

Crystallization from $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{M}^{\text{II}}\text{O}$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$) Melts and the Structure of $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$

N. Yu. Strutynska, I. V. Zatovsky, M. M. Yatskin, N. S. Slobodyanik, and I. V. Ogorodnyk

Shevchenko National University, Volodymyrs'ka ul. 64, Kyiv, 01033 Ukraine

e-mail: Strutynska_N@bigmir.net

Received September 29, 2011

Abstract—We have studied general trends of phosphate crystallization from $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{M}^{\text{II}}\text{O}$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$) high-temperature solutions at $\text{Na}/\text{P} = 1.0-1.4$, $\text{M}^{\text{II}}/\text{Fe} = 1.0$, and $\text{Fe}/\text{P} = 0.15$ or 0.3 , and identified the stability regions of the phosphates $\text{Na}_4\text{M}^{\text{II}}\text{Fe}(\text{PO}_4)_3$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$), NaFeP_2O_7 , and $\text{Na}_2\text{NiP}_2\text{O}_7$. The synthesized compounds have been characterized by X-ray powder diffraction and infrared spectroscopy. The structure of $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ (sp. gr. $R\bar{3}c$, $a = 8.83954(13)$ Å, $c = 21.4683(4)$ Å) has been determined by Rietveld powder diffraction analysis.

DOI: 10.1134/S0020168512040176

INTRODUCTION

There is great interest in NASICON-type phosphates (NZP , $\text{NaZr}_2(\text{PO}_4)_3$), motivated by their attractive physicochemical properties, such as high ionic conductivity, small thermal expansion coefficients, good catalytic and luminescent properties, and chemical and thermal stability [1–5], which is essential for designing novel functional materials. NASICON-type compounds with the general formula

$\text{A}'_x\text{A}''_y\text{A}'''_z(\text{PO}_4)_3$, ($\text{A}' = \text{Na}^+, \text{Ag}^+, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$, A'' , $\text{A}''' = \text{tri-, tetra-, or pentavalent metals}$) have a considerable number of compositions and crystallize in a trigonal or monoclinic structure [6, 7].

In this paper, we report a study of chemical interactions of $\text{Fe}_2\text{O}_3 + \text{M}^{\text{II}}\text{O}$ ($\text{M}^{\text{II}} = \text{Ni}, \text{Mg}$) oxide mixtures with sodium phosphate melts and identify conditions for phosphate formation, including new NZP-type compounds. The synthesized phosphates were characterized by X-ray powder diffraction and infrared spectroscopy. The structure of the new phosphate $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ was determined by Rietveld powder diffraction analysis.

EXPERIMENTAL

Phosphate crystallization from $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{M}^{\text{II}}\text{O}$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$) melts was studied at Na/P atomic ratios from 1.0 to 1.4 and fixed $\text{M}^{\text{II}}/\text{Fe}$ (1.0) and Fe/P (0.15 and 0.3) ratios. The starting chemicals used were analytical-grade NaPO_3 , Na_2CO_3 , Fe_2O_3 , MgO , and NiO .

Appropriate ratios of the starting reagents were ground in an agate mortar, placed in a platinum crucible, heated to 1000°C , and homogenized at this tem-

perature for 2 h. Crystallization was initiated by cooling the homogenized melt to $870-650^\circ\text{C}$ (depending on melt composition) at a rate of $25-50^\circ\text{C}/\text{h}$. To check the completion of oxide dissolution and determine the crystallization onset temperature, melt samples were taken at intervals and examined by optical microscopy. The reaction products were boiled in distilled water in order to remove the residual flux.

