

Substitution in Barium-Fluoride Apatite: The Crystal Structures of $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$, $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ and $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$

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The crystal structures of the apatites $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ (I), $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ (II) and $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$ (III) have been determined by single-crystal X-ray diffraction. All three compounds crystallize in a hexagonal apatite-like structure. The unit cells and space groups are: I, $a = 10.153(2)$, $c = 7.733(1)\text{Å}$, $P6_3/m$; $a = 9.9392(4)$, $c = 7.4419(5)\text{Å}$, $P\bar{6}$; III, $a = 9.786(2)$, $c = 7.281(1)\text{Å}$, $P\bar{3}$. The structures were refined by normal full-matrix crystallographic least squares techniques. The final values of the refinement indicators R_w and R are: I, $R_w = 0.026$, $R = 0.027$, 613 observed reflections; II, $R_w = 0.081$, $R = 0.074$, 579 observed reflections; III, $R_w = 0.062$, $R = 0.044$, 1262 observed reflections.

In I, the Ba(1) atoms located in columns on threefold axes, are coordinated to nine oxygen atoms; the Ba(2) sites form triangles about the F site and are coordinated to six oxygen atoms and one fluoride ion. The fluoride ions are statistically displaced $\sim 0.25\text{Å}$ from the Ba(2) triangles. This displacement of the F ions is analogous to the displacement of OH ion in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

The structures of II and III contain disordered cations. In II there is disorder between La and Na in the column cation sites as well as triangle sites. In III, Nd and Na ions are ordered in the column sites, but there is disorder among Ba and the remaining Nd and Na ions in the triangle sites to give an average site population of $\frac{2}{3}\text{Ba}$, $\frac{1}{6}\text{Nd}$, $\frac{1}{6}\text{Na}$. The coordination of the rare earth ions and Na ions in the ordered column sites are nine and six oxygens, respectively, in accord with the greater charge of the rare earth ions as compared with Na. The F ions in both II and III suffer from considerable disorder in position, and their locations are not precisely known.

Introduction

The apatite structure-type has been known since 1930 when Náray-Szábo determined the structure of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$,

the mineral fluorapatite (1). The extent of the hospitality of the apatite-type framework to different ions is revealed by such overviews as those provided by Wyckoff (2) who lists many examples of apatites and Kreidler (3), who discusses the concept of stability field of apatites based on ionic radii considerations. There have been several recent crystallographic studies on apatites: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F})_2$, i.e., the mineral hydroxyapatite (4-6); $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, the mineral fluorapatite (7); $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ doped with the rare earth cation Nd (8); $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ (9); and $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$ (10). These investigations have revealed

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some of the complexity of apatite structural chemistry.

Mayer, Roth and Brown (11) prepared apatites of Ca, Sr, and Ba in which there was coupled substitution of a rare earth and an Na ion for two alkaline earth cations. The constancy of the $P6_3/m$ space group for the substituted Ca and Sr apatites as shown by precession photographs is best explained by disorder over all cation sites. However, the substituted Ba apatites have lower space-group symmetry than the usual apatite space group, $P6_3/m$.

Here we report the results of a crystallographic study of a step-wise replacement of Ba ions in $Ba_{10}(PO_4)_6F_2$. There is a paucity of structural data and experience on which to base predictions of the course of ionic substitutions in apatites. Even the structural details in $Ba_{10}(PO_4)_6F_2$, particularly the location of the fluoride ions, were unknown before this investigation, which therefore included a "determination" and refinement of the $Ba_{10}(PO_4)_6F_2$ structure.

The study reported here of the crystal structures of $Ba_{10}(PO_4)_6F_2$ (I), $Ba_6La_2Na_2(PO_4)_6F_2$ (II) and $Ba_4Nd_3Na_3(PO_4)_6F_2$ (III) reveals that the ionic substitutions bring such drastic local changes in the crystal structures that the physical and chemical properties of these nominally similar materials must differ considerably.

Experimental Methods

Samples were made by heating stoichiometric amounts of phosphates, fluorides and oxides according to the procedures given by Mayer *et al.* (11). Because of the small size of available single crystals, no attempt was made to grind spheres. Instead, single and roughly equant crystals were selected for data collection.

All data were measured by counter methods using θ - 2θ scans. Reflections from I

and II were measured on a Picker¹ 4-circle diffractometer equipped with Mo radiation and a highly oriented graphite monochromator ($\theta_m = 6.06^\circ$), and operated by programs supplied by Lenhart (12). The unit cell parameters were calculated from 30 2θ values measured automatically on the diffractometer using $Mo(K\alpha_1)$ radiation. The data from III were measured using $Mo(K\alpha)$ radiation with an automated GE¹ goniostat equipped with a beta-filter and operated according to procedures given by Reimann, Mighell and Mauer (13). The unit cell parameters were calculated from 2θ values measured on a powder pattern taken on a Philips powder diffractometer. The wavelength of 0.70930 Å was assumed for $Mo(K\alpha_1)$. The raw data from the Picker diffractometer were processed by the unpublished program MTAPE, written by Schroeder and Dickens, and those from the GE diffractometer by the XRAY67 system program DIFOPT, written by F. A. Mauer of the National Bureau of Standards. All redundant data sets were merged using the unpublished program DMERGE, written by Dickens and Schroeder. Data on the crystals used, details of the data collections and results of the refinements are given in Table I.

Structure Refinements

$Ba_{10}(PO_4)_6F_2$ (I)

X-ray examination of a single crystal of $Ba_{10}(PO_4)_6F_2$ fixed the unit cell as that of a normal apatite with no supercell. The laue group is $6/m$ and the reciprocal lattice has the extinction $000l: l = 2n + 1$. These data, together with the requirements of the apatite

¹Certain commercial equipment, instruments or material are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

TABLE I
CRYSTAL DATA FOR I, II, AND III

	I	II	III
a, Å	10.153(2)	9.9392(4)	9.786(2)
c, Å	7.733(1)	7.4419(5)	7.281(1)
ρ calc, g · cm ⁻³	4.76	4.58	4.55
Space group	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> 6̄	<i>P</i> 3̄
Total reflections	1239	1050	4006
Unique set	628	586	1264
Observed ^a	613	579	1262
R(equiv)	0.037	0.039	0.047
Crystal size, mm	~0.05 cube	~0.05 cube	disc. radius ~0.12 mm thickness ~0.08 mm
μ (Mo), cm ⁻¹	136	123	116
Scan speed, °/sec	0.5	1.0	4
Background time, sec	40	40	10
Absorption Correction	Spherical	Spherical	None
Final R ^b	0.026	0.074	0.044
R _w ^b	0.028	0.081	0.062
Extinction domain size, ^b cm	0.32(9) × 10 ⁻⁵	0.47(b) × 10 ⁻⁴	0.41(4) × 10 ⁻⁶

^a Observed reflections are those with intensity $I > 2\sigma(I)$.

