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Strontium phosphates with β-$Ca_3(PO_4)_2$-type structures: $Sr_9NiLi(PO_4)_7$, $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$, and $Sr_{9.08}Ni_{1.04}K_{0.76}(PO_4)_7$†

Alexei A. Belik,[a]‡ **Fujio Izumi,***[a] **Takuji Ikeda,**[a] **Artem P. Malakho**[b] **and Bogdan I. Lazoryak**[c]

[a]*Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. E-mail: IZUMI.Fujio@nims.go.jp*
[b]*Department of Materials Science, Moscow State University, Leninsky Gory, Moscow 119899, Russia*
[c]*Department of Chemistry, Moscow State University, Leninsky Gory, Moscow 119899, Russia*

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Strontium phosphates, $Sr_9NiLi(PO_4)_7$ (Li-SNP), $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$ (Na-SNP), and $Sr_{9.08}Ni_{1.04}K_{0.76}(PO_4)_7$ (K-SNP), lying near boundary compositions $Sr_{9+2x}Ni_{1+x}A_{1-6x}(PO_4)_7$ (A = Li, Na, and K) were synthesized by the solid state method at 1000 °C. Second-harmonic generation showed that Li-SNP is centrosymmetric whereas Na- and K-SNP are non-centrosymmetric. Li-SNP crystallized in space group $I2/m$, and Na- and K-SNP are isotypic with β-$Ca_3(PO_4)_2$ (space group: $R3c$) in contrast to A-free $Sr_{9.333}Ni_{1.167}(PO_4)_7$ ($x = 1/6$) belonging to space group $R\bar{3}m$. Structure and lattice parameters of Na- and K-SNP were refined by the Rietveld method from X-ray powder diffraction data. Na- and K-SNP have six metal sites: M1–M6. The M1–M3 sites are fully occupied by Sr, and the M5 site by Ni. Occupancies, g, of the M4 site are g(Sr) = 0.04, g(Ni) = 0.02, and g(Na) = 0.88 in Na-SNP, and g(Sr) = 0.08, g(Ni) = 0.04, and g(K) = 0.76 in K-SNP. The M6 site is vacant in the same manner as with β-$Ca_3(PO_4)_2$.

Introduction

$Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$, and solid solutions including them as end members, have been extensively studied as (a) luminescence materials,[1–4] *e.g.*, $Ca_3(PO_4)_2:Sn^{2+}$, $Ca_3(PO_4)_2:Mn^{2+}$, and $(Sr,Zn)_3(PO_4)_2:Sn^{2+}$, and (b) catalysts,[5,6] *e.g.*, $Ca_{3-x}M_x(PO_4)_2$ (M = Co, Ni, and Cu). Solid solutions $Ca_{10.5-z}Ni_z(PO_4)_7$ and $Sr_{9+y}Ni_{1.5-y}(PO_4)_7$ are formed in compositional ranges of $0 \leqslant z \leqslant 1.167$[7] and $0.14 \leqslant y \leqslant 0.39$,[8] respectively. Phosphates with nominal compositions of $A'_{9.333}Ni_{1.167}(PO_4)_7$ (A′ = Ca and Sr) are commercial catalysts for dehydrogenation, *e.g.*, for converting 1- and 2-butenes to butadienes, and for oxydehydrogenating lower aliphatic alkanes and alkenes to dienes.[6]

$Ca_3(PO_4)_2$ occurs as four modifications above room temperature (RT): α, α′, β, and β′.[9,10] A variety of Ca-containing solid solutions with β-$Ca_3(PO_4)_2$-type structures have been prepared, *e.g.*, $Ca_9M'(PO_4)_7$ (M′ = Al, Sc, Cr, Fe, Ga, In, and rare-earth metals)[11] and $Ca_9MA(PO_4)_7$ (M = Mg, Ca, Mn, and Co; A = Li, Na, and K).[12] Chemical reactivities and physical properties, such as catalysis, luminescence, and nonlinear optical behavior,[13] of β-$Ca_3(PO_4)_2$-related compounds strongly depend on cationic distribution among six metal sites, M1–M6. For example, Cu^{2+} ions at the M4 site play an important role in the catalysis of solid solutions $Ca_{10.5-z}Cu_z(PO_4)_7$ ($0 \leqslant z \leqslant 1$).[5] Catalytic activity is considerably reduced by substituting Na^+ ions for Cu^{2+} ions at the M4 site in solid solutions $Ca_{10-z/2}Na_zCu_{0.5}(PO_4)_7$ ($0 \leqslant z \leqslant 1$).[5]

$Sr_3(PO_4)_2$ has three polymorphs above RT: α, β, and γ.[1,2] The β- and γ-forms are thermodynamically stable in temperature ranges of (1305–1410) °C and (1410–1620) °C, respectively, but not quenchable to RT. β-$Sr_3(PO_4)_2$ was regarded as isotypic with β-$Ca_3(PO_4)_2$.[1] Solid solutions $Sr_{3-x}M_x(PO_4)_2$ with the β-$Sr_3(PO_4)_2$-type structure were prepared for M = Mg ($0.27 \leqslant x \leqslant 1.08$),[1] M = Zn ($0.27 \leqslant x \leqslant 0.81$),[1] and M = Cd ($0.36 \leqslant x \leqslant 0.63$).[2] β-$Sr_3(PO_4)_2$-type structures were also stabilized at RT by substituting tervalent cations such as Al^{3+} for Sr^{2+} ions.[14] Some Sr-containing phosphates that presumably have the β-$Ca_3(PO_4)_2$-type structure were reported in the literature, *e.g.*, $(Sr_{8.45}Ce_{0.55})MnLi_{0.45}(PO_4)_7$.[3]

