FORMATION OF DOUBLE DIVALENT METAL–AMMONIUM CONDENSED PHOSPHATES IN THE NH_4PO_3 MELT

ANATOLY SELEVICH, ELENA GRUSHEVICH, LUDMILA IVASHKEVICH,
GALINA KRUL, NATALIA ILUSHCHENKO, and ANATOLY LESNIKOVICH

Physico-Chemical Research Institute of Belarusian State University,
14 Leningradskaya Str., Minsk, 220050, Belarus

Abstract Thermal behavior of the $\text{MO–NH}_4\text{PO}_3$ systems where $\text{M} = \text{Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd, and Pb}$ was studied at 300 and 400 °C. General regularities of formation of double divalent metal-ammonium phosphates were established. Conditions of preparation of some known and novel binary divalent metal-ammonium phosphates, $\text{M}(\text{NH}_4)_2(\text{PO}_3)_4$ ($\text{M} = \text{Mg, Ca, Mn, Co, Zn, and Cd}$), $\text{M}(\text{NH}_4)_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Sr and Pb}$), $\text{MNH}_4(\text{PO}_3)_3$ ($\text{M} = \text{Mg, Co, Ni, Cu, Zn, and Pb}$), $\text{MNH}_4\text{P}_3\text{O}_9$ ($\text{M} = \text{Mg, Ca, Mn, and Cd}$), $\text{Ba}_2\text{NH}_4(\text{PO}_3)_5$, $\text{Cu}_3(\text{NH}_4)_2\text{P}_8\text{O}_{24}$, and $\text{Ba}(\text{MH}_4)_4(\text{PO}_3)_6$ were determined. Preliminary XRD studies have been performed for powder samples of $\text{Ba}_2\text{NH}_4(\text{PO}_3)_5$ (space group Pc , unit cell dimensions $a = 8.649(1)$, $b = 7.312(1)$, $c = 13.873(2)$ Å; $\beta = 128.14(1)^\circ$) and $\text{Ba}(\text{NH}_4)_4(\text{PO}_3)_6$ (space group $P31c$, unit cell dimensions $a = 11.1911(2)$, $c = 8.9375(2)$ Å).

INTRODUCTION

Double metal-ammonium condensed phosphates are of great practical interest because they reveal flame retardant properties in polyamides.^{1, 2)} As a rule, the compounds are prepared by heating corresponding oxides or hydroxides with ammonium monophosphates. However, this technique has specific limitations.³⁾ Our recent investigations showed that ammonium polyphosphate NH_4PO_3 (APP) was convenient reagent for the preparation of double ammonium-containing condensed phosphates.^{4–8)} The use of APP allowed to synthesize several new double condensed phosphates which cannot be prepared by other techniques.

Conditions of the preparation of double tetravalent metal-ammonium tetraphosphates $\text{M}(\text{NH}_4)_2\text{P}_4\text{O}_{13}$ where $\text{M} = \text{Si, Ge, Sn, and Ti}$ were elaborated earlier.⁶⁾ The aim of this study was to establish regularities of the formation of double divalent metal-ammonium condensed phosphates in the APP melt, to develop a convenient technique for synthesis of well-known and novel phosphates, and to characterize novel obtained compounds.

EXPERIMENTAL

Reagent-grade $\text{Mg}(\text{OH})_2$, CaCO_3 , $\text{Sr}(\text{NO}_3)_2$, BaO , MnO_2 , $\text{Co}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$, CdCO_3 , $\text{Pb}(\text{NO}_3)_2$, PbO , and NH_4PO_3 were used as starting materials. It was shown earlier⁷⁾ that the temperature range of 300–400 °C was optimal for obtaining double divalent metal-ammonium condensed phosphates. In the present work, reactions of the above compounds with APP were studied at the temperatures 300 and 400 °C at the molar ratios $\text{MO} : \text{APP} = 1:3$, $1:5$, and $1:8$. Prepared mixtures were held at the above temperatures in air. Progress of the reactions was monitored by periodic sampling using X-ray diffraction (XRD) and optical microscopy. Crystalline phases were separated from the mother fluxes by washing with water on a glass filter and dried at room temperature.

