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# Synthesis of Cerium Phosphates by Thermal Polycondensation of Mixtures $CeO_2$–$NH_4H_2PO_4$ and Investigation of Their Structure

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Processes of thermal condensation in the mixtures $CeO_2$ and $NH_4H_2PO_4$ at 200–1400°C have been studied with the methods of differential thermal analysis, chemical and X-ray analysis, paper chromatography, and IR spectroscopy. Methods for obtaining double phosphates of cerium–ammonium $Ce_3(NH_4)_2H(PO_4)_5$, $CeNH_4HP_3O_{10}$, $CeNH_4P_4O_{12}$ (monoclinic), and $Ce(NH_4)_2(PO_3)_5$ have been elaborated. The structure of $Ce(NH_4)_2(PO_3)_5$ has been determined. The compound is monoclinic; unit cell parameters are $a = 8.598(3)$ Å, $b = 11.733(3)$ Å, $c = 13.375(4)$ Å, $\beta = 90.48(2)°$, $Z = 4$; space group *Cc*. $Ce(NH_4)_2(PO_3)_5$ is a polyphosphate with five tetrahedra in the identity period of the chains. On the basis of the obtained data a scheme for interaction of crystalline and amorphous heating products of the mixtures $CeO_2$ and $NH_4H_2PO_4$ dependent on the initial ratio of components P/Ce and temperature has been devised. © 1988 Academic Press, Inc.

## Introduction

For synthesis of phosphates of rare-earth elements heating of oxides or metal salts with phosphoric acid is usually performed. Polycondensation reactions, occurring in the mixtures, have been studied in detail (*1, 2*). Solid-state synthesis with application of ammonium phosphates has been used previously to obtain several phosphates of rare-earth elements including double-ammonium-containing compounds with different degrees of condensation of phosphate anion (*3–5*). However, polycondensation mechanism in the mixture metal oxide–ammonium phosphate has been investigated insufficiently. The aim of the present paper is to establish the basic regularities of the reactions occurring in the mixture $CeO_2$–$NH_4H_2PO_4$, conditions for isolation of individual compounds, their properties, and structure.

## Experimental

For the synthesis $CeO_2$ and $NH_4H_2PO_4$ were used (in some cases also $Ce(NO_3)_3 \cdot 6H_2O$ and $Ce(NH_4)_2(NO_3)_6$), especially pure and of analytical grade. The P/Ce ratio of components in mixtures of the starting materials was changed within the range 0.1–20. The samples were heated in open corundum crucibles in an electric furnace with automatic temperature regulation; the precision was ±0.5°. The heating rate was 5°/min or 0.2–0.5°/min (for the synthesis of ammonium-containing phosphates); treatment time was varied from 1–200 hr. X-ray analysis was performed on a diffractometer DRON-1 to identify products and establish

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the succession of the reactions (radiation Cu$K\alpha$, Ni-filter). Thermal analysis was performed on a derivatograph of the Paulik–Paulik–Erdey Q-1000 system; IR spectra were taken on a spectrophotometer UR-20 for the samples compressed with KBr. To perform chromatographic analysis ~0.1 g of phosphate was mixed with ~5 g of ion-exchange resin IR-100 or SNK-25E for 4 hr. After filtration and neutralization the solutions were chromatographed on paper FN-11 in dioxan solvent.

Chemical analysis was carried out to determine the contents of cerium, phosphorus, and nitrogen: cerium was determined after decomposition of the sample with concentrated $H_2SO_4$ and division on cationite KU-2-I2P, phosphorus, in the form of phosphorus molybdenum blue complex, and nitrogen was determined on a Hewlett–Packard 185 CHN analyzer. Analytical data for cerium–ammonium phosphates are given in Table I.

Determination of the structure of $Ce(NH_4)_2(PO_3)_5$ has been performed with X-ray intensities collected on a Syntex $P2_1$ diffractometer, radiation Mo$K\alpha$, graphite monochromator, scanning $\theta$–2 $\theta$, sin $\theta/\lambda \leq 0.65$. Out of 1950 reflexes 1934 with $1 > 2\sigma$ were used. After anisotropic refinement of the nonhydrogen atoms $R = 4.9\%$.

## Results and Discussion

### *Investigation of Thermal Interaction*

According to thermal analysis data (*7*) reaction of $CeO_2$ with ammonium phosphate begins almost immediately after the melting of $NH_4H_2PO_4$ at approximately 200°C and proceeds stepwise and a number of unstable intermediate materials are formed. Their composition is particularly controlled by the starting ratio of the components P/Ce and by the conditions of thermal treatment. Preliminary experiments showed that on rapid heating (5–12°C/min) of mixtures when P/Ce > 10, the only crystalline phase is ultraphosphate $CeP_5O_{14}$, which is formed exclusively at 600°C. However, with ratios P/Ce < 5 at 300–400°C diphosphate of Ce(IV) $CeP_2O_7$ and long-chain phosphate of Ce(III) $Ce(PO_3)_3$ were found. By slow heating and varying the treatment time (0.2–0.5°C/min, $\tau > 10$ hr) in the interval 220–400°C we succeeded in isolating several double phosphates of cerium(III, IV) and ammonium with different condensation degrees which exist within a comparatively narrow temperature range. This is related to the presence of an amorphous well-soluble phase in the samples which presents a mixture of condensated ammonium phosphates and/or polyphosphoric acids (above 400°C). When heated the amorphous materials interact with crystalline phosphates which lead to decomposition of the latter and formation of new compounds, having, as a rule, a higher degree of condensation.

