

Characterization of a New Calcium Ultraphosphate, $\text{Ca}_3(\text{P}_5\text{O}_{14})_2$

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$\text{Ca}_3(\text{P}_5\text{O}_{14})_2$ was prepared by the solid-state reaction of CaBPO_5 and $(\text{NH}_4)_2\text{HPO}_4$ as small single crystals. The cell dimensions were calculated in the monoclinic system using its powder diffraction pattern and were found to be $a = 8.695(5)$, $b = 8.999(6)$, $c = 12.940(1)$ Å, $\beta = 91.89(5)^\circ$, and the space group is probably $P2_1/m$ (No. 11) or $P2_1$ (No. 4) with $Z = 4$. The compound was characterized by SEM, IR spectroscopy, and EDX analysis of the single crystals. © 1997 Academic Press

INTRODUCTION

CaBPO_5 with stillwellite structure was synthesized by solid-state reactions and its crystal structure was solved using the Rietveld method (1, 2). In this work we used $(\text{NH}_4)_2\text{HPO}_4$ as a flux. The reaction of CaBPO_5 with an excess amount of $(\text{NH}_4)_2\text{HPO}_4$ was studied at 600°C in a platinum crucible for the purpose of growing large single crystals of CaBPO_5 .

A 1:7 molar ratio of CaBPO_5 and $(\text{NH}_4)_2\text{HPO}_4$ was subjected to solid-state reaction at 600°C for a week. In this procedure, the formation of BPO_4 was observed together with small crystals of a new compound within a matrix of high viscosity. These single crystals were separated from the bulk and washed with hot water. The characterization of the reaction products was achieved by X-ray powder diffraction, IR spectroscopy, and SEM techniques.

Until now, the lanthanide ultraphosphates, $\text{LnP}_5\text{O}_{14}$, ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb}$) have been synthesized by different workers using different techniques with orthorhombic, pseudoorthorhombic, monoclinic, and triclinic structures (3–21). Beucher (4) has reported that the rare earth ultraphosphates crystallize in three different forms, monoclinic-I ($P2_1/c$), monoclinic-II ($C2/c$), and orthorhombic ($Pcmm$). Hong and Pierce (12) stated that La–Gd ultraphosphates have monoclinic-I and Tb–Lu ultraphosphates show monoclinic-II structure. On

the other hand cerium ultraphosphate was reported to have triclinic (JCPDS 38-89 Ref. 16) and an orthorhombic structure (20) but with a different space group ($Pnc2$) than given before. EPR studies of $\text{GdP}_5\text{O}_{14}$ and the refinement of crystal structure of $\text{EuP}_5\text{O}_{14}$ with the space group $P2_1/b$ has been carried out by Parrot *et al.* (18). The unit cell parameters were found to be $a = 8.774$, $b = 12.946$, $c = 8.925$ Å and $\gamma = 90.46^\circ$ with $Z = 4$. X-ray powder diffraction data of $\text{BiP}_5\text{O}_{14}$ was given later by Hilmer *et al.* (22). The low temperature form is monoclinic-I and the high temperature form is orthorhombic. Ultraphosphates of alkaline earth metals of the type with $M_3(\text{P}_5\text{O}_{14})_2$ are not reported in the literature up to now. Calcium ultraphosphate with the formulas of $\text{CaP}_4\text{O}_{11}$ and $\text{Ca}_2\text{P}_6\text{O}_{17}$ were reported by Hill *et al.* (23), Beucher (24), and Durif (9). Tordjman *et al.* (25), Averbuch *et al.* (26), and Schneider *et al.* (27) also reported the ultraphosphate with the formula of $\text{CaP}_4\text{O}_{11}$ and the structure of a cyclic tetraphosphate. The d spacings of $\text{CaP}_4\text{O}_{11}$ were not in agreement with the data of $\text{LnP}_5\text{O}_{14}$, $\text{BiP}_5\text{O}_{14}$, and $\text{Ca}_3(\text{P}_5\text{O}_{14})_2$.

EXPERIMENTAL DETAILS

Materials and Instrumentation

The following chemicals were used in the synthesis of products. $(\text{NH}_4)_2\text{HPO}_4$ was reagent grade (from Merck). CaBPO_5 was prepared in the laboratory as described in the previous publication (2). For making IR pellets spectroscopic grade KBr is used and FT-IR (Nicolet 510 FT-IR spectrometer with $400\text{--}4000\text{ cm}^{-1}$ range) was employed to record the infrared spectra. A STOE powder diffractometer (STADIP with position sensitive detector, silicon monochromator and $\text{CuK}\alpha_1$ radiation, $\lambda = 1.54056$ Å) was used to record the diffraction data. The refinement of the unit-cell parameters was done by the Huber least squares refinement program. Crystalline aggregates were photographed with a Jeol scanning microscope (JSM-6400). Chemical analysis of the products was done by the EDX technique on washed and selected crystalline aggregates to determine the P/Ca ratio.