^b Values from final cycle.

structure, fix the space group as *P*6₃/*m*, which is the normal space group of a pure unsubstituted apatite. Starting values for the atomic positional parameters could have been taken from Ca₁₀(PO₄)₆F₂, since the Ba structure appeared to be of the apatite type. However, to allow least-squares refinement to proceed smoothly these parameters were found more precisely from an electron-density synthesis phased by the Ba(1) atom, which is in a special position on a threefold axis. All atoms were found and the structure was refined with isotropic temperature factors to $R_w = 0.052$ using the program RFINE4 (14). Scattering factors were taken from references (15) and (16). The structure was then refined with anisotropic temperature factors to $R_w = 0.033$. Allowance was made for secondary isotropic extinction and anomalous dispersion. The fluorine atom at this time was placed in a special position at the intersection of the mirror plane and 6₃ axis at $z = 0.25$, but its apparent thermal

parameters of $U_{11} = 0.015(3) \text{ \AA}^2$, $U_{33} = 0.13(1) \text{ \AA}^2$, corresponding to amplitudes of 0.12 Å and 0.36 Å respectively, indicated that this atom is probably disordered on both sides of the mirror plane in a manner similar to that of the OH ion in Ca₁₀(PO₄)₆(OH)₂ (4). When the fluoride was allowed to move off the mirror plane, to become randomly disordered over a site on each side, its apparent thermal parameters refined to the more physically reasonable values $U_{11} = 0.015(3) \text{ \AA}^2$, $U_{33} = 0.06(3) \text{ \AA}^2$. The final value of R_w is 0.026 for 613 reflections.²

² A table of observed and calculated structure factors has been deposited as NAPS Document No. 03324. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering, however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside the U.S. and Canada postage is \$3.00 for a photocopy or \$1.50 for a fiche.

The largest correlation coefficients between refined parameters were -0.90 between z and U_{33} for F and 0.68 between the scale factor and U_{11} of Ba(1). There were six other correlation coefficients between 0.60 and 0.70 . The highest peaks in a difference electron-density synthesis calculated after the final refinement were 2.6 electrons/ \AA^3 and are attributed to the background. The atomic parameters for the $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ structure are given in Table II. Refinement proceeded to the limit of the experimental data, and the derived parameters are physically reasonable.

$\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ (II)

The combination of Laue symmetry $6/m$, the presence of $000l$ reflections with $l = 2n + 1$ and the requirements of allowing an apatite-type structure in a normally-sized apatite unit cell (i.e., with no superlattice) fix the space group of $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ as $P\bar{6}$. This space group contains mirror planes perpendicular to threefold axes. Thus it requires that all cations in a given cation-column in the apatite framework be identical on the average but does not relate adjacent cation columns. A stoichiometrically convenient ordering of the cations would place La^{3+} next to La^{3+} in the cation

columns, which is expected to be somewhat unfavorable energetically. To find any possible larger cell, a search for measurable X-ray intensity at intervals of $\frac{1}{4}$ and $\frac{1}{6}$ of the distance between all accessible and unique reciprocal lattice points based on the cell given in Table I was carried out with the diffractometer. No such superlattice reflections were found.

The structural parameters were obtained from an electron-density synthesis based on the cation positions in the $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ structure. In the early refinement of the structure (to $R_w \cong 0.10$), the La ions were considered to be "Ba" since La and Ba have almost identical X-ray scattering factors. The program was allowed to distribute Ba and Na ions over all cation sites, and the results pointed to disorder³ of "Ba" and Na ions in the cation columns, with mostly "Ba" ions in the cation triangles. All temperature factors were assumed to be isotropic. There were large apparent thermal parameters for all oxygen atoms, and some troublesome correlations between parameters of the two PO_4

³ Disorder is possible because the estimated site occupancies are obtained by averaging over many nominally identical sites. For example, 90% Ba and 10% Na at site $M(2)$ means that 90% of these sites are occupied by Ba and 10% by Na.

TABLE II
FINAL PARAMETERS IN $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$

Atom	x^a	y	z	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	3333 ^c	6667	6(1)	125(2)	125	55(2)	63	0	0
Ba(2)	2583(1)	192(1)	2500	115(2)	97(2)	85(2)	48(2)	0	0
P	319(2)	6302(2)	2500	86(8)	83(8)	86(8)	39(7)	0	0
O(1)	-1404(6)	5180(6)	2500	7(2)	17(3)	15(3)	1(2)	0	0
O(2)	1174(6)	5414(6)	2500	16(3)	18(2)	13(3)	12(2)	0	0
O(3)	791(4)	7318(4)	888(5)	19(2)	18(2)	11(2)	7(2)	-1(2)	5(2)
F ^d	0	0	2812(50)	15(2)	15	65(28)	8	0	0

^a All positional parameters are $\times 10^4$.

^b The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ and are multiplied by 10^4 for Ba and P atoms and by 10^3 for the remaining atoms.

^c Parameters without estimates of standard deviations (in parentheses) are fixed by symmetry.

^d The F ion is disordered and was assigned an occupancy of 0.50.

groups (which are non-equivalent in space group $P\bar{6}$).

The detailed cation occupancies at this stage were (i) essentially 100% "Ba" in $M(1)$, the triangle sites at $z = \frac{1}{2}$, (ii) 90% "Ba" and 10% Na in $M(2)$, the triangle sites at $z = 0$, (iii) 50% "Ba", 50% Na in $M(3)$ the column sites at $\frac{2}{3}, \frac{1}{3}, z$ and (iv) 67% "Ba", 33% Na in $M(4)$, the column sites at $\frac{1}{3}, \frac{2}{3}, z$. In subsequent refinements, the positional parameters of all oxygen atoms were refined independently, but their temperature factors were kept isotropic. Oxygen atoms related by the pseudo-symmetry element 6_3 were constrained to have identical temperature factors. The satisfactory refinement of the $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ structure to the limit of the experimental data suggests that swamping effects of the heavily scattering cations on the refinement are not causing these problems. They decrease the deviations of the derived parameters but do not introduce artifacts into such details as the geometry and apparent motion of the PO_4 group. The local coordinations of the Nd and Na cations in the $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$ structure (see below) are 9 and 6 respectively, and La is expected to have the same coordination as Nd. In $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$, therefore, the space group is forcing an averaging of these two coordinations, and it is this averaging which makes refinement of the PO_4 groups difficult.

The two F ions per cell were difficult to locate. The initial electron density maps indicated electron density at several positions along $0, 0, z$. However, after refinement of the other atoms, the electron-density maps indicated two prominent pairs of peaks on either side of the cation triangles. During refinement of a model in which both peaks were assigned as F ions with isothermal temperature factors constrained to be equal to one another, one F ion moved away from the cation triangle while the other did not move significantly.

The final refinements contained constraints derived from chemical inter-

pretations. The F ion associated with the cation triangle at $z = \frac{1}{2}$ $M(1)$ gave interatomic distances of 2.4 Å, whereas that associated with the triangle at $z = 0$ gave interatomic distances of 2.8 Å. This suggests more La in site $M(1)$ than in $M(2)$; $M(1)$ contains no Na. Site $M(3)$ has a 9-coordination with distances 2.44–2.80 Å, which mandates the inclusion of La there. Although $M(4)$ also has 9-coordination, the distances are similar to those of Ba in (I); its occupancy was therefore divided between Ba and Na. The average occupancy in $M(3)$ was then assumed to be $\frac{1}{2}$ La and $\frac{1}{2}$ Na. The remaining La was placed at $M(1)$, which was assumed to be $\frac{2}{3}$ Ba and $\frac{1}{3}$ La with fixed occupancy. The program was allowed to distribute remaining cations over sites $M(2)$ and $M(4)$. The apparent contents varied with other noncompositional constraints applied. Values of $R = 0.074$, $R_w = 0.081$ were obtained for 579 reflections with observable intensity. Final atomic parameters are listed in Table III.²

$\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$ (III)

Precession photographs showed the Laue symmetry to be $\bar{3}$. No systematic absences were observed, and a search with the diffractometer produced no evidence for a superlattice.

