Monoclinic
$P2_1/c$
$a = 15.555\,(2)$ Å
$b = 7.5692\,(6)$ Å
$c = 17.362\,(7)$ Å
$\beta = 90.598\,(14)°$
$V = 2044.0\,(9)$ Å^3
$Z = 8$
$D_x = 4.977$ Mg m^{-3}
D_m not measured

Cell parameters from 26 reflections
$\theta = 1.8–8.5°$
$\mu = 11.538$ mm^{-1}
$T = 293\,(2)$ K
Rectangular block
0.26 × 0.18 × 0.08 mm
Dark grey metallic

Data collection

Siemens *P*4 four-circle diffractometer
Bisecting ω scans
Absorption correction: numeric
$T_{\min} = 0.152$, $T_{\max} = 0.409$
10 021 measured reflections
8167 independent reflections

$R_{\rm int} = 0.0559$
$\theta_{\max} = 26°$
$h = -1 \rightarrow 24$
$k = -1 \rightarrow 11$
$l = -27 \rightarrow 27$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0388$
$wR(F^2) = 0.0732$
$S = 0.699$
8167 reflections
127 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0093P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 1.679$ e Å^{-3}
$\Delta\rho_{\min} = -1.625$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Rb1	0.85862 (6)	0.02746 (14)	0.00788 (5)	0.0281 (2)
Rb2	0.34667 (6)	0.45606 (15)	0.97831 (6)	0.0298 (2)
Rb3	0.07657 (6)	0.4674 (2)	0.89068 (5)	0.0310 (2)
Rb4	0.55711 (6)	0.0548 (2)	0.09933 (6)	0.0367 (3)
In1	0.31611 (4)	0.72107 (9)	0.16956 (4)	0.01758 (14)
In2	0.90699 (4)	0.21146 (9)	0.27031 (4)	0.01658 (13)
In3	0.18136 (4)	0.23595 (9)	0.17727 (4)	0.01747 (14)
In4	0.40668 (4)	0.23851 (9)	0.24018 (4)	0.01798 (14)
Sb1	0.97431 (4)	0.53666 (9)	0.32768 (3)	0.01620 (12)
Sb2	0.16409 (4)	0.55444 (9)	0.09520 (3)	0.01652 (13)
Sb3	0.32931 (4)	1.06473 (8)	0.10988 (4)	0.01645 (13)
Sb4	0.25209 (4)	0.16508 (8)	0.82458 (4)	0.01753 (13)
Sb5	0.47704 (4)	0.53923 (9)	0.16277 (4)	0.01711 (13)
Sb6	0.24813 (4)	0.78693 (9)	0.82086 (4)	0.01772 (13)

Table 2. *Selected geometric parameters (Å, °)*

In1—Sb3	2.8083 (10)	In3—Sb1$^{\rm iii}$	2.8534 (9)
In1—Sb6$^{\rm i}$	2.8425 (14)	In3—Sb4$^{\rm v}$	2.8730 (13)
In1—Sb5	2.8602 (9)	In3—Sb3$^{\rm vi}$	2.8983 (9)
In1—Sb2	2.9638 (10)	In4—Sb5	2.8663 (10)
In2—Sb1$^{\rm ii}$	2.8494 (10)	In4—Sb3$^{\rm vi}$	2.8704 (12)
In2—Sb1	2.8506 (10)	In4—Sb5$^{\rm iii}$	2.8847 (10)
In2—Sb2$^{\rm iii}$	2.8532 (12)	In4—Sb4$^{\rm v}$	2.9215 (10)
In2—Sb6$^{\rm iv}$	2.8720 (10)	Sb4—Sb6$^{\rm vi}$	2.8637 (9)
In3—Sb2	2.8118 (10)		

Symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $x, y - 1, z$.