Strontium phosphates including bivalent cations, $Sr_{9+y}M_{1.5-y}(PO_4)_7$ (M = Mn, Fe, Co, Ni, Cu, and Cd),[8,15] and tervalent cations, $Sr_9M'(PO_4)_7$ (M′ = Sc, Cr, Fe, Ga, and In),[16] are structurally related to β-$Ca_3(PO_4)_2$. $Sr_{9+y}M_{1.5-y}(PO_4)_7$ crystallizes in space group $R\bar{3}m$ with lattice parameters of $a \approx 10.6$ Å and $c \approx 19.7$ Å. On the other hand, $Sr_9M'(PO_4)_7$ is monoclinic, possessing space group $I2/a$ and lattice parameters of $a \approx 18.0$ Å, $b \approx 10.7$ Å, $c \approx 18.4$ Å, and $\beta \approx 133°$. $Sr_{9+y}M_{1.5-y}(PO_4)_7$ and $Sr_9M'(PO_4)_7$ are of structural interest because these two contain some atoms with highly disordered arrangements.[8,16]

During the course of an investigation on solid solutions with general formulae of $Sr_{9+2x}M_{1+x}A_{1-6x}(PO_4)_7$ (A = Li, Na, and K), we have found that the introduction of A^+ ions into $Sr_{9+y}M_{1.5-y}(PO_4)_7$ (M = Mn, Ni, and Cd) causes changes in the crystallographic symmetry of the parent $R\bar{3}m$ structure. In this work, we have prepared $Sr_9NiLi(PO_4)_7$ (Li-SNP), $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$ (Na-SNP), and $Sr_{9.08}Ni_{1.04}K_{0.76}(PO_4)_7$ (K-SNP), measured their second-harmonic generation (SHG) responses and infrared (IR) spectra, determined the space group and lattice parameters of Li-SNP, and refined structure parameters of Na- and K-SNP from X-ray powder diffraction (XRD) data. Structural differences between A-SNP (A = Na and K) and

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† Electronic supplementary information (ESI) available: IR spectra of A-SNP (A = Li, Na and K) and $Sr_{9.333}Ni_{1.167}(PO_4)_7$ (Fig. S1). Main bond lengths and angles for Na- and K-SNP (Table S1). Conditions of XRD experiments and parts of refinement results for Na- and K-SNP (Table S2). See http://www.rsc.org/suppdata/jm/b2/b204808f/

‡ Postdoctoral fellow from Department of Chemistry, Moscow State University, Leninsky Gory, Moscow 119899, Russia.

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β-$Ca_3(PO_4)_2$-type compounds will be discussed on the basis of their crystal data.

Experimental

Synthesis

$Sr_{9+2x}Ni_{1+x}A_{1-6x}(PO_4)_7$ (A = Li, Na, and K) were synthesized from mixtures of $SrCO_3$ (99.999%), NiO (99.0%), A_2CO_3 (A = Li, Na, and K; 99.0%), and $NH_4H_2PO_4$ (99.999%) by the solid state method. The mixtures were contained in alumina crucibles, heated under air while raising the temperature very slowly from RT to 600 °C, and allowed to react at 1000 °C for 120 h with three intermediate grindings. The products were then quenched to RT.

At first, we tried to prepare stoichiometric compounds $Sr_9NiA(PO_4)_7$ (A = Li, Na, and K; $x = 0$) by analogy with $Ca_9MA(PO_4)_7$ (M = Mg, Ca, Mn, and Co; A = Li, Na, and K).[12] Li-SNP was monophasic whereas the products with A = Na and K consisted of two phases: a phase isotypic with β-$Ca_3(PO_4)_2$ and $ASrPO_4$, where A = Na (ICDD PDF #33-1282) and K (ICDD PDF #33-1045). This finding suggests that $Sr_9NiA(PO_4)_7$, if at all, decomposed to the two phases:

$$(1 + x)Sr_9NiA(PO_4)_7 \rightarrow Sr_{9+2x}Ni_{1+x}A_{1-6x}(PO_4)_7 + 7xASrPO_4 \qquad (1)$$

Mass fractions of $ASrPO_4$ in the samples with the nominal compositions $Sr_9NiA(PO_4)_7$ were calculated at 0.0171 (A = Na) and 0.0353 (A = K) from scale factors refined in their Rietveld analyses described later. Values of x calculated from the mass fractions on the basis of reaction (1) were $x \approx 0.0186$ for A = Na and $x \approx 0.0382$ for A = K.

Pure samples could be prepared for Na-SNP, K-SNP and $Sr_{9.333}Ni_{1.167}(PO_4)_7$ ($x = 1/6$) whereas samples with nominal compositions $Sr_{9.02}Ni_{1.01}Na_{0.94}(PO_4)_7$ ($x = 0.01$) and $Sr_{9.04}Ni_{1.02}K_{0.88}(PO_4)_7$ ($x = 0.02$) comprised the β-$Ca_3(PO_4)_2$-related phase and $ASrPO_4$. Reflections due to unknown impurities appeared in the XRD patterns of $Sr_{9+2x}Ni_{1+x}Li_{1-6x}(PO_4)_7$ ($x < 0$). Thus, Li-, Na-, and K-SNP are situated near boundaries of the A-rich side in the solid solutions $Sr_{9+2x}Ni_{1+x}A_{1-6x}(PO_4)_7$. Li-, Na-, and K-SNP were light yellow while $Sr_{9.333}Ni_{1.167}(PO_4)_7$ was light pink.

XRD procedures

XRD data of the products were measured at RT on a Siemens D500 Bragg–Brentano-type powder diffractometer operated at 30 kV and 30 mA. The diffractometer was equipped with an incident-beam quartz monochromator to obtain Cu Kα_1 radiation (wavelength, $\lambda = 1.5406$ Å) and a Braun position-sensitive detector. Si (NIST Standard Reference Material 640b) was used as an external standard material for diffraction angles, 2θ. For phase identification, XRD data were collected in a 2θ range from 10° to 80° with a step interval of 0.02°. For Rietveld refinements of Na- and K-SNP, XRD data were collected in a 2θ range of 10° to 140° with a step width of 0.02°.

