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The Pyrophosphate $NaFeP_2O_7$: A Cage Structure

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The high-temperature form of $NaFeP_2O_7$ crystallizes in the monoclinic $P2_1/c$ space group with a = 7.3244(13), b = 7.9045(7), c = 9.5745(15) Å, β = 111.858(13)°, and Z = 4. The structure has been refined from 3842 reflections leading to $R = 0.040$ and $R_w = 0.047$. The structure of II-$NaFeP_2O_7$ can be described by alternately stacking layers containing the FeO_6 octahedra and layers formed by the P_2O_7 groups, parallel to (001). Elongated cages are formed where two Na^+ ions are located. The structure is compared with that of $KAlP_2O_7$. Both structures are built up from blocks of three polyhedra, $[FeP_2O_{11}]$ or $[AlP_2O_{11}]$, including a small O_{oct}–O_{tet}–O_{oct} angle. These blocks are connected in such a way that several types of tunnels appear in each structure.

Introduction

The adaptability of PO_4 tetrahedra and P_2O_7 groups to a framework built up of WO_6 octahedra has been recently discussed (*1–4*). In this respect, the phosphates AMP_2O_7 (A = Na, K; M = Fe, Al) could be interesting, owing to the presence of metallic elements such as Fe or Al, which can exhibit an octahedral environment and are present in smaller amounts than phosphorus. $NaFeP_2O_7$ has been isolated by Gamondes *et al.* (*5*); at 1023K, this compound undergoes an irreversible phase transition from a low-temperature form (called I) to a high-temperature one (called II). The X-ray powder patterns pointed out that I-Na FeP_2O_7 was isostructural with $KAlP_2O_7$ and $KFeP_2O_7$, whereas II-$NaFeP_2O_7$ was isostructural with $NaAlP_2O_7$ (*6*). More recently, it has been shown that this family is much more extended (*7*). In the first group, the structure of $KAlP_2O_7$ has been studied by Nam Ng and Calvo (*8*), but nothing is known about the structure of the second group, if we except the fact that Gamondes *et al.* proposed the structure of II-Na FeP_2O_7 and $NaAlP_2O_7$ was related to that of the previously investigated α $Cu_2P_2O_7$ (*9*). Thus the present paper deals with the structure of $NaFeP_2O_7$-phase II, which represents the second series of compounds.

Experimental

Crystals of II-$NaFeP_2O_7$ were prepared by heating a mixture of 38.30% (mole) $NaHCO_3$, 10.64% Fe_2O_3, and 51.06%

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$NH_4H_2PO_4$, corresponding to 1 mole Na FeP_2O_7 and 0.2 mole $Na_4P_2O_7$. The mixture was slowly heated to 1173K in a Pt crucible and then melted at 1373K for 1 hr: after melting, it was cooled at a rate of 10K/hr to 1173K and quenched at room temperature. Clear and pink crystals of $NaFeP_2O_7$ were obtained in a matrix of a dark-yellow vitreous phase; the crystals were separated from the glass by washing in hot water.

The crystal selected for the structure determination was an optically transparent plate, limited by the {100}, {010}, and {001} forms with the dimensions 190 × 70 × 700 μm. The Laue patterns showed a monoclinic symmetry and the cell parameters, measured on precession and Weissenberg films, were confirmed later by diffractometric techniques, with a least-squares refinement based on 25 reflections: a = 7.3244(13), b = 7.9045(7), c = 9.5745(15) Å, β = 111.858(13)°. These parameters are very similar to those given by Gamondes *et al.* (*6*) and the systematic absences ($0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$) confirmed the $P2_1/c$ space group.

TABLE I

POSITIONAL PARAMETERS WITH esd's FOR $NaFeP_2O_7$ ($B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j \beta_{ij} a_i a_j$)