Solution of the structure was accomplished in space group $P\bar{3}$. Early refinements made by assuming the scattering by Nd to be equal to that of Ba and allowing the program to distribute seven "Ba" ions together with three Na ions over all ten cation sites gave reasonable R factors. All temperature factors were assumed to be isotropic. These refinements showed that the cation at $\frac{1}{3}, \frac{2}{3}, 0$ is a weaker scatterer than the cation at $\frac{1}{3}, \frac{2}{3}, \sim\frac{1}{2}$. Interatomic distances suggested that the cation at $\frac{1}{3}, \frac{2}{3}, \sim\frac{1}{2}$ is Nd. Atom positions for the PO_4 group were located from a difference Fourier synthesis. Additional refinement cycles with Na at $\frac{1}{3}, \frac{2}{3} \sim 0$, Nd at $\frac{1}{3}, \frac{2}{3} \sim \frac{1}{2}$ and Ba at the remaining cation sites and including

TABLE III
FINAL PARAMETERS IN $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$

Atom	x^a	y	z	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$M(1)^c$	2551(4)	227(4)	5000 ^d	14(2)	8(2)	8(1)	7(2)	0	0
$M(2)$	210(6)	7665(6)	0	21(3)	34(3)	38(2)	13(3)	0	0
$M(3)$	6667	3333	2199(10)	11(2)	11	39(4)	5	0	0
$M(4)$	3333	6667	2514	19(2)	19	8(2)	10	0	0
P(1)	3762(30)	4140(24)	5000	20(10)	31(12)	32(9)	15(9)	0	0
P(2)	6185(20)	5930(17)	0	11(7)	2(8)	17(6)	4(6)	0	0
B									
O(1)	497(6)	351(6)	500	3.4(6)					
O(2)	453(9)	590(9)	500	3.6(5)					
O(3)	277(6)	351(5)	350(5)	4.6(6)					
O(4)	490(6)	621(6)	0	3.4(6)					
O(5)	536(9)	410(9)	0	3.6(5)					
O(6)	726(6)	638(5)	179(5)	4.6(6)					
F(1) ^e	0	0	463(25)	4.2(1.5)					
F(2)	0	0	197(14)	4.2(1.5)					

^a Positional parameters are $\times 10^4$ for M and P atoms and $\times 10^3$ for the remaining atoms.

^b The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}klb^{*}c^{*})]$ and are multiplied by 10^3 .

^c The content of site $M(1)$ is $\frac{2}{3}$ Ba and $\frac{1}{3}$ La with fixed occupancy. Site $M(3)$ was assigned as $\frac{1}{2}$ La and $\frac{1}{2}$ Na. The least squares program was allowed to distribute the remaining Ba and Na between the sites $M(2)$ and $M(4)$. Final values were $M(2)$ 90.4% Ba and 9.6% Na; $M(4)$ 64.5% Ba and 35.5% Na.

^d Parameters without estimated standard deviations (in parentheses) are fixed by symmetry.

^e Both F ions are considered disordered with half occupancy.

the PO_4 group gave $R = 0.055$. Anisotropic temperature factors refined to reasonable values.

From the stoichiometry, it is obvious that at least one Nd and one Na ion must reside in the triangle cation sites along with Ba ions. Hence, the structure contains a set of disordered cations in the triangles with the averaged occupation of each site being $\frac{2}{3}$ Ba, $\frac{1}{6}$ Nd and $\frac{1}{6}$ Na. This averaged occupation was employed in subsequent refinements. A difference Fourier synthesis showed prominent peaks at 0, 0, 0.06 and 0, 0, 0.45. These peaks were assigned to the F ions, with a fixed occupancy of one-half employed to preserve stoichiometry. The U_{33} thermal parameter for the F ion at 0, 0, ~ 0.45 refined to the very high value of ~ 0.3 and the position of the ion shifted towards 0, 0, $\frac{1}{2}$. Another cycle was tried in which F ions were

placed at 0, 0, 0 and 0, 0, $\frac{1}{2}$ with the result that U_{33} for the ion at 0, 0, 0 refined to a value of ~ 0.3 while the value of U_{33} for the F ion at 0, 0, $\frac{1}{2}$ refined to ~ 0.17 . This suggests a model which has one F ion at 0, 0, $\frac{1}{2}$ and the second F ion disordered over positions 0, 0, ~ 0.06 and 0, 0, ~ -0.06 . This model refined well and converged to $R = 0.044$, $R_w = 0.062$. The average value for the ratio of parameter shift to error was 0.11. No significant peaks were observed in a difference electron density synthesis; the highest peak, $\sim 2.5 e/\text{\AA}^3$, was located at 0, 0, 0.

The temperature factors of both fluoride ions were more reasonable than previously obtained values. The apparent rms amplitudes of vibration perpendicular and parallel to the threefold axis are approximately 0.2 and 0.4 \AA , respectively for both F ions. The

TABLE IV
 FINAL PARAMETERS IN $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$

Atom	x^a	y	z	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M^c	2507(1)	222(1)	2599(1)	174(3)	109(3)	145(3)	63(2)	25(1)	2(1)
Nd	$\frac{1}{3}^d$	$\frac{2}{3}$	223(1)	107(3)	107	145(3)	54	0	0
Na	$\frac{1}{3}$	$\frac{2}{3}$	5204(7)	306(18)	306	141(21)	153	0	0
P	3815(2)	4118(2)	2405(2)	125(7)	137(7)	181(8)	76(6)	-2(6)	11(6)
O(1)	4581(6)	5889(6)	2762(8)	22(2)	14(2)	33(3)	10(2)	-3(2)	-5(2)
O(2)	5075(7)	3635(7)	2186(8)	26(3)	30(3)	29(3)	21(2)	-1(2)	-4(2)
O(3)	2809(7)	3835(6)	663(8)	22(3)	22(2)	30(3)	13(2)	-8(2)	-2(2)
O(4)	2688(7)	3125(8)	3939(9)	20(3)	36(3)	35(3)	13(3)	8(2)	18(3)
F(1) ^e	0	0	556(50)	47(7)	47	73(52)	24	0	0t
F(2)	0	0	5000	37(6)	37	221(25)	19	0	0

^a All positional parameters are $\times 10^4$.

^b The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ and are multiplied by 10^4 for all atoms except O and F where they are multiplied by 10^3 .

^c The contents of M are $\frac{2}{3}$ Ba, $\frac{1}{6}$ Nd and $\frac{1}{6}$ Na.

^d Parameters without estimated standard deviations (in parentheses) are fixed by symmetry.