Synthesized compounds were identified by XRD, chemical analysis, and quantitative thin-layer chromatography (QTLC). X-ray powder diffraction data were obtained with HZG 4A powder diffractometer (Carl Zeiss, Jena). The CuK_α radiation was selected by a Ni filter. The powder diffraction patterns were scanned in a step mode with a step width of 0.02° (2θ). Indexing of the diffraction patterns was performed with the program TREOR90.⁹⁾ Standard procedures were used for chemical analysis of barium (gravimetry), phosphorus (photocolorimetry), and ammonia (the Keldal method).¹⁰⁾ The phosphate anions were identified by QTLC using the method proposed by Prodan et al.¹¹⁾

RESULTS AND DISCUSSION

MgO– NH_4PO_3 system. In accordance with obtained data, formation of two well known, $\text{MgNH}_4(\text{PO}_3)_3$ and $\text{MgNH}_4\text{P}_3\text{O}_9$, and a new $\text{Mg}(\text{NH}_4)_2(\text{PO}_3)_4$ ^{7, 8, 12)} double magnesium-ammonium condensed phosphates was detected in the system. It was found that an increase of ammonium polyphosphate excess in mixtures expanded a crystallization temperature range of double magnesium-ammonium condensed phosphates in general case and double magnesium-ammonium polyphosphates in particular. An increase of temperature from 300 to 400 °C and of reaction time was found to cause the step-by-step crystallization of the following compounds:

It was found that 300 °C and the molar ratio $\text{MgO} : \text{APP} = 1:5$ were optimal for the $\text{Mg}(\text{NH}_4)_2(\text{PO}_3)_4$ preparation. $\text{MgNH}_4\text{P}_3\text{O}_9$ was obtained at the same ratio of reagents at 400 °C. Polyphosphate $\text{MgNH}_4(\text{PO}_3)_3$ crystallizes in the system as admixture.

CaO– NH_4PO_3 system. Tables 1 and 2 show kinetics of the formation of crystalline calcium phosphates in the CaO–APP mixtures at 300 and 400 °C. Known double cyclotriphosphate $\text{CaNH}_4\text{P}_3\text{O}_9$ and a new polyphosphate $\text{Ca}(\text{NH}_4)_2(\text{PO}_3)_4$ crystallize in the system.^{8, 12)}

TABLE 1 Crystalline products formed in the CaO–APP mixtures at 300 °C.

Reaction time, h	CaO : APP molar ratio		
	1 : 3	1 : 5	1 : 8
1	Ca(NH ₄) ₂ (PO ₃) ₄ CaNH ₄ P ₃ O ₉	Ca(NH ₄) ₂ (PO ₃) ₄	Ca(NH ₄) ₂ (PO ₃) ₄
2	Ca(NH ₄) ₂ (PO ₃) ₄ CaNH ₄ P ₃ O ₉	Ca(NH ₄) ₂ (PO ₃) ₄	Ca(NH ₄) ₂ (PO ₃) ₄
10	CaNH ₄ P ₃ O ₉	CaNH ₄ P ₃ O ₉	CaNH ₄ P ₃ O ₉
50	Ca(PO ₃) ₂	Ca(PO ₃) ₂	Ca(PO ₃) ₂

TABLE 2 Crystalline products formed in the CaO–APP mixtures at 400 °C.

Reaction time, h	CaO : APP molar ratio		
	1 : 3	1 : 5	1 : 8
0.2	CaNH ₄ P ₃ O ₉	Ca(NH ₄) ₂ (PO ₃) ₄ CaNH ₄ P ₃ O ₉	Ca(NH ₄) ₂ (PO ₃) ₄
0.5	CaNH ₄ P ₃ O ₉	Ca(NH ₄) ₂ (PO ₃) ₄ CaNH ₄ P ₃ O ₉	Ca(NH ₄) ₂ (PO ₃) ₄ CaNH ₄ P ₃ O ₉
1	CaNH ₄ P ₃ O ₉	CaNH ₄ P ₃ O ₉	CaNH ₄ P ₃ O ₉
15	Ca ₂ P ₄ O ₁₂	Ca ₂ P ₄ O ₁₂	Ca ₂ P ₄ O ₁₂