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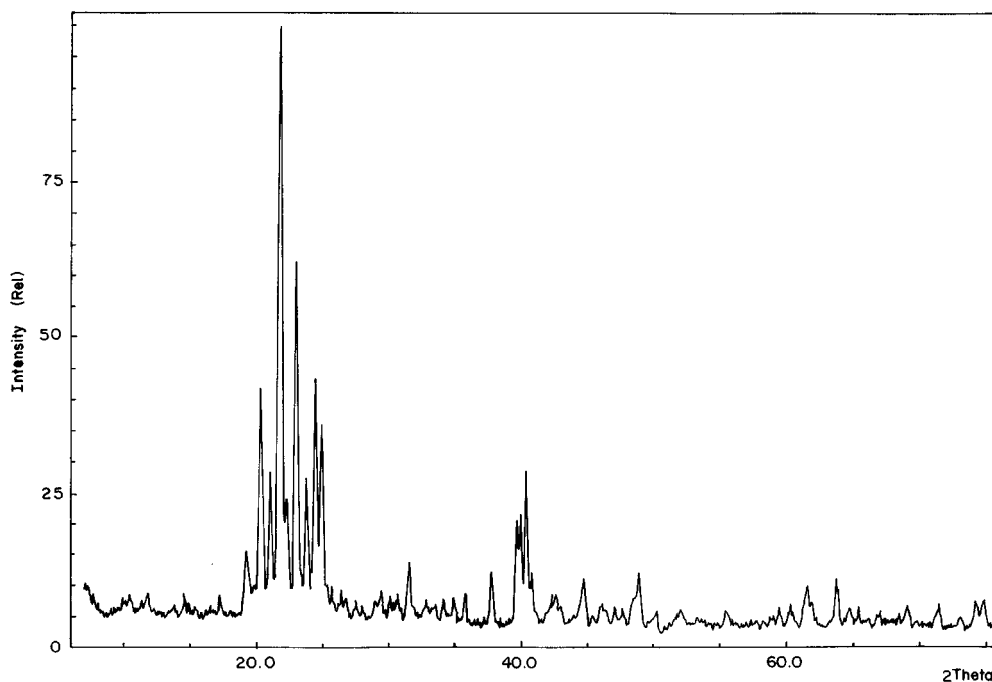
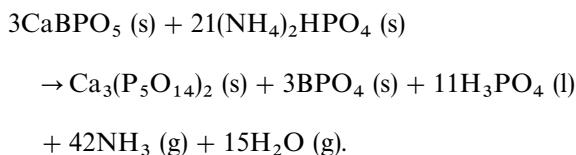


FIG. 1. X-ray powder pattern of the product obtained from $\text{CaBPO}_5 + 7(\text{NH}_4)_2\text{HPO}_4$ solid-state reaction.

Procedure

The reaction $\text{CaBPO}_5 + 7(\text{NH}_4)_2\text{HPO}_4$ was studied at 600°C . We obtained crystalline products containing the new compound by heating the mixture very slowly in covered platinum crucibles (2 K/min heating rate). The temperature was held at 500°C for 2 weeks and/or 600°C for 1 week and then the sample was cooled down to room temperature slowly. Colorless, needle shaped crystals were observed in the highly viscous melt (Fig. 1). The product was washed with hot water to remove the noncrystalline matrix and was dried at 100°C . A new unidentified compound was observed in the X-ray powder diffraction pattern together with BPO_4 . The reaction was repeated with $\text{NH}_4\text{H}_2\text{PO}_4$ instead of $(\text{NH}_4)_2\text{HPO}_4$, but the X-ray powder diffraction results were the same.

The reaction process for the composition under investigation may be defined with the equation



No suitable products for single crystal investigations were obtained. Therefore the powder diffraction pattern was used to determine the crystal system. The chemical composition

of the new phase, $\text{Ca}_3(\text{P}_5\text{O}_{14})_2$, was derived from EDX analysis (Ca/P ratio).

