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Rare Earth Substituted Fluoride–Phosphate Apatites

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Compositions with the general formula $Ln_xM_{10-2x}Na_x(PO_4)_6F_2$ (Ln = La, Pr, Nd, Sm, Eu, Dy, Er, Lu, and Y; M = Ca, Sr, and Ba) have been prepared and studied by X-ray diffraction methods. The hexagonal apatite like structure was indicated by the powder patterns of all the compounds (with Ba compounds only when Ln = La through Sm). Single crystal precession data reveal that the crystal lattice of all the compositions in the Ca and Sr system have space group $P6_3/m$, the $Ln_2Ba_6Na_2(PO_4)_6F_2$ compounds crystallize in space group $P\bar{6}$ and the $Ln_3Ba_4Na_3(PO_4)_6F_2$ compounds in the trigonal space group $P3$. Order and disorder mechanisms of the substitution and its dependence on size and polarization effects are discussed.

Introduction

Apatites with the general formula $M_{10}(XO_4)_6Y_2$, in which M stands for Ca, Sr, Ba, Pb, and Cd, X for P, As, V, Mn, Cr, Si, and Ge, and Y for F, Cl, and OH are widely studied because of their biological and industrial importance. Apatite-like materials, natural and synthetic, occur with a large variety of ions. Ca hydroxyapatite is an idealization of the main constituent of bone mineral; Ca fluoroapatite is found in phosphate deposits; and apatites activated by Sn, Sb, or Mn or doped by rare earths are useful luminescence and laser materials.

The crystal structure of the apatites has been extensively studied (*1–4*). Apatites crystallize in a hexagonal lattice with two formula units in each cell. In compounds such as $Ca_{10}(PO_4)_6(OH)_2$ the ten metal ions are distributed among two nonequivalent crystallographic sites. Four Ca ions (Ca_I) are located along the threefold axes and the other six (Ca_{II}) are symmetrically located about the sixfold screw axes. Ca_I is surrounded by three oxygen triangles. The two smaller ones are arrayed one above and one below Ca_I, with the third, larger, triangle almost at the same height along z as Ca_I. Ca_{II} is surrounded by six oxygens and one Y^- ion ($Y^- = F^-$, Cl^-, or OH^-). Hydroxy- and chloroapatites have monoclinic unit cells which are a distorted version of the hexagonal apatite. When Y^- is F^-, it is placed at the center of and coplanar with a triangle of Ca_{II} ions. If Y^- is OH^- the oxygen are somewhat displaced along the z direction from the plane of the triangles formed by the Ca_{II} ions. The rather large Cl^- ions are located approximately at z levels of zero and $\frac{1}{2}$, between planes of Ca_{II} triangles, and not at approximate z values of $\frac{1}{4}$ and $\frac{3}{4}$ as are OH^- and F^-.

One interesting aspect of apatite research is the study of substituted apatites. The presence of M ions in two different crystallographic sites and the differences in the arrangement of the Y^- ions in the apatite structure raise the questions: (1) what are the governing factors

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of the substitution process, (2) will the substituted compounds be structurally ordered and (3) will the structure remain apatitic after substitution?

The present investigation was conducted to try to answer the above questions by preparing a series of fluoride-phosphate apatites of Ca, Sr, and Ba with the alkaline earth cations partially substituted by rare earth and sodium ions. Rare earths have been investigated in apatites as dopants (*5–7*) or as one of the metal ions in silicate-apatites (*8–10*). The present work is the first systematic investigation of the incorporation of mixed rare earth–alkali ions in fluoride-phosphate apatites.

Experimental

Starting materials used were $Ca_3(PO_4)_2$, $SrHPO_4$ or $BaHPO_4$, the fluorides of Ca, Sr and Ba, oxides and phosphates of the rare earths (Ln) La, Pr, Nd, Sm, Eu, Dy, Er, Lu, and Y and Na_3PO_4. The $LnPO_4$ rare earth phosphates were prepared by heating $(NH_4)_2HPO_4$ and Ln_2O_3 at about 500°C for 2–3 hr, grinding the mixture, and reheating at 1100°C for 4–12 hr. All the materials were of 99.9% purity or higher.

The general formula of the compounds used in this study was $Ln_x^{III}M_{10-2x}^{II}Na_x^{I}(PO_4)_6F_2$. The charge balance and full occupancy of the structural sites was maintained by coupled substitution of La^{3+} and Na^{1+} for $2M^{2+}$. Most of the preparations had the compositions: $Ln_2M_6Na_2(PO_4)_6F_2$, $Ln_3M_4Na_3(PO_4)_6F_2$ and $Ln_4M_2Na_4(PO_4)_6F_2$. The samples were prepared by weighing out stoichiometric amounts and grinding them in an agate mortar. As a rule, 250–300 mg of the mixture was then put in a 30 mm long platinum tube, and closed but not sealed. The samples were heated to 1100°C in an electric furnace for 4–24 hr.

