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Preparation and Characterization of Some Crystalline Condensed Cerium–Ammonium Phosphates

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The present paper is a part of our systematic investigation of M_2^IO–Ce_2O_3–P_2O_5 systems (*1, 2*), undertaken because the properties of Ce^{3+} compounds are of interest in the field of ultrafast luminophors (*3*). We describe chemical preparations and give the main crystallographic features for three forms of $(NH_4)_2O \cdot Ce_2O_3 \cdot 4P_2O_5$ and for $(NH_4)_2Ce(PO_3)_5$, a new structural type of long chain polyphosphate.

Experimental

Starting materials in each case were reagent grade diammonium hydrogen monophosphate, $(NH_4)_2HPO_4$, and cerium chloride heptahydrate, $CeCl_3 \cdot 7H_2O$. Mixtures of these two salts were heated in open carbon crucibles. Thermal treatments were made in two steps. First the temperature was increased to 433 K at a rate of 3°/min and kept constant for 3 hr. Subsequently, the temperature was increased to 573–623 K with the same heating rate. Table I reports details of these preparations. The existence of the $(NH_4)_2Ce(PO_3)_5$ compound has been observed earlier (*4*).

X-Ray diffraction powder diagrams were recorded at low scan speed ((1°/8)θ/min) using a Philips Norelco diffractometer operating with copper radiation $K\alpha$. Space groups have been determined by the Weissenberg

TABLE I

TYPICAL MIXING QUANTITIES OF RAW MATERIALS FOR SINGLE CRYSTAL GROWTH OF BINARY CERIUM-AMMONIUM POLY- AND METAPHOSPHATES

Product	$(NH_4)_2HPO_4$ (g)	$CeCl_3 \cdot 7H_2O$ (g)	Temperature and time of crystallization	Crystal morphology
$NH_4Ce(PO_3)_4$	13.2	0.7	623 K; 10 hr	Square monoclinic antiprisms
$NH_4CeP_4O_{12}$ (cubic)	13.2	1.9	603 K; 14 hr	Tetrahedra
$NH_4CeP_4O_{12}$ (monoclinic)	2.4	0.8	573 K; 18 hr	Needle-shaped
$(NH_4)_2Ce(PO_3)_5$	5.4	1	593 K; 20 hr	Diamond-like