RESULTS AND DISCUSSION

The powder pattern was indexed in the monoclinic system with the cell parameters $a = 8.695(5)$, $b = 8.999(6)$, $c = 12.940(1)$ Å, $\beta = 91.89(5)^\circ$, and $Z = 4$. The systematic extinctions and the presence of $0k0$ for $k = 2n$ lead to the space group $P2_1/m$ (No.11) or $P2_1$ (No. 4). The X-ray powder data are given in Table 1 and Fig. 1. Careful examination of the powder data showed closed similarity to the data of $\text{GdP}_5\text{O}_{14}$ (3), $\text{BiP}_5\text{O}_{14}$ (22), or $\text{EuP}_5\text{O}_{14}$ (28) but there are appreciable differences in some stronger d spacings. It was observed that the Miller indices are not in agreement with the $\text{GdP}_5\text{O}_{14}$ data (3). On the other hand some of the d spacings and hkl values are in accord with the data of $\text{BiP}_5\text{O}_{14}$ except that a and c designations are interchanged if the similar parameters with GdPO_4 are used. The unit-cell parameters for $\text{GdP}_5\text{O}_{14}$ are $a = 8.734$, $b = 8.887$, $c = 12.926$ Å, and $\beta = 90.60^\circ$ and for $\text{BiP}_5\text{O}_{14}$ (JCPDS No. 36-5) they are $a = 12.920$, $b = 8.931$, $c = 8.694$ Å, and $\beta = 90.538^\circ$.

The crystals were photographed with a scanning electron microscope (Fig. 2). The chemical analysis by EDX (selected crystalline aggregates) showed that the P/Ca ratio is about 3.31 which corresponds to the stoichiometric formula, $\text{Ca}_3(\text{P}_5\text{O}_{14})_2$.

TABLE 1
X-ray Powder Diffraction Data of the Products Obtained From Solid State Reaction of $\text{CaBPO}_5 + 7(\text{NH}_4)_2\text{HPO}_4$

I/I_0	d_{obs}	d_{calc}	hkl	I/I_0	d_{obs}	d_{calc}	hkl
5	12.45	12.93	001	10	2.3787	2.3789	$\bar{1}33$
4	7.45	7.38	011	18	2.2648	2.2729	224
4	5.11	5.10	102	19	2.2505	2.2475	040
11 ^a	4.60	—	—	27 ^a	2.2300	2.2211	025, 224
7	4.55	4.55	$\bar{1}12$	9	2.2079	2.2143	041
5	4.46	4.44	020, 112	5	2.1347	2.1290	401, 314
38	4.34	4.34	200	5	2.1156	2.1172	410, 134
4	4.27	4.25	021	8	2.0234	2.0218	116
23	4.20	4.16	201	4	1.9667	1.9608	305, 332
100	4.053	4.075	201	3	1.9551	1.9546	420
18	3.974	3.992	120	3	1.9289	1.9241	421
58	3.857	3.831	$\bar{1}21, 013$	3	1.9032	1.8988	242, 206
4	3.794	3.773	$\bar{2}11, 121$	5	1.8722	1.8711	413
21	3.732	3.712	211	9	1.8589	1.8556	422, 333
38 ^a	3.629	—	—	3	1.8128	1.8089	017, $\bar{1}44$
31	3.563	3.549	202	3	1.7553	1.7538	341, $\bar{3}06$
4	3.511	3.508	113	3	1.6565	1.6532	$\bar{3}43, 145$
4	3.369	3.373	122	4	1.5537	1.5505	$\bar{1}54, 44\bar{1}$
3	3.314	3.301	212	4	1.5322	1.5320	$\bar{5}23$
4	3.228	3.232	004	7	1.5063	1.5042	406, $\bar{1}28$
3	3.075	3.061	$\bar{1}04$	5	1.4975	1.4973	$\bar{5}31, 060$
5	3.027	3.019	221	8	1.4587	1.4568	443, 062
4	2.9609	2.9500	$\bar{1}23$	3	1.4241	1.4222	426, $\bar{1}09$
4	2.9051	2.8941	300	4	1.3584	1.3560	346, 603
10	2.8283	2.8327	130	5	1.3190	1.3192	$\bar{5}43$
4	2.7248	2.7187	032	5	1.2764	1.2758	526, 544
4	2.6234	2.6239	024	4	1.2734	1.2736	$\bar{5}17$
5	2.5656	2.5579	$\bar{2}23$	5	1.2676	1.2659	363, $\bar{6}15$
6	2.5082	2.5002	223, 312				

^a BPO_4 (JCPDS Card No. 34-132).

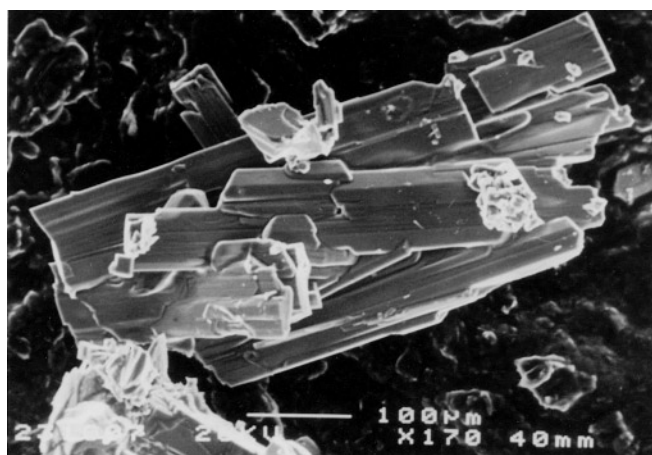


FIG. 2. SEM photograph of selected crystalline aggregates of the title compound.