^e This F ion is disordered with half occupancy.

latter value is somewhat high and suggests that the F ions may actually occupy several positions about 0, 0, ~ 0.06 and 0, 0, $\frac{1}{2}$ with an overall separation of the same magnitude as the amplitude of thermal vibration. This would be expected to be the case because of the disordered arrangements of cations of widely differing (1.0 Å to 1.33 Å) ionic radii that surround the F ions. The atomic parameters are given in Table IV.²

Description of the Structures

All three structures are hexagonal with the apatite-type structure given in general terms in Fig. 1. $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ is the most symmetrical, with space group $P6_3/m$ and an asymmetric unit comprising two Ba ions, one PO_4 group and one half of a disordered F ion. The $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ structure is very similar to the $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ structure (4).

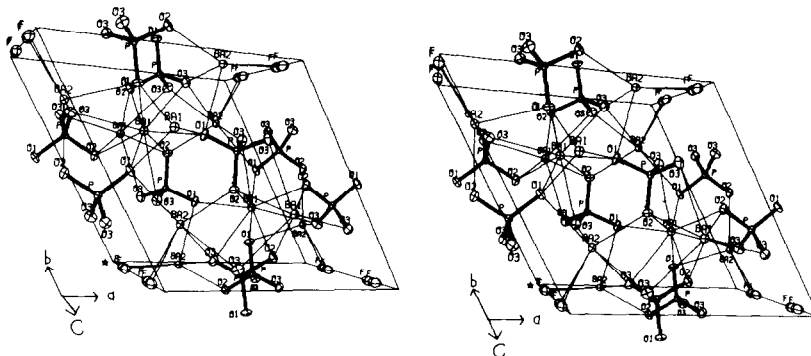


FIG. 1. The unit cell of $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ representing the apatite structure in general. Cation sites $6h$ (triangular) and $4f$ (column) are labelled Ba(2) and Ba(1), respectively. The origin of the coordinate system is marked by a star.

On the average, $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ is the next most symmetrical structure with space group $P\bar{6}$. For the purpose of examining this structure, space group $P\bar{6}$ may be rewritten as $P3/m$. The mirror plane imposes the restrictions that on the average (i) all column cations be identical, (ii) the PO_4 groups be aligned with respect to $[001]$ and separated by $c/2$ and (iii) in conjunction with the perpendicular threefold axis, that the cation triangles be strictly perpendicular to $[001]$ and separated by $c/2$. However, this apatite probably has only $P3$ symmetry or less at the local, unaveraged level.

The $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$ structure as refined in space group $P\bar{3}$ has cation columns that are fully ordered with alternating Nd and Na ions. However, these ions are not quite equally spaced along the column. Because there are more than enough Nd and Na ions to fill the column sites, Ba, Nd and Na ions are disordered in the triangle sites. In this structure the cation triangles are required by the threefold axis to be perpendicular to $[001]$, but their spacing along $[001]$ differs slightly from $c/2$. Also, the PO_4 groups are tipped with respect to $[001]$ in III because they do not have the orientational restriction of the mirrors present in I and II. Because each cation site in the triangles contain $\frac{2}{3}$ Ba, $\frac{1}{6}$ Nd and $\frac{1}{6}$ Na on average (i.e.

two triangles contain 4 Ba^{2+} ions, one Nd^{3+} ion and one Na^+ ion), the local symmetry in III must be lower than $P\bar{3}$.

The Ionic Environments in $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ (I)

Ba(2) is present in the triangular cation sites (Fig. 2). It is coordinated to seven atoms, including one fluoride ion and a PO_4 edge [O(3), O(3')]. The six distances to oxygen fall in the range 2.664 to 2.906 Å; the Ba(2)–F distance is 2.544 Å (Table V). The distance from Ba(2) to the center of the triangle is 2.531 Å, and the F ion is displaced 0.24(3) Å from the plane of the Ba(2) triangle. Ba(1), located in columns on threefold axes, is coordinated to nine oxygen atoms with distances 2.712 to 3.046 Å. The coordination includes the shared PO_4 edge [O(2)–O(3)].

The PO_4 group has mirror symmetry, with oxygens O(1) and O(2) lying in the mirror plane. The P–O distances do not differ significantly and average to the very reasonable value 1.535 Å. The O(2), O(3) and O(3), O(3') edges are the shortest, in accord with their being PO_4 edges coordinated to cations. Each oxygen atom in the PO_4 group is coordinated to three Ba ions.

The fluoride ion is coordinated to three Ba(2) ions, and is displaced from the plane of the Ba(2) triangles by 0.24(3) Å. If neigh-

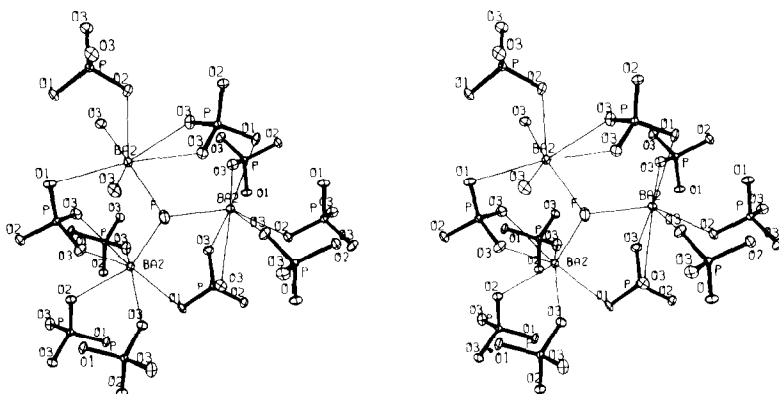


FIG. 2. The environment of Ba(2) (triangular cation sites) in $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$. Some PO_4 groups have been omitted for clarity.

TABLE V
STRUCTURAL DETAILS IN $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$

1. Cations			
Ba(1)-O(1, 1', 1'')	2.727(4)Å	Ba(2)-O(1)	2.906(6)Å
Ba(1)-O(2, 2', 2'')	2.712(5)	Ba(2)-O(2)	2.664(6)
Ba(1)-O(3, 3', 3'')	3.046(5)	Ba(2)-O(3, 3')	2.738(4)
Ba(2)-F	2.543(4)	Ba(2)-O(3'', 3'')	2.842(4)
2. Anions			
P-O(1)	1.539(7)Å	O(1)-O(2)	2.508(9)Å
P-O(2)	1.533(7)	O(1)-O(3)	2.529(6)
P-O(3)	1.534(5)	O(2)-O(3)	2.489(7)
		O(3)-O(3')	2.492(6)
O(1)-P-O(2)	109.5(3)°	O(2)-P-O(3)	108.5(3)°
O(1)-P-O(3)	110.8(3)	O(3)-P-O(3')	108.7(3)
O(1)-Ba(1, 1')	2.727(4)Å	O(2)-Ba(1, 1')	2.712(5)Å
O(1)-Ba(2)	2.906(6)	O(2)-Ba(2)	2.664(6)
O(3)-Ba(1)	3.046(5)	O(3)-Ba(2')	2.842(4)
O(3)-Ba(2)	2.738(4)		

boring F ions along [001] are on adjacent sides of their associated Ba(2) triangles, the F-F distance is $(c/2) - 0.48 = 3.357 \text{ \AA}$, where 0.48 \AA is the separation between the two possible F sites associated with a particular Ba(2) triangle and related by the mirror plane. The ionic radius of fluorine is 1.16 \AA , (17) so the above F-F approach of 3.357 \AA indicates a fairly weak F-F interaction. In particular, it is improbable that there is enough of an F-F interaction to order the F ions in the columns. It therefore appears that placement of adjacent F ions along [001] is essentially random, and although the symmetry at the local level cannot be $6_3/m$ if F does not lie on the mirror plane, it is to be expected that the actual deviations from this symmetry would be small for all atoms other than F. This is confirmed by the reasonableness and the small deviation from isotropy in the apparent thermal parameters of atoms other than F. Since the component of the Ba-F dipole along [001] is very small, any monoclinic version of the $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ structure probably would exist only at low temperatures. A monoclinic version of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is required for OH-OH chains ordered by hydrogen bond-

ing and is manifested by the existence of a superlattice of the hexagonal unit cell ($b' = 2b$, space group = $P2_1/b$, monoclinic axis assigned to be c) (6).