0022-4596/83 $3.00

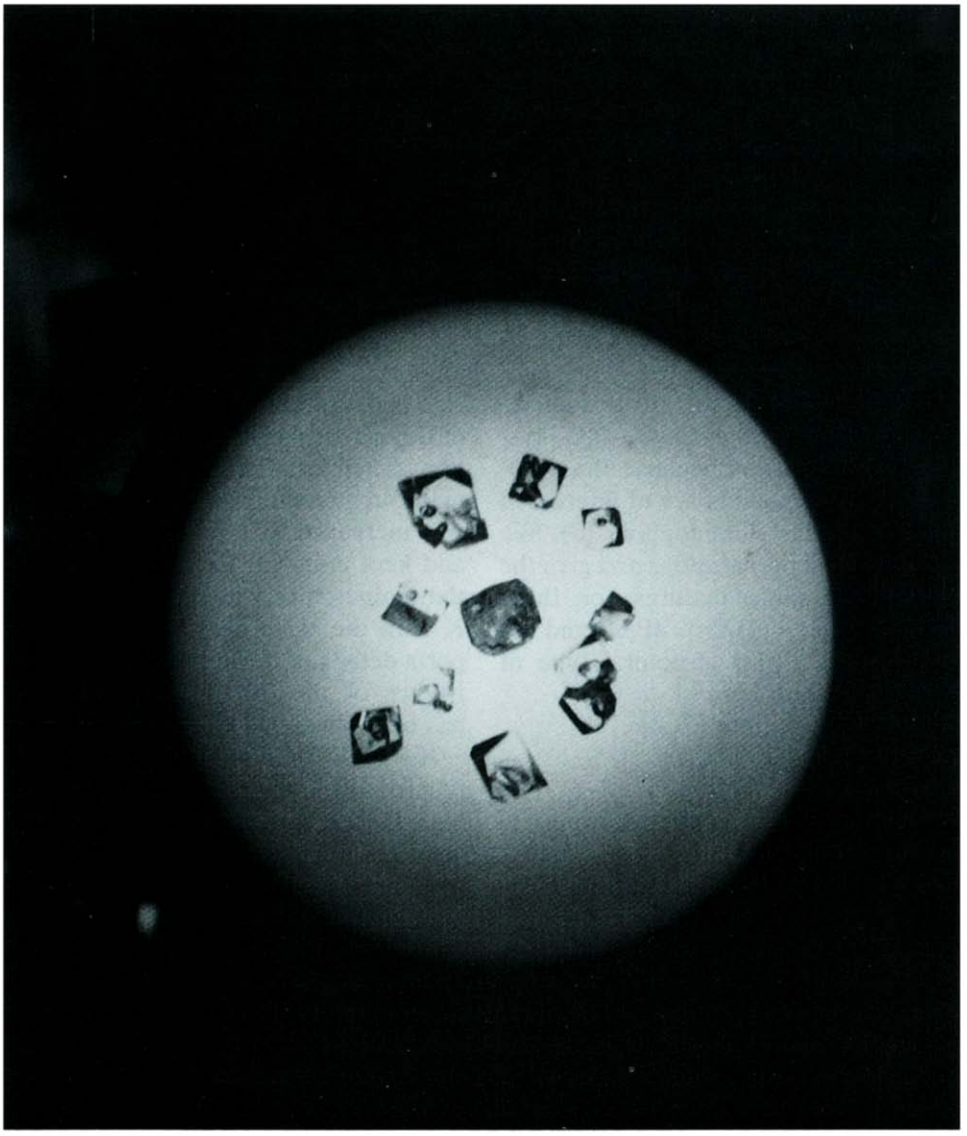

FIG. 1a. Crystal morphology of $NH_4Ce(PO_3)_4$.