TABLE I

Lattice Constants of Rare Earth–Calcium–Sodium Fluoroapatites

	a (Å)	*c* (Å)
$Nd_2Ca_6Na_2(PO_4)_6F_2$	9.406	6.907
$Nd_3Ca_4Na_3(PO_4)_6F_2$	9.421	6.923
$Nd_4Ca_2Na_4(PO_4)_6F_2$	9.436	6.956
$Eu_2Ca_6Na_2(PO_4)_6F_2$	9.374	6.882
$Eu_3Ca_4Na_3(PO_4)_6F_2$	9.374	6.882
$Eu_4Ca_2Na_4(PO_4)_6F_2$	9.374	6.882
$Y_2Ca_6Na_2(PO_4)_6F_2$	9.358	6.866
$Y_3Ca_4Na_3(PO_4)_6F_2$	9.344	6.837
$Y_4Ca_2Na_4(PO_4)_6F_2$	9.313	6.826

The completeness of the reaction was analyzed by examination of powder diffraction patterns obtained with an X-ray diffractometer, using Cu*K*α radiation (λ = 1.5418 Å).

Single crystals were found in many preparations and were examined with an X-ray diffraction precession camera using polaroid film techniques and unfiltered Mo radiation.

Results

Tables I and II list the lattice constants of the compounds, the powder patterns of which could be indexed on the basis of an apatite-like hexagonal structure. Most of the patterns contained sharp, well resolved peaks; however, the Er–Lu compositions did not give single phase material. The lattice parameters of the different rare earth phases with the same alkaline earth ion decrease in order of decreasing radius of the rare earth ion. The changes in the lattice parameters, as the amount of the rare earth increases, correspond

TABLE II

Lattice Constants of Rare Earth–Strontium (Barium)–Sodium Fluoroapatites

	a (Å)	*c* (Å)
$La_2Sr_6Na_2(PO_4)_6F_2$	9.690	7.219
$Nd_2Sr_6Na_2(PO_4)_6F_2$	9.640	7.168
$Eu_2Sr_6Na_2(PO_4)_6F_2$	9.620	7.142
$Er_2Sr_6Na_2(PO_4)_6F_2$	9.605	7.112
$Nd_3Sr_4Na_3(PO_4)_6F_2$	9.638	7.168
$Eu_3Sr_4Na_3(PO_4)_6F_2$	9.557	7.041
$La_2Ba_6Na_2(PO_4)_6F_2$	9.947	7.450
$La_3Ba_4Na_3(PO_4)_6F_2$	9.856	7.369
$Pr_3Ba_4Na_3(PO_4)_6F_2$	9.813	7.300
$Nd_2Ba_6Na_2(PO_4)_6F_2$	9.910	7.399
$Nd_3Ba_4Na_3(PO_4)_6F_2$	9.786	7.281
$Sm_3Ba_4Na_3(PO_4)_6F_2$	9.759	7.243

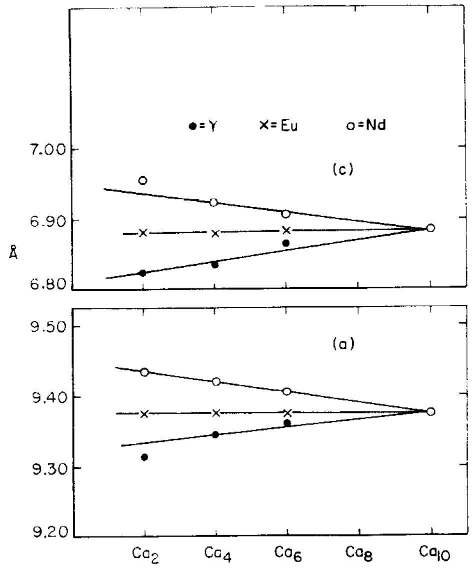

FIG. 1. Lattice constants vs Calcium content in the $Ln_xCa_{10-2x}Na_x(PO_4)_6F_2$ system.

to the size ratio between the rare earth and alkaline earth ions in the same compound. In Fig. 1 are plotted changes of the lattice constants vs the Ca content for the Nd, Eu and Y compounds.

Attempts to prepare Ba compounds with rare earths smaller than Sm resulted in a single phase different from apatite. Also, the patterns of the Ba compounds having four La or Nd ions always showed an excess of La or Nd phosphate, showing that four such ions is more than the maximum amount the structure can absorb. Specimens with the composition $Ln_5Na_5(PO_4)_6F_2$ were prepared with Ln = La, Nd, and Eu. Their patterns always contained lines of the rare earth phosphates and 2 or 3 lines of another unidentified phase, but no indication of an apatite phase.

