$AM^{V}M^{III}(PO_4)_3$: New Mixed-Metal Phosphates Having NASICON and Related Structures‡

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Introduction

$NaZr_2(PO_4)_3$[1] is the prototype of an extensive family of solid materials that are referred to as NASICONs or NZPs in the literature.[2,3] The widespread interest in this family stems from the seminal discovery[4] of fast sodium ion transport in the silicophosphate series $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ (NASICON), which possesses the $NaZr_2(PO_4)_3$ (NZP) framework.[1,5] The $Zr_2(XO_4)_3$ framework, consisting of ZrO_6 octahedra and XO_4 (X = P, Si) tetrahedra linked by corners, provides an interconnected interstitial space where the mobile sodium or other cations are located. Besides fast-ion conductivity, members of this family have been explored for other properties as well, such as immobilization of radioactive nuclides,[6] low thermal expansion,[7] and ion-exchange[8] and redox insertion/extraction reactions.[9] The unique $M_2(XO_4)_3$ framework of the NASICON/NZP structure enables a variety of chemical substitutions to be made both at the framework and at the interstitial sites enclosed by the framework. A recent review by Alamo[3] lists all the possible NASICON derivatives obtained so far by various chemical substitutions. Here, we report a new chemical substitution in the NZP structure, viz., $2Zr^{IV} \rightarrow M^{V} + M^{III}$, where M^{V} = Nb or Ta and M^{III} = Ti, V, Cr, Fe, or Al, that has enabled us to synthesize several members of the general formula $AM^{V}M^{III}(PO_4)_3$. To our knowledge, $NaNbTi(PO_4)_3$ is the only member of this series that has been previously reported[10] as a part of $Na_xNbTi(PO_4)_3$. Besides enlarging the NZP structure field to include several $M^{V}-M^{III}$ combinations at octahedral sites in the framework, the present work also shows the possibility of oxidative deintercalation of sodium from $NaMTi^{III}(PO_4)_3$ and $NaMV^{III}(PO_4)_3$ leaving the NZP framework intact.

Experimental Section

$NaM^{V}M^{III}(PO_4)_3$ phosphates for M^{V} = Nb or Ta and M^{III} = Ti or V were prepared by reacting preheated stoichiometric mixtures of Na_2CO_3, $M^{V}_2O_5$, TiO_2/V_2O_5, and $(NH_4)_2HPO_4$ at 950 °C for 3 days in a flowing hydrogen atmosphere (~10 mL/min). Similar phosphates for M^{III} = Cr, Fe, or Al were prepared by direct solid state reactions in air employing Cr_2O_3, Fe_2O_3, or Al_2O_3. The corresponding lithium compounds were prepared by the same method using Li_2CO_3 at 800 °C for 24 h. Deintercalation of sodium from $NaMTi(PO_4)_3$ and $NaMV(PO_4)_3$ (M = Nb, Ta) was carried out[9c] by passing chlorine through a suspension of ~2 g of the powder in 50 mL of $CHCl_3$. Oxidation states of titanium and vanadium in the compounds were determined by redox potentiometric titration using Ce(IV) as oxidizing agent.

The new phosphates were characterized by powder X-ray diffraction (XRD) (JEOL JDX-8P X-ray diffractometer, Cu Kα radiation), infrared absorption spectroscopy (Bio-Rad, SKC-3200 FTIR spectrometer), and ^{27}Al NMR spectroscopy (Bruker MSL-300 spectrometer operating at 78.21 MHz). Lattice parameters were derived from least-squares refinement of the powder X-ray diffraction data using PROSZKI program[11] that includes LAZY PULVERIX.