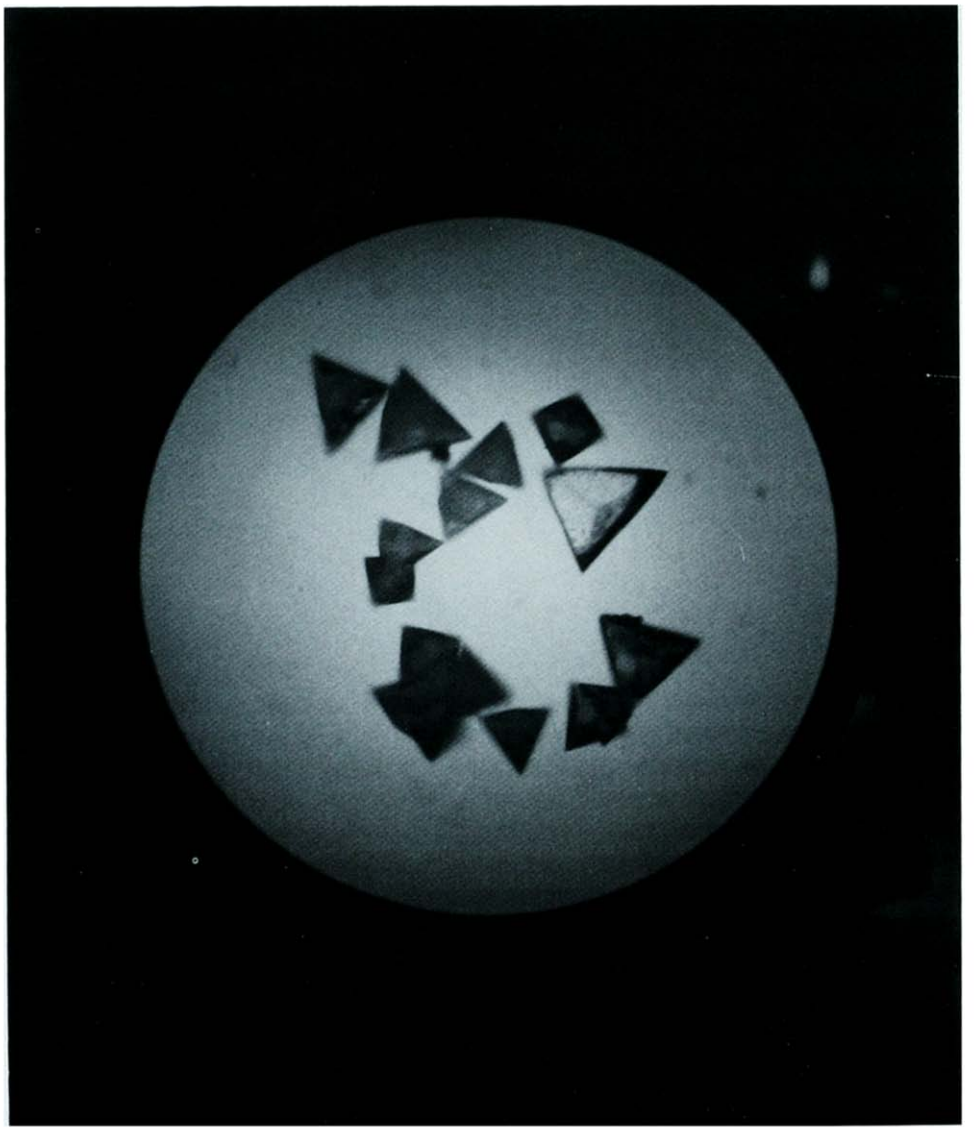

FIG. 1b. Crystal morphology of $NH_4CeP_4O_{12}$ (cubic).

FIG. 1c. Crystal morphology of $NH_4CeP_4O_{12}$ (monoclinic).