Data collection: Siemens *P*4 diffractometer software. Cell refinement: *XSCANS* (Siemens, 1994). Data reduction: *XSCANS*. Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1995).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blase, W., Cordier, G., Poth, L. & Weil, K. G. (1995). *Z. Kristallogr.* **210**, 60.
Cordier, G. & Ochmann, H. (1991). *Z. Kristallogr.* **197**, 281–282; *ibid.* 283–284; *ibid.* 285–286.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Siemens (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1995). *SHELXTL/PC*. Version 5.04. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Triclinic $Fe_3Al_2Si_3$ and Orthorhombic $Fe_3Al_2Si_4$ with New Structure Types

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Abstract

The title compounds, dialuminium triiron trisilicide and dialuminium triiron tetrasilicide, crystallize with new structure types. The coordination polyhedra in $Fe_3Al_2Si_3$ derive from icosahedra and those in $Fe_3Al_2Si_4$ from hexagonal cuboctahedra.

Comment

The ternary system Fe–Al–Si contains numerous ternary compounds. Six crystallize with known structures:

$FeAl_2Si$ (own structure type; German, Zavodnik, Yanson & Zarechnyuk, 1989), $FeAl_{2.4}Si_{0.6}$ (Na_3As structure type; German, Zarechnyuk, Ventskovskii, Yanson, Lizogub & Manyako, 1991), $FeAl_3Si_2$ (superstructure of $PdGa_5$; Gueneau, Servant, d'Yvoire & Rodier, 1995*a*), $Fe_{1.7}Al_4Si$ (own structure type; German, Belskii, Yanson & Zarechnyuk, 1989), $Fe_2Al_3Si_3$ (own structure type; Gueneau, Servant, d'Yvoire & Rodier, 1995*b*) and $Fe_2Al_{7.4}Si$ (own structure type; Corby & Black, 1977). Other compounds are known to exist but have not yet been characterized. An example is the compound of approximate composition '$Fe_3Al_3Si_2$' which was first reported by Takeda & Mutuzaki (1940). Here we present its structure and show that its refined composition is $Fe_3Al_2Si_3$. Another example is a compound of unknown composition which was reported as orthorhombic with cell parameters $a = 6.09$, $b = 9.96$, $c = 3.74$ Å (Jaeniche, 1936). Here we present its crystal structure and show that its refined composition is $Fe_3Al_2Si_4$, and that one of the reported cell parameters has to be doubled. Both structures are ordered and although they are of similar composition, they have rather different topologies.

$Fe_3Al_2Si_3$ (space group $P\bar{1}$) contains three iron, two aluminium and three silicon sites whose atomic environments are shown in Fig. 1. The coordination polyhedra resemble distorted icosahedra with some vertices unoccupied or containing an additional atom. The shortest bond distances between the different atom types are Fe—Al = 2.394, Fe—Si = 2.304, Al—Si = 2.468 Å, while those between the same atom types are Fe—Fe = 2.689, Al—Al = 2.538, Si—Si = 2.440 Å.

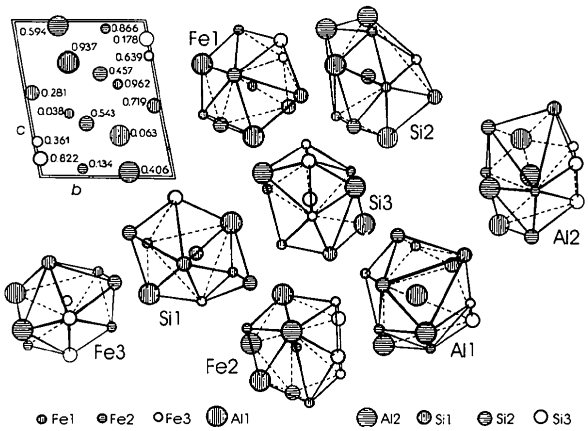

Fig. 1. The structure of $Fe_3Al_2Si_3$ viewed along [100] showing the coordination polyhedra.