The XRD data were analyzed by the Rietveld method with RIETAN-2000.[17] Coefficients for analytical approximation to atomic scattering factors for Sr, Ni, P, A (A = Na and K), and O were taken from ref. 18. The split pseudo-Voigt function of Toraya[19] was fitted to each reflection profile, and an 11th-order Legendre polynomial to the background. Partial profile relaxation[17] was applied to 012, 104, 110, 122, 214, 300, $02\underline{10}$, and 220 reflections to improve fits in these reflections at the last stages of the structure refinements. Isotropic atomic displacement parameters, U, with the isotropic Debye–Waller factor represented as $\exp(-8\pi^2 U\sin^2\theta/\lambda^2)$ were assigned to all the sites.

Mass fractions of phases were calculated from scale factors refined by the Rietveld analyses of the XRD data. In two-phase refinements of the samples with the nominal compositions $Sr_9NiA(PO_4)_7$ (A = Na and K), only scale factors and lattice parameters were refined for $ASrPO_4$ with structure parameters fixed at those of $NaBaPO_4$[21] for A = Na and those of $KSrPO_4$[20] for A = K.

Synchrotron XRD data of Li-SNP were measured at RT on a powder diffractometer (BL15XU at SPring-8) with the Debye–Scherrer geometry using a Ge(111) analyzer. Incident beams from an undulator were monochromatized to $\lambda = 0.85001$ Å with rotated inclined Si(111) double crystal monochromators. The sample was contained in a quartz-glass capillary tube with an inner diameter of 0.3 mm and rotated at a speed of 6.3 rad s^{-1}. The synchrotron XRD data were collected in a 2θ range from 5.3° to 80.01° with a step interval of 0.003° and a counting time of 1.1 s per step. The resulting data were analyzed with RIETAN-2000 by the Le Bail method using initial integrated intensities estimated from a partial structure.

SHG measurements

SHG responses of the powder samples were measured in a reflection scheme. A Q-switch pulsed Nd : YAG laser operated at a wavelength of $\lambda_\omega = 1064$ nm was used as the radiation source with a repetition rate of 4 impulses per second and a duration of impulses of about 12 ns. The laser beam was split into two beams to excite the radiation at the halved wavelength, $\lambda_{2\omega} = 532$ nm, simultaneously in samples to be measured and a reference sample of polycrystalline α-SiO_2. The incident-beam peak power was about 0.1 MW on a spot 3 mm in diameter on the surface of the sample.

IR spectroscopy

IR spectra were recorded by the Nujol mull method on a Nicolet Magna-750 Fourier spectrometer in a wavenumber ($\tilde{\nu}$) range from 4000 cm^{-1} to 400 cm^{-1}.

Results

Characterization of the products

No SHG signals were observed in Li-SNP and $Sr_{9.333}Ni_{1.167}(PO_4)_7$, which shows them to be centrosymmetric. On the other hand, Na- and K-SNP gave small SHG responses of $I_{2\omega}/I_{2\omega}$ (SiO_2) ≈ 0.8 and $I_{2\omega}/I_{2\omega}$ (SiO_2) ≈ 0.7, respectively. These facts offer evidence that Na- and K-SNP are non-centrosymmetric.

Parts of reflections in the XRD pattern of Li-SNP were split in contrast with those of $Sr_{9.333}Ni_{1.167}(PO_4)_7$. We assumed that the splitting resulted from lowering of the crystallographic symmetry from the trigonal system in $Sr_{9.333}Ni_{1.167}(PO_4)_7$ to a monoclinic one in Li-SNP. The hexagonal (h) unit cell for $Sr_{9.333}Ni_{1.167}(PO_4)_7$ could be transformed into a monoclinic (m) one for Li-SNP in such a way that $\boldsymbol{a}_m = \boldsymbol{a}_h - \boldsymbol{b}_h$, $\boldsymbol{b}_m = \boldsymbol{a}_h + \boldsymbol{b}_h$, and $\boldsymbol{c}_m = (-\boldsymbol{a}_h + \boldsymbol{b}_h + \boldsymbol{c}_h)/3$. This transformation yielded a centrosymmetric space group $C2/m$ (No. 12, unique axis b, cell choice 1)[22] and lattice parameters of $a_m \approx 18.3$ Å, $b_m \approx 10.60$ Å, $c_m \approx 8.95$ Å, and $\beta_m \approx 133°$ ($Z = 2$). All the reflections with intensity ratios, I/I_1 (I: peak intensity, I_1: peak intensity of the strongest 222 reflection), greater than *ca.* 0.01 in the XRD pattern of Li-SNP could be indexed from this monoclinic unit cell. However, the XRD pattern of Li-SNP exhibited weak additional reflections, which indicates that Li-SNP has a superlattice and/or symmetry lower than $C2/m$.

To determine the space group and lattice parameters of Li-SNP, we analyzed its synchrotron XRD data (Figs. 1 (c) and 2 (c)). Li-SNP was found to be monoclinic with a c parameter twice as large as that in the $C2/m$ model described above. Superlattice reflections in Li-SNP were considerably broadened in comparison with main reflections (Fig. 2 (c)). Reflection conditions derived from indexed reflections were $h + k + l = 2n$