Atom	x	y	z	B_{eq}
Na	0.28768(18)	0.47768(18)	0.29340(15)	1.58(2)
Fe	0.25959(3)	0.00883(3)	0.24937(3)	0.28(1)
P(1)	0.07355(6)	0.25412(5)	0.45559(4)	0.25(1)
P(2)	0.67295(6)	0.21144(5)	0.45472(5)	0.28(1)
O(1)	0.87705(18)	0.15348(17)	0.44124(16)	0.52(2)
O(2)	0.18938(21)	0.28450(17)	0.62093(14)	0.61(2)
O(3)	0.01146(18)	0.41546(16)	0.36353(15)	0.48(2)
O(4)	0.18136(22)	0.13467(19)	0.39169(16)	0.67(2)
O(5)	0.53313(19)	0.08587(18)	0.35008(15)	0.58(2)
O(6)	0.69212(21)	0.20154(17)	0.61750(14)	0.54(2)
O(7)	0.63560(19)	0.39363(16)	0.39793(15)	0.51(2)

The data were collected on a CAD-4 Enraf–Nonius diffractometer at 294K with Mo$K\alpha$ monochromatized radiation (λ = 0.7107 Å). The intensities were measured up to $2\theta = 90°$ by the ω-2θ technique with a maximum scan width of 1.28° and a counter slit aperture of 2 mm. The background intensity was measured on both sides of each reflection. A periodic control verified the stability of the sample. Among the 3884 measured reflections, only 3853 which had $\sigma(I)/I \leq 0.333$ were corrected for Lorentz and polarization effects, then for absorption with a program based on the crystal

TABLE II

$NaFeP_2O_7$: ANISOTROPIC THERMAL PARAMETERS

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	0.01897(47)	0.02535(51)	0.02517(56)	0.00226(38)	0.01272(43)	0.01093(42)
Fe	0.00454(8)	0.00411(6)	0.00334(5)	−0.00020(6)	0.00185(7)	−0.00038(8)
P(1)	0.00389(14)	0.00399(13)	0.00288(14)	0.00032(12)	0.00163(11)	−0.00031(12)
P(2)	0.00405(14)	0.00437(13)	0.00320(14)	−0.00041(9)	0.00146(11)	0.00061(11)
O(1)	0.00446(41)	0.00620(38)	0.01221(51)	−0.00020(31)	0.00419(39)	0.00100(35)
O(2)	0.01294(52)	0.00643(38)	0.00413(42)	0.00023(34)	0.00028(38)	−0.00188(35)
O(3)	0.00606(41)	0.00608(38)	0.00752(47)	0.00108(32)	0.00178(36)	0.00322(35)
O(4)	0.01294(52)	0.00953(44)	0.00896(47)	0.00375(38)	0.00806(43)	−0.00119(38)
O(5)	0.00530(41)	0.00918(41)	0.00864(47)	−0.00326(35)	0.00153(36)	−0.00330(38)
O(6)	0.01291(49)	0.00665(38)	0.00390(42)	0.00064(35)	0.00398(39)	0.00153(31)
O(7)	0.00932(47)	0.00541(38)	0.00864(47)	0.00185(32)	0.00554(39)	0.00337(34)

Note. These values were obtained from $U_{ij} = \frac{1}{2\pi^2} \beta_{ij}\ a_i\ a_j$, where β_{ij} appear through $\exp(-\beta_{ij}\ h_i\ h_j)$ and a_i are the modulus of the direct lattice vectors.

morphology.[1] The linear absorption coefficient was 36.92 cm^{-1} and the minimum and maximum transmission factors were 0.456 and 0.771.

The structure was determined from Patterson function and subsequent difference synthesis. The atomic parameters were refined by full-matrix least squares. Scattering factors for Fe^{3+}, Na^+, and P were from Cromer and Waber (*10*), corrected for anomalous dispersion (*11*), and for O^{2-} from Suzuki (*12*). A linear weighting scheme was adjusted according to $\langle w\,|F_0| - |F_c|\rangle$ in terms of sin θ/λ. For 11 intense reflections, the calculated structure factor was larger than the observed value, probably due to the secondary extinction; they were eliminated in the final refinement. The refinement with anisotropic thermal coefficients for each atom led to

$$R = \Sigma\big||F_0| - |F_c|\big| / \Sigma|F_0| = 0.040$$

and

$$R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.047.$$

The final atomic and anisotropic thermal parameters are listed in Tables I and II, respectively, and Fig. 1 shows the projection of the structure along the c axis. All the atoms are in general position.