The synthesized compounds were identified by chemical analysis, X-ray fluorescence analysis, and X-ray diffraction (XRD). XRD patterns were collected on a Shimadzu XRD-6000 powder diffractometer in reflection geometry (CuK_α radiation, $\lambda = 1.54178$ Å, bent graphite monochromator) in a continuous $\theta-2\theta$ scan mode at a rate of $1.0^\circ/\text{min}$ in the range 2θ $5.0^\circ-110.0^\circ$. Intensity data for structure analysis were also collected on the XRD-6000: step-scan mode with a step of 0.02° and a counting time per data point of 8 s. The crystal structure of $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ was refined by the Rietveld method with FullProf 2011 [8]. The peak profile function was modeled using the pseudo-Voigt function with an anisotropic Thompson–Cox–Hastings divergence [9]. As the input model, we used the atomic position coordinates in the structure of $\text{Na}_4\text{NiFe}(\text{PO}_4)_3$. The raw powder XRD data, calculated profile, and difference plot are presented in Fig. 1. The intensity data collection conditions are summarized in Table 1. Table 2 lists the atomic positional parameters, and the main bond distances in oxygen coordination polyhedra are presented in Table 3. More detailed structural data can be obtained from the ICSD database: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany; depository number CSD-423 538.

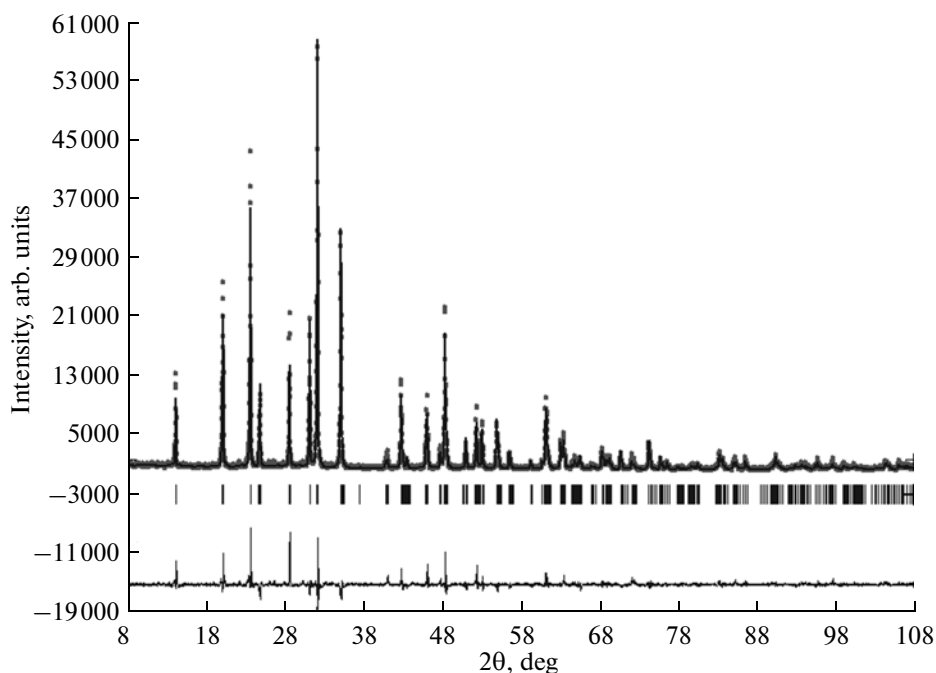


Fig. 1. Raw powder XRD data, calculated profile, and difference plot for $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$.

Infrared spectra were measured on a Nicolet Nexus 470 FTIR spectrophotometer in the frequency range $400\text{--}4000\text{ cm}^{-1}$ using KBr pellets.

RESULTS AND DISCUSSION

Phase relations. Our results for the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{M}^{\text{II}}\text{O}$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$) systems demonstrate that, under isothermal conditions (1000°C), a mixture of polyvalent metal oxides dissolves in sodium phosphate melts in 1–2 h at $\text{Fe}/\text{P} = 0.15$ and in 2–4 h at $\text{Fe}/\text{P} = 0.3$. During subsequent cooling of homogeneous high-temperature solutions, we identified the crystallization regions of compounds and mixtures of crystalline phases, whose composition depended on the initial Na/P and Fe/P ratios (Table 4).