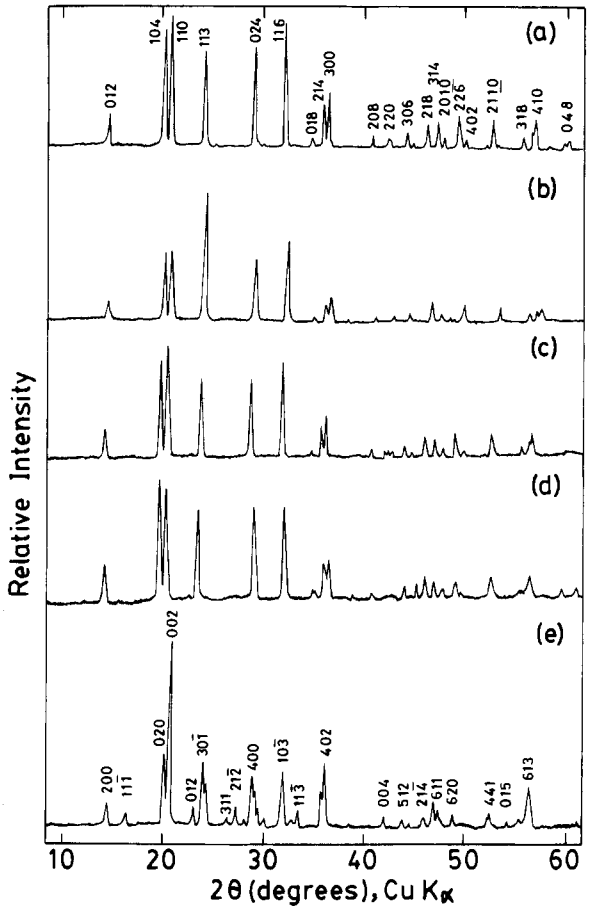

Figure 1. X-ray powder diffraction patterns of (a) $NaTaCr(PO_4)_3$, (b) $NaNbAl(PO_4)_3$, (c) $NaTaV(PO_4)_3$, (d) $TaV(PO_4)_3$, and (e) $LiNbV(PO_4)_3$.

Results and Discussion

The basic structural unit of the NZP framework is $[Zr_2P_3O_{12}]^-$, which consists of two ZrO_6 octahedra joined by three PO_4 tetrahedra.[1] This unit repeats along the *c* direction forming columns which are in turn connected by PO_4 tetrahedra to form the framework. A number of substitutions at the zirconium site of NZP have been investigated, giving rise to a variety of NASICON derivatives.[3] A straightforward substitution would be $2Zr^{IV} \rightarrow M^{V} + M^{III}$, which has not been explored in the literature. Accordingly, we investigated the formation of NZP-type phases of the general formula $AM^{V}M^{III}(PO_4)_3$, for M^{V} = Nb or Ta with a number of trivalent metals. We could readily prepare such phases for M^{III} = Cr, Fe, or Al by direct solid state reactions of the constituents in air, while the syntheses of the corresponding M^{III} = Ti or V phases required hydrogen reduction of preheated stoichiometric mixtures containing TiO_2 or V_2O_5. While we could obtain NZP-type phases for A = Na or Li, our attempts to prepare similar phases for A = K resulted in multiphasic mixtures containing both Langbeinite and NASICON/NZP-type structures.

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Table 1. Composition, Color, and Lattice Parameters of $AM^{V}M^{III}(PO_4)_3$ Phosphates and their Derivatives

