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The Crystal Structure of $Ca_6Eu_2Na_2(PO_4)_6F_2$

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The crystal structure of $Ca_6Eu_2Na_2(PO_4)_6F_2$ has been determined by single crystal X-ray diffraction. The unit cell constants are $a = 9.385(2)$, $c = 6.893(3)$ Å and the space group is $P6_3/m$. The structure was refined by normal full matrix least squares techniques. The final value of the refinement indicator is $R = 0.065$, based on 419 reflections.

The structure of $Ca_6Eu_2Na_2(PO_4)_6F_2$ contains disordered cations in both the triangle and column positions. The occupation of the six triangle sites is $\frac{1}{4}$Eu and $\frac{3}{4}$Ca and of the four column sites $\frac{1}{2}$Na, $\frac{4}{10}$Ca, and $\frac{1}{10}$Eu.

Introduction

Most apatite type compounds crystallize in a $P6_3/m$ hexagonal structure. This structure contains two crystallographically nonequivalent sites for the location of the cations; six cations are located in the $6h$ site, the so-called triangle site, and four occupy the $4f$ column positions. In every case of substitution the question arises whether substitution proceeds in an ordered way or whether the cation sites will be occupied statistically.

The above mentioned problems have been studied in relation to alkaline earth fluoride apatites substituted by rare earth and sodium ions. The general formula of these compounds was $M_{10-2x}Ln_xNa_x(PO_4)_6F_2$ (M = Ca, Sr, Ba; Ln = rare earths). Symmetry conditions found for the substituted Ca and Sr compounds show that the $P6_3/m$ space group characteristic for apatites persists after substitution (*1*). The substituted Ba compounds crystallize in the $P\bar{6}$ and $P\bar{3}$ space groups. Crystal structure analysis of these compounds has shown (*2*) that in $Ba_6La_2Na_2(PO_4)_6F_2$, La and Na occupy in a disordered way the column positions as well as the triangle positions, while in $Ba_4Nd_3Na_3(PO_4)_6F_2$, Nd and Na are ordered in the column sites but there is a disorder of the rest of these ions in the triangle position. The general trend in the substituted Ba compounds was also found for the similar lead compounds (*3*), and seems to indicate a preference by the rare earth ions to occupy the column positions.

The constancy of the $P6_3/m$ space group in the substituted Ca compounds does not necessarily mean that rare earth and sodium ions are statistically disordered in these compounds. Therefore, the question of how cations are distributed in a substituted Ca apatite has to be clarified and was, in fact, the subject of the present work. The structure analysis of $Ca_6Eu_2Na_2(PO_4)_6F_2$ was carried out and the results show that Eu prefers, in this case, to occupy the triangle positions of the $P6_3/m$ lattice.

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Experimental

$Ca_6Eu_2Na_2(PO_4)_6F_2$ was prepared in a solid state reaction as had been described elsewhere (*1*). A clear crystal, measuring approximately 0.10 × 0.12 × 0.15 mm, was selected out of the product and mounted on a PW1100/20 Philips four-circle computer controlled diffractometer. Mo$K\alpha$ (λ = 0.71069 Å) radiation with a graphite crystal monochromator was used. The cell constants obtained by the method of least-squares with 2θ values of 22 reflections are a = 9.385(2), c = 6.893(3) Å, and V = 525.8(5) Å^3.

The intensity data were collected using the θ–2θ scan method. The scan range for each reflection was 1.0° with a constant scan time of 20 sec. Background measurements were made for 10 sec at each side of a scan. There were 552 unique data within the three sets of data measured to a maximum 2θ of 60°. ψ scanning of a few reflections indicated about 10% absorption.

The data were corrected for Lorenz and polarization effects. No absorption correction was applied. Only 419 reflections having structure factor greater than $6\sigma(F)$ were used to refine the structure.