As seen from Tables 1 and 2, the temperature 300 °C and the molar ratio CaO : APP = 1:5 are optimal for the preparation of Ca(NH₄)₂(PO₃)₄. For the synthesis of CaNH₄P₃O₉, 400 °C and the same molar ratio of components should be recommended. An increase of temperature and reaction time gives rise to the consecutive crystallization of the following compounds:

SrO–NH₄PO₃ system. Only one double condensed phosphate, well known strontium-diammonium cyclotetraphosphate Sr(NH₄)₂P₄O₁₂,¹²⁾ was found in the SrO–APP system. The optimal conditions for the preparation of the compound are the temperature 300 °C and the molar ratio SrO : APP = 1:5. An increase of temperature and reaction time results in the consecutive crystallization of Sr(NH₄)₂P₄O₁₂ and then Sr(PO₃)₂. In contrast to the two above systems, no double strontium-monoammonium condensed phosphates were detected.

BaO–NH₄PO₃ system. Two novel double barium-ammonium polyphosphates, Ba(NH₄)₄(PO₃)₆ and Ba₂NH₄(PO₃)₅, were found in the BaO–APP system. The mixture of these compounds were obtained earlier⁵⁾ and, unfortunately, incorrectly identified as BaNH₄(PO₃)₄. Table 3 shows indexed powder XRD data for Ba(NH₄)₄(PO₃)₆. The compound is isostructural with BaCs₄(PO₃)₆.¹²⁾ 300 °C and the molar ratio BaO : APP = 1:8 are acceptable for the preparation of Ba(NH₄)₄(PO₃)₆. Indexed powder XRD data for Ba₂NH₄(PO₃)₅ are presented in Table 4. The phosphate is isostructural with Ba₂K(PO₃)₅ and Ba₂Cs(PO₃)₅.¹²⁾ The optimal conditions for preparation of the compound are 300 °C and the molar ratio BaO : APP = 1:3. An increase of temperature and

reaction time causes the step-by-step crystallization of the following compounds in the system:

TABLE 3 Indexed powder XRD data (CuK_α radiation) for $\text{Ba}(\text{NH}_4)_4(\text{PO}_3)_6$ (space group $P31c$, unit cell dimensions $a = 11.1911(2)$, $c = 8.9375(2)$ Å).

hkl	$2\theta_{\text{calc}}$, deg	$2\theta_{\text{obs}}$, deg	d_{obs} , Å	I, %	hkl	$2\theta_{\text{calc}}$, deg	$2\theta_{\text{obs}}$, deg	d_{obs} , Å	I, %
1 0 0	9.117	9.119	9.6903	45	3 0 2	34.222	34.224	2.6179	20
1 0 1	13.466	13.465	6.5707	39	3 1 1	34.825	34.823	2.5743	28
1 1 0	15.825	15.827	5.5948	100	2 0 3	35.338	35.340	2.5378	1
0 0 2	19.852	19.851	4.4689	1	2 2 2	37.911	37.913	2.3712	8
2 0 1	20.835	20.836	4.2599	<1	2 1 3	38.936	38.936	2.3112	9
2 1 0	24.278	24.279	3.6630	59	3 1 2	39.074	39.075	2.3034	12
1 1 2	25.489	25.487	3.4920	20	0 0 4	40.333	40.332	2.2344	6
2 1 1	26.272	26.273	3.3893	24	3 2 0	40.540	40.540	2.2235	10
2 0 2	27.122	27.127	3.2845	34	3 0 3	41.185	41.182	2.1902	2
3 0 0	27.589	27.593	3.2301	36	3 2 1	41.833	41.829	2.1579	12
3 0 1	29.374	29.375	3.0381	3	4 0 2	42.402	42.403	2.1300	3
1 0 3	31.388	31.389	2.8476	3	4 1 0	42.719	42.719	2.1149	5
2 1 2	31.555	31.557	2.8328	13	1 1 4	43.583	43.582	2.0750	1
2 2 0	31.963	31.967	2.7974	19	4 1 1	43.960	43.960	2.0581	2
3 1 0	33.305	33.302	2.6883	4	3 1 3	45.408	45.405	1.9959	7