Precession photographs were taken of single crystals found in many preparations. The Ba compounds yielded a large number of especially good quality crystals. The crystals studied had fairly regular shapes and their length was 0.1–0.2 mm. Single crystals of the following compositions were studied by the precession method: $Nd_2Ca_6Na_2(PO_4)_6F_2$, $Eu_2Ca_6Na_2(PO_4)_6F_2$, $Eu_4Ca_2Na_4(PO_4)_6F_2$, $Y_3Ca_4Na_3(PO_4)_6F_2$, $Eu_3Sr_4Na_3(PO_4)_6F_2$, $La_2Ba_6Na_2(PO_4)_6F_2$, $La_3Ba_4Na_3(PO_4)_6F_2$, and $Nd_3Ba_4Na_3(PO_4)_6F_2$. Systematic extinctions of the reflections were determined in most cases from the *hk*0, *hk*1 and *h*0*l*, *h*1*l* reciprocal planes of the apatite structure. The results show that in all the Ca and Sr compounds the systematic extinctions of the reflections were identical with those ($00l{:}\,l = 2n + 1$) for the apatite structure. The situation is different in the case of the Ba compounds. In the case of $La_2Ba_6Na_2(PO_4)_6F_2$, the upper level photographs of the *hk*0 plane prove the presence of sixfold symmetry and a mirror plane perpendicular to c^* is apparent in the *h*0*l* section; however, the 00*l* reflections were observed for all values of *l*, thus indicating the lack of 6_3 screw symmetry usually found in the apatite structure. For $La_3Ba_4Na_3(PO_4)_6F_2$ and $Nd_3Ba_4Na_3(PO_4)_6F_2$, photographs of the *hk*1 plane show the presence of only a threefold symmetry; in the *h*0*l* plane no mirror could be detected, and, as in the former case, all the 00*l* reflections were present.

Discussion

The results confirm the existence of fluoride-phosphate apatites in systems which contain the alkaline, alkaline earth, and rare earth metal ions. The powder diffraction patterns of all the compounds were alike, characteristic of the hexagonal apatite structure. However, single crystal data of the Ca and Sr compounds differ significantly from those of the Ba compounds. In the case of all the Ca and Sr compounds, symmetry conditions identical with those of the $P6_3/m$ space group of the apatites were observed. These findings along with site-occupancy considerations, indicate that the substitution of the rare earth and sodium ions in the Ca or Sr sites proceeds in a disordered way, and that these ions are statistically distributed among all the cation positions of the $P6_3/m$ lattice.

In the case of the Ba systems the compounds possess two different, but apatite-related, space groups. Results show the lack of screw symmetry in the $Ln_2Ba_6Na_2(PO_4)_6F_2$ composition, otherwise present in the $P6_3/m$ space group. The space group $P\bar{6}$, containing a threefold axis perpendicular to a mirror plane, has been selected from the $6/m$ Laue symmetry group, as the only one allowing an apatite-like structure of this composition, the cations being in the following equivalent position sets: 3 (k) $x,y,\frac{1}{2}$; 3 (j) $x,y,0$; 2 (i) $\frac{2}{3}, \frac{1}{2},z$; 2 ($h$) $\frac{1}{3},\frac{2}{3},z$.

The symmetry of the $P6_3/m$ group is further reduced in the $Ln_3Ba_4Na_3$–fluoride-phosphates. $Ln_3Ba_4Na_3(PO_4)_{10}F_2$ has space group $P3$, which is a subset of $P6_3/m$ and $P\bar{6}$. $P3$ is the only trigonal space group which allows an apatite-like structure of this stoichiometry. The equivalent position sets available for the atoms in space group $P3$ will be: 3 (d) x,y,z; 1 (c) $\frac{2}{3},\frac{1}{3},z$; 1 ($b$) $\frac{1}{2},\frac{2}{3},z$. Results of a complete structure analysis of the Ba compounds will be discussed in a subsequent publication (*11*).

Analysis of the results obtained in this work raise a number of questions:

1. What causes the substitution to be ordered in the Ba apatites and disordered in case of the Ca and Sr apatites?
2. What is the reason for the instability of the apatite structure, when elements smaller than Sm substitute for Ba in $Ba_{10}(PO_4)_6F_2$. Why is $Ln_{3.5}Ba_3Na_{3.5}(PO_4)_6F_2$ the apparent limiting composition in the Ba system, as judged from extrapolation of the cell contents of $Ln_xBa_{10-2x}Na_x(PO_4)_6F_2$ preparations?
3. Why is the ordering different in the two different compositions of the Ba system, resulting in lattices with different space groups?
4. Why do the $Ln_5Na_5(PO_4)_6F_2$ compositions not crystallize in the apatite structure?