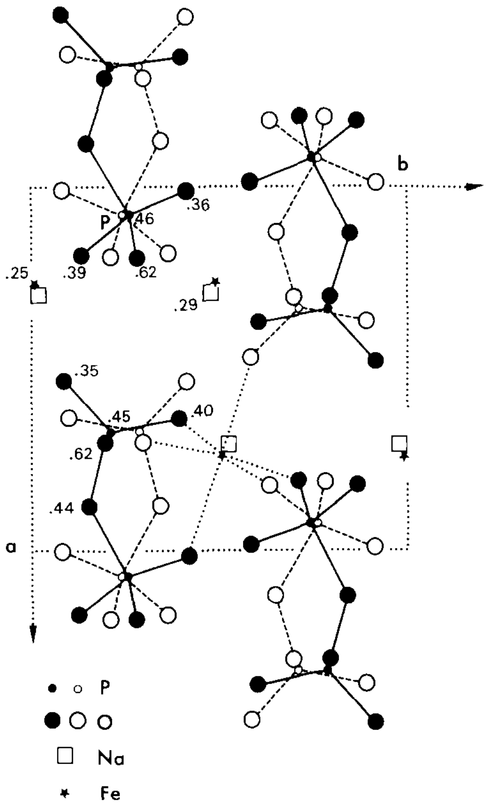

FIG. 1. $NaFeP_2O_7$: Projection of the structure along [001].

Description of the Structure and Discussion

The pyrophosphate $NaFeP_2O_7$ can be described as a cage structure whose host lattice "FeP_2O_7" is built up from corner-sharing octahedra and P_2O_7 groups (Fig. 2). The pyro group is formed from two slightly dis-

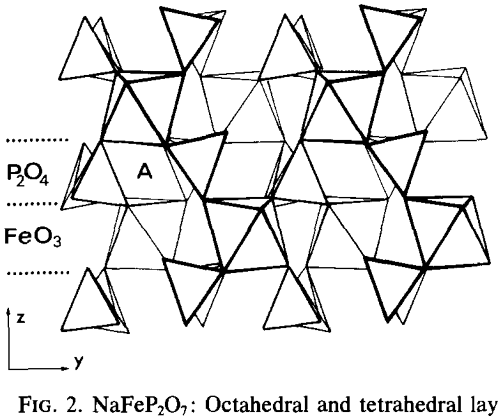

FIG. 2. $NaFeP_2O_7$: Octahedral and tetrahedral layers drawn from the projection onto (100). "A" designates a rhombic tunnel.

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[1] See NAPS document No. 03985 for 23 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 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. \$1.50 for postage of any microfiche orders.

TABLE III

GEOMETRY OF THE P_2O_7 GROUPS AND ENVIRONMENT OF Fe^{3+} AND Na^+ IN $NaFeP_2O_7$

Bond	Distance (Å)	Bond	Angle (°)
P(1)–P(2)	2.590(1)	P(1)–O(1)–P(2)	132.86(9)
P(1)–O(1)	1.605(1)	O(1)–P(1)–O(2)	107.72(8)
P(1)–O(2)	1.511(1)	O(1)–P(1)–O(3)	107.52(8)
P(1)–O(3)	1.520(1)	O(1)–P(1)–O(4)	104.16(8)
P(1)–O(4)	1.500(2)	O(2)–P(1)–O(3)	113.83(8)
		O(2)–P(1)–O(4)	110.60(8)
P(2)–O(1)	1.614(2)	O(3)–P(1)–O(4)	112.39(8)
P(2)–O(5)	1.508(1)		
P(2)–O(6)	1.514(2)	O(1)–P(2)–O(5)	100.38(8)
P(2)–O(7)	1.528(1)	O(1)–P(2)–O(6)	109.51(8)
		O(1)–P(2)–O(7)	106.71(8)
		O(5)–P(2)–O(6)	115.45(8)
		O(5)–P(2)–O(7)	113.37(8)
		O(6)–P(2)–O(7)	110.54(8)
FeO_6 octahedron		Na environment	
Fe–O(2)	1.994(1)	Na–O(1)	2.533(2)
Fe–O(3)	2.014(1)	Na–O(2)	2.580(2)
Fe–O(4)	1.938(2)	Na–O(3)	2.408(2)
Fe–O(5)	1.969(1)	Na–O(5)	2.384(2)
Fe–O(6)	2.044(1)	Na–O(6)	2.662(2)
Fe–O(7)	2.053(2)	Na–O(7)	2.457(2)
		Na–O(4)	3.064(2)
		Na–O(7)	2.975(2)

