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New Titanium–Vanadium Phosphates of Nasicon and Langbeinite Structures, and Differences between the Two Structures toward Deintercalation of Alkali Metal[1]

K. Kasthuri Rangan and J. Gopalakrishnan[2]

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore—560 012, India

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Mixed metal phosphates of the general formula $A_xTiV^{III}(PO_4)_3$, where A = Na, K, or Ba and ($0 < x \leq 3$), have been synthesized. While the sodium phosphate, $Na_3TiV(PO_4)_3$, adopts the NASICON structure, the potassium compound, $K_2TiV(PO_4)_3$, crystallizes with the langbeinite structure. $BaTiV(PO_4)_3$ is dimorphic, adopting the NASICON structure at lower temperatures and the langbeinite structure at higher temperatures. $Ba_{1.5}V_2(PO_4)_3$ and $BaKV_2(PO_4)_3$, on the other hand, crystallize only with the langbeinite structure. Oxidative deintercalation of sodium from $Na_3TiV(PO_4)_3$ readily occurs, yielding $Na_xTiV(PO_4)_3$ ($x \sim 1.0$) and retaining the NASICON framework, while a similar deintercalation of potassium does not occur from the langbeinite $K_2TiV(PO_4)_3$, revealing a difference in reactivity between the two structures: NASICON, being a skeleton structure with an interconnected interstitial space, facilitates mobility of alkali metal ions through the crystal, while langbeinite, being a true cage structure, does not permit a similar mobility.

INTRODUCTION

Phosphates of the formula $A_xM_2(PO_4)_3$, consisting of a $M_2(PO_4)_3$ framework formed by corner-sharing MO_6 octahedra and PO_4 tetrahedra, crystallize mainly in the NASICON [$Na_3Zr_2PSi_2O_{12}$] and the langbeinite [$K_2Mg_2(SO_4)_3$] structures (Fig. 1). While the $M_2(XO_4)_3$ (X = P, Si) framework of the NASICON structure provides an interconnected interstitial space through which charge-compensating A cations can diffuse, giving rise to fast-ion conductivity (1, 2), the langbeinite structure is a cage structure that accommodates large A cations in the cages (3). The structure adopted by a given $A_xM_2(PO_4)_3$ seems to depend on, among others, the size of the A cation and the value of x (4). Thus, while the sodium-containing phosphates $NaM_2^{IV}(PO_4)_3$ (5) and $Na_3M_2(PO_4)_3$ (6) adopt the NASICON structure, $K_2Ti_2(PO_4)_3$ and $K_2M^{III}M^{IV}(PO_4)_3$ phosphates crystallize with the langbeinite structure (7, 8). Interestingly, the NASICON framework is retained by $M^VM^{IV}(PO_4)_3$ (M^V = Sb, Nb, Ta; M^{IV} = Ti, Ge, Nb) without the A-site cations (9, 10). We have recently shown that the phosphate, $V_2(PO_4)_3$, with the NASICON framework can be prepared by redox deintercalation of sodium from $Na_3V_2(PO_4)_3$ (11).

In view of the importance of phosphates possessing skeletal structures in general (12) and the NASICON structure in particular (13, 14) toward ion exchange, fast-ion conduction, redox chemistry, and so on, we considered it important to synthesize new titanium–vanadium phosphates of the formula $A_xM_2(PO_4)_3$ (M = Ti and/or V), and investigate their structure and reactivity. We have been able to synthesize several titanium–vanadium phosphates of both NASICON and langbeinite structures depending on the nature of A-site cation. Furthermore, we have observed a difference in reactivity between the NASICON and langbeinite phosphates, $Na_3TiV(PO_4)_3$ and $K_2TiV(PO_4)_3$, toward redox deintercalation of alkali metal atoms. We report the results of these investigations in this paper.

EXPERIMENTAL

Phosphates of the formula $A_xTiV(PO_4)_3$ for A = Na, K, and/or Ba were prepared by the following method: A mixture of TiO_2, V_2O_5, $(NH_4)_2HPO_4$, and alkali/alkaline earth carbonate taken in the required proportion was first heated at 600°C for 24 hr to decompose the ammonium phosphate. The mixture was then ground and reduced in a flowing hydrogen (~15 ml/min) atmosphere at 900–950°C for 24 hr. For the sodium- and potassium-containing compounds, synthesis was carried out using starting compositions with $x = 2$ and 3. After the reduction, the products were washed with distilled water to

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[2] To whom correspondence should be addressed.