The Ionic Environments in $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ (II)

The least-squares occupancy refinements for the cations in II show that both the triangle sites are completely filled within experimental error. One triangle contains only heavy ions. The second contains some Na. Each of the two crystallographically different columnar sites is unequally occupied by a heavy and a light scatterer on average. Although the X-ray diffraction results cannot easily distinguish between La and Ba, and such distinction is made more difficult here because of the presence of positional disorder and site substitution, the cation environment distances definitely require that most of the Ba ions be in the triangle sites. Thus the columnar sites must contain a disordered mixture of Ba, La and Na.

The environments of the cations are shown in Fig. 3 and structural details are given quantitatively in Table VI. The $M(1)$ cation

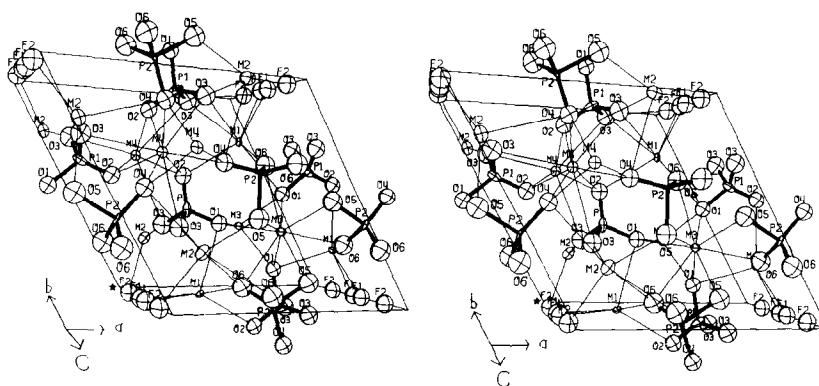


FIG. 3. The unit cell of $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$. The cations are labelled $M(i)$. For details of the contents see Table III. The origin of the coordinate system is marked by a star.

in a triangle cation site at $z = \frac{1}{2}$ is considered to be coordinated to seven atoms, because the two F sites are only $\approx 0.5 \text{ \AA}$ apart and cannot be occupied simultaneously. The $M(2)$ cation, in the second triangle cation site, spaced $c/2$ along $[001]$ from the first, is coordinated to two fluorines and six oxygens. The distances to the center of the cation triangles are 2.43 \AA for both $M(1)$ and $M(2)$.

These distances are approximately midway between those in I and III.

Although the columnar cations in II are effectively disordered, we believe that the ordered sequence found in III (see below) exists at the local level. Judging from III, we presume that the local environments usually contain nine oxygens when the central ion is La and six when it is Na. The structural

TABLE VI
STRUCTURAL DETAILS IN $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$

1. Cations			
$M(1)-\text{O}(1)$	2.93(5) \AA	$M(2)-\text{O}(4)$	3.17(5) \AA
$M(1)-\text{O}(2)$	2.71(9)	$M(2)-\text{O}(5)$	2.60(9)
$M(1)-\text{O}(3, 3')$	2.83(6)	$M(2)-\text{O}(6, 6')$	2.87(6)
$M(1)-\text{O}(6, 6)$	2.57(4)	$M(2)-\text{O}(3, 3)$	2.74(4)
$M(1)-\text{F}(1, 1')$	2.45(5)	$M(2)-\text{F}(2, 2')$	2.84(6)
$M(3)-\text{O}(1, 1', 1'')$	2.74(4)	$M(4)-\text{O}(4, 4', 4'')$	2.62(5)
$M(3)-\text{O}(5, 5', 5'')$	2.44(7)	$M(4)-\text{O}(2, 2', 2'')$	2.52(6)
$M(3)-\text{O}(6, 6', 6'')$	2.80(5)	$M(4)-\text{O}(3, 3', 3'')$	2.99(5)
2. Anions			
$\text{P}(1)-\text{O}(1)$	1.61(7) \AA	$\text{P}(2)-\text{O}(4)$	1.43(7) \AA
$\text{P}(1)-\text{O}(2)$	1.52(8)	$\text{P}(2)-\text{O}(5)$	1.58(8)
$\text{P}(1)-\text{O}(3, 3')$	1.41(5)	$\text{P}(2)-\text{O}(6, 6')$	1.62(5)
$\text{O}(1)-\text{O}(2)$	2.62(10)	$\text{O}(4)-\text{O}(5)$	2.36(10)
$\text{O}(1)-\text{O}(3)$	2.45(8)	$\text{O}(4)-\text{O}(6)$	2.62(8)
$\text{O}(2)-\text{O}(3)$	2.41(8)	$\text{O}(5)-\text{O}(6)$	2.49(8)
$\text{O}(3)-\text{O}(3')$	2.23(5)	$\text{O}(6)-\text{O}(6')$	2.66(5)
$\text{O}(1)-\text{P}(1)-\text{O}(2)$	114(3) $^\circ$	$\text{O}(4)-\text{P}(2)-\text{O}(5)$	103(3) $^\circ$
$\text{O}(1)-\text{P}(1)-\text{O}(3)$	108(3)	$\text{O}(4)-\text{P}(2)-\text{O}(6)$	118(3)
$\text{O}(2)-\text{P}(1)-\text{O}(3)$	111(4)	$\text{O}(5)-\text{P}(2)-\text{O}(6)$	102(3)
$\text{O}(3)-\text{P}(1)-\text{O}(3')$	104(3)	$\text{O}(6)-\text{P}(2)-\text{O}(6')$	110(3)

details are clouded, however, because of extreme positional disorder of the PO_4 groups. $M(3)$ has bonding distances within the expected range (taken from $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$) and is fairly well centered in its coordination polyhedron. The column cations are not equally spaced in their columns. The $M(3)$ ions are separated by approximately $c/2$ (distances 3.687 and 3.755 Å), whereas the $M(4)$ ions are separated by 3.293 and 4.149 Å.