Note. The calculation of the standard deviations does not take the thermal motion corrections into account.

torted PO_4 groups having one common oxygen. The PO_3 terminal groups are in a nearly eclipsed configuration; for instance, the dihedral angle between the O(3)–P(1)–P(2) and O(7)–P(2)–P(1) planes is about 12°. The bond lengths and angles are given in Table III. The bridge bonds are slightly longer than the average terminal bonds (1.510 and 1.517 Å for the P(1) and P(2) atoms, respectively); they are similar to those observed in other pyrophosphates (*8*). The P–O–P bridge angle is larger than the 123° value found in $KAlP_2O_7$ (*8*). Each PO_4 tetrahedron shares its corners with three octahedra and one tetrahedron, while a FeO_6 octahedron shares all its apices with PO_4 tetrahedra. The FeO_6 octahedra are nearly regular, with O–Fe–O angles between 84.32 and 94.30° (Table III). All the P_2O_7 groups have a lengthening direction parallel to **a**. The arrangement of the polyhedra allows us to distinguish two sorts of layers parallel to (001): the octahedral layers with the composition FeO_3 and the tetrahedral layers with the composition P_2O_4 (Figs. 2 and 3). These layers are alternately stacked along **c** in such a way that every P_2O_7 group shares four corners with one octahedral layer, and the two other corners with the other octahedral layer. This framework forms small rhombic tunnels running along **a**, which are labeled as A in Fig. 2. An octahedral layer is connected with the adjacent tetrahedral layer in such a manner that a P_2O_7 group shares two of its corners with the same octahedron. This results in blocks of three polyhedra $[FeP_2O_{11}]$ (Fig. 4), which can be used as structural units for describing the structure of this compound. In this

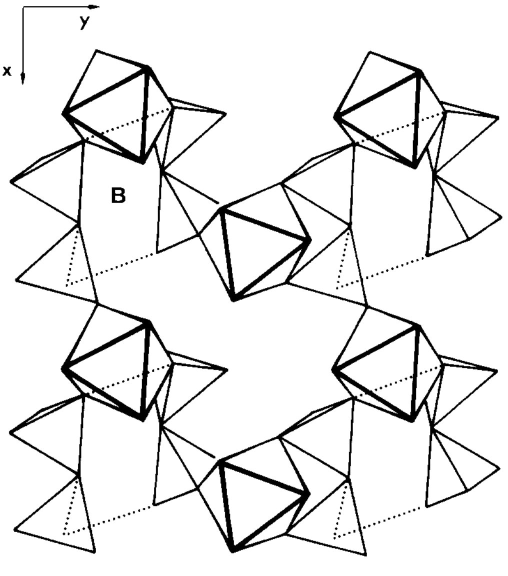

FIG. 3. Relative arrangement of the FeO_6 octahedra and P_2O_7 groups in $NaFeP_2O_7$. The "aeschynite"-type windows (B) are bounded by dotted lines.

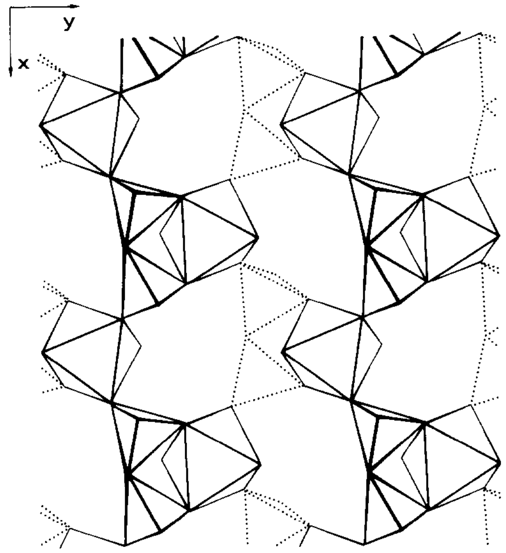

FIG. 4. $NaFeP_2O_7$: Layer parallel to (001) built up from the $[FeP_2O_{11}]$ units. The P_2O_7 groups in dotted lines lie below the mean plane of the layer.

case, new layers parallel to (001) are built up from such structural units which share their corners, as shown in Fig. 4.