TABLE I

Elemental Analysis of Cerium–Ammonium Phosphates

| Compound | Found, % |  |  | Calculated, % |  |  |
|---|---|---|---|---|---|---|
|  | Ce | P | N | Ce | P | N |
| $Ce_3(NH_4)_2H(PO_4)_5$ | 44.69 | 16.47 | 2.96 | 45.09 | 16.61 | 3.19 |
| $CeNH_4HP_3O_{10}$ | 33.62 | 22.56 | 3.51 | 34.00 | 22.50 | 3.40 |
| $CeNH_4P_4O_{12}$ | 29.52 | 25.79 | 2.98 | 29.56 | 26.14 | 2.96 |
| $Ce(NH_4)_2(PO_3)_5$ | 24.34 | 27.77 | 4.86 | 24.54 | 27.12 | 4.91 |

As primary products of interaction of $CeO_2$ and $NH_4H_2PO_4$ double phosphates of cerium(IV)–ammonium are formed. At 220–240°C in a wide concentration range bright yellow fine crystals of monophosphate $Ce_3(NH_4)_2H(PO_4)_5$ (*8*) have been isolated. This compound is unstable when heated—at approximately 250°C gradual decomposition sets in (Fig. 1a), accompanied by partial reduction of Ce(IV) to Ce(III) and formation of amorphous intermediate products. According to the data of

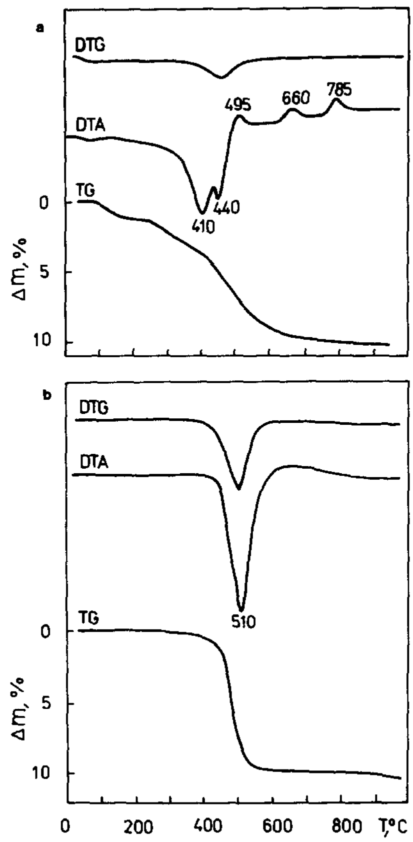

FIG. 1. Curves of thermoanalysis of $Ce_3(NH_4)_2H(PO_4)_5$ (a) and $CeNH_4HP_3O_{10}$ (b).

X-ray analysis of quenched reaction products at 550°C $CeP_2O_7$ and $CePO_4$ (monoclinic) are formed:

$$Ce_3(NH_4)_2H(PO_4)_5 \xrightarrow[-O_2]{250-300°C} \text{amorphous phase} \xrightarrow[-NH_3,\ -H_2O,\ -O_2]{500-550°C} 2CeP_2O_7 + CePO_4 \quad (1)$$

A further increase in temperature leads to decomposition of diphosphate $CeP_2O_7$ and to complete reduction of cerium(IV) according to the following equation:

$$CeP_2O_7 \xrightarrow[-O_2]{550-790°C} CePO_4 + Ce(PO_3)_3 \quad (2)$$

Exothermic effects on the differential thermal analysis (DTA) curve at 700–800°C are caused by crystallization of mono- and polyphosphates of Ce(III) (Fig. 1a).

In the presence of decomposition products of ammonium phosphate, $Ce_3(NH_4)_2H(PO_4)_5$ when heated for more than 10 hr converts into a new crystalline phase $CeNH_4HP_3O_{10}$ (initial ratio in the mixture P/Ce > 5) or $CeP_2O_7$ (at P/Ce = 3–5). Double acidic triphosphate of cerium(III)–ammonium presents a white fine crystalline substance which is stable up to ~400°C. At 460–510°C on the DTA curve of cerium–ammonium triphosphate a pronounced endothermic effect is observed (Fig. 1b), which corresponds to the procedure of the following reaction:

