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Crystal structures and magnetic properties of iron (III)-based phosphates: $Na_4NiFe(PO_4)_3$ and $Na_2Ni_2Fe(PO_4)_3$

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ABSTRACT

Crystal structures from two new phosphates $Na_4NiFe(PO_4)_3$ (**I**) and $Na_2Ni_2Fe(PO_4)_3$ (**II**) have been determined by single crystal X-ray diffraction analysis. Compound (I) crystallizes in a rhombohedral system (S. G: *R-3c*, $Z=6$, $a=8.7350(9)$ Å, $c=21.643(4)$ Å, $R_1=0.041$, $wR_2=0.120$). Compound (**II**) crystallizes in a monoclinic system (S. G: *C2/c*, $Z=4$, $a=11.729(7)$ Å, $b=12.433(5)$ Å, $c=6.431(2)$ Å, $\beta=113.66(4)^{\circ}$, $R_1=0.043$, $wR_2=0.111$). The three-dimensional structure of (**I**) is closely related to the Nasicon structural type, consisting of corner sharing $[(Ni/Fe)O_6]$ octahedra and $[PO_4]$ tetrahedra forming $[NiFe(PO_4)_3]^{4+}$ units which align in chains along the *c*-axis. The Na^+ cations fill up trigonal antiprismatic sites within these chains. The crystal structure of (**II**) belongs to the alluaudite type. Its open framework results from $[Ni_2O_{10}]$ units of edge-sharing $[NiO_6]$ octahedra, which alternate with $[FeO_6]$ octahedra that form infinite chains. Coordination of these chains yields two distinct tunnels in which site Na^+.

The magnetization data of compound (I) reveal antiferromagnetic (AFM) interactions by the onset of deviations from a Curie–Weiss behaviour at low temperature as confirmed by Mössbauer measurements performed at 4.2 K. The corresponding temperature dependence of the reciprocal susceptibility χ^{-1} follows a typical Curie–Weiss behaviour for $T > 105$ K. A canted AFM state is proposed for compound (II) below 46 K with a field-induced magnetic transition at $H \approx 19$ kOe, revealed in the hysteresis loop measured at 5 K. This transition is most probably associated with a spin-flop transition.

1. Introduction

Inorganic phosphates cover a large class of diverse materials whose applications include: catalysts, solid electrolytes for batteries [1–7], linear and non-linear optical components [8–11] and laser materials [12,13]. However, the study of phosphates has become more popular particularly after the development of the compounds containing $[A_2(XO_4)_3]$ fragments in the underlying framework. Common structure types are Garnet, Nasicon, Alluaudite, $[Sc_2(WO_4)_3]$ and Langbeinite (Figs. 1–4). In general, these structures have the same type of framework, but with different types of holes, cavities, tunnels for cations accommodation. Physical and chemical properties of all these types of compounds depend strongly on their crystal structure. Nasicon and Alluaudite structure types of interest for this study and therefore described in more detail.

1.1. Nasicon compounds

The basic structure of these compounds was first described by Hagman and Kierkegaard [14]. These phosphates have been widely studied in many fields, because of their various properties such as conductivity, low expansion coefficients and catalytic activity [15–19]. They have fascinated much awareness in recent past, as they facilitate a large scope for preparing number of materials with variation in their constituent metal ions and composition [20–24]. These materials have the general formula $B_pA_nA'_m(PO_4)_3$ where B is a monovalent cation Na^+, Ag^+, Cu^+, H^+, H_3O^+, $NH_4{}^+$, or a divalent one such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} or Cu^{2+}, while *A* and *A'* can be filled with tri-, tetra- or pentavalent transition metal ions. Thus the structure can be tailored by substituting at *B*, *A*, and/or *A'* sites which gives rise to a large number of com-

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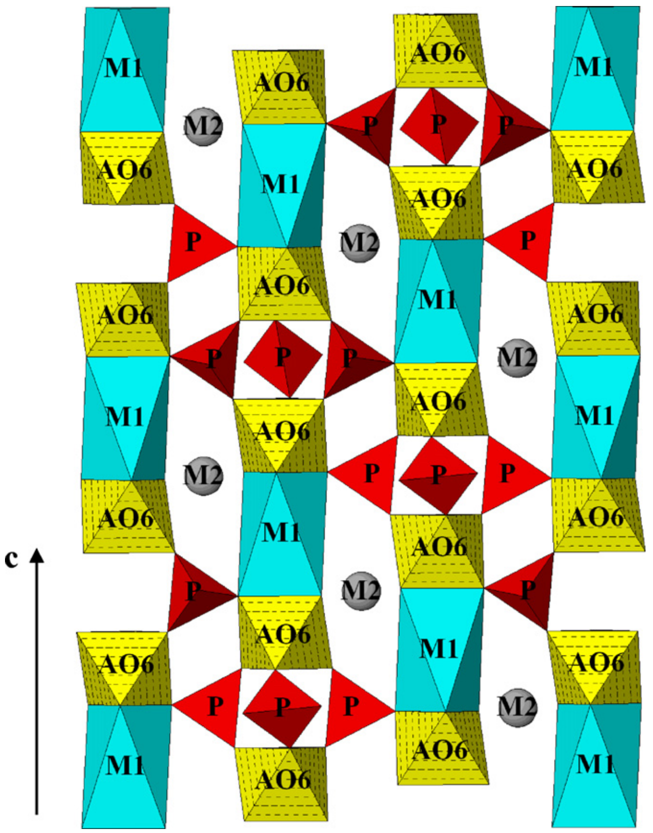

Fig. 1. The structure of Nasicon showing the M(1) (type 1) and M(2) sites (type 2).