This framework delimits elongated cages where the Na^+ ions are located; these cages are bounded by four pyrophosphate groups, eight octahedra, and four tetrahedra; it results in two sorts of windows: very distorted pentagonal windows and four-angled windows whose shape is similar to that of the tunnels observed in diaspore and in aeschynite (*13*). The former, which are built up from one P_2O_7 group, two octahedra, and one tetrahedron, form small distorted pentagonal tunnels running along $[\bar{1}10]$; the latter are not only formed from octahedra, contrary to aeschynite or diaspore, but are built up from two P_2O_7 groups and two octahedra, as shown in Fig. 3, and form small tunnels running along the [001] direction. Each cage encloses two Na^+ ions which are bound to six oxygen atoms (Table III), forming a very distorted octahedron (Fig. 5). The second neighbors for Na are two oxygen atoms at 2.975 and 3.064 Å (Fig. 5b, Table III). The others lie beyond 3.45 Å from the Na atom.

These results point out that the structure of this compound cannot be derived from that of α $Cu_2P_2O_7$, contrary to the proposition of Gamondes *et al.* (*6*).

On the other hand, a comparison can be made with the structure of the homologous potassium pyrophosphate $KAlP_2O_7$, which is also built up from corner-sharing octahedra and pyrophosphate groups (*8*). The "AlP_2O_7" framework of this phase can also be described by the association of $[AlP_2O_{11}]$ units formed of one P_2O_7 group and one octahedron, which are shown in Fig. 6. However, the configuration of the pyrophos-

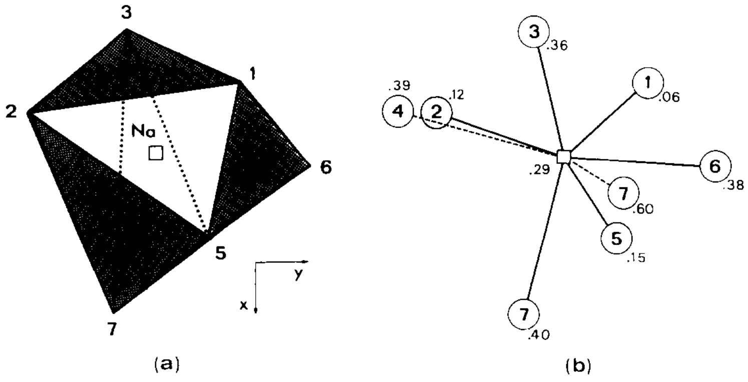

FIG. 5. $NaFeP_2O_7$: Representation of (a) the distorted NaO_6 octahedron and (b) the Na^+ environment, drawn from a projection along [001]. The oxygen atoms are labeled as in Table I.

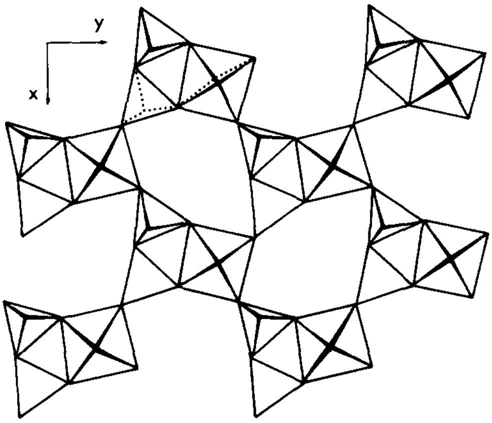

FIG. 6. $KAlP_2O_7$: Projection onto (001) showing the $[AlP_2O_{11}]$ units and the tunnels running along c.

