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Crystallochemistry and structural study of some nasicon-like phosphates

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Abstract

The phosphates $Na_{1-3x}Eu_xTi_2(PO_4)_3$, $M_{0.5}Ti_2(PO_4)_3$ and $M_{0.5}FeNb(PO_4)_3$ (M is a divalent cation) belong to the Nasicon structural family. The structures have been determined by the Rietveld refinement of the powder X-ray diffraction patterns. The space group is $R\bar{3}$ for $Na_{0.25}Eu_{0.25}Ti_2(PO_4)_3$ and $Ca_{0.5}Ti_2(PO_4)_3$ and $R\bar{3}c$ for $M_{0.5}FeNb(PO_4)_3$ (M = Cd, Ca, Sr, Pb, Ba). The change of space group, which is related to the cation distribution, is discussed with regard to the composition of the phosphates. © 1997 Elsevier Science S.A.

Keywords: Cationic distribution; Crystallochemistry; Nasicon; Phosphate; Structure

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1. Introduction

Nasicon-type phosphates have been studied extensively in the context of various fields of solid state chemistry: fast alkali ion conduction [1], low thermal expansion ceramics [2,3] and luminescence [4]. More recently, the introduction of copper or silver into the structure has extended the potential applications of such materials to various catalytic processes, for example the dehydrogenation reaction, periodic catalytic activity, etc. [5,6].

Nasicon-type phosphates can be expressed by the general formula $M_xA_2(PO_4)_3$. The structure consists of a three-dimensional framework of PO_4 tetrahedra and AO_6 octahedra sharing corners. Within this covalent framework exist two additional cationic sites usually labelled M(1) and M(2). The M(1) site is an antiprism sharing faces with the octahedron AO_6 site. The M(2) site is a large cage bounded by 10 oxygens. Cations of various size and charge can be introduced in both sites. The cationic distribution in the M(1) site can be analyzed in the context of the $R\bar{3}c$ and $R\bar{3}$ space groups (SG). This paper reviews very recent structural determinations of such new phosphates with the object of determining the influence of the composition on the cationic ordering. The phases of composition $Na_{1-3x}Eu_xTi_2(PO_4)_3$ $(0 \leq x \leq 0.25)$, $M_{0.5}Ti_2$

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Table 1
Parameters in the equivalent hexagonal cell of $\mathrm{Na_{1-3x}Eu_xTi_2(PO_4)_3}$, $\mathrm{M_{0.5}Ti_2(PO_4)_3}$ (M = Mn, Cd, Ca, Sr, Pb), and $\mathrm{M_{0.5}FeNb(PO_4)_3}$ (M = Cd, Ca, Sr, Pb, Ba)

Compound	a_h (±0.004 Å)	c_h (±0.02 Å)	c_h/a_h	Ref.
$\mathrm{Na_{1-3x}Eu_xTi_2(PO_4)3}$				
$x = 0$	8.492	21.78	2.564	[12]
$x = 0.05$	8.459	21.84	2.581	[7]
$x = 0.10$	8.410	21.90	2.604	[7]
$x = 0.15$	8.393	21.97	2.617	[7]
$x = 0.20$	8.370	22.00	2.628	[7]
$x = 0.25$	8.354	22.03	2.637	[7]
$\mathrm{Mn_{0.5}Ti_2(PO_4)_3}$	8.520	21.09	2.475	[8]
$\mathrm{Cd_{0.5}Ti_2(PO_4)_3}$	8.456	21.56	2.549	[9]
$\mathrm{Ca_{0.5}Ti_2(PO_4)_3}$	8.376	22.02	2.628	[9,15]
$\mathrm{Sr_{0.5}Ti_2(PO_4)_3}$	8.307	22.53	2.712	[9]
$\mathrm{Pb_{0.5}Ti_2(PO_4)_3}$	8.298	22.71	2.736	[9]
$\mathrm{Cd_{0.5}FeNb(PO_4)_3}$	8.612	21.63	2.512	[10,11]
$\mathrm{Ca_{0.5}FeNb(PO_4)_3}$	8.584	21.92	2.554	[10,11]
$\mathrm{Sr_{0.5}FeNb(PO_4)_3}$	8.556	22.51	2.631	[10,11]
$\mathrm{Pb_{0.5}FeNb(PO_4)_3}$	8.541	22.67	2.654	[10,11]
$\mathrm{Ba_{0.5}FeNb(PO_4)_3}$	8.483	23.16	2.730	[10,11]

$\mathrm{(PO_4)_3}$ (M = Mn, Cd, Ca, Sr, Pb), and $\mathrm{M_{0.5}FeNb(PO_4)_3}$ (M = Cd, Ca, Sr, Pb, Ba) will be described. The elaboration process and the structural determination have been described previously [7–11]. All the X-ray powder diagrams can be indexed assuming a rhombohedral cell and the order of magnitude of the parameters calculated in an equivalent hexagonal cell (a_h, c_h) is consistent with the Nasicon-type structure (Table 1). The related interatomic distances are given in Table 2.