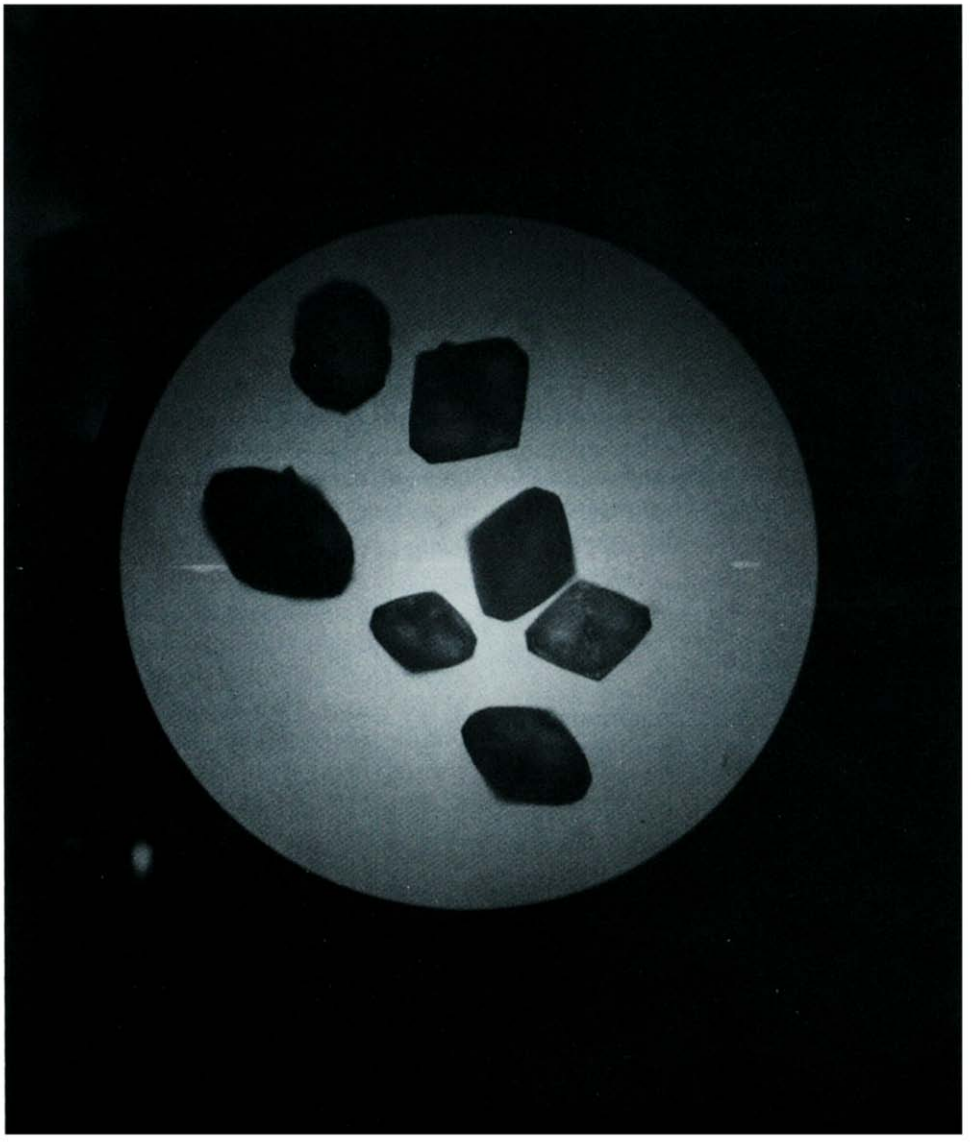

FIG. 1d. Crystal morphology of $(NH_4)_2Ce(PO_3)_5$.

TABLE II

CRYSTALLOGRAPHIC CHARACTERISTICS OF BINARY CERIUM–AMMONIUM POLY- AND METAPHOSPHATES

Compound	System	Space group	Unit cell parameter a(Å) α(°)	Unit cell parameter b(Å) β(°)	Unit cell parameter c(Å) γ(°)	Z	V (Å^3)	Density, D_x (g/cm^3)
$NH_4Ce(PO_3)_4$	Monoclinic	$P2_1/n$	10.474(6)	9.011(4) 106.64(3)°	10.947(7)	4	989.86	3.18
$NH_4CeP_4O_{12}$	Cubic	$I\bar{4}3d$	15.164(3)			12	3487.19	2.71
$NH_4CeP_4O_{12}$	Monoclinic	$C2/c$	7.930(3)	12.634(5) 110.05(3)°	10.699(5)	4	1006.94	3.13
$(NH_4)_2Ce(PO_3)_5$	Triclinic	$P\bar{1}$	7.254(2) 90.07(2)°	13.372(3) 107.3(1)°	7.277(2) 90.42(2)°	2	673.06	2.85

technique. Unit cell parameters have been refined by a least squares method using the powder data.

Infrared spectra were recorded on an IR-580 Perkin–Elmer spectrophotometer using pellets formed by mixing the specimens with KBr.

Results and Discussion

Under the experimental conditions described in Table I, four different binary cerium–ammonium poly- and metaphosphates have been prepared (Fig. 1). Their crystallographic characteristics are summarized in Table II. Indexed X-ray diffraction patterns are reported in Tables III–VI. Each crystalline form presents typical structural features:

$NH_4Ce(PO_3)_4$, square monoclinic prisms, is a long chain polyphosphate isotypic with $RbNd(PO_3)_4$ (*5*). Two infinite (PO_3) chains, with a period of eight tetrahedra run along the [101] direction. Cerium atoms have an eightfold coordination while NH_4 groups have nine oxygen neighbors. The main crystallographic features of this salt are reported in Table II.

$NH_4CeP_4O_{12}$ (cubic), tetrahedral crystals, is a binary metaphosphate isotypic with $CsNdP_4O_{12}$ (*6*). $(P_4O_{12})^{-4}$ anions are rings of four PO_4 tetrahedra, linked by shared oxygen atoms. Cerium atoms have an eightfold coordination while NH_4 groups have nine oxygen neighbors. The parame-

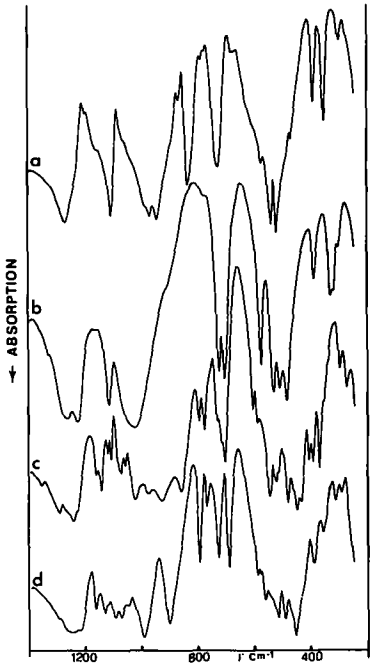

FIG. 2. Infrared absorption spectra of (a) $NH_4CeP_4O_{12}$ (cubic); (b) $NH_4CeP_4O_{12}$ (monoclinic); (c) $NH_4Ce(PO_3)_4$; (d) $(NH_4)_2Ce(PO_3)_5$.