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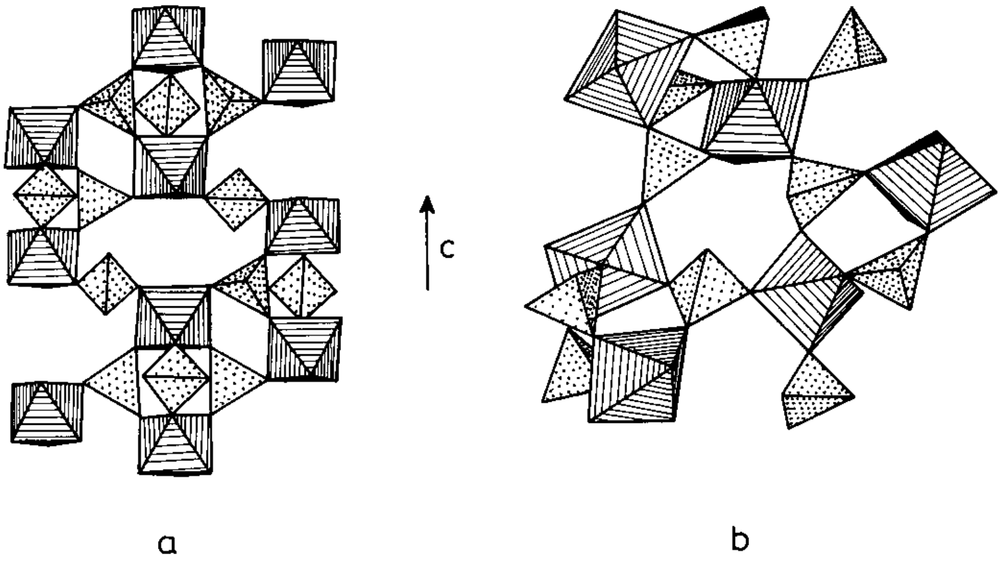

FIG. 1. $M_2(XO_4)_3$ frameworks of (a) NASICON and (b) langbeinite structures.

remove excess alkali, if any, and dried at 100°C in a vacuum oven. Deintercalation of alkali metal was investigated by passing chlorine through a suspension of the solid phosphate in $CHCl_3$. Oxidation states of titanium and vanadium (reducing power) in the products were determined by a redox potentiometric titration using Ce(IV) as an oxidizing agent. The solid phosphates were characterized by X-ray powder diffraction (JEOL JDX-8P X-ray powder diffractometer, CuK_α radiation) and magnetic susceptibility measurements down to 20 K (Lewis Coil Force magnetometer, model 2000, at 5 k G). Lattice parameters were derived from least-squares refinement of the powder diffraction data from single phases.

RESULTS AND DISCUSSION

We have prepared a number of titanium–vanadium phosphates of the formula $A_xTiV(PO_4)_3$ for A = Na, K, and/or Ba, by a novel method involving hydrogen reduction of a preheated mixture of the constituents containing TiO_2 and V_2O_5. Earlier, we successfully employed this method for the synthesis of $Na_3V_2(PO_4)_3$ (11). We list in Table 1 the compositions, lattice parameters, and other characteristics of the new phosphates synthesized. We see that while the sodium compound crystallizes with the NASICON structure (Fig. 2, Table 2) having the formula $Na_3Ti^{III}V^{III}(PO_4)_3$, where both titanium and vanadium are

TABLE 1

Composition, Color, and Lattice Parameters of Titanium–Vanadium Phosphates Possessing Nasicon/Langbeinite Structures

Compound	Color	Reducing power of the sample		Lattice parameters (Å)		Structure
		Found	Expected[a]	a	c	
$Na_3Ti^{III}V^{III}(PO_4)_3$	Brown	3.00 ± 0.02	3.00	8.759(3)	21.699(4)	NASICON
$Na_xTi^{IV}V^{IV}(PO_4)_3$[b] ($x \sim 1.00$)	Green	0.96 ± 0.02	1.00	8.460(5)	21.619(8)	NASICON
$K_2Ti^{IV}V^{III}(PO_4)_3$	Green	2.10 ± 0.03	2.00	9.855(3)	—	Langbeinite
$BaTi^{IV}V^{III}(PO_4)_3$[c]	Light yellow	2.10 ± 0.02	2.00	8.336(6)	23.370(7)	NASICON
$BaTi^{IV}V^{III}(PO_4)_3$[d]	Dark gray	2.10 ± 0.03	2.00	9.922(2)	—	Langbeinite
$Ba_{1.5}V^{III}_2(PO_4)_3$	Gray	3.96 ± 0.02	4.00	9.884(3)	—	Langbeinite
$BaKV^{III}_2(PO_4)_3$	Greenish yellow	3.94 ± 0.02	4.00	9.873(2)	—	Langbeinite

