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Synthesis and Characterization of New Nickel Phosphates, $ANi_4(PO_4)_3$ (A=K, Rb)

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Quaternary nickel orthophosphates, $ANi_4(PO_4)_3$ (A=Alkali metals) have been extensively investigated because they show interesting properties such as ionic conductivities, optical, and magnetic behaviors.[1-9] They are built up from NiO_6 octahedra and PO_4 tetrahedra. These basic building blocks are connected *via* common oxygen atoms to form the three-dimensional frameworks and the alkali metal ions reside in the empty space.

For $NaNi_4(PO_4)_3$, two different structures have been reported and this can be caused by the different reaction conditions. While $NaNi_4(PO_4)_3$ prepared as single crystals with the use of NaCl flux at 1373 K crystallizes in the space group Amam and show a partial disorder of one of the PO_4 tetrahedra,[3] $NaNi_4(PO_4)_3$ and $KNi_4(PO_4)_3$ synthesized with alkali metal nitrate at 1073 K as powders adopt an ordered structure with the space group *Pnnm*.[4] As far as we know, no structural studies of $KNi_4(PO_4)_3$ from single crystal diffraction data have been reported yet and $RbNi_4(PO_4)_3$ is a new compound. In this paper we report on the synthesis and structural investigations using single crystals of two nickel orthophosphates, $KNi_4(PO_4)_3$ and $RbNi_4(PO_4)_3$.

Experimental

Synthesis.

$KNi_4(PO_4)_3$: $KNi_4(PO_4)_3$ was prepared by the reaction of elements with the use of the reactive halide-flux technique. A combination of the pure elements, Ni powder (Alfa Aesar 99.8%), S powder(Sigma-Aldrich) and P powder (Sigma-Aldrich 99%) were mixed in a fused silica tube in molar ratio of Ni:P:S=4:5:6 and then KCl (Alfa Aesar 99%) was added. The mass ratio of the reactants and the halide was 1:3. The tube was evacuated to 0.133 Pa, sealed, and heated gradually (30 K/h) to 1023 K, where it was kept for 72 h. The tube was cooled to room temperature at the rate of 6 K/h.

$RbNi_4(PO_4)_3$: $RbNi_4(PO_4)_3$ was prepared by the reaction of elements with the use of the reactive halide-flux technique. A combination of the pure elements, Ni powder (Alfa Aesar 99.8%), Se powder (Sigma-Aldrich) and P powder (Sigma-Aldrich 99%) were mixed in a fused silica tube in molar ratio of Ni:P:Se=3:4:8 and then RbCl (Alfa Aesar 99%) was added. The mass ratio of the reactants and the halide was 1:2. The tube was evacuated to 0.133 Pa, sealed, and heated gradually (20 K/h) to 923 K, where it was kept for 72 h. The tube was cooled to room temperature at the rate of 12 K/h.

In both cases, the excess halide was removed with distilled water and yellow needle-shaped crystals were obtained. The role of chalcogens in the reactions is not clear but it is helpful to obtain the product as single crystals. The crystals are stable in air and water. A qualitative X-ray fluorescence analysis of the crystals indicated the presence of K or Rb, Ni, and P. The compositions of the compounds were determined by single-crystal X-ray diffraction.

Crystallographic Studies. The structures of $ANi_4(PO_4)_3$ (A=K, Rb) were determined by single crystal X-ray diffraction methods. Preliminary examination and data collection were performed with Mo $K\alpha_1$ radiation ($\lambda = 0.71073$ Å) on a RIGAKU R-ASXIS RAPID diffractometer. The cell constants and an orientation matrix were determined from least-squares, using the setting angles in the range $3.0^o < \theta < 27.5^o$. The crystallographic details are described in Table 1. Intensity data were collected with the ω scan technique.

The intensity statistics and systematic absences are consistent with the orthorhombic space group, *Pnnm*. The initial positions for all atoms were obtained by using direct methods of the SHELXS-86 program.[10] The structure was refined by full-matrix least-squares techniques with the use of the SHELXL-97 program.[10] The data for $ANi_4(PO_4)_3$ (A=K, Rb) were corrected for absorption using the multi-scan method.[11] In case of $KNi_4(PO_4)_3$, the final cycle of refinement performed on F_o^2 with 1183 unique reflections afforded residuals wR2 = 0.059 and the conventional R index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.024. For $RbNi_4(PO_4)_3$, the final cycle of refinement performed on F_o^2 with 1202 unique reflections afforded residuals wR2=0.091 and the conventional R index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.035.