System $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{MgO}$. When a $\text{Fe}_2\text{O}_3 + \text{MgO}$ mixture is dissolved in a melt with $\text{Na}/\text{P} = 1.0$ ($\text{Fe}/\text{P} = 0.15$, $\text{Fe}/\text{Mg} = 1.0$), homogenization takes about 1 h. Subsequent cooling to 770°C at a rate of 25°C leads to melt vitrification, without formation of crystalline phases. From melts with $\text{Na}/\text{P} = 1.2\text{--}1.3$ below 800°C , we obtained two types of crystals. XRD examination showed that the mixture consisted of $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ and NaFeP_2O_7 (PDF2, no. 00-036-1454). At $\text{Na}/\text{P} = 1.4$, the high-temperature solution experienced vitrification at 700°C . Increasing the concentration of oxides ($\text{Fe}/\text{P} = 0.3$, $\text{Fe}/\text{Mg} = 1.0$) in the melt extends the phase field of $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$, which forms as phase-pure material in the range $\text{Na}/\text{P} = 1.2\text{--}1.4$. At the same time, we observe crystallization of two compounds in the metaphosphate sec-

tion: $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ and NaFeP_2O_7 . The composition of the synthesized ternary orthophosphate $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ was determined by elemental analysis (found: Na, 20.17 wt % (calculated, 20.12 wt %); Mg, 5.28 wt % (5.32 wt %); Fe, 12.28 wt % (12.22 wt %); P,

Table 1. Intensity data collection conditions and crystal data for $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$

Crystal system	Trigonal
Space group	$R\bar{3}c$
Unit-cell parameters	
a , Å	8.83954(13)
c , Å	21.4683(4)
V , Å ³	1452.74(4)
Z	6
Diffractometer	Shimadzu XRD-6000
Wavelength, Å	1.54187
Temperature, K	293
$2\theta_{\min}$; $2\theta_{\max}$, deg	8.0; 110.0
Measured reflections	414
R_p	10.667
R_B	2.700
R_I	7.768
wR	13.626
wR_{exp}	4.103

Table 2. Atomic position coordinates in the structures of $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>
Mg/Fe	12 <i>c</i>	0	0	0.14896(14)
Na1	6 <i>b</i>	0	0	0
Na2	18 <i>e</i>	−1/3	−0.0244(7)	0.08333
P1	18 <i>e</i>	−1/3	−0.3723(4)	0.08333
O1	36 <i>f</i>	0.1767(6)	0.2041(7)	0.1915(2)
O2	36 <i>f</i>	0.1917(6)	0.0275(7)	0.0895(3)

20.41 wt % (20.33 wt %). The XRD pattern of the mixed orthophosphate could be indexed in trigonal symmetry, sp. gr. $R\bar{3}c$. This compound has the NASICON structure, which was refined by powder XRD.

System $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{NiO}$. Crystallization from high-temperature solutions in this system yields

mixed ortho- and diphosphates. At $\text{Na}/\text{P} = 1.0$ and 1.4 ($\text{Fe}/\text{P} = 0.15$, $\text{Fe}/\text{Ni} = 1.0$) and temperatures from 1000 to 700°C, we observed glass formation, without crystallization. At Na/P from 1.2 to 1.3, cooling to 780°C led to crystallization of a phase mixture. In contrast to the above system, three phases were concurrently formed: the ternary orthophosphate $\text{Na}_4\text{NiFe}(\text{PO}_4)_3$ and binary diphosphates NaFeP_2O_7 (PDF2, no. 00-036-1454) and $\text{Na}_2\text{NiP}_2\text{O}_7$ (PDF2, no. 00-052-1256) [10]. Increasing the concentration of oxides ($\text{Fe}/\text{P} = 0.3$, $\text{Fe}/\text{Ni} = 1.0$), we obtained phase-pure $\text{Na}_4\text{NiFe}(\text{PO}_4)_3$ in the range $\text{Na}/\text{P} = 1.2-1.4$. This compound precipitates below 950°C, and the melt solidifies even at 900°C. According to powder XRD data, $\text{Na}_4\text{NiFe}(\text{PO}_4)_3$ also has a trigonal structure (sp. gr. $R\bar{3}c$, $a = 8.801(1)$ Å, $c = 21.623(5)$ Å), in agreement with previous data [11]. At $\text{Na}/\text{P} = 1.0$ and temperatures from 1000 and 880°C, we observed the formation of $\text{Na}_4\text{NiFe}(\text{PO}_4)_3$ and NaFeP_2O_7 .

