

Preparation and Properties of $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ in the Pseudobinary System $\text{NH}_4\text{H}_2\text{PO}_4\text{-TiO}_2$

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Phase equilibria in the system $\text{NH}_4\text{H}_2\text{PO}_4\text{-TiO}_2$ were studied and a new compound ($\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$) with Nasicon-type structure was synthesized. Its stability range was established. X-Ray and thermal properties were investigated and another new compound ($\text{Ti}_4\text{P}_6\text{O}_{23}$) with the Nasicon-type structure was obtained by heat treatment at 770°C. © 1985 Academic Press, Inc.

1. Introduction

Compounds with a $\text{NaZr}_2\text{P}_3\text{O}_{12}$ -type structure have been investigated in relation to the superionic conductor, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (Nasicon) (1, 2). Moreover, various types of substitutional solid solutions observed are of interest for crystal chemistry. We have prepared $\text{NH}_4\text{Zr}_2\text{P}_3\text{O}_{12}$ and $\text{HZr}_2\text{P}_3\text{O}_{12}$ for study as proton conductors, ion exchangers and catalysts (3). Expecting to obtain material superior to $\text{HZr}_2\text{P}_3\text{O}_{12}$, we have prepared $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ and studied on its thermal stability. The results are reported below.

2. Experimental

$\text{NH}_4\text{H}_2\text{PO}_4$ and TiO_2 were used as starting materials. Three kinds of mixtures with P/Ti ratios equal to 1/1, 2/1, and 3/2 were prepared by mixing the starting materials in an agate mortar with ethyl alcohol. The mixture was dried and sealed in an Au cap-

sule with no water added, and then heated for 48 hr under 0.15–0.20 GPa using a cold-seal high-pressure vessel. Temperature (Table I) was measured by an internal thermocouple adjacent to the capsule.

Run products were washed with distilled water and the identification of phases was carried out by X-ray diffraction and optical microscopy. Lattice parameters and infrared (ir) spectra were obtained by methods similar to those described before (3). Thermogravimetric curves and differential thermal analysis were run in air with an ULVAC TA-5000 Model HM-20E at a heating rate of 10°C/min.

Chemical analyses of synthetic crystals were carried out with an electron probe microanalyzer (JXA 5A). Single crystals of TiO_2 and ZrP_2O_7 were used as standards. Homogeneity of the materials to be analyzed were carefully examined prior to chemical analyses. Apparent concentrations were corrected by the procedure proposed by Bence and Albee (4).

TABLE I
RESULTS OF EXPERIMENTS AT 0.15–0.2 GPa

P/Ti ratio of starting material	Temperature (°C)	Crystalline products
3/2	580	123 + (111)
3/2	535	123 + (111)
3/2	520	123 + 111
3/2	509	111
3/2	480	111 + (123)
3/2	480	111
1/1	530	111 + 123
1/1	520	111 + (123)
1/1	470	111 + (u)
1/1	400	111
2/1	590	123 + (111)
2/1	570	123 + (111)
2/1	550	123 + 111
2/1	525	111 + (u)
2/1	460	111 + (u)

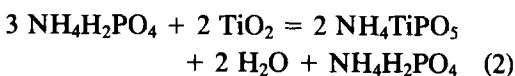
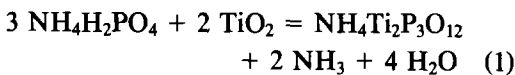
Note. Symbols: 123, $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$; 111, NH_4TiPO_5 ; u, undetermined phase; (), minor product.

3. Results and Discussion

3.1. Stability of $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$

Crystalline products obtained were mainly composed of $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ and NH_4TiPO_5 which showed similar X-ray diffraction patterns to those of rhombohedral $\text{TlTi}_2\text{P}_3\text{O}_{12}$ and orthorhombic TlTiPO_5 , respectively (5, 6). Experimental results on the stabilities of these compounds are listed in Table I.

$\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ with a very small amount of NH_4TiPO_5 was produced above 515°C from the starting material with a P/Ti ratio of 3/2. NH_4TiPO_5 was the main product formed below 515°C. Chemical reactions may be expressed as



NH_4TiPO_5 was always present in products synthesized from starting material with

P/Ti ratios equal to 1/1. $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ was formed above 520°C together with NH_4TiPO_5 . $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ was the main product obtained above 570°C by using the starting material with the P/Ti ratio equal to 2/1, but it was absent below 525°C.

