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Structure Determination of Calcium Neodymium Potassium Double Phosphate $CaKNd(PO_4)_2$

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Abstract

The structure of $(Ca_{1.5}Nd_{1.5})K_{1.5}(PO_4)_3$ $[CaKNd(PO_4)_2]$ has been determined using single-crystal X-ray diffraction data. The material crystallizes in the hexagonal system with space group $P6_222$ ($P6_422$) and the parameters (refined from powder data) $a = 7.033 (5)$ and $c = 6.397 (5)$ Å, $Z = 1$. The least-squares anisotropic refinement led to $R = 0.042$ for 407 reflexions. The structure is similar to that of hexagonal $LnPO_4$ except that the K atom occupies a large tunnel in the lattice and the Ln position is statistically occupied by both Nd and Ca atoms. It is made up of (Nd,Ca)–PO_4–(Nd,Ca)– chains running along the c axis, linked to similar chains by corner sharing with four PO_4 tetrahedra coplanar with the (001) plane.

Introduction

The importance of new luminophores has recently motivated research on new materials containing rare-earth ions. Phosphors containing neodymium ions can be used as high-power microlaser sources.

The study of the optical properties of various phosphates such as NdP_5O_{14} (Albrand, Attig, Fenner, Jeser & Mootz, 1974), $KNdP_4O_{12}$ (Hong, 1975), $K_3Nd(PO_4)_2$ (Hong & Chinn, 1976) has shown that such phases possess a covalent two- or three-di-

mensional framework in which the rare-earth ion is found relatively isolated ($d_{Ln-Ln} \simeq 5$ Å).

The phosphates $LnPO_4$ (Ln = La, Ce, Nd) seem to crystallize in two allotropic varieties. One has the monazite-type structure with monoclinic symmetry, the second has hexagonal symmetry, its structure being characterized by large tunnels running along the c axis. Ordinarily, the $LnPO_4$ hexagonal phases are hydrated ($LnPO_4 \cdot \frac{1}{2}H_2O$), but no evidence exists proving that the presence of water is necessary for stabilizing their structure (Mooney, 1950; Mooney-Slater, 1962).

The existence of the large tunnels in the lattice has l Et-Tabirou & Daoudi (1980) to prepare phases such as $ACaNd(PO_4)_2$ (A = K, Rb, Cs) with the large alkali ions inserted in the tunnels.

The necessity of studying and giving an interpretation of the optical properties of such phases has led us to carry out a detailed structural determination of $CaKNd(PO_4)_2$.

Preparation and characterization

The starting materials $(NH_4)_2HPO_4$, K_2CO_3, $CaCO_3$ and Nd_2O_3 are mixed together in stoichiometric amounts and pressed into discs. These are first heated for several hours at 673 K followed by two heat treatments for 48 h at 1323 K with interposed grinding.

Single crystals were grown by recrystallization of the powder at 1873 K in a sealed platinum tube, followed by slow cooling.

The X-ray powder patterns of the ground crystals suggest an isotypy with hexagonal $LnPO_4$. A qualitative X-ray fluorescence analysis shows only the

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Table 1. *Positional parameters and anisotropic temperature factors* $(\times 10^4 \text{ Å}^2)$ *for* $CaKNd(PO_4)_2$ *(e.s.d.'s are in parentheses)*

Anisotropic temperature-factor expression: $\exp\left[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23})\right]$.

		x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd,Ca	$3(c)$	$\frac{1}{2}$	0	0	95 (3)	66 (4)	51 (2)	$U_{22}/2$		
K	$3(b)^*$	0	0	$\frac{1}{2}$	386 (30)	U_{11}	1126 (126)	$U_{11}/2$		
P	$3(d)$	$\frac{1}{2}$	0	$\frac{1}{2}$	136 (10)	73 (12)	57 (8)	$U_{22}/2$		
O	$12(k)$	0.4397 (10)	0.1384 (9)	0.3535 (9)	234 (26)	129 (20)	111 (20)	96 (19)	−16 (18)	29 (17)

* The occupancy factor for the K atom in this site is 50%.

