

## Lead Phosphate Apatites Substituted by Rare Earth, Sodium, and Potassium Ions

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Rare earth-substituted lead apatites of the  $Pb_{10-2x}Ln_xM_x(PO_4)_6Y_2$  ( $Ln = La, Nd, Eu, Gd, Dy$ , and  $Y$ ;  $M = Na$  and  $K$ ;  $Y = F$  and  $Cl$ ) systems were prepared and studied by X-ray diffraction and infrared methods. The powder patterns of all the compounds show the apatite-like hexagonal structure. Single-crystal precession data reveal that the space group of the  $Pb_6Ln_2Na_2(PO_4)_6F_2$  compounds is probably  $P\bar{6}$  while that of  $Pb_6Ln_2K_2(PO_4)_6F_2$  is  $P6_3/m$ . Analysis of the ir spectra of substituted Ca, Ba, and Pb compounds show the effect of substituted ions on the spectra and support the assumption that substitution in the Ba and Pb systems is an ordered process. Ordering of the substituted ions in the systems studied is discussed in view of changes in lattice parameters, size conditions, and polarizing properties of the ions.

### Introduction

Apatites of the general formula  $M_5(XO_4)_3Y$  are studied because of their biological importance,  $Ca_5(PO_4)_3OH$  being the mineral constituent of bone, and because of their possible application as hosts for laser materials. Phosphate deposits contain  $Ca_5(PO_4)_3F$ , often together with some of the rare earth elements.

The substitution process of apatites has been studied in the Ca, Sr, Ba systems (1, 2), the substituents being rare earth and sodium ions.

Apatites crystallize in a hexagonal lattice with two  $M_5(XO_4)_3Y$  formula units per unit cell. In  $M_{10}(PO_4)_6F_2$  the 10  $M$  ions occupy two crystallographically nonequivalent positions, four  $M_I$  ions at the  $4f$  site, along a threefold axis, with a nine-fold coordination, and six  $M_{II}$  ions at the  $6h$  site, around a six-fold screw axis, with a seven-fold coordination. In the investigation of the

substituted compounds, attention was focused on whether the substituted ions have any site preference when inserted in the apatite lattice, or if they are disordered at the cation sites (1, 2). The orientation of the phosphate groups in the substituted compounds was also of interest, because the phosphate group might suffer distortion when coordinated to ions of different size, charge, and polarizability.

In barium phosphate fluoride apatite, the charge-balanced substitution with rare earth and sodium ions resulted in ordered substitution (3). Two Ba apatites were found with an apatite-related structure, but with lower symmetry:  $Ba_6La_2Na_2(PO_4)_6F_2$  with space group  $P\bar{6}$  and  $Ba_4Nd_3Na_3(PO_4)_6F_2$  with the space group  $P\bar{3}$ . In both cases rare earth and sodium ions occupy mainly the  $M_I$  column positions and the rest of the ions the  $M_{II}$  triangle positions.

The present study attempts to answer the question of solid solution formation and site

preference in rare earth-substituted lead phosphate apatites.  $\text{Pb}^{2+}$  differs from the alkaline earth ions, having higher atomic number and higher atomic weight. The ionic radii of  $\text{Pb}^{2+}$  are somewhat smaller than those of  $\text{Ba}^{2+}$ . The Pb bonds are more covalent and Pb is less polarizing than the alkaline earths. The crystal structure of the lead apatites was found to be hexagonal with the space group  $P6_3/m$ . As in other apatites, cations are distributed among the  $6h$  and  $4f$  equivalent sites. Lead apatites are also known with the hexad  $Y$  anion being completely vacant (4), with the general formula  $\text{Pb}_4M(\text{PO}_4)_3$  ( $M = \text{Na}$  or  $\text{K}$ ), and they represent the only known apatites with  $\text{K}^+$  incorporated in them. The monovalent ions are located in the  $4f$  sites together with the lead ions (5). The presence of lone pairs of electrons in the Pb atoms in the vicinity of the hexad site seems to explain why this site remains empty. Rare earth-doped lead sodium apatites with anion deficiency were also studied (6).