TABLE 4 Indexed powder XRD data (CuK_α radiation) for $\text{Ba}_2\text{NH}_4(\text{PO}_3)_5$ (space group Pc , cell dimensions $a = 8.649(1)$, $b = 7.312(1)$, $c = 13.873(2)$ Å; $\beta = 128.14(1)^\circ$).

hkl	$2\theta_{\text{calc}}$, deg	$2\theta_{\text{obs}}$, deg	d_{obs} , Å	I, %	hkl	$2\theta_{\text{calc}}$, deg	$2\theta_{\text{obs}}$, deg	d_{obs} , Å	I, %
0 1 0	12.095	12.102	7.3073	20	0 1 3	27.368	27.367	3.2563	31
1 0 0	13.005	13.010	6.7993	9	1 2 0	27.680	27.685	3.2196	5
1 0 -2	13.099	13.093	6.7563	9	2 1 0	28.931	28.937	3.0831	39
0 1 1	14.572	14.558	6.0798	41	2 1 -4	29.107	29.111	3.0650	12
1 1 -1	15.859	15.854	5.5853	12	1 1 -4	29.349	29.357	3.0399	21
0 0 2	16.235	16.245	5.4519	26	1 2 1	31.148	31.158	2.8682	29
1 1 -2	17.865	17.880	4.9569	12	3 0 -2	32.028	32.023	2.7927	22
0 1 2	20.294	20.310	4.3690	10	2 2 -3	33.133	33.128	2.7020	32
2 0 -2	20.522	20.534	4.3218	9	2 1 1	34.338	34.337	2.6096	17
1 1 -3	22.826	22.834	3.8914	27	3 1 -4	34.464	34.459	2.6006	10
2 1 -2	23.888	23.892	3.7214	28	0 2 3	34.767	34.761	2.5787	9
0 2 0	24.327	24.342	3.6536	3	0 1 4	35.086	35.085	2.5556	6
2 1 -1	25.212	25.217	3.5288	73	1 2 -4	36.384	36.380	2.4676	3
0 2 1	25.679	25.688	3.4652	100	3 1 -1	37.227	37.217	2.4140	5
2 0 0	26.182	26.203	3.3982	12	0 3 1	37.792	37.787	2.3789	11
2 0 -4	26.374	26.372	3.3768	93	2 0 2	38.876	38.872	2.3149	3
1 0 2	26.496	26.501	3.3607	61	3 0 0	39.723	39.738	2.2664	2
1 0 -4	26.639	26.638	3.3437	27					

MnO– NH_4PO_3 system. It was shown earlier¹³⁾ that MnO_2 reacted with APP reducing Mn(IV) to Mn(II). Two double divalent manganese condensed phosphates, $\text{Mn}(\text{NH}_4)_2(\text{PO}_3)_4$ and orthorhombic $\text{MnNH}_4\text{P}_3\text{O}_9$, were found in the system. The optimal conditions for the formation of these compounds are the same as for isotypical

calcium phosphates. An increase of temperature and reaction time results in the consecutive crystallization of the following compounds:

CoO–NH₄PO₃ system. Two crystalline forms of double cobalt-ammonium polyphosphate $\text{CoNH}_4(\text{PO}_3)_3$, rhombohedral (*r*) and orthorhombic (*o*), and cobalt-diammonium polyphosphate $\text{Co}(\text{NH}_4)_2(\text{PO}_3)_4$ were found in the CoO–APP system. The consecutive crystallization of the following compounds was found by increasing the temperature and reaction time:

NiO–NH₄PO₃ system. In accordance with XRD data, three phosphates were detected in the NiO–APP system. An increase of temperature and reaction time were found to cause the consecutive crystallization of the following compounds:

Unfortunately, because of high solubility of X-phase, it was not isolated and identified.

CuO–NH₄PO₃ system. An increase of temperature and reaction time were found to cause the consecutive crystallization of the compounds in the system CuO–APP:

Cyclooctaphosphate $\text{Cu}_3(\text{NH}_4)_2\text{P}_8\text{O}_{24}$ was detected in the system as admixture at the temperature 300 °C and the molar ratio CuO : APP = 1:3.