$$CeNH_4HP_3O_{10} \xrightarrow[-NH_3,\ -H_2O]{460-510°C} Ce(PO_3)_3 \quad (3)$$

However, in the presence of the amorphous phase, where phosphorus is abundant, $CeNH_4HP_3O_{10}$ at 300°C already forms homogeneous melts with complex anionic composition. With a temperature increase resulting from the intensive evolution of $NH_3$ a reductive gassy medium is formed which favors the transition of Ce(IV) into Ce(III) and crystallization of predominantly cerium(III) phosphates. For the first time we have received at 380–400°C double phosphates of cerium–ammonium $Ce(NH_4)_2(PO_3)_5$ and $CeNH_4P_4O_{12}$ (monoclinic modification) which crystallize from mixtures with the starting ratios P/Ce > 10 and P/Ce = 5–10, respectively (*9*, *10*). Cubic modification of $CeNH_4P_4O_{12}$ and polyphosphate $CeNH_4(PO_3)_4$ obtained by Rzaigui and Ariguib (*11*) on interaction of $CeO_2$ with decomposition products of $NH_4H_2PO_4$ is not formed. In addition, with a reduction in the ratio P/Ce, polyphosphate of Ce(IV) $Ce(PO_3)_4$ crystallizes as admixture.

Monoclinic modification of cyclophosphate $CeNH_4P_4O_{12}$ is isotypic with regard to the previously described $PrNH_4P_4O_{12}$

(*4*). Crystals are transparent and birefringent; they are insoluble in water but are slowly decomposed by concentrated $H_2SO_4$. On the DTA curve of double cyclotetraphosphate of cerium–ammonium (Fig. 2a) an endothermic effect is observed at 600°C which corresponds to the decomposition reaction:

$$CeNH_4P_4O_{12} \xrightarrow[-NH_3,\ -H_2O]{460\text{–}600^\circ C} Ce(PO_3)_3 + CeP_5O_{14} \qquad (4)$$

Flat exothermic effect at ~670°C corresponds to the crystallization of poly- and ultraphosphates of cerium.

Double phosphate $Ce(NH_4)_2(PO_3)_5$ is isolated in the form of large birefringent crystals. The composition of this compound has no analogs in phosphate series of rare-earth elements, and it will be discussed later. When $Ce(NH_4)_2(PO_3)_5$ is heated above 400°C decomposition occurs in two stages corresponding to two endothermic effects at 460 and 550°C (Fig. 2b). It has been established by X-ray analysis that $CeNH_4P_4O_{12}$ is formed as an intermediate decomposition product:

$$Ce(NH_4)_2(PO_3)_5 \xrightarrow[-NH_3,\ -H_2O]{400\text{–}460^\circ C} CeNH_4P_4O_{12} + \text{amorphous phase} \qquad (5)$$

It is of interest that, according to analysis of gas evolution, cleavage of $NH_3$ slightly precedes elimination of $H_2O$, which suggests that in the initial stages of decomposition intermediate products of the type $Ce(NH_4)_{2-x}H_x(PO_3)_5$ are formed where $x = 0\text{–}1$.

Further increase of temperature leads to decomposition of cyclotetraphosphate $CeNH_4P_4O_{12}$ and to interaction of the products with amorphous phase which presents a mixture of polyphosphoric acids $(HPO_3)_n$:

$$CeNH_4P_4O_{12} + \text{amorphous phase} \xrightarrow[-NH_3,\ -H_2O]{550\text{–}670^\circ C} CeP_5O_{14} \qquad (6)$$

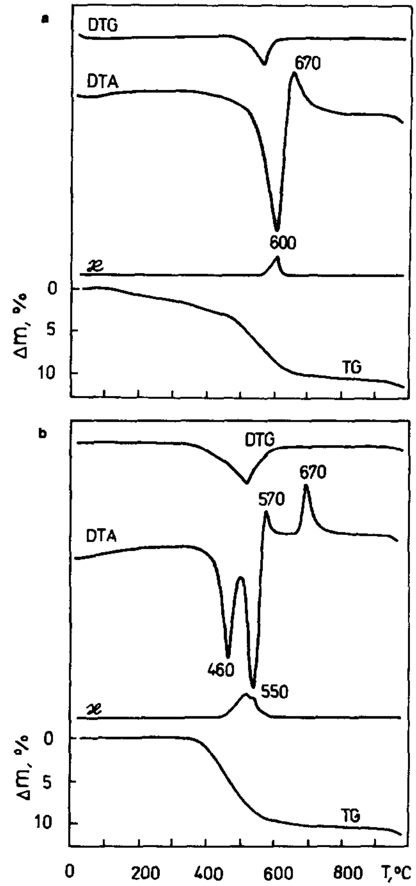

FIG. 2. Curves of thermoanalysis and relative electric conductivity (ϰ) $CeNH_4P_4O_{12}$ (a) and $Ce(NH_4)_2(PO_3)_5$ (b).

It has been confirmed by X-ray analysis and IR spectra of samples quenched from 600–700°C that exothermic effects on the DTA curve at 570 and 670°C are related to the formation and crystallization of ultraphosphate $CeP_5O_{14}$. At ~900°C on DTA curves of $CeNH_4P_4O_{12}$ and $Ce(NH_4)_2(PO_3)_5$ endothermic effects are observed accompanied by loss of weight (Fig. 2). This is conditioned by gradual decomposition of $CeP_5O_{14}$ and expulsion of $P_4O_{10}$ and by transition into glassy state at ~1100°C.