X-ray diffraction data and structure determination

presence of Ca, Nd and K as heavy-atom components. The analysis by flame spectroscopy for the K and Ca concentration gave the following results: Ca: 9.7 (theor.), 9.5 (exp.); K: 9.5 (theor.), 9.1 (exp.)%. The IR absorption spectrum of the powder in Nujol between 800–1700 cm^{-1} and 2200–4000 cm^{-1} gives no evidence for the presence of water in the compound. Furthermore a DTA curve shows no peak due to water loss.

The single-crystal X-ray diffraction patterns indicate unambiguously a $6/mmm$ hexagonal Laue symmetry and the systematic extinction $00l$: $l \neq 3n$. These are compatible with the space group $P6_222$ (or the enantiomorphic $P6_422$).

The unit cell contains one formula unit $(Ca_{1.5}Nd_{1.5})K_{1.5}(PO_4)_3$ $[D_m = 3.74 (2), D_c = 3.757$ Mg m$^{-3}]$.

A small crystal having a flat diamond-like shape with maximum and minimum diameters of 0.22 and 0.19 mm and a thickness of 0.14 mm was mounted along the c-axis direction. The intensities were measured on a three-circle automatic diffractometer (Enraf–Nonius CAD-3) with Mo $K\alpha_1$ graphite-monochromated radiation $(\lambda = 0.70929 \text{ Å})$ and a multiple $\theta/2\theta$ scanning technique up to $\theta_{max} = 45°$. Three standard reflections were measured for every batch of 50 reflections with no significant fluctuation in their intensities. 407 independent reflections $[I > 3\sigma(I)]$ were obtained (after six equivalents were averaged) and corrected for Lorentz and polarization factors, but not for absorption $[\mu(\text{Mo } K\alpha) = 8.95 \text{ mm}^{-1}]$.

A preliminary Fourier synthesis was calculated using the LnPO$_4$ model, equally confirmed by a three-dimensional Patterson synthesis, and both revealed the O atom positions. A further refinement was carried out with the Ln position occupied half by Ca and half by Nd atoms and its occupancy factor allowed to vary. No change greater than the e.s.d. was observed and the distribution was fixed at 1:1 = Nd:Ca for this site. A

new Fourier analysis was made with this model, revealing a significant electron density maximum at the $3(b)$ position $(00\frac{1}{2},00\frac{1}{2},00\frac{5}{6})$. This position corresponds to the axis of the large infinite tunnel in the LnPO$_4$ structure and was assumed to be half occupied by a K atom. Refining the occupation factor of this site produced no significant difference from 50% and it was fixed at this value.

Refinement first by isotropic and then by anisotropic full-matrix least squares (Busing, Martin & Levy, 1962) led to a final $R = \sum \|F_o| - |F_c\|/\sum |F_o| = 0.042$. A final difference synthesis showed no significant residual electron density.

Scattering factors were those of McMaster, Kerr del Grande, Mallet & Hubbel (1969).

The final positional and thermal parameters are given in Table 1. Table 2 gives the interatomic distances.*

Table 2. *Interatomic distances* (Å) *for* $CaKNd(PO_4)_2$ *with e.s.d.'s in parentheses*

(Nd,Ca) polyhedron		K polyhedron	
4 × (Nd,Ca)—O	2.580 (6)	4 × K—O	2.894 (6)
4 × (Nd,Ca)—O	2.363 (6)	4 × K—O	2.988 (6)

P tetrahedron		Cation–cation distances	
4 × P—O	1.555 (6)	(Nd,Ca)—(Nd,Ca)	4.112 (2)
2 × O—O	2.482 (12)	(Nd,Ca)—K	3.674 (2)
2 × O—O	2.521 (12)	(Nd,Ca)—P	3.199 (2)
2 × O—O	2.614 (12)	(Nd,Ca)—P	3.675 (2)
		K—P	3.517 (2)
		K—K	4.264 (2)
		(K—K)	2.132 (2)*

* This distance is not significant since the K atom occupies the three positions of the $3(b)$ site only with a value of 50%.