$Fe_3Al_2Si_4$ (space group *Cmcm*) contains two iron, one aluminium and three silicon sites whose atomic environments are shown in Fig. 2. The coordination polyhedra resemble distorted hexagonal cuboctahedra in which some vertices are unoccupied. The coordination polyhedron of Al can also be considered as a trigonal prism with five additional coplanar neighbours in which the central atom is shifted outside the prism. Such coordination also occurs in Ni_2GeGa (Bhargava & Schubert, 1974). The shortest bond distances between the different atom types in this system are Fe—Al = 2.562, Fe—Si = 2.309, Al—Si = 2.570 Å, while those between the same atom types are Fe—Fe = 2.529, Al—Al = 2.624, Si—Si = 2.413 Å. The Al atoms form quasi-infinite undulating chains running along [001]. The structure can also be regarded as built up from identical planar networks which are situated at $x = 0$ and $x = 1/2$, and are mutually shifted by $b/2$ (see the right-hand side of Fig. 2).

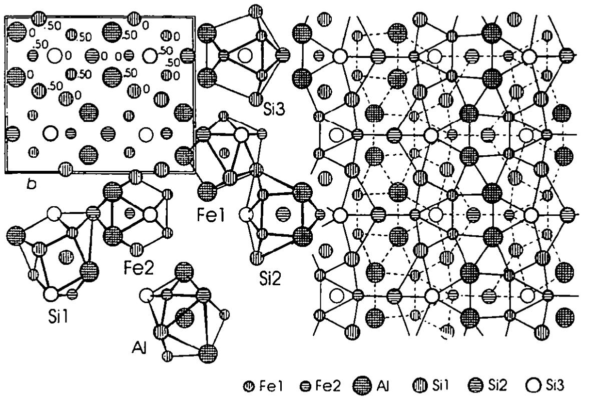

Fig. 2. The structure of $Fe_3Al_2Si_4$ viewed along [100] showing the coordination polyhedra and identical planes situated at $x = 0$ and $x = \frac{1}{2}$, and mutually shifted by **b**/2.

Experimental

Single crystals of $Fe_3Al_2Si_3$ and $Fe_3Al_2Si_4$ were found in the alloys prepared by arc melting the element mixtures (99.99% Fe, 99.98% Al and 99.98% Si) under an argon atmosphere and annealing for 700 h at 873 and 773 K, respectively. The nominal compositions for the two systems are $Fe_{32.5}Al_{37.5}Si_{30}$ and $Fe_{22.5}Al_{40}Si_{37.5}$, respectively.

$Fe_3Al_2Si_3$

Crystal data

$Fe_3Al_2Si_3$
$M_r = 305.76$
Triclinic
$P\bar{1}$
$a = 4.6512\,(16)$ Å
$b = 6.3261\,(24)$ Å
$c = 7.499\,(3)$ Å
$\alpha = 101.375\,(23)°$
$\beta = 105.923\,(17)°$
$\gamma = 101.237\,(19)°$
$V = 200.63\,(14)$ Å^3
$Z = 2$
$D_x = 5.062$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 9–25°$
$\mu = 11.821$ mm^{-1}
$T = 293$ K
Plate
$0.048 \times 0.048 \times 0.016$ mm
Grey

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–θ scans
Absorption correction: by integration from crystal shape (*LSABS*; Blanc, Schwarzenbach & Flack, 1991)
$T_{min} = 0.5471$, $T_{max} = 0.8353$
2562 measured reflections
1168 independent reflections
1046 observed reflections $[F > 1\sigma(F)]$
$R_{int} = 0.07$
$\theta_{max} = 30°$
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = -10 \rightarrow 10$
2 standard reflections frequency: 60 min intensity decay: 0.9–1.0%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.031$
$S = 1.27$
1046 reflections
74 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.00095$
$\Delta\rho_{max} = 1.74$ e Å^{-3}
$\Delta\rho_{min} = -2.32$ e Å^{-3}
Extinction correction: Becker & Coppens (1975)
Extinction coefficient: 2603 (195)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Fe_3Al_2Si_3$*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe1	0.03790 (19)	0.29782 (14)	0.41027 (12)	0.0087 (3)
Fe2	0.13449 (19)	0.31956 (13)	0.05623 (11)	0.0071 (3)
Fe3	0.36147 (19)	0.02378 (13)	0.22702 (11)	0.0084 (3)
Al1	0.0633 (4)	0.6522 (3)	0.2757 (3)	0.0088 (6)
Al2	0.4058 (4)	0.6734 (3)	0.0383 (3)	0.0095 (6)
Si1	0.2808 (4)	0.0509 (3)	0.5372 (3)	0.0117 (6)
Si2	0.5428 (4)	0.4147 (3)	0.3476 (3)	0.0093 (5)
Si3	0.8222 (3)	0.0191 (3)	0.1174 (3)	0.0079 (5)