In mixtures with the initial ratio P/Ce < 5 formation of double phosphates cerium–

ammonium at 300–400°C is not characteristic (in several samples a small admixture of $\mathrm{CeNH_4P_4O_{12}}$ has been detected). The main crystallization product is $\mathrm{CeP_2O_7}$ the stability of which increases considerably with the increased $\mathrm{CeO_2}$ mixture. Decomposition of diphosphate (Fig. 3b) proceeds stepwise and intermediate products $\mathrm{Ce(PO_3)_3}$ and $\mathrm{Ce(PO_3)_4}$ are formed. Polyphosphate of Ce(IV) is unstable when heated above 490°C: at 535°C on the DTA curve an endothermic effect is observed which corresponds to decomposition according to the following scheme:

$$\mathrm{Ce(PO_3)_4} \xrightarrow[-\mathrm{O_2},\ -\mathrm{P_4O_{10}}]{490\text{–}535^\circ\mathrm{C}} \mathrm{Ce(PO_3)_3} \qquad (7)$$

The exothermic effect at ~545°C corresponds to crystallization of $\mathrm{Ce(PO_3)_3}$. Taking these data into account the decomposition process can be formulated as follows:

$$\begin{aligned} &\mathrm{CeP_2O_7} \xrightarrow[-\mathrm{O_2}]{390\text{–}430^\circ\mathrm{C}} \mathrm{Ce(PO_3)_3} \\ &\quad + \mathrm{Ce(PO_3)_4} + \text{amorphous phase} \xrightarrow[-\mathrm{O_2}]{470\text{–}545^\circ\mathrm{C}} \\ &\quad \mathrm{Ce(PO_3)_3} + \text{amorphous phase} \xrightarrow{>630^\circ\mathrm{C}} \\ &\qquad \mathrm{Ce(PO_3)_3} + \mathrm{CePO_4}(\text{monoclinic}) \qquad (8) \end{aligned}$$

If the samples alongside $\mathrm{CeP_2O_7}$ have amorphous phase (see Eq. (8)) reaction is completed by crystallization of $\mathrm{Ce(PO_3)_3}$ at ~500°C. Above 850°C slow evolution of $\mathrm{P_4O_{10}}$ (endothermic effect at 850°C on DTA curves, Fig. 3) and gradual transition of polyphosphate into $\mathrm{CePO_4}$ (monoclinic) begins. However, at a heating rate 5–10 deg/min in the interval 1100–1200°C cerium phosphate glass can be obtained. By chemical analysis and optical spectrum it has been established that cerium is present in glass predominantly in the trivalent state; however, with an increase of $\mathrm{CeO_2}$ concentration the contents of Ce(IV) increases and produces the amber color of the glass. Ce(IV) contents in terms of $\mathrm{CeO_2}$ reaches 1.15 mole%.

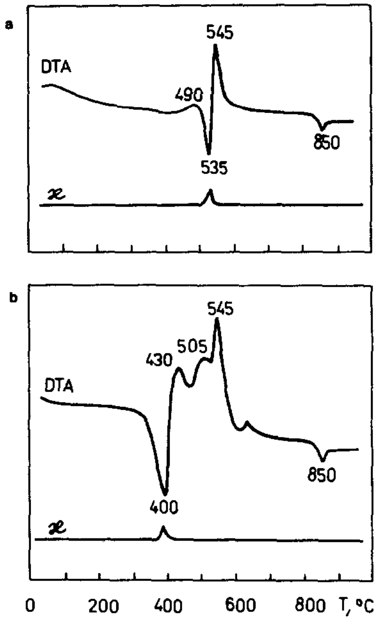

FIG. 3. Curves of thermoanalysis and relative electric conductivity (ϰ) $\mathrm{Ce(PO_3)_4}$ (a) and $\mathrm{CeP_2O_7}$ (b).

In mixtures with a large excess of $\mathrm{CeO_2}$ the only product of interaction above 610–630°C is $\mathrm{CePO_4}$ (monoclinic). As a result of partial oxidation of Ce(III) to Ce(IV) at high temperature (>1000°C) samples have a greenish color.

### *Structural Studies*

Out of the synthesized cerium–ammonium phosphates with unknown structure the most interesting was $\mathrm{Ce(NH_4)_2(PO_3)_5}$. The structure of the compound $\mathrm{CeNH_4H(PO_3)_5}$ from phosphate series $\mathrm{Ce(NH_4)_{2-x}H_x(PO_3)_5}$, which was discussed above, was described in (*12*) and later (*13*) the structure of $\mathrm{Ce(NH_4)_2(PO_3)_5}$ was determined. Comparison of the data (*13*) with triclinic $\mathrm{Ce(NH_4)_2(PO_3)_5}$ synthesized in (*11*) and structurally investigated in (*14*) shows that it is one and the same compound.

