THE SODIUM YTTERBIUM ORTHOPHOSPHATE $Na_{3(1+x)}Yb_{(2-x)}(PO_4)_3$

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ABSTRACT :

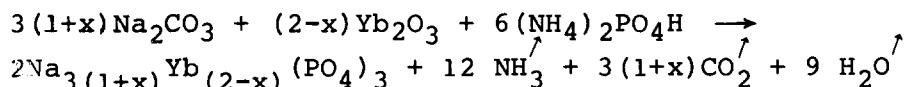A new sodium ytterbium orthophosphate with general formula $Na_{3(1+x)}Yb_{(2-x)}(PO_4)_3$ $(0.07 \leqslant x \leqslant 0.50)$ has been prepared and characterized. Its crystal structure has been determined from a single crystal for $x = 0.50$. The space group is $R\bar{3}c$, the lattice constants are : $a = 9.12(1)$ Å, $c = 21.81(6)$ Å. The structure of $Na_{4.50}Yb_{1.50}(PO_4)_3$ is related to that of $NaZr_2(PO_4)_3$. The PO_4 tetrahedra and the $(Yb,Na)O_6$ octahedra form a three-dimensional skeleton in which the remaining sodium atoms are inserted. This structural type is also found for the phases $Na_{4.50}Ln_{1.50}(PO_4)_3$ (Ln = Tm, Lu) and $Na_{4.50}Ln_{1.50}(AsO_4)_3$ (Ln = Er, Tm, Yb, Lu).

The study of the sodium rare-earth orthophosphates has allowed to prepare several phases with formula $Na_3Ln(PO_4)_2$ where Ln is a rare earth going from lanthanum to erbium [1]. The structural analysis of $Na_3Nd(PO_4)_2$ shows that its structure can be derived from that of glaserite $K_3Na(SO_4)_2$ with an order between the sodium and neodymium atoms [2].

In attempt to prepare these phases for the heaviest rare earths Ln = Tm, Yb, Lu, we found a new non-stoichiometric phase with general formula $Na_{3(1+x)}Ln_{(2-x)}(PO_4)_3$. A detailed determination of its homogeneity range and crystal structure has been carried out when the rare earth is ytterbium.

Experimental procedure

$Na_{3(1+x)}Yb_{(2-x)}(PO_4)_3$ has been prepared from a stoichiometric mixture of sodium carbonate, diammonium hydrogenophosphate $(NH_4)_2PO_4H$ and Yb_2O_3 oxide according to the reaction :

$$3(1+x)Na_2CO_3 + (2-x)Yb_2O_3 + 6(NH_4)_2PO_4H \longrightarrow$$

$$2 Na_{3(1+x)}Yb_{(2-x)}(PO_4)_3 + 12 NH_3\uparrow + 3(1+x)CO_2\uparrow + 9 H_2O\uparrow$$

This mixture has been heated slowly in a platinum crucible up to 450°C under a nitrogen flow in order to bring about a progressive decomposition of $(NH_4)_2PO_4H$. Two successive heatings at 1050°C - one for 5 hours followed by grinding and one another for 15 hours - were necessary to obtain pure materials. An X-ray diffraction study indicates a single phase for x values between 0.07 and 0.50.

The symmetry and cell constants have been obtained from a single crystal with composition $Na_{4.50}Yb_{1.50}(PO_4)_3$ which has been prepared from a polycrystalline sample having the same composition heated to 1150°C for 16 hours and then cooled slowly. The small single crystals are colorless with a rectangular shape.
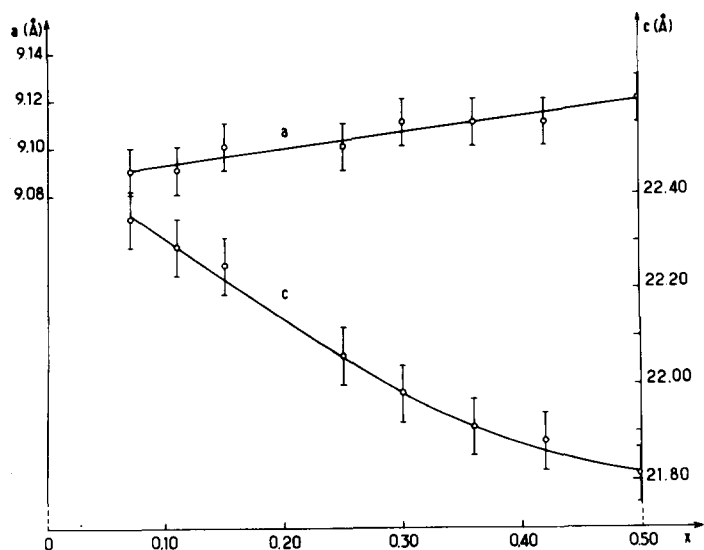
The structural analysis was carried out on a crystal with dimensions $0.06 \times 0.09 \times 0.09$ mm^3 mounted along the c-axis. Weissenberg photographs indicate a Laüe symmetry $\bar{3}m$, the systematic extinctions hkl: $(-h+k+l) \neq 3n$ and $h\bar{h}l$: $l \neq 2n$ are consistent with the space groups R3c or $R\bar{3}c$. The refined lattice parameters are:
a = 9.12(1) Å,
c = 21.81(6)Å.
The cell contains