Table 2. *Selected geometric parameters (Å) for $Fe_3Al_2Si_3$*

$Fe1^{i}$—$Si1^{i}$	2.304 (3)	$Al2^{ii}$—$Si3^{iii}$	2.468 (3)
$Fe2^{i}$—$Al2^{i}$	2.394 (3)	$Al2^{ii}$—Al2	2.538 (3)
$Fe2^{i}$—$Fe3^{i}$	2.6887 (15)	$Si1^{i}$—$Si1^{iv}$	2.440 (3)

Symmetry codes: (i) $1+x, y, z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, -y, -z$; (iv) $1-x, -y, 1-z$.

$Fe_3Al_2Si_4$

Crystal data

$Fe_3Al_2Si_4$
$M_r = 333.85$
Orthorhombic
Cmcm
$a = 3.6687$ (15) Å
$b = 12.385$ (7) Å
$c = 10.147$ (5) Å
$V = 461.1$ (4) Å^3
$Z = 4$
$D_x = 4.809$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 19 reflections
$\theta = 6.14$–$23.96°$
$\mu = 10.557$ mm^{-1}
$T = 293$ K
Plate
$0.096 \times 0.048 \times 0.004$ mm
Grey

Data collection

Philips PW1100 four-circle diffractometer
ω–2θ scans
Absorption correction: by integration from crystal shape (*LSABS*; Blanc, Schwarzenbach & Flack, 1991)
$T_{min} = 0.6445$, $T_{max} = 0.9573$
1668 measured reflections
402 independent reflections
378 observed reflections $[F > 1\sigma(F)]$
$R_{int} = 0.087$
$\theta_{max} = 29.98°$
$h = -5 \rightarrow 5$
$k = -17 \rightarrow 17$
$l = -14 \rightarrow 14$
2 standard reflections frequency: 60 min intensity decay: 4.4–5.5%

Refinement

Refinement on F
$R = 0.061$
$wR = 0.039$
$S = 1.685$
378 reflections
31 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.00096$
$\Delta\rho_{max} = 2.00$ e Å^{-3}
$\Delta\rho_{min} = -2.03$ e Å^{-3}
Extinction correction: Becker & Coppens (1975)
Extinction coefficient: 500
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Fe_3Al_2Si_4$*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe1	0	0.14896 (9)	0.12537 (13)	0.0040 (3)
Fe2	0	0.35285 (15)	1/4	0.0052 (5)
Al1	0	0.05746 (18)	0.6086 (3)	0.0053 (7)
Si1	0	0.31907 (16)	0.0150 (3)	0.0050 (6)
Si2	0	0.5448 (2)	1/4	0.0074 (9)
Si3	0	0.7396 (3)	1/4	0.0073 (9)

Table 4. *Selected geometric parameters (Å) for $Fe_3Al_2Si_4$*

$Fe1^{i}$—$Fe1^{ii}$	2.529 (3)	$Al1^{vi}$—$Si1^{vii}$	2.570 (3)
$Fe1^{i}$—$Al1^{iii}$	2.562 (3)	$Al1^{vi}$—$Si1^{i}$	2.570 (3)
$Fe2^{i}$—$Si3^{iv}$	2.309 (3)	$Al1^{vi}$—$Al1^{viii}$	2.624 (4)
$Fe2^{i}$—$Si3^{v}$	2.309 (3)	$Si2^{v}$—$Si3^{v}$	2.413 (5)