A difference Fourier synthesis calculated with phases based on the final parameters shows no peak heights greater than 1.11 and 1.91 e/Å^3. No unusual trends were found in the goodness of fit as a function of F_o, $\sin\theta/\lambda$ and Miller indices. Final values of the atomic coordinates and equivalent isotropic displacement parameters are given in Tables 2, 3. Anisotropic displacement parameters and complete tabulations on the X-ray studies can be found in CIF format in the Supporting Information Section.

Solid-State UV/Vis Spectroscopy. Optical diffuse reflec-

Table 1. Crystal data and structure refinement for $ANi_4(PO_4)_3$

	$KNi_4(PO_4)_3$	$RbNi_4(PO_4)_3$
Formula weight, amu	558.85	605.22
Space group	*Pnnm*	*Pnnm*
a, Å	9.4908 (3)	9.4837 (4)
b, Å	16.2378 (6)	16.3458 (6)
c, Å	6.1553 (2)	6.1846 (2)
V, $Å^3$	948.59 (6)	958.72(6)
Z	4	4
T, K	290 (1)	290 (1)
Radiation	Graphite Monochromated MoKα (λ = 0.71073 Å)	Graphite Monochromated MoKα (λ = 0.71073 Å)
Linear absorption coefficient, mm^{-1}	8.83	13.35
Crystal size, mm^3	0.42 × 0.10 × 0.08	0.60 × 0.08 × 0.06
Scan type	ω	ω
θ limits, deg.	$3.0^o < \theta < 27.5^o$	$3.0^o < \theta < 27.5^o$
Data collected	± h, ± k, ± l	± h, ± k, ± l
No. of unique data with $F_o^2 > 0$	1183	1202
No. of unique data with $F_o^2 > 2\sigma(F_o^2)$	1117	1016
wR2 (all data)	0.059	0.091
R (on Fo for $F_o^2 > 2\sigma(F_o^2)$)	0.024	0.035
Goodness-of-fit on F^2	1.107	1.113
Min. and Max. residual Electron density ($e/Å^3$)	−0.96 and 1.11	−2.09 and 1.91

tance measurements of the powdered sample were performed at room temperature using a Shimadzu UV-2400 PC spectrophotometer operating in the range of 200-800 nm. $BaSO_4$ powder was used as reference material. The absorption data were calculated from the diffuse reflectance data with the use of the Kubelka-Munk relation.[12]

Table 2. Atomic coordinates, equivalent isotropic displacement parameters and bond valence sums (BVSs) for $KNi_4(PO_4)_3$

	X	y	z	Ueq*	BVS
K	0.2029(1)	0.4687(1)	0	0.0221(2)	1.1173
Ni1	0.0342 (1)	0.9074(1)	0	0.0078(2)	1.9556
Ni2	0.5133 (1)	0.1426(1)	0	0.0084(2)	1.8734
Ni3	0.2521 (1)	0.2039(1)	0.2506 (1)	0.0078(2)	1.9246
P1	0.4604 (1)	0.3372(1)	0	0.0069(2)	4.9217
P2	0.0474(1)	0.2799(1)	0	0.0068(2)	4.9129
P3	0.2941(1)	0.0363(1)	0	0.0072(2)	4.9597
O1	0.6228 (3)	0.3252(2)	0	0.0103(5)	1.9738
O2	0.1145 (3)	0.7256(2)	0	0.0091(5)	2.0163
O3	0.4124 (2)	0.3824(1)	0.2007 (3)	0.0114(4)	1.9503
O4	0.1098 (3)	0.1897(1)	0	0.0087(5)	2.1386
O5	0.3886 (3)	0.2475 (2)	0	0.0087(5)	1.9833
O6	0.6351 (3)	0.0459 (2)	0	0.0139(6)	1.9536
O7	0.3402 (2)	0.0901(1)	0.1978 (3)	0.0106(4)	1.9268
O8	0.1069 (2)	0.3178 (1)	0.2085 (3)	0.0113(4)	1.8826
O9	0.1344 (3)	0.0201 (2)	0	0.0120(6)	2.0046