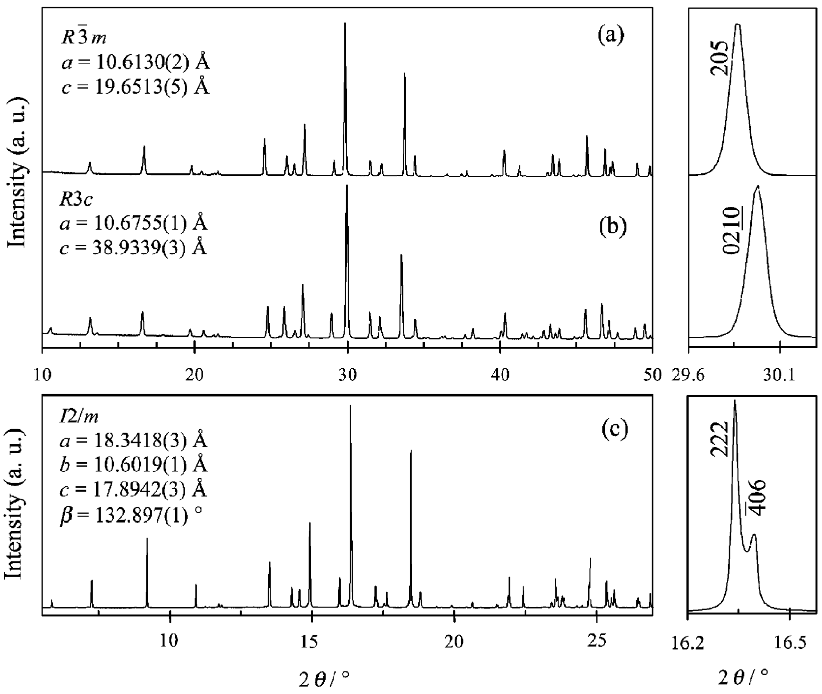

Fig. 1 Portions of XRD patterns for (a) $Sr_{9.333}Ni_{1.167}(PO_4)_7$, (b) $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$, and (c) $Sr_9NiLi(PO_4)_7$ in d ranges from 8.84 Å to 1.82 Å and from 3.02 Å to 2.95 Å.

for hkl, giving space group $I2/m$ (No. 12, unique axis b, cell choice 3).[22]

Because Li atoms are hardly visible by X-ray diffraction, the full structure of Li-SNP, particularly structure parameters of Li, needs to be determined by neutron powder diffraction. In this work, we refined only lattice parameters of Li-SNP from the synchrotron XRD data not by the Rietveld method, but by the Le Bail method. Final lattice parameters were a = 18.3418(3) Å, b = 10.6019(1) Å, c = 17.8942(3) Å, and β = 132.897(1)°. It is interesting to note that Li-SNP and $Sr_9M'(PO_4)_7$ (M′ = Sc, Cr, Fe, Ga, and In)[16] have the same sublattice structure of space group $C2/m$ whereas the space groups of their superlattices differ from each other.

XRD patterns of Na- and K-SNP were very similar to that of $Sr_{9.333}Ni_{1.167}(PO_4)_7$ (space group: $R\bar{3}m$; $a \approx 10.61$ Å and $c \approx 19.65$ Å) except for the appearance of weak additional reflections (Figs. 1 and 2). All the reflections in their XRD patterns could be indexed on the basis of a trigonal system and a superlattice with $a \approx 10.70$ Å and $c \approx 38.90$ Å (hexagonal axes). Reflection conditions in Na- and K-SNP were $-h + k + l = 3n$ for hkl and $h + l = 3n$, $l = 2n$ for $h\bar{h}l$ (hexagonal axes, obverse setting),[22] affording a possible non-centrosymmetric space group $R3c$ (No. 161). This finding supports the idea that Na- and K-SNP are structurally related to β-$Ca_3(PO_4)_2$, having space group $R3c$ and lattice parameters of a = 10.439 Å and c = 37.375 Å.[9]

IR spectra of A-SNP and $Sr_{9.333}Ni_{1.167}(PO_4)_7$ showed absorption bands assigned to P–O stretching and O–P–O bending vibrations at (1250–800) cm^{-1} and (650–500) cm^{-1}, respectively. The IR spectra of Na- and K-SNP were similar to each other but somewhat different from those of Li-SNP and $Sr_{9.333}Ni_{1.167}(PO_4)_7$. The IR spectra of Li-SNP and $Sr_{9.333}Ni_{1.167}(PO_4)_7$ were similar to each other despite the different crystallographic symmetry of these phosphates, which is ascribed to analogous chemical environments of PO_4^{3-} ions in centrosymmetric Li-SNP and $Sr_{9.333}Ni_{1.167}(PO_4)_7$.

Structure refinements of Na- and K-SNP

Structure parameters of β-$Ca_3(PO_4)_2$[9] were used as the initial ones in Rietveld refinements of Na- and K-SNP. Ca^{2+} ions occupy the M1 (18b; $x \approx 0.73$, $y \approx 0.86$, and $z \approx 0.43$), M2 (18b; $x \approx 0.62$, $y \approx 0.82$, and $z \approx 0.23$), and M3 (18b; $x \approx 0.13$, $y \approx 0.27$, and $z \approx 0.33$) sites in β-$Ca_3(PO_4)_2$[9] and $Ca_9MA(PO_4)_7$ (M = Mg, Mn, and Co; A = Li, Na, and K).[12] In Na- and K-SNP, these three sites were fully occupied by Sr^{2+} ions, *i.e.*, g(Sr) = 1 for the M1–M3 sites, where g denotes the occupancy. Ni^{2+} ions were located at the octahedral M5 site (6a; $z = 0$) with g(Ni) = 1 in a similar way to other small bivalent cations in $Ca_9MA(PO_4)_7$ and $Ca_{9.5}Cu(PO_4)_7$.[23] We assumed the M4 site (6a; $z \approx 0.18$) to have g(Sr) = 0.04, g(Ni) = 0.02, and g(Na) = 0.88 in Na-SNP and g(Sr) = 0.08, g(Ni) = 0.04, and g(K) = 0.76 in K-SNP to make these occupancies consistent with the compositions of A-SNP.