$\mathrm{Ce(NH_4)_2(PO_3)_5}$ is monoclinic, with space group *Cc*, $a = 8.598(3)$ Å, $b = 11.733(3)$ Å, $c = 13.375(4)$ Å, $\beta = 90.48(2)^\circ$, $Z = 4$, $V =$

TABLE II

ATOMIC COORDINATES IN THE STRUCTURE OF $Ce(NH_4)_2(PO_3)_5$

| Atoms | $X(\sigma_x)$ | $Y(\sigma_y)$ | $Z(\sigma_z)$ |
|---|---|---|---|
| Ce | 0.0000(0) | 0.0955(1) | 0.2500(0) |
| P(1) | 0.2078(4) | 0.1954(3) | 0.4868(3) |
| P(2) | 0.1740(4) | 0.3804(3) | 0.1619(2) |
| P(3) | 0.4259(4) | 0.3917(3) | 0.4697(3) |
| P(4) | 0.1972(4) | 0.5761(3) | 0.4437(3) |
| P(5) | 0.3356(4) | 0.8932(3) | 0.1715(3) |
| O(1) | 0.2696(12) | 0.4605(8) | 0.4854(8) |
| O(2) | 0.0194(15) | 0.0994(9) | 0.0609(8) |
| O(3) | 0.0098(12) | 0.4434(8) | 0.1676(8) |
| O(4) | 0.3382(12) | 0.7763(8) | 0.2114(8) |
| O(5) | 0.2412(15) | 0.9810(10) | 0.2225(9) |
| O(6) | 0.0385(13) | 0.5506(10) | 0.4025(8) |
| O(7) | 0.3597(14) | 0.2673(9) | 0.4571(10) |
| O(8) | 0.1881(15) | 0.3508(9) | 0.0445(9) |
| O(9) | 0.4996(13) | 0.4203(8) | 0.3713(8) |
| O(10) | 0.3107(14) | 0.6376(9) | 0.3793(9) |
| O(11) | 0.0932(14) | 0.7377(11) | 0.0409(9) |
| O(12) | 0.2893(16) | 0.8968(9) | 0.0574(9) |
| O(13) | 0.1692(13) | 0.2651(8) | 0.2109(8) |
| O(14) | 0.2963(12) | 0.4748(10) | 0.1994(8) |
| O(15) | 0.1586(14) | 0.1360(9) | 0.3940(7) |
| N(1) | 0.4933(29) | 0.2079(13) | 0.2459(22) |
| N(2) | 0.3314(19) | 0.8819(15) | 0.4488(14) |

TABLE III

ANISOTROPIC THERMAL PARAMETERS

| Atom | $B_{11}(\sigma)$ | $B_{22}(\sigma)$ | $B_{33}(\sigma)$ | $B_{12}(\sigma)$ | $B_{13}(\sigma)$ | $B_{23}(\sigma)$ |
|---|---|---|---|---|---|---|
| Ce | 0.81(2) | 0.47(2) | 0.48(2) | −0.03(3) | −0.07(1) | 0.00(2) |
| P(1) | 0.81(11) | 0.86(11) | 1.40(12) | −0.22(9) | 0.09(9) | 0.10(9) |
| P(2) | 0.70(11) | 0.71(10) | 0.73(10) | 0.14(9) | −0.08(8) | −0.35(8) |
| P(3) | 0.68(12) | 0.62(10) | 1.49(13) | −0.06(8) | 0.16(10) | −0.02(9) |
| P(4) | 0.79(12) | 0.83(10) | 1.40(12) | 0.12(9) | 0.40(9) | 0.01(9) |
| P(5) | 0.85(12) | 0.78(11) | 0.79(11) | 0.12(8) | 0.14(9) | 0.18(8) |
| O(1) | 1.5(4) | 0.3(3) | 1.7(4) | 0.4(3) | 0.5(3) | 0.2(3) |
| O(2) | 1.7(5) | 1.9(4) | 1.0(4) | 0.1(3) | 0.0(3) | −0.3(3) |
| O(3) | 1.0(4) | 0.5(3) | 2.0(4) | 0.3(3) | 0.5(3) | 0.1(3) |
| O(4) | 1.1(4) | 0.8(3) | 2.0(4) | 0.0(3) | −0.1(3) | 0.6(2) |
| O(5) | 2.1(5) | 1.8(4) | 2.1(4) | 0.9(4) | 0.6(4) | 0.0(4) |
| O(6) | 1.4(4) | 1.9(4) | 1.7(3) | −0.8(3) | −0.1(3) | −0.1(3) |
| O(7) | 1.5(5) | 0.7(4) | 3.6(5) | −0.1(3) | 0.6(4) | −0.4(4) |
| O(8) | 2.0(5) | 0.9(4) | 2.1(4) | −0.1(3) | 0.6(4) | −0.1(3) |
| O(9) | 1.6(4) | 0.9(3) | 1.4(4) | −0.2(3) | 0.5(3) | 0.3(3) |
| O(10) | 2.0(4) | 0.7(3) | 2.4(4) | 0.1(3) | 1.6(4) | 0.6(3) |
| O(11) | 1.5(4) | 2.2(5) | 2.3(4) | 0.9(4) | 0.6(4) | 0.9(4) |
| O(12) | 2.1(5) | 2.1(5) | 1.0(4) | 1.0(3) | −0.5(3) | 0.0(3) |
| O(13) | 1.6(4) | 0.8(3) | 1.9(4) | 0.2(3) | −0.1(3) | −0.6(3) |
| O(14) | 1.0(4) | 2.1(4) | 1.9(4) | 1.1(3) | −0.8(3) | −0.7(3) |
| O(15) | 2.5(5) | 1.4(4) | 0.9(3) | −0.7(3) | −1.1(3) | −0.2(3) |
| N(2) | 2.1(5) | 3.9(8) | 4.4(8) | −1.0(5) | 0.9(5) | −1.0(6) |
| N(1) | 1.4(5) | 2.5(5) | 4.4(7) | −0.6(7) | 0.4(5) | −1.0(9) |