2. The phosphates of composition $\mathrm{Na_{1-3x}Eu_xTi_2(PO_4)_3}$ $(0 \leq x \leq 0.25)$

The phosphates of general formula $\mathrm{Na_{1-3x}Eu_xTi_2(PO_4)_3}$ $(0 \leq x \leq 0.25)$ have the Nasicon-type structure. The substitution of europium for sodium induces a decrease of a_h and an increase of c_h.

The structure of the phase with composition $x = 0$ has been solved previously with the $R\bar{3}c$ SG [12], whereas the structure of the $\mathrm{Na_{0.25}Eu_{0.25}Ti_2(PO_4)_3}$ phase was solved in the context of the $R\bar{3}$ SG [7]. The projection of the polyhedra typical of the respective cationic distribution is given in Fig. 1. In $\mathrm{NaTi_2(PO_4)_3}$ the sodium is located at the center of M(1) and the Na–O distance, 2.472 Å, is slightly larger than the distance calculated from the ionic radii, 2.42 Å [13]. For $\mathrm{Na_{0.25}Eu_{0.25}Ti_2(PO_4)_3}$ the sodium and europium are randomly located in half of the M(1) sites with a 1–1 ordering along the c-axis between the full and empty sites (M(1) and M(1)$_{\mathrm{va}}$. in Fig. 2). In this case the metal–oxygen distance, 2.489 Å, is less than the distance between the center of the vacancy and the surrounding oxygens at 2.596 Å. Such a high value is the consequence of the electrostatic repulsions between the plane of oxygens perpendicular to the c-axis. Therefore, the Ti–O distance close to the empty M(1) site (1.859 Å) is less than the Ti–O distance facing the full M(1) site (1.982 Å). This latter distance is exactly the Ti–O distance of the bond near the sodium site in $\mathrm{NaTi_2(PO_4)_3}$ [12]. The transition

Table 2
Cation–oxygen interatomic distances in $\mathrm{Na_{0.25}Eu_{0.25}Ti_2(PO_4)_3}$, $\mathrm{Ca_{0.5}Ti_2(PO_4)_3}$ and $\mathrm{M_{0.5}FeNb(PO_4)_3}$ (M = Cd, Ca, Sr, Pb, Ba)

Compound and space group	M–O distances (Å) in the M(1) site	Fe/Nb–O or Ti–O distances (Å)	P–O distances (Å)	Ref.
$\mathrm{Na_{0.25}Eu_{0.25}Ti_2(PO_4)_3}$, $R\bar{3}$	2.489 × 6	Ti(1)–O: 1.852 × 3 1.983 × 3 Ti(2)–O: 1.859 × 3 1.902 × 3	1.517 1.551 1.582 1.594	[7]]
$\mathrm{Ca_{0.5}Ti_2(PO_4)_3}$, $R\bar{3}$	2.427 × 6	Ti(1)–O: 1.930 × 3 2.004 × 3 Ti(2)–O: 1.862 × 3 1.938 × 3	1.548 1.558 1.561 1.571	[9]
$\mathrm{Cd_{0.5}FeNb(PO_4)_3}$, $R\bar{3}c$	2.390 × 6	1.895 × 3 1.979 × 3	1.580 × 2 1.569 × 2	[10] [11]
$\mathrm{Ca_{0.5}FeNb(PO_4)_3}$, $R\bar{3}c$	2.464 × 6	1.927 × 3 1.973 × 3	1.514 × 2 1.551 × 2	[10] [11]
$\mathrm{Sr_{0.5}FeNb(PO_4)_3}$, $R\bar{3}c$	2.592 × 6	1.920 × 3 1.912 × 3	1.547 × 2 1.587 × 2	[10] [11]
$\mathrm{Pb_{0.5}FeNb(PO_4)_3}$, $R\bar{3}c$	2.607 × 6	1.925 × 3 1.947 × 3	1.546 × 2 1.574 × 2	[10] [11]
$\mathrm{Ba_{0.5}FeNb(PO_4)_3}$, $R\bar{3}c$	2.713 × 6	1.969 × 3 1.956 × 3	1.539 × 2 1.535 × 2	[10] [11]