[a] Corresponds to the number of electrons per formula unit required for the oxidation of titanium and vanadium.

[b] Prepared by deintercalation.

[c] Prepared at 800°C.

[d] Prepared at 950°C.

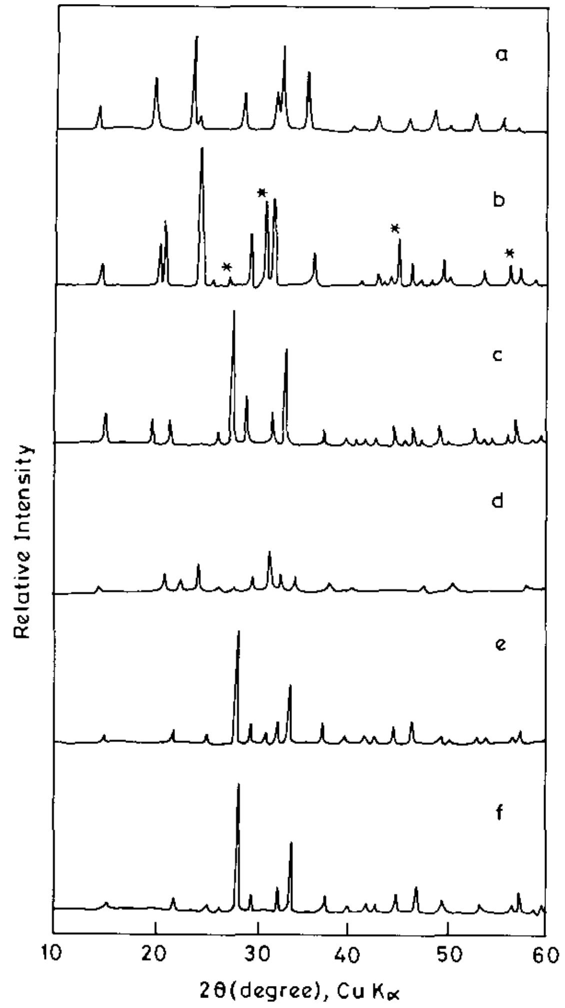

FIG. 2. X-ray powder diffraction patterns of (a) $Na_3TiV(PO_4)_3$, (b) $Na_xTiV(PO_4)_3$ ($x \sim 1.0$), (c) $K_2TiV(PO_4)_3$, (d) $BaTiV(PO_4)_3$-NASICON, (e) $BaTiV(PO_4)_3$-langbeinite, and (f) $BaKV_2(PO_4)_3$. (Asterisks in (b) denote peaks due to deintercalated NaCl.)

TABLE 2

X-Ray Powder Diffraction Data for $Na_3TiV(PO_4)_3$

h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}[a]
0	1	2	6.215	6.217	28	31
1	0	4	4.407	4.413	56	65
1	1	0		4.380		37
1	1	3	3.746	3.746	100	100
0	0	6	3.619	3.617	20	26
0	2	4	3.105	3.108	48	72
2	1	1	2.840	2.842	35	29
1	1	6	2.788	2.789	89	83
3	0	0	2.529	2.529	62	76
1	3	1	2.094	2.094	18	12
1	2	8	1.969	1.970	14	17
2	2	6	1.872	1.873	25	29
0	0	12	1.814	1.808	7	12
1	3	7	1.740	1.741	25	29
3	1	8	1.661	1.662	18	15
2	2	9	1.620	1.621	6	4

[a] Calculated by LAZY PULVERIX program using the position parameters of $Na_3Cr_2(PO_4)_3$ (18).