FIG. 1
Cell parameters evolution versus composition x
for $Na_{3(1+x)}Yb_{(2-x)}(PO_4)_3$ phases.

six formula units ($d_{mes.}$ = 3.94(8) gcm^{-3}, $d_{calc.}$ = 4.11 gcm^{-3}). Fig. 1 shows the cell parameters variations as a function of x for $Na_{3(1+x)}Yb_{(2-x)}(PO_4)_3$.

Determination of the structure

The structure has been solved from a Patterson synthesis using 266 independent reflections collected on an Enraf-Nonius CAD3 three-circle automatic diffractometer using MoKα radiation (λ = 0.70942 Å). Because of the observed correlations during refinement, between the positions x,y,z and $\bar{x}$, $\bar{y}$, $\bar{z}$, the space group R3c was adopted. The full-matrix least-squares isotropic refinement led to an R-factor of 0.063.

The final values of the positional and thermal parameters are given in Table I and the significant interatomic distances in Table II.

TABLE I

Final positional and thermal parameters for $Na_{4.50}Yb_{1.50}(PO_4)_3$

Atom	Site	x	y	z	B($Å^2$)
(Yb,Na)	12c	0	0	0.1575(1)	2.22(4)
Na(1)	6b	0	0	0	4(1)
Na(2)	18e	0.6445(33)	0	1/4	2.6(8)
P	18e	0.3137(13)	0	1/4	1.9(2)
O(1)	36f	0.1874(29)	0.1744(27)	0.0847(10)	3.7(4)
O(2)	36f	0.2042(27)	-0.0222(27)	0.1950(9)	3.5(4)

TABLE II

Selected bond distances (±0.005 Å) in $Na_{4.50}Yb_{1.50}(PO_4)_3$

(Yb,Na)-O(1)	3×2.292	Na(1)-O(1)	6×2.478
(Yb,Na)-O(2)	3×2.134	Na(1)-O(2)	6×3.626
		Na(2)-O(1)	2×2.560
P-O(1)	2×1.481	Na(2)-O(1)	2×2.551
P-O(2)	2×1.508	Na(2)-O(2)	2×2.622
		Na(2)-O(2)	2×2.913
		Na(2)-O(2)	2×3.233

Description and discussion

A partial projection of the structure of $Na_{4.50}Yb_{1.50}(PO_4)_3$ along the c-axis is given in Fig. 2. This structure, which may be written $Na_4[Yb_{1.50}Na_{0.50}](PO_4)_3$, consists of a three-dimensional framework of PO_4 tetrahedra and $(Yb,Na)O_6$ octahedra, the remaining Na^+ ions occupying the Na(1) and Na(2) sites, large size holes of 6-fold and 10-fold coordination respectively. In the framework each octahedron is linked to six PO_4 tetrahedra and each tetrahedron to four octahedra by common corners. The $[Na(1)O_6]$ octahedron shares opposite faces with $(Yb,Na)O_6$ octahedra, giving rise to $(Yb,Na)O_6$ $[Na(1)O_6](Yb,Na)O_6$ groups oriented in a parallel direction
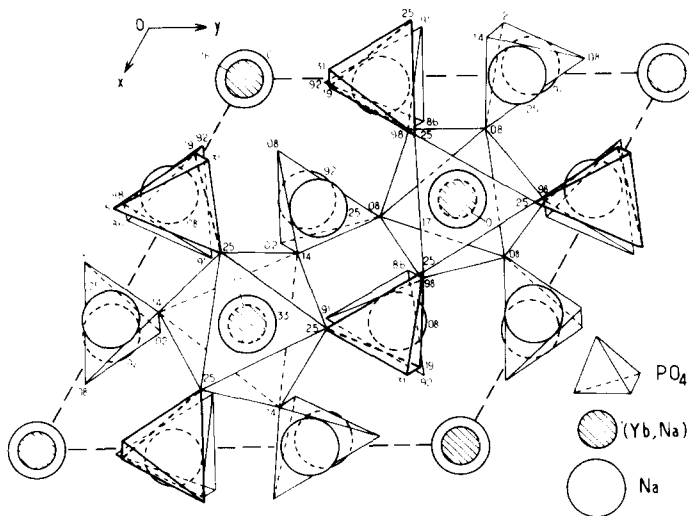
FIG. 2