1349 Å$^3$. The coordinates of atoms are presented in Table II, the list of anisotropic thermal parameters is given in Table III, and structure factors are available from the authors. $Ce(NH_4)_2(PO_3)_5$ is a chain polyphosphate with anionic chains $(PO_3)_\infty$, running along the *ab* diagonals of the unit cell with a period of five tetrahedra $PO_4$ (Fig. 4). Cationic polyhedra of cerium and ammonium link anionic chains into a three-dimensional structure. Interatomic distances and valence angles are presented in Table IV. A comparison of $Ce(NH_4)_2(PO_3)_5$ structure with the triclinic form described in (*14*) shows that geometrical characteristics of polyphosphate anion and cationic polyhedrons practically coincide. Parameters of the triclinic cell ($a_t$ = 7.241(5) Å, $b_t$ = 13.314(8) Å, $c_t$ = 7.241(5) Å, $\alpha$ = 90.35(5)°, $\beta$ = 107.50(5)°, $\gamma$ = 90.28(5)°) after deriving the mean value $\alpha = \gamma$ = 90.32° are transformed into monoclinic: $\mathbf{a}_m = \mathbf{a}_t + \mathbf{c}_t$, $\mathbf{b}_m = -\mathbf{a}_t + \mathbf{c}_t$, $\mathbf{c}_m = \mathbf{b}_t$: $a_m$ = 8.563 Å, $b_m$ = 11.679 Å, $c_m$ = 13.314 Å, $\alpha = \gamma$ = 90.0°, $\beta$ = 90.54°. The presence of a glide plane perpendicular to diagonal $-\mathbf{a}_t + \mathbf{c}_t$ with translation $c/2$, that can be seen in Fig. 1 of Ref. (*14*), is direct evidence for lowering of sym-

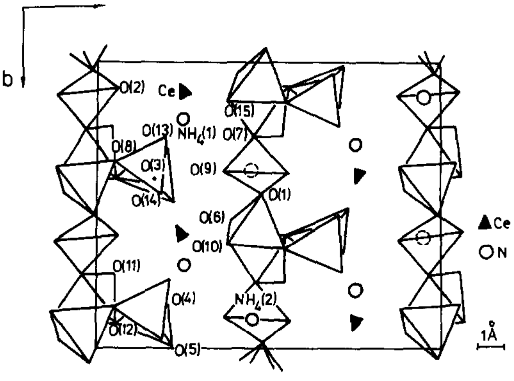

FIG. 4. Structure of $Ce(NH_4)_2(PO_3)_5$, projection upon the plane *bc*.

metry in the triclinic form $Ce(NH_4)_2(PO_3)_5$. It can be shown that in a triclinic setting coordinate relations of atoms connected by this plane are as follows:

$$x + z = x' + z'$$
$$y = y' + \tfrac{1}{2}. \qquad (9)$$

### TABLE IV

### INTERATOMIC DISTANCES (Å) AND VALENCE ANGLES (°) IN $Ce(NH_4)_2(PO_3)_5$

| | | | | |
|---|---|---|---|---|
| P(1) | O(7) | O(11) | O(12) | O(15) |
| O(7) | 1.608(12) | 2.56(2) | 2.43(2) | 2.46(2) |
| O(11) | 113.3(7) | 1.456(13) | 2.52(2) | 2.53(2) |
| O(12) | 98.5(6) | 111.6(7) | 1.595(12) | 2.48(2) |
| O(15) | 115.4(6) | 118.7(7) | 107.3(6) | 1.482(11) |
| P(2) | O(3) | O(8) | O(13) | O(14) |
| O(3) | 1.596(11) | 2.51(2) | 2.56(2) | 2.50(2) |
| O(8) | 102.7(6) | 1.613(13) | 2.45(2) | 2.58(2) |
| O(13) | 111.6(6) | 103.6(6) | 1.503(10) | 2.60(2) |
| O(14) | 107.3(6) | 111.4(6) | 119.1(6) | 1.506(12) |
| P(3) | O(1) | O(2) | O(7) | O(9) |
| O(1) | 1.583(II) | 2.47(2) | 2.43(2) | 2.55(2) |
| O(2) | 108.4(6) | 1.459(12) | 2.50(2) | 2.55(2) |
| O(7) | 100.4(6) | 110.6(7) | 1.574(12) | 2.45(2) |
| O(9) | 111.5(6) | 118.8(7) | 105.6(7) | 1.503(12) |
| P(4) | O(1) | O(6) | O(8) | O(10) |
| O(1) | 1.591(10) | 2.50(2) | 2.45(2) | 2.54(2) |
| O(6) | 108.1(6) | 1.497(12) | 2.56(2) | 2.57(2) |
| O(8) | 100.5(6) | 111.4(7) | 1.600(12) | 2.46(2) |
| O(10) | 111.0(6) | 118.9(7) | 105.3(7) | 1.492(12) |
| P(5) | O(3) | O(4) | O(5) | O(12) |
| O(3) | 1.610(II) | 2.53(2) | 2.47(2) | 2.45(2) |
| O(4) | 110.0(6) | 1.472(II) | 2.55(2) | 2.53(2) |
| O(5) | 105.9(6) | 119.2(7) | 1.481(13) | 2.46(2) |
| O(12) | 100.7(6) | 112.3(6) | 107.0(7) | 1.575(12) |