present in the III oxidation state, the potassium compound adopts the langbeinite structure (Fig. 2) having the composition $K_2Ti^{IV}V^{III}(PO_4)_3$. Both the chemical analysis (Table 1) and magnetic susceptibility measurements support the formulation. The effective magnetic moment, μ_{eff}, of the sodium compound obtained from the Curie–Weiss plot of the inverse molar susceptibility, χ_M^{-1}, versus temperature, T (Fig. 3), is 3.33 BM., while the value expected for the formula $Na_3Ti^{III}V^{III}(PO_4)_3$ with $Ti^{III}: 3d^1$ and $V^{III}: 3d^2$ configuration is 3.31 BM. On the other hand, the potassium compound has the formula $K_2Ti^{IV}V^{III}(PO_4)_3$, which is consistent with oxidation state analysis (Table 1) and magnetic susceptibility data (Fig. 3). The μ_{eff} of 2.95 BM obtained for this compound is close to the value (2.83 BM) expected for $V^{III}: 3d^2$ electronic configuration. The change in composition and structure of the titanium–vanadium phosphates as we change the A cation from Na to K is significant. Similar results, viz., the sodium compound adopting a NASICON structure and the potassium compound adopting a langbeinite structure, have been reported for $Na_3Ti_2(PO_4)_3$ (6) and $K_{2-x}Ti_2(PO_4)_3$ (7).

We have prepared a new phosphate, $BaTi^{IV}V^{III}(PO_4)_3$, that is dimorphic. When the synthesis of this composition is carried out at 800°C, we see predominantly a NASICON phase (Table 3) that transforms to the langbeinite structure at higher temperatures (950°C) (Table 4). We could quench the NASICON phase for this composition as seen from the powder diffraction pattern (Fig. 2). Since langbeinite is a more dense structure than NASICON, formation of the NASICON structure at lower temperatures, and of

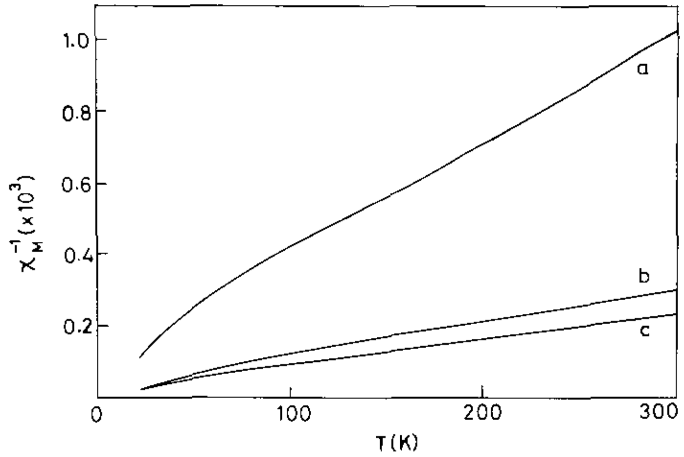

FIG. 3. Temperature dependence of the magnetic susceptibility for (a) $Na_xTiV(PO_4)_3$ ($x \sim 1.0$), (b) $K_2TiV(PO_4)_3$, and (c) $Na_3TiV(PO_4)_3$.

TABLE 3
X-Ray Powder Diffraction Data for NASICON–$BaTiV(PO_4)_3$

h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
0	1	2	6.151	6.142	4
1	1	0	4.171	4.168	52
0	0	6	3.892	3.895	38
1	1	3	3.678	3.675	61
0	2	4	3.074	3.071	35
1	1	6	2.849	2.846	100
0	1	8	2.710	2.708	20
1	2	2	2.652	2.657	18
3	0	0	2.408	2.407	15
2	0	8	2.270	2.271	3
0	0	12	1.947	1.947	4
2	2	6	1.838	1.838	10

the langbeinite structure at higher temperatures would indicate that the NASICON phase is metastable for this composition. The densities of NASICON and langbeinite forms of $BaTiV(PO_4)_3$ calculated from the unit cell parameters are, respectively, 3.20 and 3.54 g/cm^3. A similar dimorphism has been reported for $K_2GaM(PO_4)_3$ (M = Zr, Hf, and Sn) (8).