Rietveld analyses of the two phosphates with the above model afforded sufficiently low R factors and reasonable U parameters for all the sites. Refinement of g(M6) (M6: 6a, $z \approx -0.13$) showed this site to be vacant in the same manner as with β-$Ca_3(PO_4)_2$.[9] Refining occupancies of the M1, M2, M3, and M5 sites resulted in convergence to unity within error limits: g(Sr) = 0.996(6), g(Sr) = 0.999(6), g(Sr) = 0.996(5), and g(Ni) = 0.993(8) for Na-SNP and g(Sr) = 0.997(6), g(Sr) = 1.001(6), g(Sr) = 0.996(6), and g(Ni) = 0.994(8) for K-SNP. These findings are in accord with the distribution of the metals among the M1−M5 sites in our structural models.

Fig. 3 shows experimental, calculated, and difference XRD patterns for Na- and K-SNP. Final structure and lattice parameters, R factors, and so forth, are listed in Table 1, where the M1, M2, M3, and M5 sites are denoted as Sr1, Sr2, Sr3, and Ni5, respectively.

Discussion

Arrows in the insets of Fig. 3 denote reflections with odd indices l in Na- and K-SNP. These weak reflections disappeared in the XRD pattern of A-free $Sr_{9.333}Ni_{1.167}(PO_4)_7$ (Fig. 1), which led to a halved c parameter (Z = 3; a = 10.6130(2) Å and c = 19.6513(5) Å) and the higher symmetry of space group $R\bar{3}m$ in comparison with Na- and K-SNP. Differences in point symmetry for sites occupied by Ni^{2+} ions is most probably

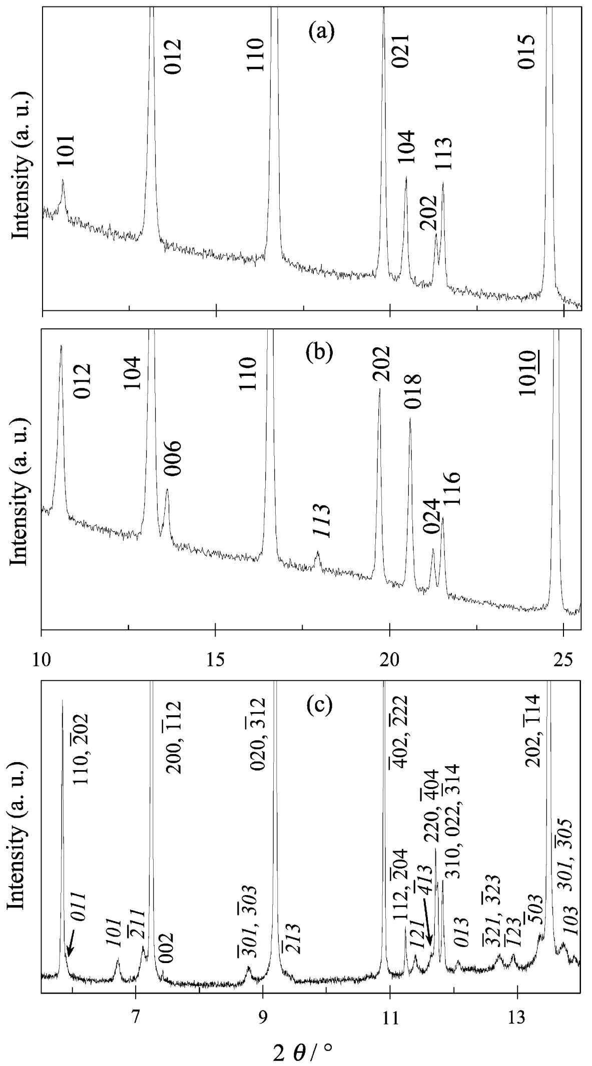

Fig. 2 Portions of XRD patterns for (a) $Sr_{9.333}Ni_{1.167}(PO_4)_7$, (b) $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$, and (c) $Sr_9NiLi(PO_4)_7$ in a *d* range from 8.84 Å to 3.49 Å with indices of reflections. Italic indices are given for superlattice reflections.

responsible for the different colors of Na/K-SNP and $Sr_{9.333}Ni_{1.167}(PO_4)_7$ described previously.[24]

Na- and K-SNP are isotypic with β-$Ca_3(PO_4)_2$[9] and $Ca_9CoA(PO_4)_7$ (A = Li, Na, and K)[12] belonging to the non-centrosymmetric space group of *R*3*c*. On the other hand, $Sr_{9.333}Ni_{1.167}(PO_4)_7$,[8] $Sr_9Fe_{1.5}(PO_4)_7$, and $Sr_{9.1}Cu_{1.4}(PO_4)_7$[15] crystallize in the centrosymmetric space group of $R\bar{3}m$, including disordered atoms in their structures. That is, Sr^{2+} ions are statistically distributed among four equivalent positions corresponding to the M3 site, $P1O_4$ tetrahedra are orientationally disordered, and Ni^{2+} and Cu^{2+} ions are disordered to occupy sites corresponding to the M4 and M6 sites. We have recently applied whole-pattern fitting based on the maximum-entropy method[25] to determination of electron-density distribution in $Sr_{9.3}Ni_{1.2}(PO_4)_7$ from synchrotron XRD data.[8] Highly disordered arrangements of Sr, Ni, P, and O atoms have been clarified by representing its structure with three-dimensional electron densities.

In the average structures of A-SNP, Sr^{2+} ions at the Sr3 site and the $P1O_4$ tetrahedra are ordered. The M4 site is partially occupied, and the M6 site is vacant. Fig. 4 illustrates PO_4^{3-} ions surrounding the M4, Ni5, and M6 sites in Na- and K-SNP. The M4 site contains Sr^{2+}, Ni^{2+}, and A^+ ions, and vacancies, while Ni^{2+} ions fully occupy the Ni5 site. The average Ni5–O distances of 2.112 Å in Na-SNP and 2.123 Å in K-SNP exclude the possibility for Sr^{2+}, Na^+, and K^+ ions to occupy the Ni5 site.