The two crystallographically discrete PO_4 groups have similar coordinations. In the $\text{P}(1)\text{O}_4$ group, $\text{O}(1)$ is coordinated to two $M(3)$ ions and $M(1)$ ion, $\text{O}(2)$ is coordinated to two $M(4)$ ions and to the $M(1)$ ion, and $\text{O}(3)$ is coordinated to $M(4)$, $M(1)$ and $M(2)$. The $[\text{O}(3), \text{O}(3')]$ edge is coordinated to $M(1)$. In the $\text{P}(2)\text{O}_4$ group, $\text{O}(4)$ is coordinated similarly to $\text{O}(1)$ in $\text{P}(1)\text{O}_4$, and $\text{O}(5)$ resembles $\text{O}(2)$. The $[\text{O}(6), \text{O}(6')]$ edge is also coordinated to an $M(2)$ ion.

The Ionic Environments in $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$ (III)

The unit cell contents are illustrated in Fig. 4 and the structural details in Table VII. Site M contains a mixture of $\frac{2}{3}$ Ba, $\frac{1}{6}$ Nd and $\frac{1}{6}$ Na. It occupies a triangle cation site and is coordinated to seven oxygen atoms and two fluoride ions with distances less than 3.2 Å (Fig. 5). The coordination includes the two PO_4 edges $[\text{O}(2'), \text{O}(4')]$ and $[\text{O}(3), \text{O}(4)]$. The distance to the center of the triangle of M sites is 2.365 Å.

A composite ionic radius may be estimated for the M ions as $\sim [\frac{2}{3}(2.7) + \frac{1}{6}(2.5) + \frac{1}{6}(2.5)] - 1.35 = 1.3$ Å, where typical smallest ionic radii for Ba, Nd and Na have been taken from Tables V and VII and the ionic radius of oxygen is taken as 1.35 Å. Thus we see that if the crystal radius of 1.2 Å given by Shannon and Prewitt (17) is taken for F ion, the closest M-F distance would be at least

TABLE VII
 STRUCTURAL DETAILS IN $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$

1. Cations			
Nd-O(1, 1', 1'')	2.533(6)Å	Na-O(1, 1', 1'')	2.482(7)Å
Nd-O(2, 2', 2'')	2.460(7)	Na-O(2, 2', 2'')	2.566(8)
Nd-O(3, 3', 3'')	2.574(6)		
M -O(1)	2.651(7)	M -O(2)	3.035(6)
M -O(3)	2.632(6)	M -O(4)	2.576(6)
M -O(3')	2.923(7)	M -O(4')	2.713(7)
M -O(4'')	2.933(7)	M -F(1)	2.786(22)
M -F(2)	2.934(4)		
2. Anions			
P-O(1)	1.528(5)Å	P-O(2)	1.533(8)Å
P-O(3)	1.543(7)	P-O(4)	1.529(7)
O(1)-O(2)	2.518(9)	O(2)-O(3)	2.572(10)
O(1)-O(3)	2.429(8)	O(2)-O(4)	2.483(10)
O(1)-O(4)	2.544(8)	O(3)-O(4)	2.471(9)
O(1)-P-O(2)	110.7(4)°	O(2)-P-O(3)	113.5(4)°
O(1)-P-O(3)	104.5(3)	O(2)-P-O(4)	108.4(4)
O(1)-P-O(4)	112.7(4)	O(3)-P-O(4)	107.1(4)
O(1)-Nd	2.533(6)Å	O(2)-Nd	2.460(7)Å
O(1)-Na	2.482(7)	O(2)-Na	2.566(8)
O(1)-M	2.651(7)	O(2)- M	3.035(6)
O(3)-Nd	2.574(6)	O(4)- M	2.576(6)
O(3)-M	2.632(6)	O(4)- M'	2.713(7)
O(3)- M''	2.923(7)	O(4)- M''	2.933(7)

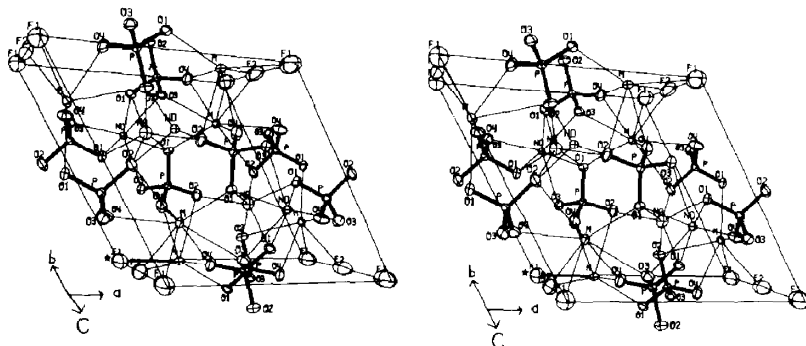


FIG. 4. The unit cell of $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$. The origin of the coordinate system is marked by a star.

$1.3 + 1.2 = 2.5 \text{ \AA}$, which suggests that F ions apparently do not quite fit in the planes of the cation triangles.

The separation of the triangles differs by $\approx 0.3 \text{ \AA}$ (3.496 vs 3.785 \AA). F(2) is midway between the two closer triangles, at a center of symmetry at $(0, 0, \frac{1}{2})$. This F ion is coordinated to six M ions at 2.933 \AA . The local symmetry must be lower than $\bar{3}$, because the triangles are not occupied by Ba alone. The apparent vibrational amplitude of 0.4 \AA parallel to c for F(2) suggests some positional disorder of $\sim 0.1\text{--}0.2 \text{ \AA}$ along c but the component sites cannot be refined independently. Fluoride ion F(1) is disordered between sites which are separated by 0.81 \AA (across the center of symmetry at $0, 0, 0$). F(1) is coordinated to three M ions at 2.786 \AA .

The column cations lie on threefold axes and consist of alternating Nd and Na ions. The separation of the Nd and Na ions along the column is almost $c/2$, the actual value being $0.498 c$ (Table VII). The Nd ion is coordinated to nine oxygens, all closer than 2.58 \AA . The coordination includes the shared PO_4 edge $[0(1), 0(3)]$. The upper and lower triangles of oxygen atoms in the coordination geometry are eclipsed and are separated by a staggered triangle (Fig. 6).

The Na ion is coordinated on to an octahedron of oxygen atoms, at distances of 2.483 and 2.566 \AA (Fig. 4). There are no shared PO_4 edges. The PO_4 groups have tilted from the positions imposed on them in $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ by the mirror planes. In this way they can accommodate the different

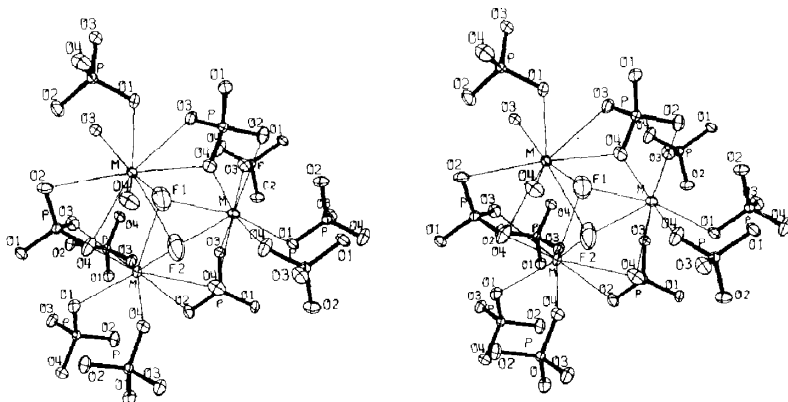


FIG. 5. The environment of triangular site cation M in $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$. The M site contains a mixture of $\frac{2}{3}$ Ba, $\frac{1}{6}$ Nd and $\frac{1}{6}$ Na. The threefold axis passes through F(1) and F(2).