We could prepare two other phosphates, $Ba_{1.5}V_2(PO_4)_3$ and $BaKV_2(PO_4)_3$, containing V(III) by the hydrogen-reduction method. Both phosphates crystallize with the langbeinite structure (Fig. 2 and Table 5). We could not, however, synthesize the potassium analog, $K_2V_2(PO_4)_3$, by our method. While the langbeinite phosphate of the formula $BaKM^{III}(PO_4)_3$ for M = Fe and Cr are known (15), no other trivalent method phosphate similar to $Ba_{1.5}V_2(PO_4)_3$ has been reported. Two different (nine-coordinated) sites for the large A atoms are available in the langbeinite structure, space group $P2_13$, of which one site with longer A–O distances is preferentially occupied (7). The other site could be partially or fully occupied, accounting for the formation of nonstoichiometric langbeinites such as $K_{2-x}Ti_2(PO_4)_3$ for $0 \leq x \leq 0.5$ (9, 16). The composition $Ba_{1.5}V_2(PO_4)_3$ would therefore correspond to the upper limit of the above series with x = 0.5 and suggest the possibility of the series $Ba_{1+y}V_2(PO_4)_3$ with mixed-valent vanadium. Significantly, the barium–molybdenum phosphate, $BaMo^{III}Mo^{IV}(PO_4)_3$, has been reported to crystallize with the NASICON structure (17).

TABLE 4
X-Ray Powder Diffraction Data for Langbeinite–$BaTiV(PO_4)_3$

h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
1	1	1	5.735	5.729	6
2	1	1	4.049	4.051	10
2	2	0	3.507	3.508	9
3	1	0	3.137	3.138	100
3	1	1	2.989	2.992	20
2	2	2	2.859	2.864	11
3	2	0	2.751	2.752	20
3	2	1	2.652	2.652	52
4	1	0	2.408	2.406	18
3	3	1	2.276	2.276	7
4	2	1	2.163	2.165	6
3	3	2	2.115	2.115	8
4	2	2	2.025	2.025	15
5	1	0	1.947	1.946	20
5	2	0	1.841	1.842	6
5	2	1	1.811	1.812	2
5	2	2	1.726	1.727	4
5	3	0	1.702	1.702	4
6	1	0	1.631	1.631	5
6	1	1	1.610	1.610	12
6	2	1	1.550	1.550	5

We recently reported that sodium could be oxidatively deintercalated from the NASICON phosphate, $Na_3V_2(PO_4)_3$, using chlorine as an oxidizing agent (11). We

TABLE 5
X-Ray Powder Diffraction Data for $BaKV_2(PO_4)_3$ and $Ba_{1.5}V_2(PO_4)_3$ Langbeinites

			$BaKV_2(PO_4)_3$				$Ba_{1.5}V_2(PO_4)_3$			
h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}[a]	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}[a]
1	1	1	5.598	5.700	5	8	5.698	5.707	4	4
2	1	0	—	4.415	—	3	4.428	4.420	3	1
2	1	1	4.031	4.031	12	12	4.031	4.035	10	9
2	2	0	3.486	3.491	5	3	3.500	3.495	11	10
2	2	1	3.290	3.291	2	2	3.296	3.295	3	12
3	1	0	3.121	3.122	100	100	3.128	3.126	100	100
3	1	1	2.974	2.977	13	18	2.979	2.980	22	29
3	2	0	2.739	2.738	18	24	2.743	2.742	13	27
3	2	1	2.637	2.639	55	63	2.640	2.642	49	63
4	1	0	2.392	2.395	13	8	2.395	2.397	12	9
3	3	1	2.265	2.265	6	8	2.268	2.268	7	9
4	2	0	—	2.208	—	1	2.209	2.210	4	2
4	2	1	2.154	2.155	6	7	2.156	2.157	5	9
3	3	2	2.103	2.105	7	8	2.108	2.107	8	9
4	2	2	2.015	2.015	16	24	2.017	2.018	18	24
4	3	0	—	1.975	—	—	1.975	1.977	2	1
5	1	1	—	1.900	—	—	1.901	1.902	18	23
4	3	2	1.833	1.833	10	8	1.834	1.836	7	8
5	2	1	—	1.803	—	—	1.804	1.805	2	1
4	4	1	1.719	1.719	7	9	1.722	1.721	5	8
5	3	0	—	1.693	—	—	1.695	1.695	3	3
5	3	1	—	1.669	—	—	1.672	1.671	1	2
6	0	0	—	1.646	—	—	1.647	1.647	2	2
6	1	0	1.623	1.623	6	7	1.623	1.625	3	3
6	1	1	1.603	1.602	18	10	1.605	1.603	15	10
6	2	0	1.562	1.561	3	3	1.564	1.563	2	4
6	2	1	1.542	1.542	7	10	1.544	1.544	7	5

[a] Calculated by LAZY PULVERIX program using the position parameters of $K_2Mg_2(SO_4)_3$ (3).