Table 3. Bond distances (Å) and angles (deg) in the oxygen coordination polyhedra in the structure of $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$

(Mg/Fe) O_6 polyhedra					
Mg/Fe–O1	$1.926(5) \times 3$	Mg/Fe–O2	$2.037(6) \times 3$	O1–Mg/Fe–O1 ⁱ	99.4(2)
O1–Mg/Fe–O2 ⁱ	169.5(2)	O2–Mg/Fe–O1 ⁱ	87.7(1)	O2–Mg/Fe–O2 ⁱ	84.9(1)
PO_4 tetrahedra					
P1–O2 ⁱ	$1.554(4) \times 2$	P1–O2 ⁱⁱ	$1.570(5) \times 2$	O1 ⁱⁱⁱ –P1–O2 ⁱ	106.1(2)
O1 ⁱⁱⁱ –P1–O2 ^{iv}	111.3(2)	O1 ⁱⁱⁱ –P1–O1 ⁱⁱ	108.4(2)	O2 ⁱ –P1–O2 ^{iv}	113.8(1)
NaO_x polyhedra					
Na1–O2	$2.492(5) \times 6$	O2–Na1–O2 ^v	180.0(1)	O2–Na1–O2 ⁱ	66.9(1)
		O2–Na1–O2 ^{vi}	113.1(1)		
Na2–O2 ⁱ	$2.366(6) \times 2$	Na2–O2 ^{vii}	$2.579(8) \times 2$	Na2–O1 ⁱ	$2.594(4) \times 2$
Na2–O1 ^{viii}	$2.825(8) \times 2$				

Note: Coordinates of equivalent positions (i) $-x + y, -x, z$; (ii) $-1/3 + x - y, -2/3 + x, 1/3 - z$; (iii) $-1/3 - x + y, -2/3 + y, -1/6 + z$; (iv) $-2/3 + x - y, -1/3 - y, 1/6 - z$; (v) $-x, -y, -z, 1/3 - z$; (vi) $x - y, x, -z$; (vii) $-y, x - y, z$; (viii) $-1/3 + x, 2/3 + x - y, 1/6 + z$.

Table 4. Crystallization of mixed phosphates from $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{M}^{\text{II}}\text{O}$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$) high-temperature solutions in the temperature range 1000–670°C

Na/P	$\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{MgO}$		$\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{NiO}$	
	0.15*	0.3*	0.15*	0.3*
1.0	Glass formation	$\text{Na}_4\text{MgFe}(\text{PO}_4)_3 + \text{NaFeP}_2\text{O}_7$	Glass formation	$\text{Na}_4\text{NiFe}(\text{PO}_4)_3 + \text{NaFeP}_2\text{O}_7$
1.2	$\text{Na}_4\text{MgFe}(\text{PO}_4)_3 + \text{NaFeP}_2\text{O}_7$	$\text{Na}_4\text{MgFe}(\text{PO}_4)_3$	$\text{Na}_4\text{NiFe}(\text{PO}_4)_3 + \text{NaFeP}_2\text{O}_7 + \text{Na}_2\text{NiP}_2\text{O}_7$	$\text{Na}_4\text{NiFe}(\text{PO}_4)_3$
1.3				
1.4	Glass formation		Glass formation	

* Fe/P.

