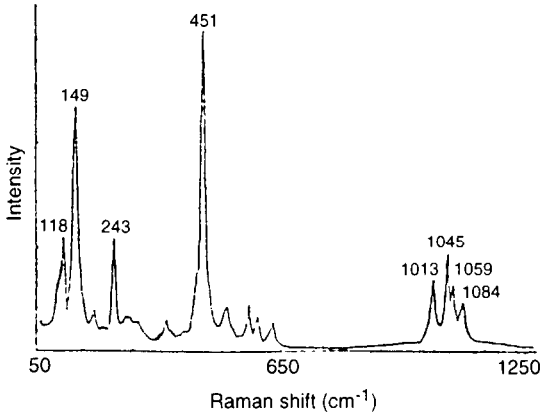

FIG. 2. Raman spectrum of the product.

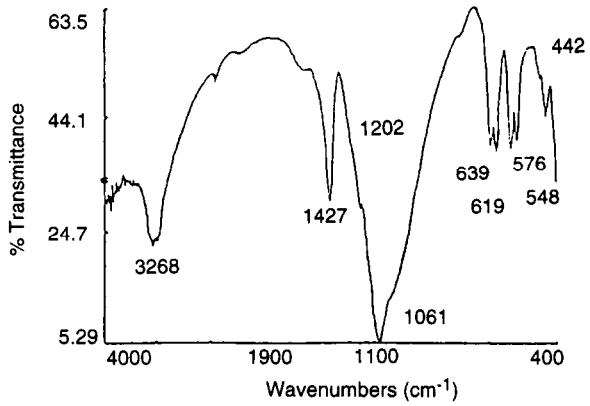

FIG. 3. IR spectrum of the product.

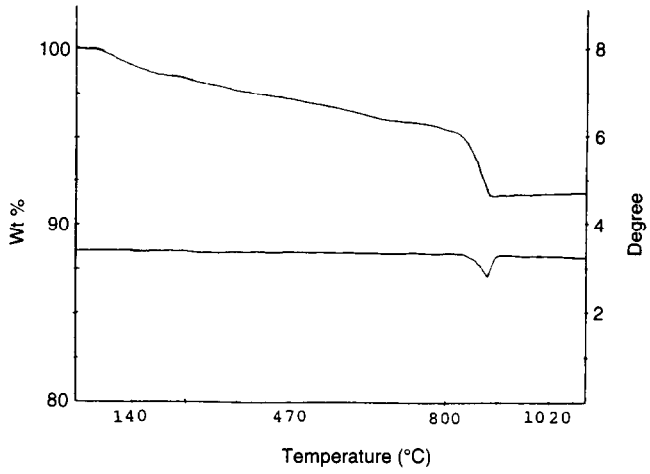

FIG. 4. DTA–TGA curve for the product.

is a mixture of SnP_2O_7 and SnO_2. The whole change may be the following reaction:

$$NH_4Sn_2(PO_4)_3 \cdot 1.7H_2O \rightarrow NH_4Sn_2(PO_4)_3 \rightarrow$$
$$NH_3 + 1.5\, SnP_2O_7 + \tfrac{1}{2}\, SnO_2 + \tfrac{1}{2}\, H_2O.$$

In summary, by using the hydrothermal crystallization method, $NH_4SN_2(PO_4)_3$, which has considerable thermal stability at temperatures lower than 760°C, has been synthesized and the pure phase is easily obtained at lower reaction temperature.

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