TABLE 6
X-Ray Powder Diffraction Data for $Na_xTiV(PO_4)_3$ ($x \sim 1.0$)

h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}[a]
0	1	2	6.066	6.065	20	25
1	0	4	4.343	4.349	29	35
1	1	0	4.220	4.230	48	50
1	1	3	3.641	3.648	100	100
2	0	2	3.466	3.469	4	7
0	2	4	3.033	3.032	29	34
2	1	1	2.747	2.747	62	15
1	1	6		2.743		42
3	0	0	2.442	2.442	21	27
2	0	8	2.178	2.175	3	3
1	1	9	2.090	2.089	7	5
2	1	7	2.058	2.062	3	2
1	3	1	2.023	2.023	5	3
1	2	8	1.935	1.934	12	10
1	3	4	1.901	1.902	4	2
0	2	10	1.863	1.862	2	3
2	2	6	1.824	1.824	14	15
0	4	2	1.806	1.806	5	7
3	2	1	1.675	1.676	2	1
4	1	0	1.598	1.599	10	10
4	1	3	1.562	1.561	4	2

[a] Calculated by LAZY PULVERIX program using the position parameters of $NaTi_2(PO_4)_3$ (19).

investigated similar deintercalation of alkali metals from the titanium–vanadium phosphates. We could readily deintercalate considerable amounts of sodium from $Na_3TiV(PO_4)_3$ using chlorine as the oxidizing agent in $CHCl_3$, according to the reaction

$$Na_3TiV(PO_4)_3 + y/2Cl_2 \rightarrow Na_{3-y}TiV(PO_4)_3 + yNaCl.$$

We could remove about two atoms of sodium, readily yielding $NaTiV(PO_4)_3$, which retains the parent NASICON structure (Table 6 and Fig. 2). In going from $Na_3TiV(PO_4)_3$ to $NaTiV(PO_4)_3$, there is a distinct decrease in the lattice parameters, which is consistent with the oxidation of vanadium and titanium from III to IV state. Chemical analysis (Table 1) and magnetic susceptibility (Fig. 3) of the deintercalated product are consistent with the formula, $NaTi^{IV}V^{IV}(PO_4)_3$. The μ_{eff} value of 1.65 BM obtained for the deintercalated phase is close to the value (1.73 BM) expected for $V^{IV}: 3d^1$. We could not obtain a completely deintercalated phase, $TiV(PO_4)_3$, even after prolonged reaction with chlorine. This is unlike the case with $Na_3V_2(PO_4)_3$, where we could readily obtain $V_2(PO_4)_3$ by this method (11).

More interestingly, we could not deintercalate potassium from $K_2TiV(PO_4)_3$ under similar conditions. Even prolonged reaction (3 days) did not result in a significant deintercalation. The lack of deintercalation reactivity of this phase in contrast to the facile deintercalation of sodium from $Na_3TiV(PO_4)_3$ is likely related to the structure. Langbeinite, being a true cage structure with small windows connecting cages (3, 7), most probably does not permit a mobility of potassium ions in $K_2TiV(PO_4)_3$, while NASICON, being a skeletal structure with an interconnected interstitial space (1), permits facile mobility of sodium ions through the crystal, resulting in deintercalation under oxidative conditions.

In summary, we have synthesized a number of titanium–vanadium phosphates of the formula $A_xTiV(PO_4)_3$ for A = Na, K, and/or Ba, which crystallize with the NASICON (A = Na) and langbeinite (A = K, Ba) structures. $BaTiV(PO_4)_3$ is dimorphic, forming in the NASICON structure at lower temperatures and the langbeinite structure at higher temperatures. Oxidative deintercalation has revealed an interesting difference in the reactivity between NASICON–$Na_3TiV(PO_4)_3$ and langbeinite–$K_2TiV(PO_4)_3$. Sodium could be topochemically deintercalated readily from $Na_3TiV(PO_4)_3$, giving $Na_x TiV(PO_4)_3$ ($x \sim 1.0$); a similar deintercalation of potassium from $K_2TiV(PO_4)_3$ does not occur.

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