TABLE III

X-RAY POWDER DATA FOR $NH_4Ce(PO_3)_4$

h k l	d_{cal} (Å)	d_{obs} (Å)	I (%)	h k l	d_{cal} (Å)	d_{obs} (Å)	I (%)
$\bar{1}$ 0 1	8.58	8.56	47	$\bar{3}$ 0 1	3.489	3.491	24
0 1 1	6.84	6.84	71	$\bar{2}$ 2 1	3.387	3.387	82
1 0 1	6.39	6.39	47	$\bar{2}$ 1 3	3.144	3.145	24
$\bar{1}$ 1 1	6.21	6.22	92	3 1 0	3.136	3.135	35
1 1 1	5.21	5.22	100	1 0 3	3.042	3.043	18
2 0 0	5.02	5.02	15	$\bar{3}$ 0 3	2.861	2.860	41
$\bar{1}$ 1 2	4.58	4.58	18	0 2 3	2.762	2.759	18
0 1 2	4.53	4.53	17	$\bar{3}$ 2 1	2.759		
$\bar{2}$ 0 2	4.29	4.29	76	$\bar{1}$ 0 5	2.182	2.178	19
$\bar{1}$ 0 3	3.642	3.640	27	$\bar{1}$ 4 1	2.179		

ters of its cubic unit cell are given in Table II.

$NH_4CeP_4O_{12}$ (monoclinic), needle-shaped crystals, is a binary metaphosphate isostructural with $NH_4PrP_4O_{12}$ (*7*). Its monoclinic unit cell contains P_4O_{12} rings. The cyclic anions provide eight and six oxygen atoms about Ce^{3+} and NH_4^+, respectively.

$(NH_4)_2Ce(PO_3)_5$, diamond-like crystals, is another type of long chain polyphosphate with a P1 triclinic unit cell. The most interesting crystallographic feature of this salt is the existence of two independent infinite $(PO_3)_n$ chains in the unit cell; one running along the **a** axis, the other along the **c** axis. Both have a period of five tetrahedra. This is the first long chain polyphosphate to exhibit such a feature. We detail this structure elsewhere (*8*).

TABLE IV

X-RAY POWDER DATA FOR $NH_4CeP_4O_{12}$ (CUBIC)

h k l	d_{cal} (Å)	d_{obs} (Å)	I (%)	h k l	d_{cal} (Å)	d_{obs} (Å)	I (%)
2 1 1	6.19	6.20	100	4 3 1 5 1 0	2.974	2.978	67
2 2 0	5.36	5.37	23	5 2 1	2.769	2.770	23
3 1 0	4.80	4.80	17	5 3 2 6 1 1	2.460	2.464	17
3 2 1	4.05	4.05	40	6 2 2	2.286	2.288	13
4 0 0	3.791	3.792	27	5 5 2 6 3 3 7 2 1	2.064	2.067	10
4 2 0	3.391	3.394	17	6 4 2	2.026	2.029	30
3 3 2	3.233	3.241	30	7 3 0	1.991	1.993	10
4 2 2	3.095	3.100	15				