### Experimental

Compositions were prepared by solid state reactions. As a rule samples were of 150–200 mg and were heated in a gold or platinum tube. In the case of  $\text{Pb}_{10-2x}\text{Ln}_x\text{Na}_x(\text{PO}_4)_6\text{F}_2$  and  $\text{Pb}_{10-2x}\text{Ln}_x\text{Na}_x(\text{PO}_4)_6\text{Cl}_2$  stoichiometric amounts of  $\text{Pb}_3(\text{PO}_4)_2$ ,  $\text{LnPO}_4$ ,  $\text{PbF}_2$ ,  $\text{NaF}$ , and  $\text{NaCl}$  were heated together in the temperature range 850–900°C for 8–12 hr. In the case of the  $\text{Pb}_{10-2x}\text{Ln}_x\text{K}_x(\text{PO}_4)_6\text{F}_2$  the starting materials were  $\text{Pb}_3(\text{PO}_4)_2$ ,  $\text{PbO}$ ,  $\text{PbF}_2$ , and  $\text{KPO}_3$  and the samples were heated for 1–2 hr. The starting materials were all of analytical grade. Compositions prepared corresponded to  $x = 1, 2$ , or  $3$  in the above general formulas.  $\text{Ln}$  were of La, Nd, Eu, Gd, and Dy.

Single crystals of  $\text{Pb}_6\text{Eu}_2\text{Na}_2(\text{PO}_4)\text{F}_2$  were grown in  $\text{NaF}$  flux and of  $\text{Pb}_6\text{Nd}_2\text{K}_2(\text{PO}_4)_6\text{F}_2$  in  $\text{PbF}_2$  flux, heating the mixtures of the

starting materials for several hours at 900 and 850°C, respectively, and then cooling at a rate of 4°C/hr.

The X-ray powder diffraction method was used for phase identification and for crystal data collection. Powdered samples were analyzed on an X-ray high-angle diffractometer using  $\text{CuK}\alpha$  monochromatized radiation. Lattice parameters were determined by a least-squares computer program. Single crystals were studied by the precession method, using unfiltered Mo radiation.

The ir spectra were taken by a Perkin-Elmer 457 spectrophotometer. The samples for these measurements were prepared by mixing 3 mg of the specimen with 500 mg  $\text{KBr}$  (dried at 110°C). Disks were prepared from these mixtures. The spectra were taken in the range of 250–1400  $\text{cm}^{-1}$ .

### Results

X-Ray diffraction patterns of the compounds of the three systems studied in this work have shown that they crystallize in an apatite-like hexagonal lattice. The space group  $P6_3/m$  is assumed in analogy with other apatite-like phases. Lattice constants and  $c/a$  values of the compounds are listed in Tables I, II, and III. The powder patterns of the compounds contained well-defined lines, indicating satisfactory crystallization. Only at composition  $x = 1$  and  $2$  were the patterns of single phase. The compositions with  $x = 3$  always had lines of  $\text{LnPO}_4$  of moderate strength. In the case of the  $\text{Pb}_{10-2x}\text{Ln}_x\text{Na}_x(\text{PO}_4)_6\text{Cl}_2$  and the  $\text{Pb}_{10-2x}\text{Ln}_x\text{K}_x(\text{PO}_4)_6\text{F}_2$  systems the Dy compounds contained  $\text{DyPO}_4$  lines at all compositions. Tables I and II show a regular decrease of the lattice constants with increasing amounts of the rare earth and Na ions. In the case of the  $\text{Pb}_{10-2x}\text{Ln}_x\text{K}_x(\text{PO}_4)_6\text{F}_2$  compounds (Table III) the changes in the lattice constant were slight, but also in this system the constants tend to decrease in the case of the Nd and Eu

TABLE I  
LATTICE CONSTANTS OF COMPOUNDS IN THE  
 $Pb_{10-2x}Ln_xNa_x(PO_4)_6F_2$  SYSTEM<sup>a</sup>

Composition	a (Å)	c (Å)	c/a
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.771	7.301	0.747
Pb <sub>8</sub> LaNa(PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.742	7.204	0.739
Pb <sub>7</sub> La <sub>1.5</sub> Na <sub>1.5</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.730	7.167	0.737
Pb <sub>6</sub> La <sub>2</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.719	7.142	0.735
Pb <sub>5</sub> La <sub>2.5</sub> Na <sub>2.5</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.730	7.142	0.735
Pb <sub>8</sub> NdNa(PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.741	7.198	0.740
Pb <sub>6</sub> Nd <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.661	7.067	0.732
Pb <sub>4</sub> Nd <sub>3</sub> Na <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.616	7.029	0.731
Pb <sub>8</sub> EuNa(PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.730	7.176	0.738
Pb <sub>6</sub> Eu <sub>2</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.655	7.058	0.731
Pb <sub>4</sub> Eu <sub>3</sub> Na <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.593	6.979	0.728
Pb <sub>8</sub> YNa(PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.712	7.170	0.738
Pb <sub>7</sub> Y <sub>1.5</sub> Na <sub>1.5</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.672	7.103	0.734
Pb <sub>6</sub> Y <sub>2</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.649	7.055	0.731