composition	color	reducing power found	reducing power expected[a]	lattice parameters (Å) a	lattice parameters (Å) c
$NaNbTi(PO_4)_3$	dark blue	0.97	1.00	8.630(4)	22.052(5)
$NaNbV(PO_4)_3$	brownish green	2.01	2.00	8.565(6)	22.078(8)
$NaNbCr(PO_4)_3$	green			8.515(6)	22.023(7)
$NaNbFe(PO_4)_3$	pale pink			8.571(5)	22.102(9)
$NaNbAl(PO_4)_3$	white			8.476(8)	21.810(5)
$NaTaV(PO_4)_3$	green	2.00	2.00	8.587(3)	22.089(6)
$NaTaCr(PO_4)_3$	green			8.546(4)	22.065(9)
$NaTaFe(PO_4)_3$	pale pink			8.580(3)	22.149(6)
$NaTaAl(PO_4)_3$	white			8.471(4)	21.928(6)
$LiNbV(PO_4)_3$	green	1.99	2.00	*b*	
$LiNbFe(PO_4)_3$	pale pink			8.589(6)	21.654(8)
$LiTaV(PO_4)_3$	green	2.00	2.00	*c*	
$LiTaCr(PO_4)_3$	green			8.535(6)	21.551(8)
$LiTaFe(PO_4)_3$	pale pink			8.608(6)	21.753(6)
$LiTaAl(PO_4)_3$	white			8.510(5)	21.230(4)
$TaV(PO_4)_3$	green	1.02	1.00	8.514(5)	21.949(8)
$NbTi(PO_4)_3$	white			8.552(2)	21.945(6)

[a] Corresponds to the number of electrons per formula unit required for the oxidation of titanium and vanadium. [b] Monoclinic: a = 12.282(9), b = 8.764(8), c = 8.590(5) Å; β = 90.90(8)°. [c] Monoclinic: a = 12.27(1), b = 8.773(8), c = 8.590(8) Å; β = 90.63(8)°.

Table 2. X-ray Powder Diffraction Data for $NaTaCr(PO_4)_3$

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}[a]
012	6.135	6.146	24	23
104	4.412	4.423	86	84
110	4.275	4.273	100	100
113	3.686	3.695	67	64
024	3.070	3.073	72	52
116	2.788	2.787	80	68
211		2.775		8
018	2.578	2.584	9	7
214	2.488	2.495	31	25
300	2.462	2.467	40	38
208	2.206	2.211	9	7
220	2.132	2.137	7	6
1,0,10	2.108	2.115	4	4
217	2.087	2.092	1	1
306	2.045	2.049	10	8
312	2.014	2.018	1	1
218	1.961	1.961	23	20
314	1.922	1.923	18	13
2,0,10	1.895	1.895	9	7
226	1.843	1.847	27	22
402	1.822	1.825	5	3
2,1,10	1.731	1.732	23	19
137	1.719	1.720	6	3
318	1.645	1.647	13	10
324	1.621	1.623	15	12
410	1.613	1.615	29	23
048	1.535	1.537	7	5

[a] Calculated by the LAZY PULVERIX program using the position parameters of $NaZr_2(PO_4)_3$.[1]

We give the XRD patterns of the representative members of $AM^{V}M^{III}(PO_4)_3$ in Figure 1; in Table 1, we list the unit cell parameters together with other characteristics of all the phosphates synthesized. We see that while most of the phases synthesized crystallize in the rhombohedral ($R\bar{3}c$) NZP structure,[1] $LiMV(PO_4)_3$ (M = Nb, Ta) crystallize in a monoclinic structure probably related to $Ni_{0.5}Zr_2(PO_4)_3$.[12] In Tables 2 and 3, we give indexed powder X-ray diffraction data for representative members of both structure types. We have also calculated the intensities of *hkl* reflections for the rhombohedral phases, using the position parameters[1] of $NaZr_2(PO_4)_3$ and assuming a random distribution of M^{V} and M^{III} atoms at the 12(c) site. We see that the agreement between the observed and calculated intensities is quite good (Table 2), suggesting that the NZP model is most likely for the rhombohedral $AM^{V}M^{III}(PO_4)_3$ phases.