ZnO–NH₄PO₃ system. Two double phosphates, well known $\text{Zn}(\text{NH}_4)_2(\text{PO}_3)_4$ and orthorhombic $\text{ZnNH}_4(\text{PO}_3)_3$,¹²⁾ were found in the system ZnO–APP. 300 °C and the molar ratio ZnO : APP = 1:5 are optimal for the $\text{Zn}(\text{NH}_4)_2(\text{PO}_3)_4$ preparation. An increase of temperature and reaction time was found to give rise to the step-by-step crystallization of the following compounds:

CdO–NH₄PO₃ system. Thermal behavior of the CdO–APP system is similar to that of CaO–APP. An increase of temperature and reaction time causes the consecutive crystallization of the compounds:

PbO–NH₄PO₃ system. Only two double phosphates, well known $\text{Pb}(\text{NH}_4)_2\text{P}_4\text{O}_{12}$ and $\text{PbNH}_4(\text{PO}_3)_3$,^{12, 14, 15)} were found in the PbO–APP system. An increase of tem-

perature and reaction time causes the consecutive crystallization of the following compounds:

Conditions of the preparation of lead-ammonium phosphates were described earlier.¹⁵⁾

SUMMARY

It was found that large majority of studied MO–APP systems (M = Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd, and Pb) demonstrated similar schemes of transformations of crystalline phases. An increase of reaction time and temperature from 300 to 400 °C causes the step-by-step crystallization of the following compounds:

The obtained results show that the use of APP is a powerful technique for preparation of large number of known and novel condensed phosphates.

REFERENCES

- 1) G.F. Levchik, S.V. Levchik, A.F. Selevich, A.I. Lesnikovich A.I., A.V. Lutsko, and L. Costa, Fire Retardancy of Polymers. The Use of Intumescence, edited by M. Le Bras *et al.*, Cambridge (UK): Royal Chem. Soc., 280 (1998).
- 2) S. Duquesne, M. Le Bras, S. Bourbigot, and R. Delobel, Phos. Res. Bull., **10**, 88 (1999).
- 3) Z.A. Konstant and A.P. Dindune, Divalen Metal Phosphates, Zinatne, Riga (1987) (In Russian).
- 4) A.F. Selevich, G.F. Levchik, and A.I. Lesnikovich and S.V. Levchik, Belarusian Patent 260A, (1994).
- 5) A.F. Selevich, S.V. Levchik, A.S. Lyakhov, G.F. Levchik, A.I. Lesnikovich, and J.-M. Catala, J. Solid State Chem., **125**, 43 (1996).
- 6) A.F. Selevich, L.S. Ivashkevich, K.I. Khurs, A.S. Lyakhov, and A.I. Lesnikovich, Phos. Res. Bull., **13**, 227 (2002).
- 7) E.V. Grushevich, A.F. Selevich, and A.I. Lesnikovich, Sviridov readings. Iss. 1. Minsk, 16 (2004) (in Russian).
- 8) A.F. Selevich, L.S. Ivashkevich, E.V. Grushevich, and A.I. Lesnikovich, Phos. Res. Bull., **18**, 93 (2005).
- 9) P.E. Werner, L. Eriksson, and M. Westdahl, J. Appl. Crystallogr., **18**, 367 (1985).
- 10) G. Charlot, Les Méthodes de la Chimie Analytique, Paris, 1956.
- 11) E.A. Prodan, I.L. Shashkova, and T.N. Galkova, Zh. Anal. Khim., **33**, 2304 (1978).
- 12) A. Durif, Crystal chemistry of condensed phosphates, Plenum Press, New York, 1995.
- 13) G.F. Levchik, S.V. Levchik, P.D. Sachok, A.F. Selevich, A.S. Lyakhov, and A.I. Lesnikovich, Thermochim. Acta, **257**, 117 (1995).
- 14) B.M. Gatehouse and L.W. Guddat, Acta Crystallogr., **C43**, 1659 (1987).
- 15) A.F. Selevich, A.S. Lyakhov, A.I. Lesnikovich, and L.S. Ivashkevich, Phos. Res. Bull., **12**, 99 (2001).