TABLE V

X-RAY POWDER DATA FOR $NH_4CeP_4O_{12}$ (MONOCLINIC)

h k l	d_{cal} (Å)	d_{obs} (Å)	I (%)	h k l	d_{cal} (Å)	d_{obs} (Å)	I (%)
1 1 0	6.42	6.42	19	0 4 2	2.674	2.675	6
0 2 0	6.32	6.32	58	$\bar{1}$ 1 4	2.617	2.616	6
0 2 1	5.35	5.35	71	3 1 0	2.436	2.437	6
1 1 1	4.80	4.80	26	2 4 0	2.409	2.409	23
$\bar{1}$ 1 2	4.69	4.69	35	1 5 0	2.393	2.392	6
2 0 0	3.725	3.723	14	$\bar{3}$ 1 3	2.390		
1 3 0	3.666	3.663	32	2 2 4	2.342	2.344	9
1 1 2	3.488	3.488	100	1 3 3	2.288	2.289	6
$\bar{1}$ 1 3	3.412	3.412	6	2 4 1	2.233	2.233	6
$\bar{2}$ 2 1	3.357	3.356	9	$\bar{3}$ 3 1	2.231		
1 3 1	3.271	3.271	19	$\bar{3}$ 3 3	2.107	2.108	6
$\bar{1}$ 3 2	3.233	3.234	65	0 6 0	2.106		
2 2 0	3.208	3.207	9	0 6 1	2.061	2.060	13
$\bar{2}$ 2 2	3.160	3.158	19	$\bar{1}$ 5 3	2.057		
0 4 0	3.157			2 2 3	2.036	2.033	13
2 2 1	2.824	2.824	8				

TABLE VI

X-RAY POWDER DATA FOR $(NH_4)_2Ce(PO_3)_5$

h k l	d_{cal} (Å)	d_{obs} (Å)	I (%)	h k l	d_{cal} (Å)	d_{obs} (Å)	I (%)
0 0 1	6.94	6.94	50	1 $\bar{1}$ 2	2.728	2.729	21
0 2 0	6.69	6.69	13	1 4 $\bar{1}$	2.647	2.647	5
0 $\bar{1}$ 1	6.17	6.17	89	1 5 $\bar{1}$	2.430	2.429	11
$\bar{1}$ 0 1	5.86	5.86	8	2 4 $\bar{1}$	2.427		
1 1 $\bar{1}$	5.36	5.36	32	$\bar{3}$ 2 1	2.278		
0 2 1	4.80	4.79	66	0 1 3	2.277	2.276	13
1 2 0	4.79			3 1 0	2.275		
$\bar{1}$ 2 1	4.41	4.40	8	2 1 $\bar{3}$	2.231	2.230	8
1 2 $\bar{1}$	4.40			$\bar{3}$ 1 2	2.230		
1 1 1	4.08	4.08	5	0 $\bar{2}$ 3	2.188		
1 3 0	3.733	3.732	24	$\bar{3}$ 2 0	2.185	2.186	5
1 2 1	3.602	3.061	18	0 2 3	2.184		
$\bar{2}$ 0 1	3.552	3.550	26	$\bar{1}$ 5 $\bar{2}$	2.139		
1 1 $\bar{2}$	3.441	3.440	74	1 5 $\bar{2}$	2.138	2.139	13
1 $\bar{1}$ $\bar{2}$	3.440			$\bar{3}$ 2 $\bar{2}$	2.137		
0 $\bar{1}$ 2	3.361	3.361	100	1 6 0	2.116	2.114	16
2 1 0	3.342	3.341	84	0 5 $\bar{2}$	2.114		
$\bar{1}$ 2 2	3.143	3.143	8	1 6 $\bar{1}$	2.080	2.078	5
1 $\bar{2}$ $\bar{2}$	3.142			2 $\bar{2}$ 2	2.049	2.045	8
0 $\bar{2}$ 2	3.084	3.083	5	$\bar{3}$ 3 0	2.041		
$\bar{2}$ $\bar{2}$ 0	3.082			$\bar{3}$ 1 1	1.994	1.992	8
0 4 1	3.016	3.016	24	3 1 $\bar{1}$	1.989		
1 4 0	3.001	3.000	18	3 2 $\bar{3}$	1.873	1.874	5
$\bar{2}$ 0 2	2.930	2.931	11	1 7 $\bar{1}$	1.814	1.814	16

The ir absorption spectra (Fig. 2) are characteristic of cyclic phosphates and linear polyphosphates (*9*), respectively.

We used these compounds and other binary condensed phosphates of the same type to investigate the Ce^{3+} luminescence in such materials. The results will be published in subsequent contributions.

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