Table 3. X-ray Powder Diffraction Data for $LiNbV(PO_4)_3$

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
200	6.150	6.140	14
11$\bar{1}$	5.471	5.513	8
020	4.439	4.382	39
002	4.301	4.294	100
01$\bar{2}$	3.858	3.856	11
30$\bar{1}$	3.708	3.718	36
301	3.670	3.673	23
31$\bar{1}$	3.363	3.387	5
21$\bar{2}$	3.267	3.286	11
400	3.079	3.070	31
022	3.053	3.067	22
320	3.023	2.991	10
12$\bar{2}$	2.959	2.968	5
10$\bar{3}$	2.797	2.797	31
411	2.730	2.733	4
01$\bar{3}$	2.714	2.721	4
11$\bar{3}$	2.675	2.665	9
20$\bar{3}$	2.501	2.501	18
402	2.481	2.479	35
040	2.212	2.191	3
004	2.151	2.147	6
51$\bar{2}$	2.060	2.058	5
20$\bar{4}$	2.029	2.036	2
21$\bar{4}$	1.971	1.984	6
611	1.931	1.935	14
522	1.910	1.907	9
620	1.855	1.855	6
503	1.848	1.849	5
441	1.743	1.743	5
324	1.737	1.735	8
015	1.685	1.685	3
251	1.653	1.653	5
613	1.623	1.624	23

The powder XRD patterns (Figure 1 and Table 3) of monoclinic $LiNbV(PO_4)_3$ and $LiTaV(PO_4)_3$ show a strong resemblance to that of $Ni_{0.5}Zr_2(PO_4)_3$.[12] Accordingly, we could index the patterns of these phases on monoclinic cells with lattice parameters a = 12.282(9) Å, b = 8.764(4) Å, c = 8.590(5) Å, β = 90.90(8)° for $LiNbV(PO_4)_3$ and a = 12.27(1) Å, b = 8.773(8) Å, c = 8.590(8) Å, β = 90.63(8)° for $LiTaV(PO_4)_3$. The monoclinic ($P2_1/n$) structure of $Ni_{0.5}Zr_2(PO_4)_3$ has been shown to be related to the structure of $Sc_2(WO_4)_3$.[12] The $Sc_2(WO_4)_3$ structure, which appears to be competitive with the NZP/NASICON structure, is adopted by $A_xM_2(XO_4)_3$ compounds for small A cations such as Li, Mg, Ni, or Cu. It is interesting that, among the various $LiM^{V}M^{III}(PO_4)_3$ phases synthesized here, only the M^{III} = V compounds crystallize with this structure.

In Figure 2, we have plotted the hexagonal a and c parameters of rhombohedral $NaNb^{V}M^{III}(PO_4)_3$ as a function of the average ionic radius[13] of the octahedral site cations. For purposes of comparison, we have also included the data for the corresponding Zr^{IV}, Ti^{IV}, and Ge^{IV} phosphates.[1] We see that the variation of a and c with the average ionic radius is almost linear for all compositions excepting the Ge^{IV} phosphate. The anomalous behavior of the Ge^{IV} phase is likely related to the fact that it adopts a different space group ($R\bar{3}$).[14] Among the new phosphates reported in this paper, those containing Al^{III} deserve

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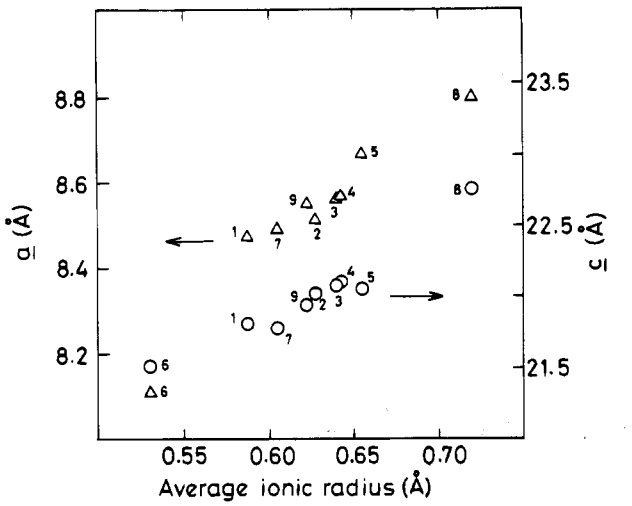

Figure 2. Variation of hexagonal a and c parameters of $NaNbM^{III}(PO_4)_3$ with the average ionic radii of Nb and M^{III}. (1) M^{III} = Al; (2) M^{III} = Cr; (3) M^{III} = V; (4) M^{III} = Fe; (5) M^{III} = Ti; (6), (7), and (8) denote corresponding data points for the Ge^{IV}, Ti^{IV}, and Zr^{IV} phosphates, respectively; (9) denotes the data point for $NbTi^{IV}(PO_4)_3$.