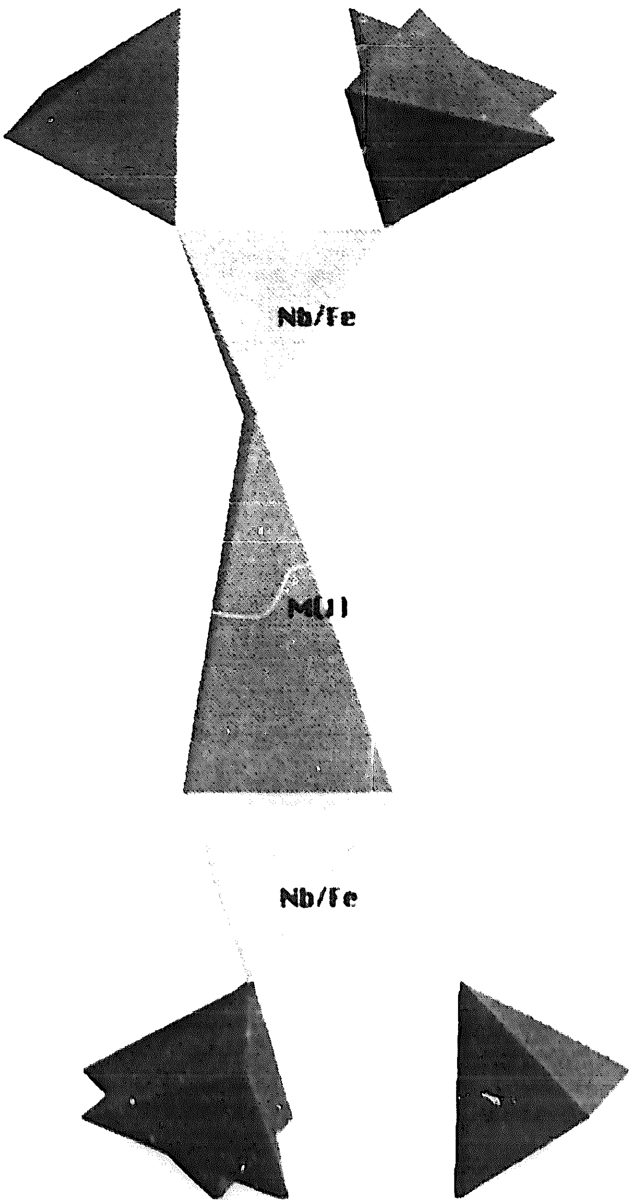

Fig. 1. Arrangement, along the c-axis, of the octahedral and antiprismatic sites in the nasicon-type structure assuming the $R\bar{3}c$ space group. The tetrahedra represent the PO_4 groups.

from the $R\bar{3}c$ to the $R\bar{3}$ SG with the variation of composition is in agreement with the conclusions of Mentre et al. [14] for the description of the solid solution $Ca_{(1-x)/2}Na_xTi_2(PO_4)_3$ and with Senbhagaram et al. for $M_{0.5}Ti_2(PO_4)_3$ compounds (M = Ca, Sr, Ba) [15].

3. The phosphates of composition $M_{0.5}Ti_2(PO_4)_3$ (M = Mn, Cd, Ca, Sr, Pb)

In the titanium phosphates containing the divalent cation M^{2+}, as the size of this cation increases, a_h decreases whereas c_h increases. On the other hand, by comparing the cell parameters of these phosphates with those of the titanium phosphates containing a monovalent cation of the same size, the value of c_h is larger and the value of a_h is smaller [e.g., $NaTi_2(PO_4)_3$ vs. $Ca_{0.5}Ti_2(PO_4)_3$ (Table 1)].

The crystal structure of the calcium phase was solved assuming the $R\bar{3}$ SG [9,14,15]. Recently, Fakrane et al. [8] have also solved the structure of $Mn_{0.5}Ti_2(PO_4)_3$ in the same SG ($R\bar{3}$). The divalent cations are located in half of the M(1) sites with the same 1–1 ordering along the c-axis between the full and empty sites. The Mn–O and Ca–O distances are 2.262 and 2.427 Å, respectively, i.e. slightly larger than the distances expected from the ionic radii of 2.23 and 2.40 Å, respectively [13]. The distances between the center of the empty M(1) site and the surrounding oxygens are larger, respectively 2.363 Å (Mn) and 2.603 Å (Ca). The Ti–O distances facing the full site are very close, 2.014 Å (Mn) and 2.005 Å (Ca), respectively.

4. The phosphates of composition $M_{0.5}FeNb(PO_4)_3$ (M = Cd, Ca, Sr, Pb, Ba)

The crystal structures of all the $M_{0.5}FeNb(PO_4)_3$ phases have been solved assuming the $R\bar{3}c$ SG [10,11]. As the size of M^{2+} increases, c_h increases but a_h decreases, whereas the c_h/a_h ratio increases. The niobium and iron atoms are distributed statistically over the octahedral sites and the M^{2+} cations are also located statistically in the M(1) sites (Fig. 1). In this family of phosphates two interesting features must be underlined: (i) the octahedral sites become progressively regular from the calcium to the barium compounds; (ii) the M^{2+}–O distances are larger than those deduced from the ionic radii for the smaller cations (Cd^{2+}, Ca^{2+}), closely match the calculated values for the intermediate cation sizes (Sr^{2+}, Pb^{2+}) and become smaller for Ba^{2+} (Table 2).