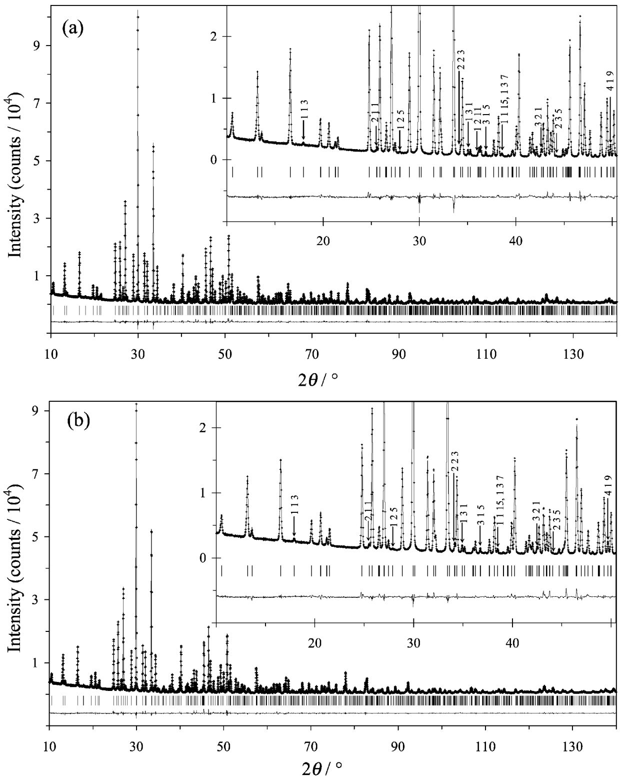

Fig. 3 Observed (crosses), calculated (solid line), and difference XRD patterns for (a) $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$ and (b) $Sr_{9.08}Ni_{1.04}K_{0.76}(PO_4)_7$. Bragg reflections are indicated by tick marks. The insets show XRD patterns in a 2*θ* range from 10° to 50.5°. Reflections with odd indices *l* are marked with arrows.

The M4 site is fully occupied by A^+ ions in $Ca_9MA(PO_4)_7$ (A = Li, Na, and K; M = Mg, Ca, Mn, and Co),[12] 50% occupied by small Cu^{2+} ions in $Ca_9Cu_{1.5}(PO_4)_7$,[23] and 50% occupied by $(Sr,Cu)^{2+}$ and $(Sr,Ca)^{2+}$ ions in $Sr_{9.1}Cu_{1.4}(PO_4)_7$,[15] $Ca_2Sr(PO_4)_2$, and $Ca_{5/7}Sr_{16/7}(PO_4)_2$.[10] Thus, the M4 site is flexible enough to accommodate cations with different oxidation states and sizes, and vacancies. Apparently large *U*(M4) parameters in Na-SNP (3.9 nm^2) and K-SNP (3.6 nm^2) are believed to reflect local static displacements arising from differences in effective ionic radii[26] among Ni^{2+} (0.69 Å), Sr^{2+} (1.18 Å), Na^+ (1.02 Å), and K^+ (1.38 Å) ions in six-fold coordination. We did not split any atoms at the M4 site because of the small *g*(Sr) and *g*(Ni) values. Partial occupation of relatively small Ni^{2+} ions at the M4 site mostly occupied by A^+ ions can be explained in terms of an empirical rule that $Z^{(n+1)+}$ ions tend to substitute for X^{n+} ions even if the $Z^{(n+1)+}$ ions have considerably smaller ionic radii than the X^{n+} ions.[27]

Each $M5O_6$ octahedron contains three M5–O24 bonds and three M5–O33 bonds, whose lengths, *l*, will be noted in parentheses here. $M5O_6$ octahedra in Na-SNP (*l*(Ni5–O) = 2.076 Å and 2.148 Å), K-SNP (*l*(Ni5–O) = 2.055 Å and 2.190 Å), $Ca_9CoNa(PO_4)_7$ (*l*(Co5–O) = 2.02 Å and 2.19 Å), and $Ca_9CoK(PO_4)_7$ (*l*(Co5–O) = 2.06 Å and 2.21 Å)[12] are more distorted than those in β-$Ca_3(PO_4)_2$ (*l*(Ca5–O) = 2.238 Å and 2.287 Å).[9] In $Sr_{9.3}Ni_{1.2}(PO_4)_7$, all of six Ni5–O bonds (2.099 Å) are equivalent to each other.

The M4 atom has three short M4–O21 and three long M4–O12 bonds: 2.394 Å and 2.995 Å (M4: Na, Sr, and Ni) in Na-SNP, 2.39 Å and 2.92 Å (M4: Na) in $Ca_9CoNa(PO_4)_7$,[12] 2.512 Å and 3.133 Å (M4: K, Sr, and Ni) in K-SNP, and 2.55 Å and 3.04 Å (M4: K) in $Ca_9CoK(PO_4)_7$.[12] M4–O bond lengths comparable to those in $Ca_9CoK(PO_4)_7$ were reported for β-$Ca_3(PO_4)_2$: *l*(Ca4–O21) = 2.538 Å and *l*(Ca4–O12) = 3.041 Å.[9]

Table 1 Fractional coordinates and isotropic atomic displacement parameters for $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$ (Na-SNP)[a] and $Sr_{9.08}Ni_{1.04}K_{0.76}(PO_4)_7$ (K-SNP)[b]