Table 3. Atomic coordinates, equivalent isotropic displacement parameters and bond valence sums (BVSs) for $RbNi_4(PO_4)_3$

	x	y	z	Ueq[a]	BVS
Rb1	0.1963(1)	0.4690(1)	0	0.0248(3)	1.2589
Ni1	0.0327(1)	0.9075(1)	0	0.0088(2)	1.9183
Ni2	0.5146(2)	0.1431(1)	0	0.0094(2)	1.8412
Ni3	0.2536(1)	0.2044(1)	0.2503(1)	0.0082(2)	1.9221
P1	0.4623(2)	0.3371(1)	0	0.0065(4)	4.9269
P2	0.0481(2)	0.2787(1)	0	0.0071(4)	4.9302
P3	0.2956(2)	0.0371(1)	0	0.0082(4)	4.9211
O1	0.6254(5)	0.3245(3)	0	0.010(1)	1.9520
O2	0.1134(5)	0.7263(3)	0	0.011(1)	2.0211
O3	0.4162(4)	0.3813(2)	0.2007(6)	0.0125(8)	1.9654
O4	0.1111(5)	0.1892(3)	0	0.009(1)	2.1294
O5	0.3895(5)	0.2480(3)	0	0.008(1)	1.9636
O6	0.6332(6)	0.0447(3)	0	0.0150(1)	1.9573
O7	0.3420(4)	0.0913(2)	0.1959(6)	0.0107(8)	1.9531
O8	0.1079(4)	0.3155(2)	0.2084(6)	0.0104(7)	1.8988
O9	0.1359(5)	0.0199(3)	0	0.0120(1)	1.9819

[a]Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

Result and Discussion

Crystal Structure. The structural studies of $ANi_4(PO_4)_3$ (A=K, Rb) demonstrate the existence of another members of the $AM_4(PO_4)_3$ family (A=Alkali metal, M=Co, Fe, Mg, Mn, Ni).[1-9] Selected bond distances and angles can be found in Table 4 and the Supporting Information Section, respectively. The title compounds are isostructural with $AM_4(PO_4)_3$ and the detailed descriptions of this structural type have been given previously.[1-9] A view down the a-axis, given in Figure 1 shows the three-dimensional framework structure and tunnels, where the alkali metal cations are located. There are three crystallographically independent Ni atoms and two types of Ni coordination are found in this structure (Figure 2). The Ni1 is coordinated by five O atoms in a trigonal bipyramidal fashion and the Ni2 and Ni3 are surrounded by six O atoms in the distorted octahedral symmetry. The P atom is coordinated to four O atoms to form the regular tetrahedron. $Ni3O_6$ octahedra form a one-dimensional chain along the c-axis by sharing edges and these chains are linked *via* $Ni2O_6$ octahedra to form the two-dimensional layer parallel to the ac plane. The edge-sharing trigonal bipyramidal $Ni1O_5$ acts as a bridge to connect the layers and finally the tetrahedral PO_4 link the Ni polyhedra to complete the three-dimensional framework, $^3_\infty[Ni_4(PO_4)_3]^-$. As a result, an empty hexagonal channel along the a-axis is formed. The free diameters of the channels are about 4.8 Å, which is similar to that of $NaNi_4(PO_4)_3$. The alkali metal cations, K^+ or Rb^+ reside in this channel through the electrostatic Coulombic interaction.

The Ni-O distances ranging from 1.949(3) to 2.320(2) Å are consistent with the sum of the ionic radii of each ions[13] except the Ni2-O7 and Ni3-O8. The P-O distances ranging

Table 4. Bond lengths [Å] for $ANi_4(PO_4)_3$

$KNi_4(PO_4)_3$		$RbNi_4(PO_4)_3$	
Ni1—O3	1.953 (2) × 2	Ni1—O3	1.961 (4) × 2
Ni1—O4	2.086 (3)	Ni1—O4	2.087 (5)
Ni1—O9	1.986 (3), 2.063 (3)	Ni1—O9	1.991 (5), 2.082 (5)
Ni2—O5	2.075 (3)	Ni2—O5	2.085 (5)
Ni2—O6	1.949 (3)	Ni2—O6	1.962 (5)
Ni2—O7	2.216 (2) × 2	Ni2—O7	2.204 (4) × 2
Ni2—O8	2.103 (2) × 2	Ni2—O8	2.120 (4) × 2
Ni3—O1	2.021 (2)	Ni3—O1	2.021 (3)
Ni3—O2	2.021 (2)	Ni3—O2	2.026 (3)
Ni3—O4	2.063 (2)	Ni3—O4	2.069 (3)
Ni3—O5	2.136 (2)	Ni3—O5	2.137 (3)
Ni3—O7	2.055 (2)	Ni3—O7	2.057 (3)
Ni3—O8	2.320 (2)	Ni3—O8	2.297 (4)
P1—O1	1.553 (3)	P1—O1	1.561 (5)
P1—O3	1.508 (2)	P1—O3	1.502 (4) × 2
P1—O5	1.607 (3)	P1—O5	1.496(3)
P2—O2	1.539 (3)	P2—O2	1.534 (5)
P2—O4	1.581 (3)	P2—O4	1.580 (5)
P2—O8	1.531 (2) × 2	P2—O8	1.531 (4) × 2
P3—O6	1.496 (3)	P3—O6	1.498 (5)
P3—O7	1.561(2) × 2	P3—O7	1.565 (4) × 2
P3—O9	1.538 (3)	P3—O9	1.540 (5)

from 1.496(3) to 1.607(3) Å appear to be typical for the PO_4 tetrahedra.[14] According to the bond valence calculations,[15] the global instability indices, Gii for $KNi_4(PO_4)_3$ and $RbNi_4(PO_4)_3$ are 0.0779 and 0.0994 v.u, respectively, which are typical of the unstrained structures.[16] The charge balance of the title compounds can be described by $[A^+]$ $[Ni^{2+}]_4$-$[P^{5+}]_3[O^{2-}]_{12}$.