| | | | | | |
|---|---|---|---|---|---|
| Ce–O(2) | 2.537(11) | N(1)–O(6) | 2.82(3) | N(2)–O(6) | 2.74(2) |
| O(4) | 2.587(10) | O(13) | 2.90(3) | O(11) | 2.92(2) |
| O(5) | 2.501(13) | O(11) | 2.90(3) | O(12) | 3.00(2) |
| O(9) | 2.619(10) | O(9) | 3.00(2) | O(10) | 3.02(2) |
| O(10) | 2.435(12) | O(4) | 3.11(3) | O(9) | 3.06(2) |
| O(13) | 2.523(10) | O(7) | 3.14(3) | O(2) | 3.09(2) |
| O(14) | 2.439(11) | O(3) | 3.28(2) | O(8) | 3.26(2) |
| O(15) | 2.398(11) | O(10) | 3.35(3) | O(5) | 3.33(2) |

All other Ce–O distances are longer than 4 Å.
Average 2.50

| | | | | | |
|---|---|---|---|---|---|
| O(1) | P(3) | P(4) | O(3) | P(2) | P(5) |
| P(3) | 1.583 | 2.94(2) | P(2) | 1.596 | 2.92(2) |
| P(4) | 135.9(7) | 1.591 | P(5) | 131.0(7) | 1.610 |
| O(7) | P(1) | P(3) | O(8) | P(2) | P(4) |
| P(1) | 1.608 | 2.99(2) | P(2) | 1.613 | 2.97(2) |
| P(3) | 138.9(8) | 1.583 | P(4) | 135.2(8) | 1.600 |
| O(12) | P(1) | P(5) | The shortest distances Ce–Ce | | |
| P(1) | 1.595 | 2.89(2) | | 2 × 7.053 | |
| P(5) | 131.4(8) | 1.575 | | 2 × 7.272 | |

### TABLE V

### X-RAY POWDER DATA FOR $Ce(NH_4)_2(PO_3)_5$

| hkl | $d_{cal}$ (Å) | $d_{obs}$ (Å) | I (%) | hkl | $d_{cal}$ (Å) | $d_{obs}$ (Å) | I (%) |
|---|---|---|---|---|---|---|---|
| 110 | 6.935 | 6.96 | 9 | $\bar{1}14$ | 3.020 | 3.016 | 18 |
| 002 | 6.687 | 6.68 | 16 | $\bar{2}23$ | 2.746 | 2.748 | 10 |
| $\bar{1}11$ | 6.174 | 6.19 | 12 | 223 | 2.728 | 2.727 | 10 |
| 020 | 5.867 | 5.89 | 1 | $\bar{2}04$ | 2.650 | 2.646 | 6 |
| 021 | 5.373 | 5.39 | 3 | 134 | 2.433 | 2.427 | 8 |
| $\bar{1}12$ | 4.830 | 4.81 | 12 | 242 | 2.275 | 2.271 | 4 |
| 112 | 4.798 | | | 331 | 2.275 | | |
| 022 | 4.410 | 4.41 | 2 | 006 | 2.229 | 2.220 | 10 |
| 113 | 3.739 | 3.735 | 10 | $\bar{3}32$ | 2.189 | 2.187 | 3 |
| 202 | 3.602 | 3.593 | 5 | 332 | 2.180 | | |
| 023 | 3.550 | 3.548 | 8 | $\bar{2}25$ | 2.125 | 2.120 | 16 |
| 131 | 3.437 | 3.437 | 9 | 243 | 2.125 | | |
| 221 | 3.351 | 3.341 | 100 | $\bar{2}44$ | 1.966 | 1.967 | 5 |
| 004 | 3.344 | | | | | | |

According to the data given in Table II (*14*) these relations are retained within several standard deviations for all atoms grouped in couples: Ce(1) and Ce(2), P(1) and P(8), P(2) and P(9), etc.

It is evident from the above statements that monoclinic and triclinic forms of $Ce(NH_4)_2(PO_3)_5$ are different ways of describing one and the same structure. Since the monoclinic system of coordinates reflects the symmetry of the structure most fully, crystallographic data for $Ce(NH_4)_2(PO_3)_5$ and isomorphous phosphate series $LnM^{I}_{2}(PO_3)_5$ described in (*11*) should be presented in the monoclinic setting.