Description and discussion of the structure

Fig. 1 gives the projection of the structure on the (001) plane. The anionic environment of the Nd and K atoms is reproduced in Figs. 2 and 3.

The structure of (Ca$_{1.5}$Nd$_{1.5}$)K$_{1.5}$(PO$_4$)$_3$ [CaKNd(PO$_4$)$_2$] can be described as a three-dimensional network made up of chains of (Nd,Ca) atoms alternating with phosphate groups, along the c axis. In such a chain each (Nd,Ca) atom is linked to two adjacent phosphate groups by edge sharing (see Fig. 2). Each chain is cross-linked to four neighboring
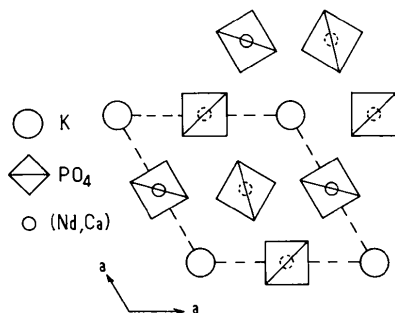

Fig. 1. Projection of the CaKNd(PO$_4$)$_2$ structure on the (001) plane.

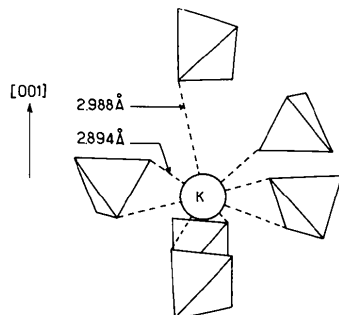Fig. 2. Environment of the K atom in CaKNd(PO$_4$)$_2$.
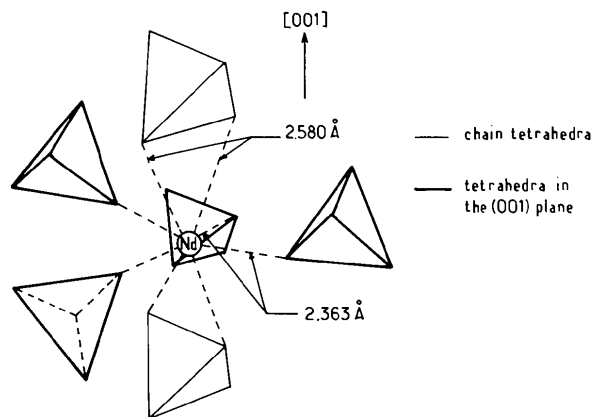

Fig. 3. Environment of the Nd atom in CaKNd(PO$_4$)$_2$.

chains by bonds which extend from the Nd or Ca atom to corners of four different phosphate tetrahedra roughly parallel to the (001) plane. Each (Nd,Ca) atom is coordinated to eight O atoms, four at distances of 2·363 Å and four at 2·580 Å. The four shorter bonds are directed towards corners of four different coplanar tetrahedra, while the longer bonds extend to two O atoms forming the edges of two tetrahedra above and below the plane of the shorter bonds (Fig. 3). A very similar configuration of Ln—PO$_4$—Ln— chains and short–long distances is found in the monazite structure, differences arising only in the mutual orientation of the chains. The hexagonal $\rightleftharpoons$ monazite transition between the two varieties of the LnPO$_4$ phases involves only some reorientations of the chains with respect to one another.

Such a symmetrical arrangement of interconnected Ln—PO$_4$—Ln— chains leaves large open tunnels running along the hexagonal axis. These tunnels are lined by O atoms at minimum cross-tunnel distances of approximately 5 Å. In these tunnels are found the potassium atoms on the 3(b) site. The figure of 1·5 K per unit cell, which is compatible with a K/Nd = 1 ratio, corresponds to the maximum occupation possibility of this position. Greater occupation would create a K—K distance which is physically impossible (2·132 Å).