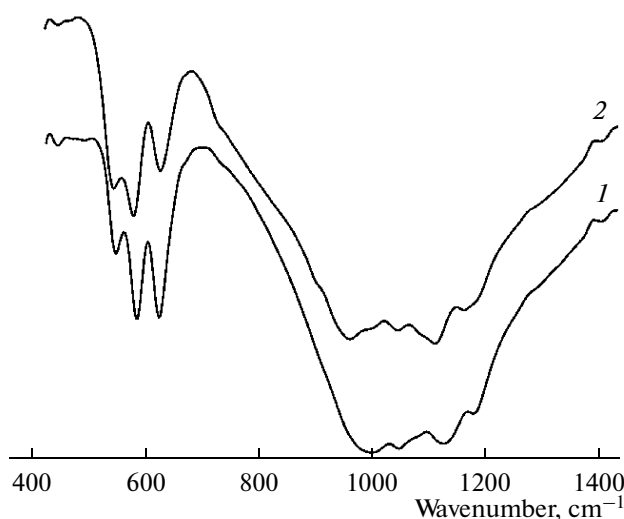


Fig. 2. Infrared spectra of the ternary orthophosphates (1) $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ and (2) $\text{Na}_4\text{NiFe}(\text{PO}_4)_3$.

Infrared spectra of the synthesized compounds. The spectra of the ternary orthophosphates $\text{Na}_4\text{M}^{\text{II}}\text{Fe}(\text{PO}_4)_3$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$) contain absorption bands that confirm the presence of the orthophosphate anion (Fig. 2): asymmetric and symmetric bending modes of the phosphate tetrahedra (δ_{as} and $\delta_{\text{s}}(\text{PO}_4)$) in the range $500\text{--}640\text{ cm}^{-1}$ and the corresponding stretching modes (ν_{s} and $\nu_{\text{as}}(\text{PO}_4)$) in the range $950\text{--}1200\text{ cm}^{-1}$. Such spectra are typical of framework phosphates with an $[\text{M}_2(\text{PO}_4)_3]_{\infty}$ anion sublattice.

Structure of the mixed orthophosphate $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$. Analysis of the structure of the synthesized ternary phosphate shows that this compound is isostructural with the $\text{Na}_4\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{PO}_4)_3$ ($\text{M}^{\text{II}} = \text{Ni}, \text{Fe}, \text{Mg}$, $\text{M}^{\text{III}} = \text{Fe}, \text{Cr}$) phosphates [11–14], which have the NASICON structure. These compounds have a three-dimensional framework made up of corner-sharing AO_6 polyhedra and PO_4 tetrahedra and con-

tain two crystallographic sites, M1 and M2, for cations that compensate for the charge of the anion sublattice, which suggests the crystallographic formula $\text{M}(1)_x\text{M}(2)_y\text{A}_n(\text{PO}_4)_3$.

The anion sublattice $[\text{MgFe}(\text{PO}_4)_3]^{4-}$ of the $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ orthophosphate is made up of isolated $(\text{Mg}/\text{Fe})\text{O}_6$ polyhedra and PO_4 tetrahedra, and its charge is neutralized by two types of sodium cations (Fig. 3).

The magnesium and iron atoms reside in the same crystallographic position (12c) and are surrounded each by six oxygens, with bond distances $d((\text{Mg}/\text{Fe})-\text{O}) = 1.926$ and 2.037 \AA (Table 3). Three O2 oxygens, 2.037 \AA from the Mg/Fe atoms, also form the coordination of Na1 (Fig. 4). The O1 oxygens, with $d((\text{Mg}/\text{Fe})-\text{O}) = 1.926\text{ \AA}$, belong to “bridging” PO_4 tetrahedra, which reside between neighboring $(\text{Mg}/\text{Fe})\text{O}_6$ polyhedra (Fig. 4). This seems to be evidence that the Na1 atoms have a significant effect on the coordination of the Mg/Fe atoms.

The P–O bond lengths in the PO_4 tetrahedra lie in the range $1.554\text{--}1.570\text{ \AA}$ and slightly exceed those in the analogous phosphates $\text{Na}_4\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ ($d = 1.533(6)\text{--}1.538(6)\text{ \AA}$ [12]) and $\text{Na}_4\text{NiFe}(\text{PO}_4)_3$ ($d = 1.533(6)\text{--}1.538(6)\text{ \AA}$ [11]). The O–P–O bond angles lie in the range 106.051° to 113.772° , typical of NASICON-type phosphates ($106.9(3)^\circ\text{--}112.1(3)^\circ$ in $\text{Na}_4\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ and $106.11(8)^\circ\text{--}112.11(8)^\circ$ in $\text{Na}_4\text{NiFe}(\text{PO}_4)_3$).