Indexed powder X-ray pattern of $Ce(NH_4)_2(PO_3)_5$ in the monoclinic system is presented in Table V.

A comparison of structures of $Ce(NH_4)_2(PO_3)_5$ and $CeNH_4P_4O_{12}$ shows their crystallochemical affinity and a certain geometric resemblance. In both phosphates cationic polyhedra $Ce^{3+}$ and $NH_4^+$ have some affinity and cation distribution in the elementary cell is similar. Loop-like sections of the polyphosphate chain in

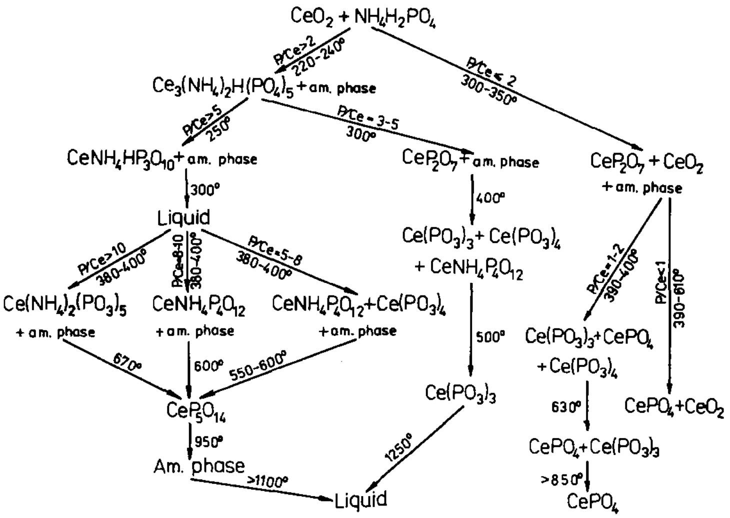

FIG. 5. The scheme of thermal interaction of $CeO_2$ with $NH_4H_2PO_4$ and its decomposition products.

$Ce(NH_4)_2(PO_3)_5$ after a slight shift of two tetrahedra can be enclosed in a cycle $P_4O_{12}$. Orientation of planes of the loops and cycles coincides in both compounds. Geometric affinity is retained in parameters of the elementary cell of polyphosphate and cyclotetraphosphate. The parameters obtained by us for $CeNH_4P_4O_{12}$ were $a$ = 7.913 Å, $b$ = 12.662 Å, $c$ = 10.686 Å, $\beta$ = 110.1°. The above data suggests that thermolysis

$$Ce(NH_4)_2(PO_3)_5 \xrightarrow[-NH_3,\ -H_2O,\ -P_4O_{10}]{460°C} CeNH_4P_4O_{12} \quad (10)$$

proceeds according to the mechanism of topotaxic reaction.

On the basis of the obtained data a scheme has been elaborated for interaction of crystalline and amorphous heating products of the mixtures $CeO_2$ and $NH_4H_2PO_4$ dependent on the starting ratio P/Ce of the components at 200–1400°C (Fig. 5).

## References

1. N. N. CHUDINOVA, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **15**(6), 931 (1979).
2. N. N. CHUDINOVA, "Chemistry of Condensed Phosphates of Trivalent Metals," Diss. Dr. Sci. (Chem.), Moscow (1979).
3. N. N. CHUDINOVA, L. P. SHKLOVER, L. M. SHKOLNIKOVA, A. E. BALANEVSKAYA, AND C. M. BALAGINA, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **14**(7), 1327 (1978).
4. R. MASSE, J. C. GUITEL, AND A. DURIF, *Acta Crystallogr. Sect. B* **33**, 630 (1977).
5. M. BEUCHER, "Les Elements des Terres Rares," Coll. No. 180, Vol. 1, p. 331, CNRS, Paris (1970).
6. A. PAUL AND R. DOUGLASS, *Phys. Chem. Glasses* **6**, 212 (1965).
7. M. A. VAIVADA AND Z. A. KONSTANT, *Izv. Akad. Nauk SSSR. Neorg. Mater.* **16**(10), 1810 (1980).
8. M. A. VAIVADA AND Z. A. KONSTANT, *Latv. PSR Zinat. Akad. Vestis Kim. Ser.* (1), 7 (1984).
9. M. A. VAIVADA AND Z. A. KONSTANT, *Latv. PSR Zinat. Akad. Vestis Kim. Ser.* (4), 496 (1978).
10. M. A. VAIVADA AND Z. A. KONSTANT, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **15**(5), 824 (1979).
11. M. RZAIGUI AND N. K. ARIGUIB, *J. Solid State Chem.* **49**, 391 (1983).
12. K. K. PALKINA, V. V. KRASNIKOV, AND Z. A. KONSTANT, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **17**(7), 1243 (1981).
13. V. V. KRASNIKOV, "Crystal Structure of Mono- and Polycrystalline Phosphates of Cerium, Iron, Vanadium," Diss. Cand. Sci. (Chem.), Riga (1982).
14. M. RZAIGUI, K. ARIGUIB, M. T. AVERBUCH-POUCHOT, AND A. DURIF, *J. Solid State Chem.* **50**, 240 (1983).