5. Discussion and conclusion

The rules governing the variation of the Nasicon-type phosphate parameters have been reported previously [16,17], but the present data allow the determination of the relation between the composition and the cationic distribution. With this in mind, the discussion will be focused on the cluster consisting of M(1) sites surrounded by octahedral sites sharing faces in the configuration of the $R\bar{3}c$ or $R\bar{3}$ SG, i.e.

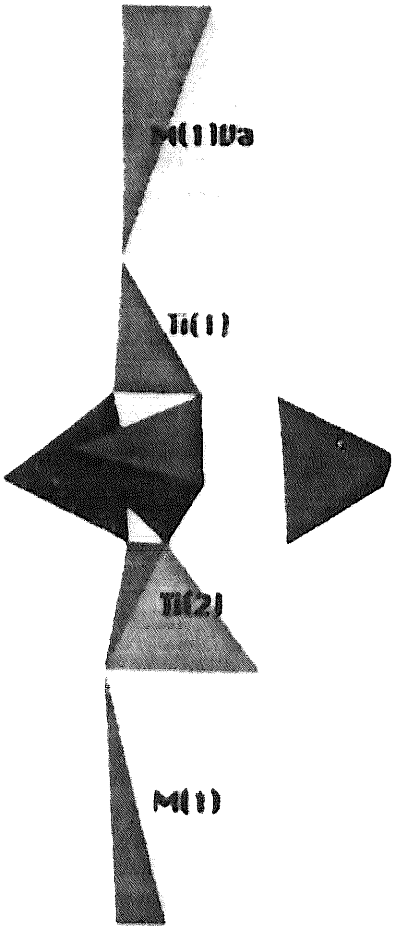

Fig. 2. Arrangement, along the c-axis, of the octahedral and antiprismatic sites in the nasicon-type structure assuming the $R\bar{3}$ space group. The tetrahedra represent the PO_4 groups (M(1)va: vacancy in the M(1) site).

with disorder or with order between the occupied and the empty sites, respectively, as shown in Figs. 1 and 2.

The value of c_h results from the coulombic attractions between the cation in M(1) and the surrounding oxygens and from the O^{2-}–O^{2-} repulsions occurring when M(1) is empty. The magnitude of a_h is governed by the size of the cation in the octahedral sites, but is extremely sensitive to expansion of the covalent network in a perpendicular direction, i.e. along the c-axis. The influence of these various factors is illustrated by the evolution of the parameters of the sodium europium phosphate family. Na^+ and Eu^{3+} in six-fold coordination have approximately the same size, respectively 1.02 and 0.95 Å. [13]. The substitution of europium for sodium leads to an increase of c_h and a decrease of a_h. These variations are induced only by the creation of the M(1) empty site. The c_h/a_h ratio increases with the europium, but its maximum value remains relatively small, 2.63.

In the $M_{0.5}Ti_2(PO_4)_3$ family the expansion of the covalent network along the c-axis is directly related to the size of M^{2+} and c_h/a_h attains, for lead phosphate, a higher value of 2.74. A parallel evolution is also observed for the iron niobium phosphates. In $Mn_{0.5}Ti_2(PO_4)_3$ and $Ca_{0.5}Ti_2(PO_4)_3$ the M(1) empty sites are somewhat larger than the M(1) occupied sites. Similar results have been obtained for $Ca_{0.5}Zr_2(PO_4)_3$ [18] and the distances between the center of the M(1) site and the surrounding oxygens, whether occupied by Ca or not, are slightly larger than those of the titanium phosphates, respectively 2.47 and 2.66 Å (Zr) vs. 2.43 and 2.60 Å (Ti).

Finally, it is of interest to discuss the apparent difference of the cationic ordering in $M_{0.5}Ti_2(PO_4)_3$ (M = Mn, Ca) and $M_{0.5}FeNb(PO_4)_3$. With regard to the respective ion size and charge, there are no crystal chemistry reasons for changing the cationic distribution. The $R\bar{3}$ SG implies two different octahedral sites. By considering the cluster of Fig. 2 several combinations of the respective distribution of niobium and iron atoms in octahedral sites and calcium atoms and vacancies in the antiprism M(1) can be assumed, e.g. Ca–Fe–Fe–Ca, Ca–Fe–Nb–Ca, etc. Each of these microscopic entities is characterized by a more or less strong distortion of the octahedral sites. Actually, the final refinement in the $R\bar{3}c$ SG represents the "mean" description of these various cationic arrangements. In contrast, in titanium compounds, only one kind of atom is located in the octahedral sites and the number of cationic arrangements on the microscopic scale is strongly reduced. Therefore, the $R\bar{3}$ SG accounts for the actual crystal structure.

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