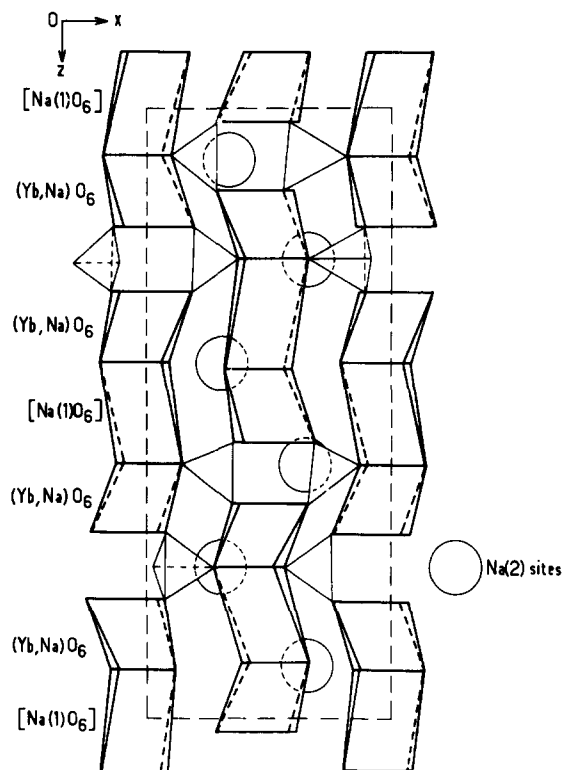Projection of third the unit cell along the c-axis of $Na_{4.50}Yb_{1.50}(PO_4)_3$

to the c-axis (Fig. 3).

The $(Yb,Na)O_6$ octahedra are occupied statistically by ytterbium and 1/9 of the present sodium ions.

A number of other phases seem to belong to the same family as $Na_4(Yb_{1.50}Na_{0.50})(PO_4)_3$: $Fe_2(SO_4)_3$ (3,4), $NaB_2(PO_4)_3$ (B = Ge,Ti,Zr) (5), $Na_3M_2(PO_4)_3$ (M = Ti,V,Cr,Fe) (6,7), $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ $(0 \leqslant x \leqslant 3)$ (8) and $Na_4Zr_2(SiO_4)_3$ (9). The three-dimensional skeleton assures in these phases the cohesion of the lattice, while the Na(1) and Na(2) sites can be empty, partially or totally occupied.

The non-stoichiometry of $Na_{3(1+x)}Yb_{(2-x)}(PO_4)_3$, when x goes from 0.07 to 0.50, can be explained by a progressive filling of the Na(2) sites, while ytterbium is replaced by sodium. The correlative substitution in the $(Yb,Na)O_6$ octahedra of the Yb^{3+} ions by much larger Na^+ ions induces a slight increase of the a parameter. On contrary, the c parameter diminishes (Fig. 1). This decrease can be explained by smaller repulsion forces between Yb^{3+} ions via the PO_4 tetrahedra along the c-axis at rising x.

FIG. 3
Projection of $Na_{4.50}Yb_{1.50}(PO_4)_3$ along the $[120]$ direction showing the different sites and their relative arrangement.

Non-stoichiometric phases of similar structure and of formulation $Na_{3(1+x)}Ln_{(2-x)}(XO_4)_3$ have been also found for Ln = Tm, Lu when X = P and for Ln = Er, Tm, Yb, Lu when X = As. The cell parameters for x = 0.50 are given in Table III.

Table III
Lattice parameters of $Na_{4.50}Ln_{1.50}(XO_4)_3$ phases

	a±0.01(Å)	c±0.06(Å)	$d_{calc.}$ (gcm^{-3})	$d_{mes.}$ ±0.08(gcm^{-3})
$Na_{4.50}Tm_{1.50}(PO_4)_3$	9.15	21.88	4.03	3.84
$Na_{4.50}Yb_{1.50}(PO_4)_3$	9.12	21.81	4.11	3.94
$Na_{4.50}Lu_{1.50}(PO_4)_3$	9.11	21.80	4.14	3.94
$Na_{4.50}Er_{1.50}(AsO_4)_3$	9.49	22.35	4.41	4.36
$Na_{4.50}Tm_{1.50}(AsO_4)_3$	9.48	22.32	4.44	-
$Na_{4.50}Yb_{1.50}(AsO_4)_3$	9.47	22.28	4.49	4.40
$Na_{4.50}Lu_{1.50}(AsO_4)_3$	9.45	22.25	4.53	-

According to J.B. Goodenough, H.Y-P. Hong and J.A. Kafalas who have studied the Na^+-ion conductivity in the $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ phases(10), such a lattice is particularly well adapted for fast-ion transport. A study of the transport properties of the phosphate phases is in progress.

References

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