Symmetry codes: (i) $-x, 1-y, \frac{1}{2}+z$; (ii) $x, 1-y, 1-z$; (iii) $x, 1+y, z$; (iv) $\frac{1}{2}-x, \frac{3}{2}-y, \frac{1}{2}+z$; (v) $-\frac{1}{2}-x, \frac{3}{2}-y, \frac{1}{2}+z$; (vi) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (vii) $1-x, 1-y, \frac{1}{2}+z$; (viii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

The atomic coordinates were standardized using *STRUCTURE TIDY* (Gelato & Parthé, 1987).

Data collection: Stoe Stadi-4 software for $Fe_3Al_2Si_3$; Philips PW1100 software for $Fe_3Al_2Si_4$. Cell refinement: *DIF*4 (Stoe & Cie, 1991) for $Fe_3Al_2Si_3$; *Xtal*3.2 *LATCON* (Hall, Flack & Stewart, 1992) for $Fe_3Al_2Si_4$. For both compounds, data reduction: *Xtal*3.2 *REFCAL LSABS* and *SORTRF*; program(s) used to solve structures: *Xtal*3.2 *GENTAN*; program(s) used to refine structures: *Xtal*3.2 *CRYLSQ*; software used to prepare material for publication: *Xtal*3.2 *BONDLA* and *CIFIO*, *STRUCTURE TIDY* (Gelato & Parthé, 1987).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1157). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Becker, P. J. & Coppens, P. (1975). *Acta Cryst.* A**31**, 417–425.
Bhargava, M. K. & Schubert, K. (1974). *J. Less Common Met.* **38**, 177–185.
Blanc, E., Schwarzenbach, D. & Flack, H. D. (1991). *J. Appl. Cryst.* **24**, 1035–1041.
Corby, R. N. & Black, P. J. (1977). *Acta Cryst.* B**33**, 3468–3475.
Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.
German, N. V., Belskii, V. K., Yanson, T. I. & Zarechnyuk, O. S. (1989). *Kristallografiya*, **34**, 735–737.
German, N. V., Zarechnyuk, O. S., Ventskovskii, A. V., Yanson, T. I., Lizogub, V. A. & Manyako, M. B. (1991). *Visn. L'viv. Derzh. Univ. Ser. Khim.* **31**, 8–10.
German, N. V., Zavodnik, V. E., Yanson, T. I. & Zarechnyuk, O. S. (1989). *Kristallografiya*, **34**, 738–739.
Gueneau, C., Servant, C., d'Yvoire, F. & Rodier, N. (1995*a*). *Acta Cryst.* C**51**, 177–179.
Gueneau, C., Servant, C., d'Yvoire, F. & Rodier, N. (1995*b*). *Acta Cryst.* C**51**, 2461–2464.
Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
Jaeniche, W. (1936). *Alum. Arch.* pp. 1–21.
Stoe & Cie (1991). *DIF*4. *Diffractometer Control Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
Takeda, H. P. & Mutuzaki, K. (1940). *Tetsu To Hagane*, **26**, 335–361.

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La Phase Monoclinique $Li_2Nb_{0,5}In_{1,5}(PO_4)_3$

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Abstract

The crystallographic characterization of dilithium niobium–indium triphosphate reveals independent PO_4 tetrahedra and distorted MO_6 octahedra with a statistical distribution of Nb and In atoms of M = (Nb + 3In)/4. The framework, built up from $M_2(PO_4)_3$ structural units, is isotypic with that of the monoclinic phases $Li_3M_2(PO_4)_3$ where M = In, Fe, Sc. The present structure differs from the $Li_3M_2(PO_4)_3$ structure in the distribution of the Li^+ cations; in particular, the partial occupation of a lithium site has not been encountered before.