The sodium atoms reside in two independent crystallographic sites: Na1 and Na2 (Fig. 3). In the former site, Na is in a regular octahedral oxygen coordination, with $d(\text{Na1}-\text{O}) = 2.492(5)\text{ \AA}$. The $\text{Na}(1)\text{O}_6$ octahedron shares faces with two neighboring $(\text{Mg}/\text{Fe})\text{O}_6$ polyhedra (Fig. 4). The other type of sodium atom resides in voids of the three-dimensional anion framework and is coordinated by eight oxygens, with $d(\text{Na2}-\text{O}) = 2.366(6)\text{--}2.825(8)\text{ \AA}$ (Table 3).

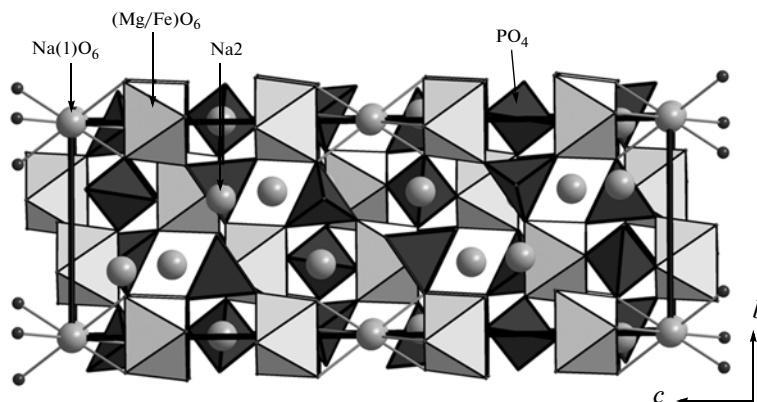


Fig. 3. Structure of $\text{Na}_4\text{MgFe}(\text{PO}_4)_3$ projected onto the bc plane.

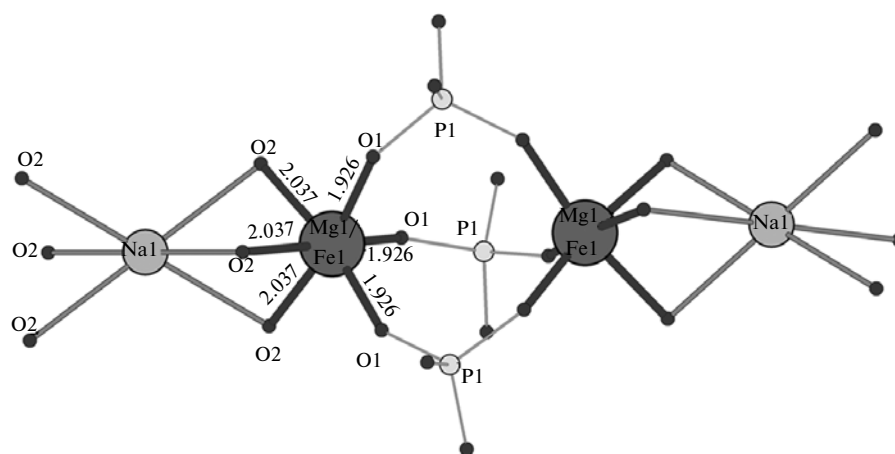


Fig. 4. Coordination of the Mg/Fe atoms and linkage between the (Mg/Fe) O_6 polyhedron and Na(1) O_6 octahedron.

CONCLUSIONS

We have studied crystallization of phosphates from $Na_2O-P_2O_5-Fe_2O_3-M^{II}O$ ($M^{II} = Mg, Ni$) high-temperature solutions at $Na/P = 1.0-1.4$, $Fe/P = 0.15$ or 0.3 , and $Fe/M^{II} = 1.0$, and established conditions for the formation of the mixed phosphates $Na_4M^{II}Fe(PO_4)_3$ ($M^{II} = Mg, Ni$), $NaFeP_2O_7$, and $Na_2NiP_2O_7$. The structure of the new ternary orthophosphate $Na_4MgFe(PO_4)_3$ has been determined by X-ray powder diffraction.