<sup>a</sup> Standard deviations in the lattice constants are all about ±0.02.

compounds, and increase in the case of the La compounds. The changes of the lattice parameters in the three systems from one rare earth to the other reflect the general lanthanide contraction of these ions. The c/a

TABLE II  
LATTICE CONSTANTS OF COMPOUNDS IN THE  
 $Pb_{10-2x}Ln_xNa_x(PO_4)_6Cl_2$  SYSTEM<sup>a</sup>

Composition	a (Å)	c (Å)	c/a
Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	9.934	7.327	0.738
Pb <sub>8</sub> LaNa(PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	9.866	7.268	0.737
Pb <sub>6</sub> La <sub>2</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	9.730	7.189	0.739
Pb <sub>8</sub> NdNa(PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	9.830	7.255	0.738
Pb <sub>6</sub> Nd <sub>2</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	9.759	7.193	0.736
Pb <sub>8</sub> EuNa(PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	9.860	7.252	0.736
Pb <sub>6</sub> Eu <sub>2</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	9.712	7.150	0.736
PbGdNa(PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	9.818	7.256	0.739
Pb <sub>6</sub> Gd <sub>2</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	9.689	7.150	0.738

<sup>a</sup> Standard deviations in lattice constants are all about ±0.002.

TABLE III  
LATTICE CONSTANTS OF COMPOUNDS IN THE  
 $Pb_{10-2x}Ln_xK_x(PO_4)_6F_2$  SYSTEM<sup>a</sup>

Composition	a (Å)	c (Å)	c/a
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.774	7.295	0.746
Pb <sub>8</sub> LaK(PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.783	7.294	0.746
Pb <sub>6</sub> La <sub>2</sub> K <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.807	7.298	0.744
Pb <sub>4</sub> La <sub>3</sub> K <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub> <sup>b</sup>	9.816	7.303	0.744
Pb <sub>8</sub> NdK(PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.771	7.279	0.745
Pb <sub>6</sub> Nd <sub>2</sub> K <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.760	7.275	0.745
Pb <sub>4</sub> Nd <sub>3</sub> K <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub> <sup>b</sup>	9.79	7.30	0.746
Pb <sub>8</sub> EuK(PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.763	7.278	0.746
Pb <sub>6</sub> Eu <sub>2</sub> K <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	9.756	7.276	0.746
Pb <sub>4</sub> Eu <sub>3</sub> K <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub> <sup>b</sup>	9.742	7.291	0.748

<sup>a</sup> Standard deviations in lattice constants are all about ±0.002 except for Nd<sup>3+</sup> with x = 3.

<sup>b</sup> Not single phase.

values at the different compositions of the  $Pb_{10-2x}Ln_xNa_x(PO_4)_6F_2$  systems decrease at the higher substitutions, indicating a more rapid change in c than in a. The more rapid change in c is illustrated also in Fig. 1, which

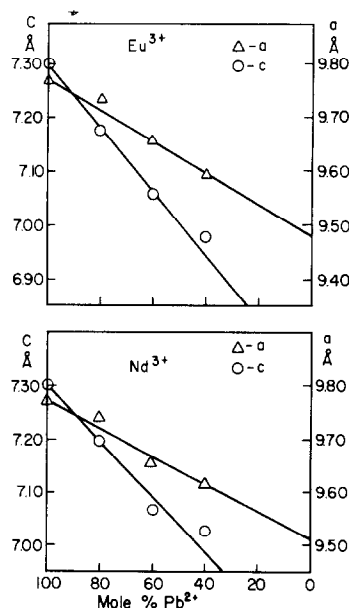


FIG. 1. Lattice constants a and c versus mole% of Pb<sup>2+</sup> in the Eu- and Nd-substituted compounds.

shows that the slope of curve *c* is much steeper than that of *a*. The *c/a* values as shown in Table II and III remain almost constant at the various substitutions, thus showing an almost equal rate of change of the two lattice constants in these two systems.