Table 4. X-ray Powder Diffraction Data for $NaNbAl(PO_4)_3$

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}[a]
012	6.088	6.089	20	16
104	4.375	4.377	40	36
110	4.240	4.238	54	47
113	3.663	3.661	100	100
024	3.043	3.045	40	30
116	2.759	2.759	64	51
211		2.752		14
018	2.550	2.556	2	2
214	2.471	2.473	9	7
300	2.445	2.447	18	23
208	2.191	2.189	4	4
119	2.106	2.104	4	5
306	2.032	2.030	6	3
218	1.945	1.945	16	16
314	1.910	1.907	6	5
2,0,10	1.873	1.875	3	3
226	1.831	1.831	14	18
402	1.811	1.810	3	3
2,1,10	1.713	1.715	11	11
137	1.708	1.704	5	5
318	1.630	1.631	9	8
324	1.610	1.609	6	7
410	1.603	1.602	12	16

[a] Calculated by the LAZY PULVERIX program using the position parameters of $NaZr_2(PO_4)_3$.[1]

a special mention, because it has been reported[15] that Al^{III} does not substitute for Zr^{IV} in the NZP structure. Our calculations of the powder XRD intensities of the Al^{III}-containing phosphates assuming the NZP structure model give a good agreement with the observed intensities (Table 4). In addition, we recorded the solid state ^{27}Al NMR spectra of $NaNbAl(PO_4)_3$ and $NaTaAl(PO_4)_3$ (Figure 3). The ^{27}Al resonances occurring at -15 and -19 ppm relative to $[Al(H_2O)_6]^{3+}$ show that Al^{III} indeed occurs at the octahedral sites,[16] as expected for the NZP structure model. It is likely that Al^{III} does not substitute for Zr^{IV} in $NaZr_2(PO_4)_3$, but it does substitute at the octahedral site of the NZP structure, when it is coupled with pentavalent cations (Nb^V or Ta^V) as in $NaNbAl(PO_4)_3$ and $NaTaAl(PO_4)_3$ reported here.

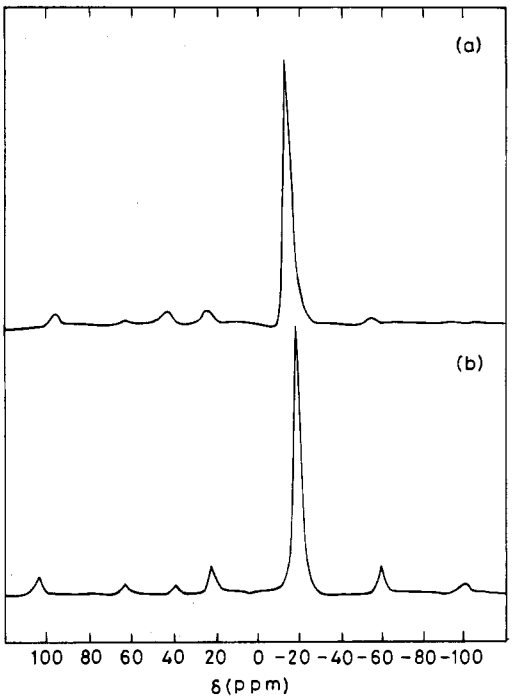

Figure 3. ^{27}Al NMR spectra of (a) $NaNbAl(PO_4)_3$ and (b) $NaTaAl(PO_4)_3$.