Solid-State UV/Vis Spectroscopy. UV/Vis absorption spectral data show that absorption peaks of crystal field splittings of the Ni^{2+} ions are around 2.78 eV for $KNi_4(PO_4)_3$ and 2.68 eV for $RbNi_4(PO_4)_3$. Usually Ni^{2+} ions with octahedral coordinations with oxygen atoms show greenish colors. According to the investigation by Rossman *et al.*, bright yellow oxides containing Ni^{2+} ions are found when the Ni^{2+} ions enter sites significantly deviated from the regular octahedral symmetry.[17] Therefore, we believe that the electronic transitions localized mainly on the distorted Ni polyhedra are responsible for the colors observed in the title compounds.

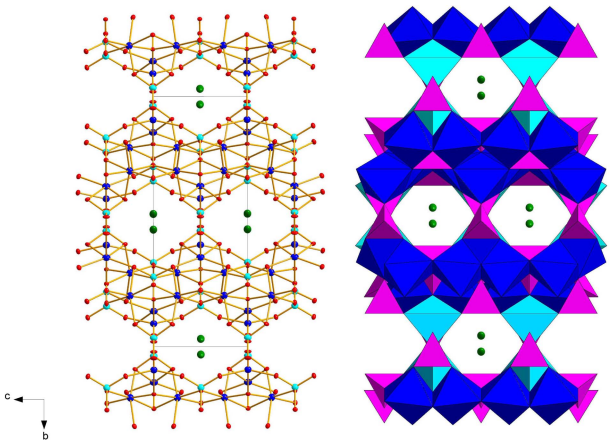

Figure 1. View of $ANi_4(PO_4)_3$ down the a-axis showing the structure of the framework. Alkali metals, Ni, P, and O atoms are represented by green, blue, turquoise, and red spheres, respectively with arbitrary radii; NiO_5, NiO_6 polyhedra are drawn in sky blue and blue, respectively. PO_4 tetrahedra are drawn in pink.

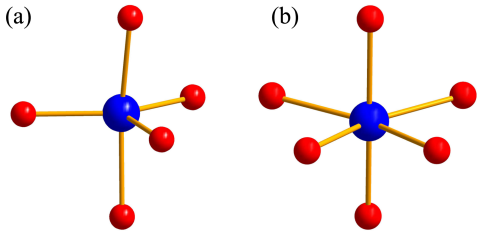

Figure 2. Basic polyhedral units around Ni atoms. Atom color codes as in Figure 1. (a) $Ni1O_5$ trigonal bipyramid (b) $Ni2O_6$ and $Ni3O_6$ octahedra.

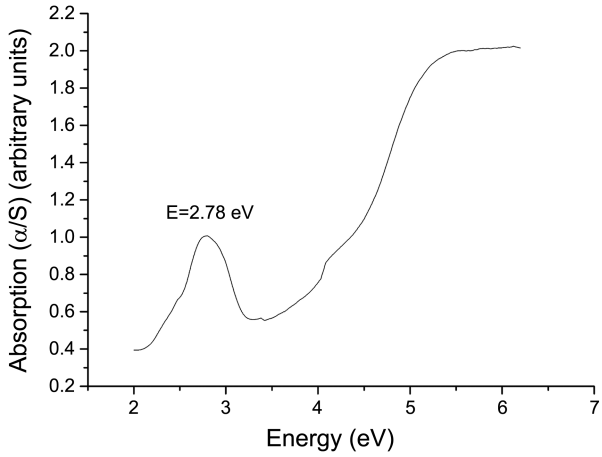

Figure 3. Solid-state UV/Vis absorption spectra of $KNi_4(PO_4)_3$.

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Supporting Information. Crystallographic data for the structures reported here have been deposited with FIZ (Deposition No. CSD-427036 and CSD-427037 for $KNi_4(PO_4)_3$ and $RbNi_4(PO_4)_3$, respectively). These data can be obtained free of charge from FIZ, D-76344, Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de).

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