Attempts were also made to prepare substituted compounds of the  $\text{Pb}_{8-2x}\text{Ln}_x\text{K}_{x+2}(\text{PO}_4)_6$  system in which the second anion site is vacant. X-Ray powder patterns of all the samples contained reflections of an unidentified phase and that of  $\text{Pb}_8\text{K}_2(\text{PO}_4)_6$ .

Single crystals of  $\text{Pb}_6\text{Eu}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$  and  $\text{Pb}_6\text{Nd}_2\text{K}_2(\text{PO}_4)_6\text{F}_2$  were studied by the X-ray precession method. X-Ray powder patterns of the same materials were found to be a single phase. The precession photographs of the  $a^*c^*$  zone of the reciprocal lattice show all the characteristics of Laue symmetry  $6/m$  with  $00l$  reflections only at  $l = 2n$  in the case of  $\text{Pb}_6\text{Nd}_2\text{K}_2(\text{PO}_4)_6\text{F}_2$ , while in the case of  $\text{Pb}_6\text{Eu}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$  the  $a^*c^*$  zone of the reciprocal lattice contained  $00l$  reflections with  $l \neq 2n$  also. It can be concluded therefore that the space group for this type of apatite is no longer  $P6_3/m$ , but most probably  $P\bar{6}$  (No. 174).

Infrared spectra of the substituted lead fluoride apatites as well as Ca and Ba apatites with similar compositions were taken. The absorption bands of the spectra were identified according to the factor group model. The results of the ir measurements are listed in Table IV. The intensity of the bands appears in parentheses. Figures 2 and 3 show a few spectra of the substituted Ca and Ba apatites. The general trend in the spectra can be summarized as follows:

1. The bands of the substituted apatites were as a rule broad.
2. The highest energy absorption was found in the case of the Ca system. The bands of the Ba system appear at somewhat lower energies. The bands of the two systems show only slight shifts from one composition to another.

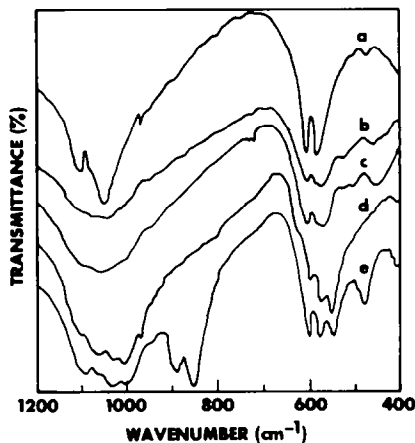


FIG. 2. Infrared spectra of: (a)  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ; (b)  $\text{Ca}_6\text{Eu}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ ; (c)  $\text{Ca}_4\text{Eu}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$ ; (d)  $\text{Ba}_6\text{Nd}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ ; (e)  $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_3\text{F}_2$ .

3. The absorption bands of the Pb system are shifted significantly to lower frequencies, compared to those of the Ca and Ba systems. The changes in composition in this system are accompanied by significant changes in the frequency of the bands. The increase of *x* in the composition causes an increase of the absorption frequencies.

## Discussion

The results obtained in this work show some of the common characteristics of the three lead apatite systems studied. The

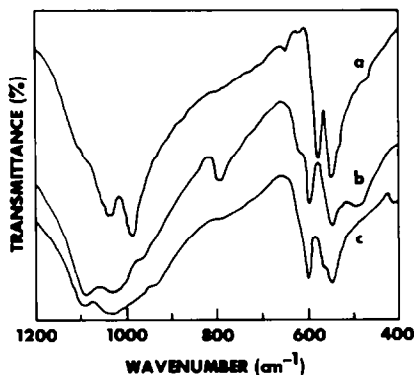


FIG. 3. Infrared spectra of: (a)  $\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2$ ; (b)  $\text{Pb}_6\text{Eu}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ ; (c)  $\text{Pb}_4\text{Eu}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$ .