Commentaire

Les conducteurs ioniques $A_xM_2(PO_4)_3$ ont un squelette structural tridimensionnel ménageant des tunnels interconnectés. Parmi eux les composés $Li_3M_2(PO_4)_3$ avec M^{III} = In, Fe, Sc (Tran Qui & Hamdoune, 1987; Bykov *et al.*, 1990) présentent au moins deux variétés polymorphiques: monoclinique $P2_1/n$ à la température ambiante, type β-$Fe_2(SO_4)_3$ (Christidis, Rentzeperis, Kirfel & Will, 1983) et orthorhombique *Pbna* à haute température, type $Sc_2(WO_4)_3$ (Abrahams & Bernstein, 1966). Dans la phase monoclinique basse température, les 12 ions lithium par maille occupent totalement trois sites de multiplicité 4; il en résulte une faible conductivité ionique ($\sigma_{293K} \sim 10^{-8}\,S\,cm^{-1}$) (Bykov *et al.*, 1990). Dans la phase orthorhombique haute température, la répartition des 12 ions lithium sur trois sites de multiplicité 8 entraîne une conductivité élevée ($\sigma_{573K} \sim 10^{-1}\,S\,cm^{-1}$) (Bykov *et al.*, 1990).

Afin d'accroître la mobilité des ions Li^+ à la température ambiante dans la phase monoclinique $Li_3In_2(PO_4)_3$, nous avons diminué leur concentration en réalisant la substitution $Li^I + 0{,}5In^{III} = \square + 0{,}5Nb^V$. L'obtention de monocristaux du composé $Li_2Nb_{0,5}In_{1,5}(PO_4)_3$ nous a permis d'en déterminer sa structure cristalline pour une meilleure connaissance des facteurs influant sur la conductivité ionique des monophosphates à charpente tridimensionnelle.

La charpente structurale, isotype de celle des phases monocliniques $Li_3M_2(PO_4)_3$ avec M = In, Fe, Sc, est composée de tétraèdres PO_4 indépendants et d'octaèdres déformés indépendants MO_6 où M est un atome moyen (Nb + 3In)/4. Trois tétraèdres PO_4 relient deux octaèdres MO_6 pour former un motif $M_2(PO_4)_3$. Ces motifs, orientés alternativement selon [021] et $[02\bar{1}]$ au sein de feuillets parallèles à (001), génèrent deux types de tunnels selon [010], l'un à section pentagonale et l'autre hexagonale (Fig. 1). Tous les atomes du squelette structural $M_2(PO_4)_3$ admettent comme pseudo-symétries les opérations du groupe d'espace orthorhombique *Pbna*, en accord avec l'existence d'une transformation displacive $P2_1/n \rightarrow Pbna$ à l'échauffement, $P2_1/n$ étant sous-groupe de *Pbna*.

Chaque atome de lithium est situé dans un environnement oxygéné sensiblement tétraédrique (Tableau 2). Les huit atomes de lithium dans la maille sont distribués sur trois sites de multiplicité 4 qui constituent des groupements indépendants (Fig. 2). Contrairement au site Li(3), les sites Li(1) et Li(2) sont partiellement occupés; les valeurs des taux d'occupation (respectivement 0,33 et 0,67) et de la courte distance Li(1)···Li(2) = 1,91 Å semblent interdire l'occupation simultanée de ces deux sites. Il doit donc en résulter, localement, soit l'existence de deux tétraèdres indépendants LiO_4, soit la présence d'un groupement Li_2O_7. On observe logiquement que les valeurs moyennes des distances Li—O dans les tétraèdres LiO_4 se classent dans l'ordre inverse des taux d'occupation: Li(1)—O = 2,09 > Li(2)—O = 2,08 > Li(3)—O = 2,05 Å. De même les atomes d'oxygène O(14), O(24) et O(34), constitutifs du tétraèdre plein $Li(3)O_4$, correspondent aux plus longues