Structure Refinement

Single crystal X-ray analysis has revealed the following data for the unit cell of $Ca_6Eu_2Na_2(PO_4)_6F_2$: the unit cell is hexagonal, laue group $6/m$, extinction $00l : l = 2n + 1$ (up to $00l$ = 0017) and space group $P6_3/m$, similar to what is known for unsubstituted apatites.

The structural parameters were obtained by least squares refinement, started with the positional parameters of the cations as found for $Ca_{10}(PO_4)_6F_2$ (*4*). The structure factors were taken from reference (*5*). To determine the location of the cations in the lattice, least squares occupancy refinements have been carried out at first with all the Ca of the composition in the $6h$ site. The results were unsatisfactory and indicated that cation with stronger scattering was needed at this site. Therefore Ca in the $6h$ site was replaced by increasing amounts of Eu, keeping the site occupancies constant and allowing the other parameters to vary. The results of the refinement indicate that the triangle sites contain 3.5 Ca and 1.5 Eu ions (actual values of occupancy 0.727(3) Ca and 0.273 Eu) and the column positions 1.6 Ca, 0.4 Eu and 2.0 Na (actual values of occupancy 0.409(3) Ca, 0.091 Eu and 0.500 Na). This means that all the Na of the composition is in the column site, while most of the Eu is in the triangle site.

The structure was refined with anisotropic temperature factors for all but the oxygen atoms of the structure. This refinement (30 param.) resulted in an R value, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.065, based on 419 reflections.[1] Final parameters are listed in Table I.

The difficulty in refining the PO_4 group might be caused by the same reason as was pointed out in case of $Ba_6La_2Na_2(PO_4)_6F_2$. The local coordination of the ions occupying the column position differ significantly, Na has six coordination while Ca and Eu have nine. Averaging of these coordinations required by the space group makes refinement of the PO_4 group difficult.

Description of the Structure

Results reveal that $Ca_6Eu_2Na_2(PO_4)_6F_2$ has the general structure of the apatites

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[1] See NAPS document No. 04088 for 2 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE I

POSITIONAL AND THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS

	X	Y	Z	U_{11} or U,Å^2	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$M(1)^a$	$\frac{1}{3}$	$\frac{2}{3}$	−0.0015(7)	0.008(1)	U_{11}	0.008(2)	$U_{11}/2$	0	0
$M(2)$	0.2357(2)	−0.0109(2)	$\frac{1}{4}$	0.0089(9)	0.0039(8)	0.0041(8)	0.0033(7)	0	0
F	0	0	$\frac{1}{4}$	0.015(6)	U_{11}	0.09(2)	$U_{11}/2$	0	0
P	0.3964(5)	0.3683(5)	$\frac{1}{4}$	0.008(2)	0.004(2)	0.007(2)	0.004(2)	0	0
O(1)	0.317(2)	0.478(2)	$\frac{1}{4}$	0.013(3)					
O(2)	0.582(2)	0.466(2)	$\frac{1}{4}$	0.009(2)					
O(3)	0.338(1)	0.254(1)	0.073(1)	0.013(2)					

Note. Estimated standard deviations in the least significant figure are given in parentheses. The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

[a] The occupancy at site 4*f* is 0.409(3)Ca, 0.091Eu and 0.500Na; at site 6*h* 0.727(3)Ca and 0.273Eu.

with all the symmetry requirements of the $P6_3/m$ space group.

The $M(2)$ cations present in the triangular positions are seven coordinated, including one fluoride ion and a shared PO_4 edge [0(3), 0(3′)]. The distances to six oxygens are in the range of 2.36–2.60 Å and the $M(2)$–F distance is 2.265 Å (Table II). The $M(1)$ cations located in the column positions are coordinated to nine oxygen atoms with distances 2.43–2.83 Å. The $M(1)$ cations (Ca, Eu, and Na) and the $M(2)$ cations (Ca and Eu) are effectively disordered at their crystallographic positions.