TABLE IV  
INFRARED BAND ASSIGNMENTS (cm<sup>-1</sup>) FOR THE PO<sub>4</sub><sup>3-</sup> IONS OF SUBSTITUTED APATITES<sup>a</sup>

Composition	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$
Nd <sub>2</sub> Pb <sub>6</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	—	485 (sh)	1080 (vs)	595 (sh)
Nd <sub>2</sub> Ca <sub>6</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	958 (sh)	517 (m)	~1125 (sh)	545 (s)
Nd <sub>2</sub> Ba <sub>6</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	970 (s)	—	1049 (vs)	585 (sh)
Eu <sub>2</sub> Pb <sub>6</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	~970 (sh)	490 (m)	1070 (vs)	577 (s)
Eu <sub>2</sub> Ca <sub>6</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	958 (sh)	530 (m)	1035 (vs)	550 (s)
La <sub>2</sub> Pb <sub>6</sub> Na <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	~950 (sh)	480 (m)	~1050 (s)	~530 (sh)
Nd <sub>3</sub> Pb <sub>4</sub> Na <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	~945 (sh)	—	~1020 (s)	—
Nd <sub>3</sub> Ba <sub>4</sub> Na <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	953 (sh)	470 (m)	1033 (vs)	550 (s)
Eu <sub>3</sub> Ca <sub>4</sub> Na <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	945 (sh)	~515 (w)	1038 (vs)	~556 (sh)
Eu <sub>3</sub> Pb <sub>4</sub> Na <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	935 (sh)	—	~1055 (vs)	578 (m)
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	968 (m)	475 (w)	1035 (sh)	~570 (m)
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	—	470 (w)	1080 (sh)	550 (s)
			—	578 (s)
			988 (vs)	547 (s)

<sup>a</sup> vs, very strong; s, strong; m, middle; w, weak; sh, shoulder.

crystal data obtained for the compounds of these systems reveal that apatite-like phases occur when a charge-balanced substitution ( $Ln^{3+}Na^{1+}$  or  $Ln^{3+}K^{1+}$ ) is made for 2  $Pb^{2+}$  ions. The data have also shown that there is a limit ( $x$  approaches 3) for the amount these ions can be inserted in the lattice of the lead apatite. Another limit is set by the size of the rare earth ions. In the case of the  $Pb_{10-2x}Ln_xNa_x(PO_4)_6Cl_2$  and  $Pb_{10-2x}Ln_xK_x(PO_4)_6F_2$  systems the Dy phases corresponded to a mixture of the starting materials rather than to an apatite phase. In the  $Pb_{10-2x}Ln_xNa_x(PO_4)_6F_2$  system substitution could proceed also with the Y ion, therefore it can be concluded that the ionic radii of  $Y^{3+}$  is about the minimum size necessary for the formation of the apatite phase in this system. The above limits in substitution reflect most probably the size ratio conditions necessary for the formation of the apatitic phase.

The  $Pb_{10-2x}Ln_xNa_x(PO_4)_6F_2$  system differs from the other two systems studied in the behavior of the  $a$  and  $c$  lattice parameters during substitution as has been demonstrated by the  $c/a$  values in this system. According to Table I  $c/a$  values decrease when  $x$  increases, thus when the amount of the rare earth and sodium ions increases. The more rapid change of  $c$  might indicate that during the substitution process a partial ordering occurs, namely, that the Pb ions occupy mainly the  $6h$  triangle position and the smaller rare earth and Na ions the  $4f$  column positions. Due to this ordering  $c$  is more sensitive to the compositional changes as the smaller ions order themselves along this axis. The single-crystal data of  $Pb_6Eu_2Na_2(PO_4)_6F_2$  which have shown the lack of screw symmetry otherwise present in the  $P6_3/m$  of the apatites suggest the distortion of the phosphate tetrahedra by the substituted cations and indicate also that ordering occurs. These findings show much similarity with results obtained in the case of substituted Ba apatites (3). The

$c/a$  values remain almost constant in the  $\text{Pb}_{10-2x}\text{Ln}_x\text{Na}_x(\text{PO}_4)_6\text{Cl}_2$  system. Constant  $c/a$  values mean that the lattice changes its dimensions, with change in composition, in the same proportion in the  $a$  as in the  $c$  direction. This could lead to the conclusion that the cations are statistically distributed at each of the cation sites of the apatite structure. In  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$  the chlorine ions are halfway between the triangles formed by the lead ions and the Pb-Cl bonds developing between Pb ions of these triangles cause shrinking of the lattice in the  $c$  direction. The  $c/a$  values of this compound are therefore lower than those of the corresponding fluoride apatite. It can be assumed therefore that despite constant  $c/a$  at different compositions of the substituted chloride apatites, there is a partial ordering of the cations and the rare earth and Na ions occupy mainly the  $4f$  column positions. Because, as pointed out above, lead chloride apatite has an already diminished  $c$  axis, this axis is not much affected by the insertion of smaller ions in the column positions and  $c/a$  does not change much.