A distribution of exactly 1·5 K per unit cell supposes the existence of an order between empty and filled 3(b) sites, inducing a doubling of the c-axis parameter. The fact that no long-range order is experimentally observed proves that the theoretical ratio of 1·5 per unit cell is not quite attained and some Schottky defects probably exist either inside the same tunnel or in adjacent tunnels. The concentration of these defects is sufficiently small as to be undetected by chemical analysis and does not disturb the short-range order in the crystal. The K atom has an eightfold coordination, surrounded by oxygen at shorter and longer K—O distances (2·894 and 2·988 Å) forming a square antiprism (Fig. 2). These distances compare well with the sum of the ionic radii (Shannon & Prewitt, 1969) of 2·89 Å.

The (Nd,Ca)—O distances (2·363 and 2·580 Å) are comparable to those found in Na$_3$Nd(PO$_4$)$_2$ (2·26–2·69 Å) (Salmon, Parent, Vlasse & Le Flem, 1978), in CePO$_4$ (2·34–2·66 Å) (Mooney, 1950) and BiPO$_4$ (2·33–2·66 Å) (Mooney-Slater, 1962), the last two compounds being isostructural with CaKNd(PO$_4$)$_2$. We can conclude then that the 50% substitution of Nd by Ca on the same site has little influence on the coordination-polyhedron distances of this atom. This obviously results from the similarity of the Nd^{3+} and Ca^{2+} effective ionic radii [Nd^{3+}(VIII) $r = 1·12$ Å; Ca^{2+}(VIII) $r = 1·12$ Å (Shannon & Prewitt, 1969)].

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The Water Molecule in Crystalline Hydrates Studied by Neutron Diffraction

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Abstract

A survey of the geometry and environment of water molecules in crystalline hydrates is presented. Histograms and correlation analyses are based on 97 crystal structures accurately determined by neutron diffraction, and include data from 183 water molecules, each donating two hydrogen bonds. The sample is analyzed according to the nature of the hydrogen-bond acceptors and of the coordinated cations. Cases of bifurcated hydrogen bonds are also discussed. The hydrogen bonds tend to be linear and the acceptors tend to be located close to the water plane. The tendency of coordination bonds to be collinear with the direction of one of the lone pairs of the O or their bisector increases with the strength of the bonds. The length of the W–H bond, which, on average, is shorter than in the gas phase, is correlated to the strength of the donated hydrogen bond and to the nature of the acceptor as well as to the type of coordination. On average, W–H is shorter for weaker hydrogen bonds, lower electronegativity of the acceptors and a triangular (as opposed to tetrahedral) type of coordination. The H–W–H angle is, on average, about $2 \cdot 5^\circ$ wider than in the gas phase; this widening is correlated to the type of coordination (larger for triangular), to the strength of the hydrogen bond, and to the $A \cdots W \cdots A$ angle between acceptors. Differences between the dimensions of water molecules in gas and solid phases are shown to be effective and not due to uncorrected thermal effects.

Introduction

Since the survey published by Ferraris & Franchini-Angela (1972) (FF hereafter), the structures of crystalline hydrates studied by neutron diffraction have quadrupled in number, and data for about 200 such structures are now available. Meanwhile, following previous work (Hamilton & Ibers, 1968; Vinogradov & Linnel, 1971), several reviews based on neutron diffraction data have been published (Falk & Knop, 1973; Fuess, 1979; Lundgren, 1974; Olovsson & Jönsson, 1976; Speakman, 1972, 1973, 1974, 1975, 1976). All these works, however, are not specifically concerned with hydrates, and an up-to-date investigation of these compounds seemed, therefore, worthwhile. In particular, the larger number of structures now available also allows one to take into consideration, in some cases, the nature of the hydrogen-bond acceptors A, and of the cations C coordinated to the water molecule. Because of the larger sample, selection criteria even stricter than those used by FF were applied. Compounds with any kind of disorder, symmetry ambiguities, uncertainties in the hydrogen-bonding scheme or in coordination, gross inaccuracy or some other flaws have been excluded. Unfortunately for our purposes, several structures had been selected for neutron diffraction studies in order to clarify order/disorder problems, and so about half of the papers scrutinized were not included in the present investigation, which was eventually based on 97