IR Studies

The IR spectrum of $\text{GdP}_5\text{O}_{14}$ was reported Sungur *et al.* (3) and Agrawal *et al.* (29) and the IR studies of several condense phosphates are given by Hilmer *et al.* (22). The high pressure Raman spectra of the $\text{LnP}_5\text{O}_{14}$ crystal was also reported (30). The spectrum of the new product which was proposed to be $\text{Ca}_3(\text{P}_5\text{O}_{14})_2$ is given in Fig. 3, which has close similarities to the $\text{GdP}_5\text{O}_{14}$ spectra (3, 29). Strong bands centered around 1342 and 1096 cm^{-1} have been assigned to asymmetric and symmetric vibrations of O–P–O in the compound. P–O–P symmetric and asymmetric stretching vibrations have been observed at about 984 and 738 cm^{-1} . Bending δ motions of O–P–O and P–O–P are on the low frequency side of the spectrum as given in Table 2.

In addition, vibrational bands for tetrahedral BO_4 groups of BPO_4 (31) have been observed between 1000 – 830 cm^{-1} and 794 – 738 cm^{-1} . The band at 611 cm^{-1} is due to the bending motion in BPO_4 (31). Osaka *et al.* (32) reported

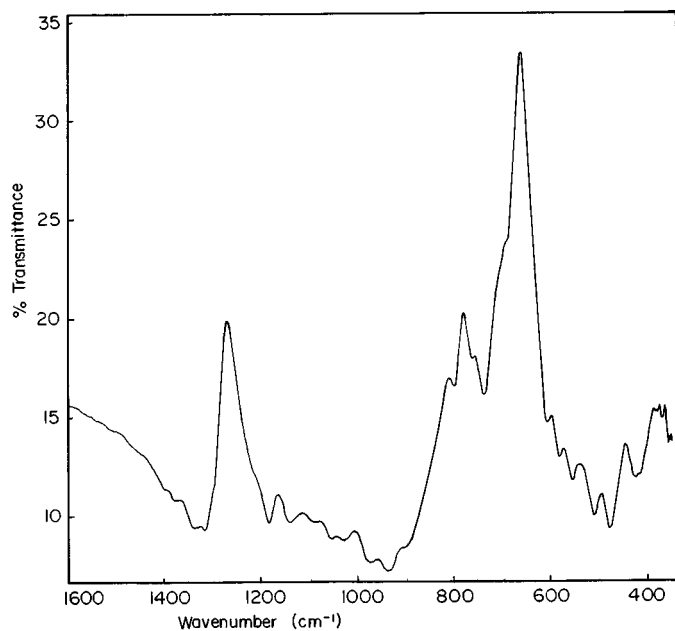


FIG. 3. IR spectrum of $\text{Ca}_3(\text{P}_5\text{O}_{14})_2 + \text{BPO}_4$.

a band at 935 cm^{-1} for high cristobalite BPO_4 which indicates the presence of a P–O–P bridging band. The doublet band at $1170/1090\text{ cm}^{-1}$ can be assigned to the B–O stretching vibration of BO_4 tetrahedra.

CONCLUSION

$\text{Ca}_3(\text{P}_5\text{O}_{14})_2$ could have some analogies with the monoclinic lanthanide ultraphosphates and bismuth ultraphosphate. The powder data showed that there are some similarities in the d spacings of $\text{BiP}_5\text{O}_{14}$ (11) and $\text{Ca}_3(\text{P}_5\text{O}_{14})_2$ but there are appreciable differences in some stronger d spacings. The X-ray powder pattern was successfully indexed using slightly larger b and c parameters than those of $\text{BiP}_5\text{O}_{14}$, where in this case $a = 8.695(5)$, $b = 8.999(6)$, $c = 12.940(1)\text{ \AA}$, and $\beta = 91.89(5)^\circ$. These should be proved by single crystal investigations if it would be possible to

TABLE 2
IR Band Locations and Empirical Assignments for
 $\text{Ca}_3(\text{P}_5\text{O}_{14})_2$

Assignments	ν , cm^{-1}
$\nu(\text{P}=\text{O})$	1377, 1342
$\nu_{\text{as}}(\text{OPO})$	1321, 1181
$\nu_{\text{s}}(\text{OPO})$	1138, 1096, 1061
$\nu_{\text{as}}(\text{POP})$	1026, 984, 934
$\nu_{\text{s}}(\text{POP})$	766, 738, 670
$\delta(\text{OPO})$	590, 555, 506, 477, 421
$\delta(\text{POP})$	365

prepare perfect single crystals. Workers are trying to grow single crystals.

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