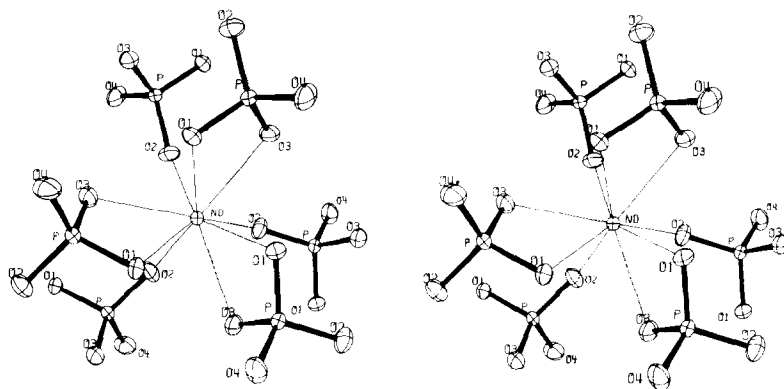


FIG. 6. The environment of Nd (column sites) in $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$.

coordination requirements of Na and Nd. Oxygen atoms O(1) and O(2) are not constrained by mirror symmetry to lie on the plane at $z = \frac{1}{4}$ and O(3) and O(4), which are coordinated to the column cations in the cases of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$, are not coordinated to the corresponding column Na ions in III.

As in the case of I, each oxygen atom is coordinated to 3 cations in III. The absence of the mirror plane has allowed the PO_4 group to twist out of this plane. Both O(1) and O(2) are coordinated to two cations in the column and one in the triangle. In I, the oxygen corresponding to O(3) is coordinated to two cations in triangles (2.74–2.84 Å) and by a long Ba–O distance (3.05 Å) to a column cation. In III, however, O(3) is coordinated to two cations in triangles and Nd in the column, while O(4) is exclusively linked to three cations in the triangle sites (Fig. 5).

Discussion

While refinement of I proceeded normally, the refinements of II and III presented severe challenges. The disordered local configurations in these structures when averaged over many unit cells produces “distorted” atoms for which the scattering properties cannot be conventionally represented. Neither were

these scattering centers resolvable into components which could be treated separately. In our refinements we required chemically sensible motion for all atoms in the phosphate groups. In the case of III where disorder is apparently less severe than in II, it was possible to refine all atoms anisotropically to give physically reasonable values for all apparent thermal parameters even though their parameters were necessarily derived for composite scatterers.

Pile-up of error on the 0, 0, z , lines in II and III obscured the locations and refinement of the F ions, which we therefore initially positioned in these salts on the basis of chemical knowledge.

In II, apparent disorder between Ba^{2+} and Na^+ or La^{3+} and Na^+ in the cation columns served to average coordination polyhedron of 9 and 6 oxygen atoms and introduced positional disorder for these oxygen atoms which was beyond the reach of the refinement method. The cause of this La/Na disorder and whether it is short or long-range is unknown at this time. Because short range disorder would invoke a significant percentage of La^{3+} – La^{3+} nearest neighbor repulsions rather than the electrostatically less repulsive configurations Na^+ – La^{3+} – Na^+ , we intuitively prefer columnar order over long ranges. Random lengths of order would blur

out the thermal diffuse scattering which would otherwise allow an estimate of the extent of the order. We do not know whether a particular column is ordered within itself but has lost registry with adjacent columns because of effects of mixed substitutions in the triangle sites or a given column is itself disordered.

The La/Na disorder could possibly arise from equilibrium not being attained in the preparative reaction. This suggests that under the appropriate conditions the space group would change from $P\bar{6}$ to $P3$ as ordering is attained. Alternate possibilities are that for some reason the entropy of the structure is too great to permit intercolumn ordering in II or that column ordering is enhanced, made possible, or made inevitable by the coupled substitution of rare earth and sodium ions into the triangle sites as in III. Clarification of these aspects requires a more detailed investigation of the phase diagram.

The present investigation has shown that (Ln/Na) coupled substitution occurs first in the columnar cation sites. This does not support the suggestion of Blasse (18) that trivalent ions will occupy mainly the triangle sites. The results of Mayer *et al* (11) indicate that the upper limit of x in $\text{Ba}_{10-2x}\text{Ln}_x\text{Na}_x(\text{PO}_4)_6\text{F}_2$ is ~ 3.5 , and that, beyond this limit, mixtures of phases occur. Presumably the columnar sites in the material with $x \sim 3.5$ are completely occupied by Ln^{3+} and Na^+ ions, and the 6 triangle sites per cell contain 3 Ba^{2+} , $1\frac{1}{2} \text{ Ln}^{3+}$ and $1\frac{1}{2} \text{ Na}^+$ ions on the average. If the reason for $x \sim 3.5$ were involved with cation-cation repulsions, a limit of $x \sim 4$ would be expected, because each column could contain ordered arrays of Ln and Na, and each triangle could contain Ba, Na and Ln staggered in such a way that there would be no Ln^{3+} - Ln^{3+} near neighbors. The following simple electrostatic considerations, involving $\sum_{ij} z_i z_j / r_{ij}$ for the cations, shed some light on Ln/Na substitution in $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$. Here we have divided the cations into noninteract-

ing sets of columns and triangle cations, although this is not strictly true because a triangle cation is slightly nearer to a column cation than to another triangle cation.

1. Ordered or Disordered Cations in Columns

a. Ordered. The sequence $\text{Ln}^{3+}\text{-Na}^+\text{-Ln}^{3+}\text{-Na}^+$ gives $+4(3 \times 1)/3.5 = +3.4$, where $\text{Ln-Na} \sim 3.5 \text{ \AA}$, and there are 4 cation-cation repulsions in the two columns of a cell.

b. Disordered case. On a local level an example would be $\text{Na}^+\text{-Ln}^{3+}\text{-Ln}^{3+}$ in one column and $\text{Na}^+\text{-Na}^+\text{-Ln}^{3+}$ in the other. For 4 columnar cations, which correspond to one unit cell, we would have in the above cases, $+(3 \times 3 + 2(1 \times 3) + 1 \times 1)/3.5 = +4.6$.

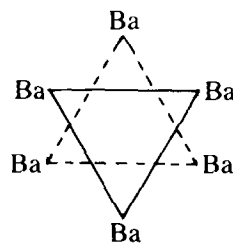
c. Ordered Ba ions in columns. e.g., $\text{Ba}^{2+}\text{-Ba}^{2+}\text{-Ba}^{2+}$ would give $+4(2 \times 2)/3.5 = +4.6$.

Thus, the above simple estimates suggest that the electrostatic repulsive forces between unlike cations tend to order the column cation and tend to produce coupled substitution of (Ln/Na) for Ba. We know this is feasible from the structure of III.