The findings of this work show differences between the  $\text{Pb}_{10-2x}\text{Ln}_x\text{K}_x(\text{PO}_4)_6\text{F}_2$  and the parallel system with Na. While charge-coupled substitution is possible in both cases, substitution causes only very slight changes in the lattice constants of the potassium-containing compounds. This is most probably due to the fact that the average ionic radii of the  $\text{K}^+$  and  $\text{Ln}^{3+}$  ions are identical or very close to the radii of  $\text{Pb}^{2+}$ . For this reason the main evidence for the formation of substituted compounds in the potassium system is the fact that the X-ray patterns of these compounds were of a single phase. Another more significant difference found was that there is no symmetry change in the potassium-bearing compounds from the  $P6_3/m$  space group. This suggests that the substituted cations do not distort the phosphate tetrahedra in a way that alters the symmetry of the  $P6_3/m$  lattice, while in the

Na system such a distortion was indicated by the decrease in symmetry from  $P6_3/m$  to the  $P6$  space group. Apparently this can be connected to the fact that the polarizing properties of  $\text{Pb}^{2+}$  are much more similar to those of  $\text{K}^+$  than of  $\text{Na}^+$ , therefore the coordination of the phosphate group to the  $\text{Pb}^{2+}$  and  $\text{K}^+$  ions proceeds with much less distortion of the phosphate group than happens in the presence of  $\text{Na}^+$  ions. As pointed out above, we did not succeed in preparing rare earth-substituted compounds of the  $\text{Pb}_8\text{K}_2(\text{PO}_4)_6$  apatite. One possible reason might be the high coordination power of the rare earth ions. When one of the anion positions is vacant in the apatite structure, as in this case, the coordination number of the rare earth ion will not be satisfied and consequently these ions will not be incorporated in the  $\text{Pb}_8\text{K}_2(\text{PO}_4)_6$ -type lattice.

The ir spectra shown in Figs. 2 and 3 were analyzed in view of the effect of the substituted ions on the internal vibration modes of the phosphate groups of the apatites. The factors which are considered in such an analysis are: the mass of the cation; its size; crystallographic site; and polarizability, as well as the nature of the cation-anion bond.

The effect of the mass of the cations can be well recognized on the appearance of the spectra. The vibration energy of the phosphate groups decreases when the mass of the cation increases. Accordingly, the bands of the spectra of the Ca compounds were found at much higher wavenumbers than the corresponding bands of the Pb and Ba compounds.

The unit-cell dimensions of the compounds change when ions of different ionic radii are substituted. These changes affect the distance between the phosphate groups, i.e., the strength of the coupling between them and consequently the frequency of the absorption bands. The effect of this factor, as well as the influence of the cation mass, is best observed in the case

of the Pb compounds. The reason for this might be the covalent character of the Pb bonds. The internal vibrational mode of the phosphate ion is more sensitive to the mass of cation, or to the lattice dimensions, when the cation-anion bond is of a stronger character.

The bands affected by the distribution of the cations in their crystallographic positions are the  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  bands.  $\nu_3$  becomes broader in all the systems. The various crystal fields acting on the stretching vibrations of the phosphates bring about a mixture of the band modes and the transitions become less clearly defined.  $\nu_2$  and  $\nu_4$ , the symmetric and antisymmetric bent modes, are different for the Ca, Ba, and Pb systems. In the Ca system where substitution is statistical, this part of the spectrum is diffused, weak splitting is observed, and there are no changes from composition to composition. In the Ba and Pb systems where substitution is ordered, the spectrum is split and new lines appear. This appearance of the spectra is most probably due to the stronger distortion of the phosphate groups caused by the ordered substitution. Apparently for the same reason  $\nu_{2a}$  appears in the Pb system as quite a strong

band. This is a forbidden band for the free phosphate group and its presence is another indication of the distortion of the phosphate group affected by the lanthanide and sodium located in the column positions.

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