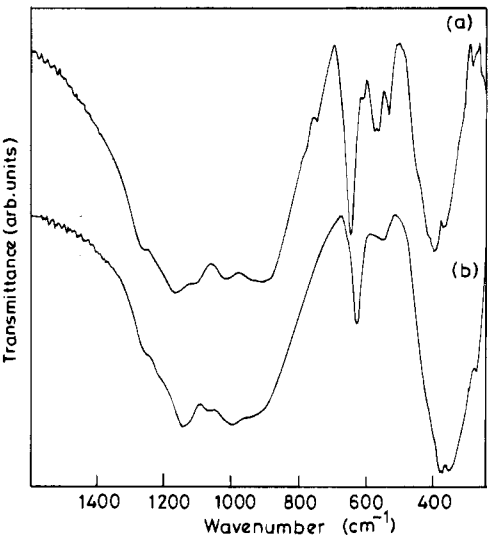

Figure 4. Infrared absorption spectra of (a) $NaTaV(PO_4)_3$ and (b) $TaV(PO_4)_3$.

We recently showed that sodium could be deintercalated from NASICON-type $Na_3V_2(PO_4)_3$ by reaction with chlorine in nonaqueous solvents.[9c] We have investigated the possibility of similar deintercalation of sodium in $NaM^VTi(PO_4)_3$ and $NaMV(PO_4)_3$. Deintercalation readily occurs, yielding $TaV^{IV}(PO_4)_3$ and $NbTi^{IV}(PO_4)_3$. Of the two, $NbTi(PO_4)_3$ has already been reported.[17] The XRD patterns (Figure 1) of these materials reveal that the NASICON framework is retained, albeit with a slight decrease in the a and c parameters (a = 8.514(5), c = 21.949(8) Å for $TaV^{IV}(PO_4)_3$). The infrared spectra of $NaTaV(PO_4)_3$ and its deintercalation product are shown in Figure 4. Both compounds show characteristic PO_4 vibrations of the NZP framework.[18] (1270–1070 cm^{-1}, $\nu_3(PO_4)$; 1010–900 cm^{-1},

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$\nu_1(PO_4)$; 670−640 cm^{-1}, $\nu_4(PO_4)$; 400−360 cm^{-1}, $\nu_2(PO_4)$). A weak band at 530 cm^{-1} in $NaTaV(PO_4)_3$, which is likely associated with $V^{III}O_6$ octahedra, is shifted to 570 cm^{-1} in the deintercalation product, consistent with the oxidation of V^{III} to V^{IV} on deintercalation.

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Additions and Corrections

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Enrique Colacio,* Jose M. Dominguez-Vera, Albert Escuer,* Raikko Kivekäs, and Antonio Romerosa: Heterodinuclear Copper(II)−Nickel(II) Complexes with Unusual Asymmetrical Bridges from a New and Versatile Dioxime Multidentate Ligand. Magneto−Structural Study.

Page 3920. In Table 6, some of the bond angles involving the Ni(II) atom were incorrectly reported. Corrected data are as follows:

O(14)−Ni−O(15A)	97.2(6)	O(14)−Ni−N(15)	73.1(2)
O(14)−Ni−N(18)	170.4(2)	O(14)−Ni−N(29)	97.9(2)
O(14)−Ni−N(25)	87.3(2)	O(14)−Ni−N(22)	88.1(2)
O(15A)−Ni−N(18)	73.6(6)	O(15A)−Ni−N(29)	87.0(7)
O(15A)−Ni−N(25)	174.8(6)	O(15A)−Ni−N(22)	98.2(6)
N(15)−Ni−N(18)	97.7(2)	N(15)−Ni−N(29)	88.0(3)
N(15)−Ni−N(25)	159.8(2)	N(15)−Ni−N(22)	99.6(3)
N(18)−Ni−N(29)	84.3(2)	N(18)−Ni−N(25)	102.0(2)
N(18)−Ni−N(22)	90.7(2)	N(22)−Ni−N(25)	84.5(2)
N(22)−Ni−N(29)	171.5(2)	N(25)−Ni−N(29)	89.7(2)

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