Atom	Site		*x*	*y*	*z*	*U*/nm^2
Sr1	18*b*	Na-SNP	0.72855(12)	0.8581(2)	0.43194(10)	0.61(3)
		K-SNP	0.72637(15)	0.8566(2)	0.43289(12)	0.68(4)
Sr2	18*b*	Na-SNP	0.61747(13)	0.8187(2)	0.22915(10)	0.53(3)
		K-SNP	0.6142(2)	0.8174(2)	0.23100(12)	0.83(4)
Sr3	18*b*	Na-SNP	0.1305(2)	0.27421(11)	0.32453(11)	0.96(3)
		K-SNP	0.1292(2)	0.27303(12)	0.32595(12)	1.23(4)
M4[c]	6*a*	Na-SNP	0	0	0.1851(3)	3.9(3)
		K-SNP	0	0	0.1837(2)	3.6(2)
Ni5	6*a*	Na-SNP	0	0	0	0.49(7)
		K-SNP	0	0	0	0.64(8)
P1	6*a*	Na-SNP	0	0	0.26323(15)	1.25(13)
		K-SNP	0	0	0.2656(2)	1.8(2)
P2	18*b*	Na-SNP	0.6848(3)	0.8510(6)	0.13405(13)	0.89(10)
		K-SNP	0.6796(3)	0.8519(7)	0.13576(15)	0.88(13)
P3	18*b*	Na-SNP	0.6596(4)	0.8442(4)	0.02946(13)	0.18(8)
		K-SNP	0.6592(5)	0.8452(5)	0.03104(15)	0.27(11)
O11	6*a*	Na-SNP	0	0	0.3035(4)	2.4(5)
		K-SNP	0	0	0.3052(4)	0.8(5)
O12	18*b*	Na-SNP	0.0102(9)	0.8695(7)	0.2524(3)	1.7(2)
		K-SNP	0.0180(10)	0.8726(8)	0.2547(3)	2.7(3)
O21	18*b*	Na-SNP	0.7503(8)	0.9054(8)	0.1711(2)	0.6(2)
		K-SNP	0.7367(10)	0.9053(10)	0.1727(3)	1.2(3)
O22	18*b*	Na-SNP	0.7403(13)	0.7576(12)	0.1180(2)	0.5(3)
		K-SNP	0.7425(12)	0.7628(12)	0.1205(3)	0.1(3)
O23	18*b*	Na-SNP	0.7229(12)	0.9916(9)	0.1137(3)	0.4(3)
		K-SNP	0.7251(13)	0.9947(10)	0.1144(3)	0.4(3)
O24	18*b*	Na-SNP	0.5126(6)	0.7543(13)	0.1346(2)	0.1(2)
		K-SNP	0.5091(7)	0.7538(14)	0.1346(2)	0.1(2)
O31	18*b*	Na-SNP	0.6073(10)	0.9445(11)	0.0442(3)	0.6(2)
		K-SNP	0.6103(12)	0.9471(12)	0.0444(3)	1.0(3)
O32	18*b*	Na-SNP	0.5889(9)	0.6929(9)	0.0482(2)	0.1(2)
		K-SNP	0.5891(10)	0.6920(10)	0.0502(3)	0.1(3)
O33	18*b*	Na-SNP	0.8245(7)	0.9212(11)	0.0361(2)	0.1(2)
		K-SNP	0.8250(8)	0.9205(13)	0.0377(2)	0.4(2)
O34	18*b*	Na-SNP	0.6216(7)	0.8194(11)	0.9915(2)	0.6(2)
		K-SNP	0.6233(8)	0.8212(13)	0.9924(2)	0.6(2)

[a] a = 10.6755(1) Å and c = 38.9339(3) Å; Z = 6; R_{wp} = 4.94%, R_{p} = 3.59%, R_{B} = 1.53%, R_F = 0.70%, and $S = R_{\mathrm{wp}}/R_{\mathrm{e}}$ = 2.01. [b] a = 10.7128(1) Å and c = 38.9492(3) Å; Z = 6; R_{wp} = 4.86%, R_{p} = 3.53%, R_{B} = 1.50%, R_F = 0.70%, and S = 1.97. [c] Occupancies, g, of the M4 site are g(Sr) = 0.04, g(Ni) = 0.02 and g(Na) = 0.88 in Na-SNP and g(Sr) = 0.08, g(Ni) = 0.04, and g(K) = 0.76 in K-SNP. The occupancies of all the other sites are 1.

M4–O bond lengths in Na-SNP and $Ca_9CoNa(PO_4)_7$ and those in K-SNP and $Ca_9CoK(PO_4)_7$ are close to each other.

Polyhedra for the M1, M2, and M3 atoms in β-$Ca_3(PO_4)_2$[9] can be represented as $Ca1O_{[7+1]}$ (seven distances lie in a range from 2.32 Å to 2.51 Å, and the eighth distance is 2.997 Å), $Ca2O_{[6+2]}$ (six bonds have l values from 2.37 Å to 2.44 Å, and two distances are 2.704 Å and 2.752 Å), and $Ca3O_{[8+1]}$ (eight bonds ranging in l from 2.38 Å to 2.65 Å, and the ninth bond with l = 3.11 Å). The replacement of Ca^{2+} ions by Sr^{2+} ions at the M1 and M2 sites led to Sr1–O and Sr2–O distances close to each other. Thus, polyhedra for the Sr1, Sr2, and Sr3 atoms in Na- and K-SNP are expressed as $Sr1O_8$, $Sr2O_8$, and $Sr3O_{[8+1]}$ (Fig. 5).

All of the Ca-containing phosphates, $Ca_{3-x}M_x(PO_4)_2$, $Ca_9M'(PO_4)_7$, and $Ca_9MA(PO_4)_7$, are isotypic with β-$Ca_3(PO_4)_2$ and crystallize in space group $R3c$ independent of the occupation of the M4 site. On the other hand, the occupation of larger Sr^{2+} ions at the M1–M3 sites causes lowering of symmetry from the trigonal system to the monoclinic one in $Sr_9M'(PO_4)_7$ and disordered arrangements of part of atoms in $Sr_{9+y}M_{1.5-y}(PO_4)_7$.