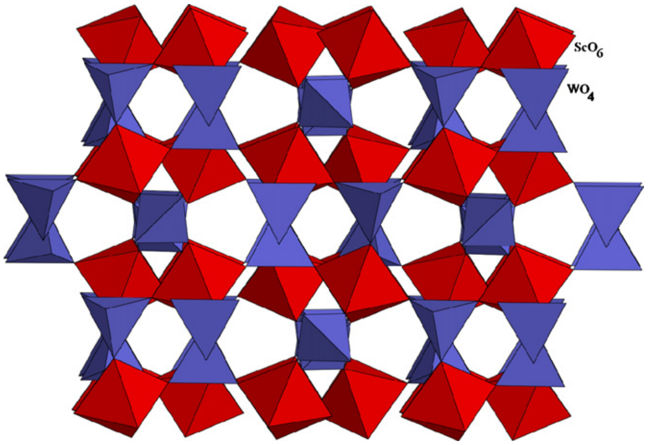

Fig. 3. The polyhedral unit cell structure of $Sc_2(WO_4)_3$ as viewed down the *a*-axis.

pounds for comparative studies. The crystal structure consists of a three-dimensional network built up from corners sharing of $[PO_4]$ tetrahedra and $[AO_6]$ ($[A'O_6]$) octahedra. Every apex of $[AO_6]$ octahedron belongs to one $[PO_4]$ tetrahedron. The two distinct interstitial voids generated within the network are known as M(1) and M(2) sites. The M(1) site is a trigonally distorted octahedron formed by the triangular faces of two $[AO_6]$ octahedra along the *c*-axis of the hexagonal cell. The M(2) sites are located in the large cavities and have an eight-fold coordination. There is one atom on a M(1) site per three atoms on a M(2) site according to the formula unit $M(1)_xM(2)_yA_n(PO_4)_3$ with $0 \leq x \leq 1$ and $0 \leq y \leq 3$. Most of the members of Nasicon type compounds so far known in the literature are described in rhombohedral $R\bar{3}c$, $R\bar{3}$ or $R32$ space groups with typical unit cell dimensions $a \sim 8$ Å and $c \sim 22$ Å, but cell

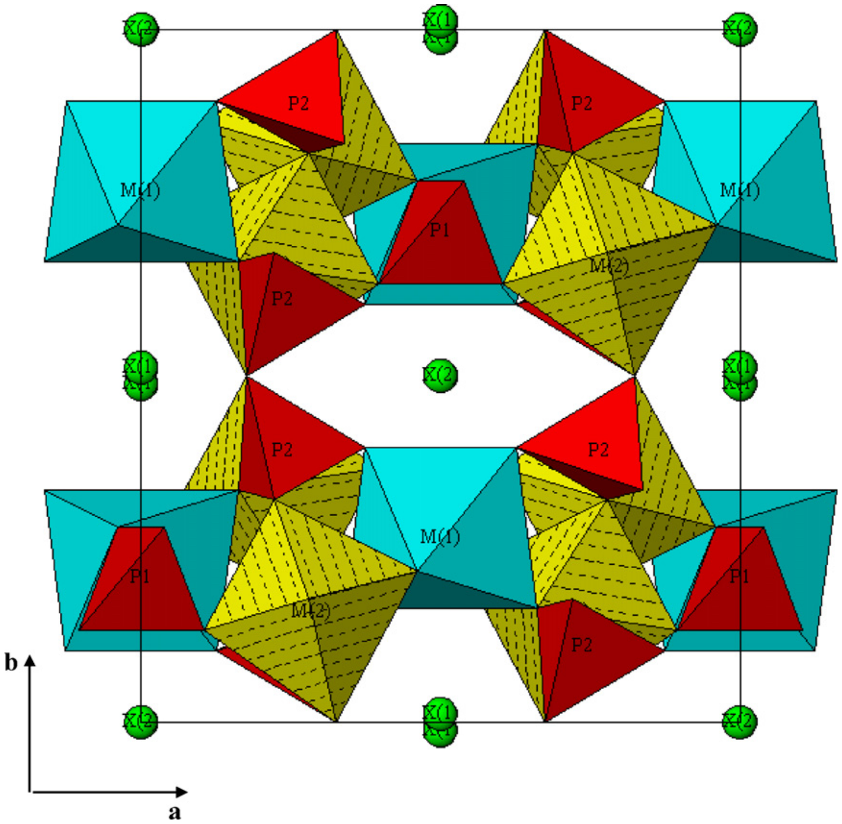

Fig. 2. Polyhedral representation of the alluaudite unit cell showing the open-framework channel structure propagating along [0 0 1].