A definite answer on the above questions cannot be given until a complete structure analysis of the compounds is completed. It can be stated, at this stage nevertheless, that these phenomena are most probably connected to size and polarizing factors. Ba^{2+}, the rare earths and Na^+ differ not only in their valence but also in their ionic radii and polarizing power.

The ordered substitution in the Ba system is most probably a consequence of the relatively large difference in size between Ba and the Ln and Na ions. The ionic radii (for an average coordination number of 8) are 1.42 Å for Ba, 1.16 Å for Na and in the range of 1.18–0.97 Å for the rare earths (*12*).

The rare earth ions, being small and highly charged, will be the strongest polarizers among the three ions participating in the Ba compounds, and their effect will be more pronounced when the structure contains proportionally less Ba. The ions affected by the different polarizing abilities of the Ln and Na ions will be the oxygens of the PO_4^{3-} groups. Preliminary structure analysis results have already shown that Ln ions in the M_I columns are 9-coordinated, whereas Na ions are 6-coordinated. Above a certain content of the Ln and Na ions, random distribution between them will be highly improbable, as this would cause too much disorder in the oxygens of the phosphate groups.

Partial or complete substitution of the alkaline earths by Na or rare earth ions in apatites or other biological systems is of great interest (*13*, *14*) because of the possible role of substitutions in dental caries. The results obtained in this work emphasize that the polarizing power of the substituted ions is an important factor determining ordering and stability of the apatitic structure. Structure fields for fluor- and chlorapatites were determined by Kreidler and Hummel (*15*) and from them the size limitations on ions for the replacement of Ca was deduced. A similar treatment was made by Ito (*16*) on silicate apatites. The size limitations for the ions (R_c) replacing Ca in fluorapatites were found to be $0.95 \leqslant R_c \leqslant 1.35$ Å. Based on these figures, the formation of $La_5Na_5(PO_4)_6F_2$ was predicted and the nonexistence of $Y_3Ca_4Na_3(PO_4)_6F_2$ was reported (*17*). Our results do not confirm these reports. While size conditions might well explain why substituted Ca compounds have been found to be disordered and the corresponding Ba compounds ordered and that Ba- apatite cannot be substituted by rare earth ions smaller than Sm, size limitations are not the only determining factors in the formation of apatite like compounds. As pointed out above, the polarization effects of the different ions and the resulting coordinations must be seriously considered when analyzing the stability range of the apatite structure.

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References

1. St. Naray-Szabo, *Z. Krist.* **75**, 387 (1930).
2. C. A. Beevers and D. B. McIntyre, *Mineral Mag.* **27**, 254 (1946).
3. K. Sudarsanan, P. E. Mackie, and R. A. Young, *Mater. Res. Bull.* 7, 1331 (1972).
4. M. I. Kay, R. A. Young, and A. S. Posner, *Nature (London)* **204**, 1050 (1964).
5. R. Mazelsky, R. C. Ohlman, and K. Steinbruegge, *J. Electrochem. Soc.* **115**, 68 (1968).
6. K. B. Steinbruegge, T. Henningsen, R. H. Hopkins, R. Mazelsky, N. T. Melamed, E. P. Riedel, and G. W. Roland, *Appl. Opt.* **11**, 999 (1972).
7. P. E. Mackie and R. A. Young, *J. Appl. Cryst.* **6**, 26 (1973).
8. J. Ito, *Amer. Mineralogist* **53**, 890 (1968).
9. W. L. Wanmaker, J. W. ter Vrugt, and J. G. Verlijsdonk, *J. Solid State Chem.* **3**, 452 (1971).
10. J. Felsche, *J. Solid State Chem.* **5**, 266 (1972).
11. B. Dickens, W. E. Brown, and I. Mayer, in preparation.
12. R. D. Shannon and C. T. Prewitt, *Acta Cryst.* **B25**, 925 (1969).
13. R. J. P. Williams, *Quart. Rev. (London)* **24**, 331 (1970).
14. M. N. Hughes, "The Inorganic Chemistry of Biological Processes," pp. 267–270, Wiley, New York (1972).
15. E. R. Kreidler and F. A. Hummel, *Amer. Mineralogist* **55**, 170 (1970).
16. J. Ito, *Amer. Mineralogist* **53**, 890 (1968).
17. E. R. Kreidler and F. A. Hummel, Ph.D. Thesis, Pennsylvania State University, 1967. University Microfilms, Inc., Ann Arbor, Michigan.