The P–O distances obtained for $Ca_6Eu_2Na_2(PO_4)_6F_2$ and those known for other apatite type compounds are listed in Table III. Comparison of the bond values in Table III leads to the conclusion that in the nonsubstituted compounds as well as in $Ba_4Nd_3Na_3(PO_4)_6F_2$ the P–O bonds vary only slightly and their average value is around 1.53 Å. The same values in $Ba_6La_2Na_2(PO_4)_6F_2$ vary significantly, while the P–O lengths of $Ca_6Eu_2Na_2(PO_4)_6F_2$ change in a more moderate way. The variation in the P–O distances might be related to the apparent distortion of the PO_4 tetrahedra. In case all the P–O bonds are similar, the PO_4 tetrahedra are less distorted. Increase in the dissimilarity of these bonds indicate more distortion of the PO_4 group. In the $P6_3/m$ and $P\bar{6}$ lattices the cation columns must be disordered to average between the nine and six coordination of the oxygen atoms to the Ba^{2+}, Ca^{2+} or rare earth (nine coordination) and Na^+ (six coordination) ions. This positional disorder causes a relatively high distortion of the PO_4 group. In $Ba_4Nd_3Na_3(PO_4)_6F_2$ ($P\bar{3}$), the presence of the six coordinated Na^+ ions in the column position does not give rise to the same high disorder of the PO_4 group and to the distortion of the PO_4 tetrahedra as was observed with $Ba_6La_2Na_2(PO_4)_6F_2$. The reason for this is that the restrictions imposed on the PO_4 group by the $P6_3/m$ or $P\bar{6}$ space groups do not exist in $P\bar{3}$, the PO_4 groups can be tilted in such a way that they can accomodate the different coordination requirements of Na and Nd. Judging from

TABLE II

BOND LENGTHS (Å) AND ANGLES (°)

$M(1)$–O(1)(×3)	2.43(1)	$M(2)$–O(3)(×2)	2.49(1)
–O(2)(×3)	2.47(1)	–F	2.265(2)
–O(3)(×3)	2.83(1)	P–O(1)	1.54(2)
$M(2)$–O(1)	2.60(1)	–O(2)	1.51(1)
–O(2)	2.43(1)	–O(3)(×2)	1.53(1)
–O(3)(×2)	2.36(1)		
O(1)–P–O(2)	112.8(8)	O(2)–P–(3)(×2)	109.0(5)
–O(3)(×2)	110.1(6)	O(3)–P–O(3)	105.5(7)

TABLE III

P–O BOND LENGTHS IN VARIOUS APATITES

	Space gr	P–O1	P–O2	P–O3	P–O4	Ref.
$Ca_{10}(PO_4)_6F_2$	$P6_3/m$	1.53	1.54	1.53		(*4*)
$Ba_{10}(PO_4)_6F_2$	$P6_3/m$	1.54	1.53	1.53		(*2*)
$Ca_6Eu_2Na_2(PO_4)_6F_2$	$P6_3/m$	1.54	1.51	1.53		Present work
$Ba_6La_2Na_2(PO_4)_6F_2$	$P\bar{6}$	$\begin{cases} 1.61 \\ 1.43 \end{cases}$	1.52 1.58	1.41 1.62		(*2*)
$Ba_4Nd_3Na_3(PO_4)_6F_2$	$P\bar{3}$	1.53	1.53	1.54	1.53	(*2*)

the P–O bond values in $Ca_6Eu_2Na_2(PO_4)_6F_2$, the PO_4 tetrahedra are less distorted than in $Ba_6La_2Na_2(PO_4)_6F_2$. The reason for this might be that the cations in $Ca_6Eu_2Na_2(PO_4)_6F_2$ are all similar in size and that Na and Ca occupying the column sites differ less in coordination power than Na and the rare earths do. The same reason might apply as to why the space group in this compound remains $P6_3/m$, as in all the apatite-like compounds.

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