2. Triangle Site Substitution

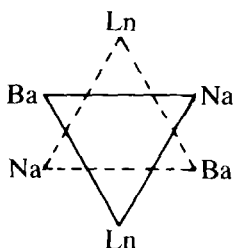
In what follows, each triangle site is considered to be 4.0 \AA from its neighbors (actually these distances are 4.1 \AA in the triangle and 4.2 \AA between triangles) and all the near-neighbor electrostatic terms for two triangles have been summed up to get the value for a unit cell. Division by two is then necessary so that all terms will not be counted twice.

a. Only Ba in triangle sites



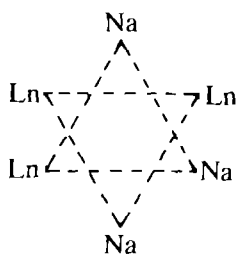
Each Ba^{2+} ion has two near neighbors in the triangle above, two in the triangle below, and two in its own triangle. The repulsive term is $+6(\text{Ba}^{2+}-\text{Ba}^{2+})/4$ per Ba ion, i.e. $+6[6(2 \times 2)/4] = +36$ for the 6 Ba ions in the 6 triangle sites in the cell, and we obtain +18 after division by two.

b. 2 Ba, 2 Ln, 2 Na in triangle sites. To minimize Ln-Ln interactions, we consider the order below:

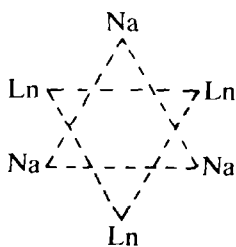


For each triangle, this gives 6 ($\text{Ln}^{3+}-\text{Na}^+$), 6 ($\text{Ln}^{3+}-\text{Ba}^{2+}$) and 6 ($\text{Na}^+-\text{Ba}^{2+}$) interactions at 4.0 Å. (For example, in the case of Ln-Na, Ln is next to Na in the triangle, and is next to Na in each of the two adjacent triangles. Na is similarly positioned with respect to Ln.) The net repulsive energy per cell for two triangles is: $+2[6(3 \times 1 + 3 \times 2 + 1 \times 2)/4]/2 = +16.5$.

c. 3 Ln, 3 Na in triangle sites. Both the possible arrangements



and



give 24 (Ln-Na), 6 [Ln-Ln] and 6 [Na-Na] repulsive terms, with a net repulsive energy of $+ \{ [24(3 \times 1) + 6(3 \times 3) + 6(1 \times 1)] / 4 \} / 2 = +16.5$.

Thus we see that coupled Ln/Na substitution for Ba is usually associated with smaller cation-cation repulsive energies. These energies cannot account for disordered cation columns or for the observed maximum limit of Ln/Na substitution. The reason for the second observation must therefore lie in the attractive electrostatic terms. Other things being equal, coupled substitution will decrease these inter-cation attractive terms as it does the inter-cation repulsive terms, and thus it may be the cation-anion terms have a determining influence.

The polarizing power of the rare earth cations Ln^{3+} induces a coordination of nine close oxygen neighbors in the cation columns in III. Concomitantly, Na has 6 near neighbors. It is therefore of interest to compare the cation-anion electrostatic attractive terms for Ba occupancy and Ln/Na occupancy. Ba is coordinated to 9 phosphate oxygens at 2.8 Å (Table V). For a charge of z_0 on the phosphate oxygens, +2 on Ba, and two Ba ions, we have an attractive term of

$$\sum_{i=1}^2 \sum_{j=1}^9 (+2)(z_0)/2.8 = 12.9 z_0.$$

When these two Ba ions are replaced with one Ln^{3+} ion (coordination: 9 oxygens at 2.5 Å) and one Na ion (coordination: 6 oxygens at 2.5 Å), the structure rearranges to accommodate the new coordination requirements, and the attractive term becomes

$$\sum_{j=1}^9 (+3)(z_0)/2.5 + \sum_{k=1}^6 (+1)(z_0)/2.5 = 13.2 z_0.$$

Thus even these electrostatic attractive terms favor substitution of Ba pairs by Ln/Na as long as the steric requirements of the new ions can be met.

When the structure packs more closely about the cation columns it must open up about the triangle sites, which usually have a coordination of 7. The smaller cations occupy the column sites preferentially because of the increased coordination, and the larger ions (Ba^{2+} here) preferentially occupy the triangle sites. In $\text{Ca}_{10-2x}\text{Ln}_x\text{Na}_x(\text{PO}_4)_6\text{F}_2$ and $\text{Sr}_{10-2x}\text{Ln}_x\text{Na}_x(\text{PO}_4)_6\text{F}_2$ the differences in cation sizes are not great enough to impose ordering into column and triangle sites. Continued substitution of Ln and Na into the triangle sites in the Ba apatites after the column sites have been filled by Ln^{3+} and Na^+ ions apparently proceeds until the coordination requirements of La^{3+} ions in the triangle sites can no longer be met. The structure must balance the requirements of three different ions of widely differing charges and sizes. The reason for the upper limit of $x = 3.5$ in the Ba apatite series thus seems to lie in the coordination requirements of the substituent cations rather than cation-cation repulsions or cation-anion attractions. The coordination requirements and hence the substitution site depend on the ionic size and charge of the substituent vs the substituted ions. There are three possibilities.

1. Coupled substitution preserving the charge balance and filling all atomic sites as in the present case.

2. Substituent atoms have charges different from those in the host structure so that ion vacancies are formed.

3. As in (2), but with incorporation of interstitial atoms.

In the present case, smaller and higher charged cations were substituted in the cation columns, and the larger cations persisted in the triangles. When there is no size factor, as in the Ca and Sr cases, there is no preferred site of substitution. Conversely, if the substituted cations are larger and less positively charged than the host cations, substitutions will probably take place in the triangle sites, with the host cations persisting in the column sites.

Coupled substitution is probably the case in the Nd_2O_3 doped fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (8). There, Nd substitutes exclusively in the triangle sites, but substitutes roughly equally in column and triangle sites when the apatite is doped with NdF_3 . In the former case, coupled substitution of Nd^{3+} and O^{2-} for Ca^{2+} and F^- could occur. O^{2-} and F^- would be almost indistinguishable to X rays, and would occupy the same set of sites, on the 6_3 axis. Substitution of Nd^{3+} in the triangle sites would allow the largest possible electrostatic interaction in the crystal, $\text{Nd}^{3+}-\text{O}^{2-}$, to make a significant contribution to the lattice energy. Coupled substitution of Nd^{3+} and F^- would make no change in the 6_3 axis population (there is no room for any appreciable amount of interstitial F ions) and so would require cation vacancies. In the absence of the $\text{Nd}^{3+}-\text{O}^{2-}$ interaction and the size factor, Nd substitutes in all cation sites. To reduce $\text{Nd}^{3+}-\text{Ca}^{2+}$ repulsions within the cation columns, the cation vacancies are likely to be in these columns.

Interest in cation substitution in apatite-like structures arises from several fields. The present work has concentrated on Ba apatite-like structures because Ba is the only alkaline earth cation which allows ordering of the Ln/Na substitutions (11). Our results show these substitutions to be unexpectedly complex. If the limit of substitution is indeed imposed by the inability of the structure to adapt to the coordination requirements, the limits of substitution will be difficult to predict *a priori*. This suggests that there is still a need to augment the background of well-documented structural details of substitutions in apatite-like compounds before predictions of such substitutions can be made with confidence.

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