3.2. Properties of $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$

Thermogravimetric curves of $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ indicate a weight loss of 6.7% in the temperature range 670 to 860°C. The weight loss is accompanied by a weak exothermic peak, suggesting that deammoniation and dehydration took place at the same time. Final crystalline product heated up to 900°C was composed of TiP_2O_7 and $\text{Ti}_5\text{P}_4\text{O}_{20}$. X-Ray diffraction patterns of these compounds are similar to those reported by previous workers (7).

Weight loss of $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ slowly took place when the sample was heated in air at constant temperature. For example, a single crystal of $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ (0.5 mm in size) was changed to an aggregate of very slightly disoriented crystals after heat treatment at 770°C for 80 min. The X-ray diffraction pattern of the heated crystals can be indexed as hexagonal with $a = 0.8406$ nm and $c = 2.2341$ nm (Table II). The X-ray pattern is similar to that of $\text{NH}_4\text{Ti}_2\text{P}_3\text{O}_{12}$ which gave the following unit cell dimensions; $a = 0.8318$ nm, $c = 2.3444$ nm. NH_4^+

TABLE II
X-RAY POWDER DATA FOR $\text{Ti}_4\text{P}_6\text{O}_{23}$

<i>hkl</i>	d_{hkl}	<i>I</i>
012	0.610	15
104	0.443	30
110	0.420	25
113	0.366	100
024	0.305	30
116	0.278	35
030	0.242	10
1,0,10	0.213	5
036	0.203	3
226	0.183	10

TABLE III
CHEMICAL COMPOSITIONS OF THE SYNTHETIC
CRYSTALS

	1	(1)	2	(2)	(3)
TiO ₂	40.23	40.11	43.46	42.87	41.86
P ₂ O ₅	53.10	53.45	56.60	57.12	55.78
G.C. ^a	6.70 ^b	6.44			2.36
Total	100.03	100.00	100.06	99.99	100.00
P/Ti	1.48	1.50	1.47	1.50	1.50

^a Gas component, (NH₃ + H₂O) or H₂O.

^b Estimated by weight loss data.

Note. (), Theoretical values of the compounds; 1, NH₄Ti₂P₃O₁₂; 2, Ti₄P₆O₂₃; 3, HTi₂P₃O₁₂.

bending and OH stretching bands are absent in an ir spectrum of the heated crystals.

Weight loss of the heated crystals was 0.4% at 900°C, indicating that 94% of the volatile components in NH₄Ti₂P₃O₁₂ were lost during the heat treatment at 770°C. Therefore, the heated crystal may be represented by the formula: (NH₄)_{0.06}Ti₂P₃O_{11.53}.

Chemical compositions of the heated and preheated crystals are listed in Table III. The analytical data are consistent with theoretical values for NH₄Ti₂P₃O₁₂ and Ti₄P₆O₂₃ within analytical uncertainty (±0.5 wt%). It is clear that the heated crystal is not HTi₂P₃O₁₂.

Heat treatment of NH₄Ti₂P₃O₁₂ at 770°C for 110 min revealed the weight loss of 6.5%, and further loss of weight did not occur by longer heating. The final product is composed of TiP₂O₇, Ti₅P₄O₂₀, and Ti₄P₆O₂₃. The weight-loss data suggest that NH₄⁺ is absent in the material with Nasicon-type

structure. Unit cell dimensions of this material (Ti₄P₆O₂₃) are $a = 0.841$ nm, $c = 2.224$ nm.

Deammoniation of NH₄Ti₂P₃O₁₂ took place slowly at 590°C in air. The materials obtained by the heat treatment for 220 hr showed no OH stretching absorption band. Examination of the X-ray powder pattern of the product showed the presence of NH₄Ti₂P₃O₁₂ and Ti₄P₆O₂₃.

3.3. Properties of NH₄TiPO₅

Weight loss mainly occurred in two temperature regions, 300 to 480°C and 550 to 680°C. X-Ray diffraction peaks of 101 and 210 split into doublets and an O-H stretching ir band at 3700 cm⁻¹ appeared after the first weight loss. The second weight loss is due to deammoniation and dehydration accompanied with loss of proton. These data suggest presence of two kinds of NH₄⁺ in the crystal. Crystallinity of the material became low after the second weight loss, but recrystallization took place at 730°C producing TiP₂O₇, Ti₄P₆O₂₃, and Ti₅P₄O₂₀.

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