The crystal symmetry of Sr-containing phosphates, $Sr_{9+y}M_{1.5-y}(PO_4)_7$, $Sr_9M'(PO_4)_7$, and A-SNP, depends on kinds and amounts of cations at sites corresponding to the M4 and M6 sites. These sites are both vacant in $Sr_9M'(PO_4)_7$ with monoclinic and centrosymmetric structures (space group: $I2/a$).

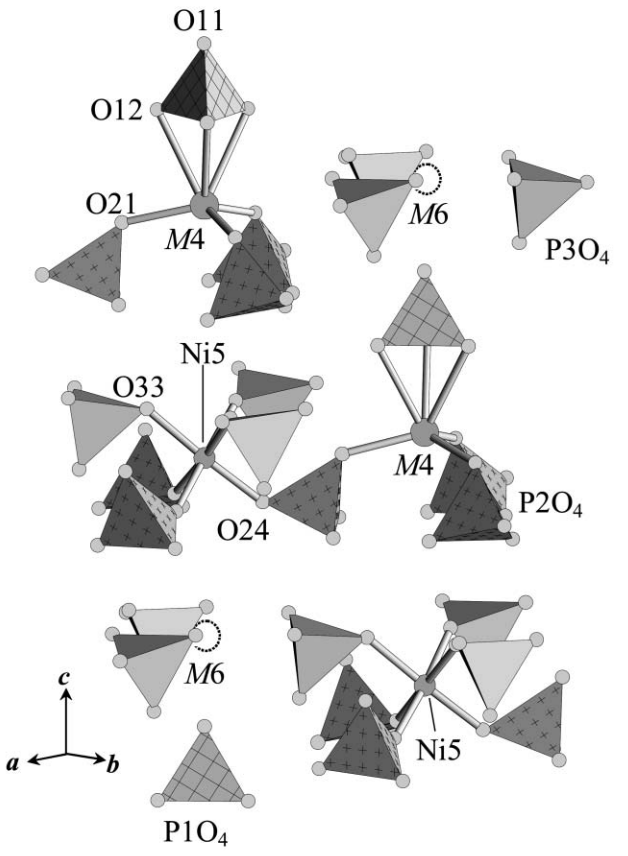

Fig. 4 Part of the structure for $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$. Tetrahedral PO_4^{3-} ions surrounding the M4, Ni5, and M6 sites are shown.

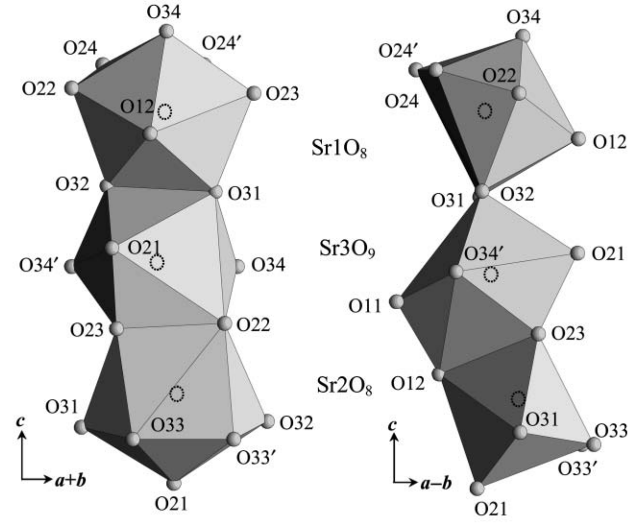

Fig. 5 Part of the structure for $Sr_{9.04}Ni_{1.02}Na_{0.88}(PO_4)_7$. $Sr1O_8$, $Sr2O_8$, and $Sr3O_9$ polyhedra are shown with numbers given for O atoms.

Li-SNP containing small Li^+ ions is also monoclinic with space group $I2/m$. $Sr_{9+y}M_{1.5-y}(PO_4)_7$, where the M4 site (M6 is equivalent to M4) is 25% occupied by $(Sr,M)^{2+}$ ions, belongs to space group $R\bar{3}m$. In Na- and K-SNP, occupation of the M4 site by large univalent A^+ ions stabilizes the β-$Ca_3(PO_4)_2$-type structure. These two phosphates contain the mixed-metal site, M4, and vacancies at the M6 site, and crystallize in the non-centrosymmetric space group of $R3c$.

A symmetrical change was also found in substitutional solid solutions $Ca_{3-x}Sr_x(PO_4)_2$: phosphates with $0 \leqslant x \leqslant 12/7$ have space group $R3c$ and a superlattice of dimensions $a \approx$ 10.5 Å and $c \approx$ 38 Å, whereas those with $13/7 \leqslant x \leqslant 16/7$

belong to space group $R\bar{3}m$ with $a \approx 11$ Å and $c \approx 19$ Å.[10] A comprehensive understanding of such symmetrical changes will help in searching for new nonlinear optical materials isotypic with or structurally related to β-$Ca_3(PO_4)_2$.

The present study has shown that introduction of Na^+ and K^+ ions into $Sr_{9+y}Ni_{1.5-y}(PO_4)_7$ yields β-$Ca_3(PO_4)_2$-type structures containing the Sr1, Sr2, Sr3, and Ni5 sites occupied completely and the mixed-metal site M4. β-$Ca_3(PO_4)_2$, $Ca_{9.333}Ni_{1.167}(PO_4)_7$, $Ca_9NiNa(PO_4)_7$ (PDF #50-0217), $Ca_9NiK(PO_4)_7$ (PDF #49-1226), Na-SNP, and K-SNP are isotypic with each other. Parts of solid solutions among these compounds may exhibit interesting physical and chemical properties characteristic of β-$Ca_3(PO_4)_2$-type structures, *e.g.*, catalytic action in a similar manner to $A'_{9.333}Ni_{1.167}(PO_4)_7$ (A' = Ca and Sr).[6]

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