REFERENCES

1. Anantharamulu, N., Rao, K.K., Vithal, M., and Prasad, G., Preparation, Characterization, Impedance and Thermal Expansion Studies of $Mn_{0.5}MSb(PO_4)_3$ ($M = Al, Fe$ and Cr), *J. Alloys Compd.*, 2009, vol. 479, nos. 1–2, pp. 684–691.
2. Feng, J.K., Lu, L., and Lai, M.O., Lithium Storage Capability of Lithium Ion Conductor $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, *J. Alloys Compd.*, 2010, vol. 501, no. 2, pp. 255–258.
3. Cushing, B.L. and Goodenough, J.B., $Li_2NaV_2(PO_4)_3$: A 3.7V Lithium-Insertion Cathode with the Rhombohedral NASICON Structure, *J. Solid State Chem.*, 2001, vol. 162, pp. 176–181.
4. Sun, J.-K., Huang, F.-Q., Wang, Y.-M., et al., Characterization of Nasicon-Type $Li_3Fe_{2-2x}Ti_xMn_x(PO_4)_3/C$ Cathode Materials, *J. Alloys Compd.*, 2009, vol. 469, pp. 327–331.
5. El Bouari, A., El Jazouli, A., Benmokhtar, S., Gravereau, P., and Wattiaux, A., Synthesis, Structure, Magnetic, Optical and Moessbauer Properties of $Na_2FeSn(PO_4)_3$, *J. Alloys Compd.*, 2010, vol. 503, pp. 480–484.
6. Boilot, J.P., Salanié, J.P., Desplanches, G., and Le Potier, D., Phase Transformation in $Na_{1+x}Si_xZr_2P_{3-x}O_{12}$ Compounds, *Mater. Res. Bull.*, 1979, vol. 14, no. 111, pp. 1469–1477.
7. Alpen, U., Bell, M.F., and Wichelhaus, W., Phase Transition in Nasicon ($Na_3Zr_2Si_2PO_{12}$), *Mater. Res. Bull.*, 1979, vol. 14, no. 10, pp. 1317–1322.
8. Rodriguez-Carvajal, J., *FullProf*, Saclay: Laboratoire Léon Brillouin (CEA-CNRS), 2006.
9. Thompson, P., Cox, D.E., and Hastings, J.B., Rietveld Refinement of Debye–Scherrer Synchrotron X-Ray Data from Al_2O_3 , *J. Appl. Crystallogr.*, 1987, vol. 20, pp. 79–83.
10. Nagorny, P.G., Slobodanik, N.S., and Petrenko, O.V., Phase Relations in the $Na_2O-P_2O_5-NiO$ System, *Zh. Neorg. Khim.*, 1998, vol. 43, no. 4, pp. 599–603.
11. Essehli, R., Bali, B.E., Benmokhtar, S., et al., Crystal Structure and Magnetic Properties of Iron(III)-Based Phosphates: $Na_4NiFe(PO_4)_3$ and $Na_2Ni_2Fe(PO_4)_3$, *J. Alloys Compd.*, 2011, vol. 509, pp. 1163–1171.
12. Hatert, F., $Na_4Fe^{2+}Fe^{3+}(PO_4)_3$, a New Synthetic NASICON-Type Phosphate, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2009, vol. 65, p. i30.
13. Manoun, B., Jazouli, A.El., Krimi, S., and Lacgar, A., Synthesis and Crystallochemistry of $Na_4CrNi(PO_4)_3$, *Powder Diffr.*, 2004, vol. 19, no. 2, pp. 162–164.
14. Delmas, C., Cherkaoui, F., and Hagenmuller, P., Ionic Conductivity in a New NASICON Related Solid Solution: $Na_{3+y}Cr_{2-y}Mg_y(PO_4)_3$. An Optical Characterization of the Skeleton Covalency, *Mater. Res. Bull.*, 1986, vol. 21, no. 4, pp. 469–477.