phate groups is staggered in the potassium compound while it is eclipsed in the case of sodium, as one can see by the comparison of Figs. 4 and 6. In both structures, the FeO_6 or AlO_6 octahedra, as well as the PO_4 tetrahedra, remain almost regular. The configuration of the P_2O_7 group is worthy of note in both compounds: O_{oct}–O_{tet}–O_{oct} angles of 64 and 70° are indeed observed in $KAlP_2O_7$ and $NaFeP_2O_7$, respectively (Figs. 3 and 6). To our knowledge, such a small angle has never been observed in other pyrophosphates containing corner-sharing P_2O_7 and octahedral groups: bivalent pyrophosphates, such as α $Cu_2P_2O_7$ (*9*), α $Co_2P_2O_7$ (*14*), and α $Mg_2P_2O_7$ (*15*), exhibit minimum O_{oct}–O_{tet}–O_{oct} angles ranging from 88.2 to 101.4° and P_2O_7 groups belonging to structures such as the bronzes $A_xP_8W_{8n}O_{24n+16}$ (*1, 2*) and $P_8W_{18}O_{52}$ (*4*), in which the octahedra are more numerous, are also characterized by greater angles, ranging from 84.4 to 88.5°. Small O_{pol}–O_{tet}–O_{pol} (pol for polyhedron) are also observed in pyrophosphates, such as, for instance, α $Ca_2P_2O_7$ (75.4°) and β $Ca_2P_2O_7$ (76.6 and 78.7°), where the cation has seven, eight, or nine neighbors (*16, 17*). In all these cases, the existence of a small O_{pol}–O_{tet}–O_{pol} angle is due to the double connection of the P_2O_7 group with the same octahedron ($NaFeP_2O_7$–$KAlP_2O_7$) or polyhedron (α and β $Ca_2P_2O_7$). In $KAlP_2O_7$ and $NaFeP_2O_7$, this confirms the great adaptability of the P_2O_7 groups to the octahedra without involving any distortion of the polyhedra. The adaptability of the P_2O_7 group to the octahedra is perhaps more striking for $KAlP_2O_7$ in that the "height" of a P_2O_7 group corresponds exactly to that of an octahedron, forming corner-sharing files of polyhedra similar to those obtained in octahedral structures, one P_2O_7 group alternating with one octahedron (Fig. 7). It results that the $[AlP_2O_7]$ host lattice of the potassium pyrophosphate, like that of Na FeP_2O_7, forms cages resulting from intersecting tunnels where the K^+ ions are located. The so-formed tunnels are, however, much wider than those observed for Na FeP_2O_7 and exhibit sizes close to those of hexagonal and tetragonal tungsten bronzes (*18, 19*). Two sorts of tunnels are indeed observed: very wide tunnels running along the [001] direction and distorted hexagonal

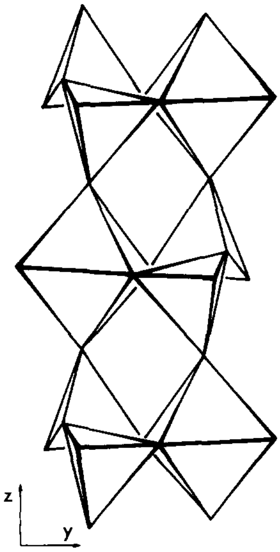

FIG. 7. Representation of a double file of AlO_6 octahedra and P_2O_7 groups obtained by a projection along a in $KAlP_2O_7$.

tunnels running along the [110] direction, formed by two types of alternating windows. The former, which correspond to four corner-sharing $[AlP_2O_{11}]$-unit crowns (Fig. 6), exhibit a mean radius of 2.77 Å, close to that observed in hexagonal tungsten bronzes or in pyrochlore (about 2.7 Å) and a minimum distance between opposite oxygen atoms of 4.68 Å; the latter, which are formed of crowns built up of two P_2O_7 groups and two octahedra, have a shape similar to that of pyrochlore but are smaller than in pyrochlore: the minimum distance between opposite oxygens are 3.49 and 3.67 Å for the two types of windows. Thus it appears that $KAlP_2O_7$, which is characterized by rather large intersecting tunnels contrary to $NaFeP_2O_7$, could be able to exhibit some mobility of the inserted cation K^+.

Conclusion

The structures of these pyrophosphates show the great adaptability of the P_2O_7 groups to the octahedra, in spite of the relatively great number of PO_4 tetrahedra (P/Fe(Al) = 2). The presence of tunnels and cages lets an analogy appear with the bronzes $A_xP_8W_{12}O_{24n+16}$ (*1, 2*) and $P_8W_8O_{24n+16}$ (*4*) in which the octahedra are much more numerous. These results let us consider the possibility of existence of intermediate phases involving the connection of PO_4 tetrahedra with WO_6 and AlO_6 (or FeO_6) octahedra simultaneously.

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