Soft-chemical routes to synthesis of solid oxide materials[†]

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Abstract. We describe three different families of metal oxides, viz., (i) protonated layered perovskites, (ii) framework phosphates of NASICON and KTiOPO$_4$ (KTP) structures and (iii) layered and three-dimensional oxides in the H–V–W–O system, synthesized by 'soft-chemical' routes involving respectively ion-exchange, redox deintercalation and acid-leaching from appropriate parent oxides. Oxides of the first family, H$_y$A$_2$B$_3$O$_{10}$(A = La/Ca; B = Ti/Nb), exhibit variable Bronsted acidity and intercalation behaviour that depend on the interlayer structure. V$_2$(PO$_4$)$_3$ prepared by oxidative deintercalation from Na$_3$V$_2$(PO$_4$)$_3$ is a new host material exhibiting reductive insertion of lithium/hydrogen, while K$_{0.5}$Nb$_{0.5}$M$_{0.5}$OPO$_4$ (M = Ti, V) are novel KTP-like materials exhibiting second harmonic generation of 1064 nm radiation. H$_x$V$_x$W$_{1-x}$O$_3$ for $x = 0.125$ and 0.33 possessing α-MoO$_3$ and hexagonal WO$_3$ structures, prepared by acid-leaching of LiVWO$_6$, represent functionalized oxide materials exhibiting redox and acid–base intercalation reactivity.

Keywords. Synthesis of oxide materials; ion-exchange; intercalation/deintercalation; acid-leaching.

1. Introduction

Synthesizing inorganic solids, especially to specification, is a challenging task because, unlike organic/molecular compounds, the factors that determine the formation, stability, structure and properties of inorganic solids are poorly understood at present (DiSalvo 1990). Accordingly, there is a tremendous current interest towards developing novel routes to solid synthesis, based on chemical principles (Gopalakrishnan 1984; Rao 1993). Such chemical methods which enable syntheses of solids at low temperatures have an added advantage in that the stringent requirement of thermodynamic phase stability can be avoided, enabling stabilization of metastable phases under ambient conditions (Stein *et al* 1993). We have been pursuing soft-chemical/low-temperature synthesis of metastable phases of perovskite, ReO$_3$, rocksalt and rutile-related structures for sometime (Rao and Gopalakrishnan 1987; Gopalakrishnan 1993). In this paper, we describe three different families of metal oxides synthesized by us in recent times using soft-chemical routes. They are (i) protonated layered perovskites, (ii) framework phosphates belonging to NASICON and KTiOPO$_4$ (KTP) structures and (iii) layered and three-dimensional oxides in the H–V–W–O system synthesized respectively by ion-exchange, redox deintercalation and acid-leaching of appropriate

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parent oxides. The new oxides, which could not have been synthesized by conventional high-temperature routes, exhibit interesting structure–property relationships of relevance to the design of solid materials for special applications.

2.   Experimental

Protonated layered perovskites, $H_yA_2B_3O_{10}(A = La/Ca; B = Ti/Nb)$, were prepared from the parent alkali metal analogues, $(K/Rb)_yA_2B_3O_{10}$, by ion-exchange in aqueous HNO_3. Intercalation of organic bases was investigated by refluxing the host materials with a 10% solution of the base in *n*-heptane around 90°C for several days. Deintercalation of alkali metal from $Na_3V_2(PO_4)_3$, $A'_xTiV(PO_4)_3$ $(A' = Na, K)$ and $KM_{0.5}M'_{0.5}OPO_4(M = Nb, Ta; M' = Ti, V)$ was investigated by passing chlorine through a suspension of the solid phosphate in $CHCl_3$. Acid-leaching of $LiVWO_6$ was carried out by treating the solid with varying concentrations of HNO_3/HCl both over a water bath and under reflux. Oxidation state of the transition metal, where essential, was determined by potentiometric titration using Ce(IV) as an oxidizing agent. Solid products were characterized by EDX, X-ray powder diffraction and thermogravimetry. Second harmonic generation (SHG) intensities of KTP-related powder materials were measured using a pulsed Q-switched Nd:YAG laser.

3.   Results and discussion

We employed three different soft-chemical routes, viz., *ion-exchange* in aqueous acids, oxidative *deintercalation* of alkali metal using chlorine in nonaqueous solvents and *acid-leaching* in aqueous acids to prepare the following series of layered and three-dimensional oxide materials.

3.1   *Protonated layered perovskites*

There are two series of layered perovskites, one is the Ruddlesden–Popper series (Ruddlesden and Popper 1957, 1958) of the general formula, $A'_2[A_{n-1}B_nO_{3n+1}]$, of which $Sr_4Ti_3O_{10}$ is a typical $n = 3$ member and the other is the Dion–Jacobson series (Dion *et al* 1981; Jacobson *et al* 1985) of the general formula, $A'[A_{n-1}B_nO_{3n+1}]$, of which $CsCa_2Nb_3O_{10}$ (Dion *et al* 1984) and $KLaNb_2O_7$ (Gopalakrishnan *et al* 1987) are typical $n = 3$ and $n = 2$ members. A few years back, we prepared a new series of titanates, $A'_2[Ln_2Ti_3O_{10}]$ where $A = K$, Rb and $Ln = La$ or rare earth (Gopalakrishnan and Bhat 1987), which are isostructural with $Sr_4Ti_3O_{10}$. Members of both the series of oxides undergo facile ion-exchange in aqueous acids to yield protonated derivatives such as $H_2La_2Ti_3O_{10}$ and $HCa_2Nb_3O_{10}$ retaining the parent layered perovskite structure. Of these, protonated oxides of the latter type are strong Bronsted acids intercalating a wide variety of organic bases (Jacobson *et al* 1987) including pyridine $(pK_a = 5.3)$ and aniline $(pK_a = 4.6)$, while members of the former series do not show such an obvious acidic property.

In an attempt to understand the relation between acidic property and structure of the layered perovskite oxides, we prepared protonated oxides of the general formula $H_yA_2B_3O_{10}-H_{1-x}La_xCa_{2-x}Nb_3O_{10} (0 < x < 1)$, $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10} (0 < x < 2)$

Table 1. Composition and lattice parameters of representative protonated layered perovskites, $H_yA_2B_3O_{10}$.

Composition	Lattice parameters (Å)		Structure type
	a	*c*	
$HCa_2Nb_3O_{10}$	3·850(6)	14·379(3)	$CsCa_2Nb_3O_{10}$
$H_{0·5}La_{0·5}Ca_{1·5}Nb_3O_{10}$	3·881(5)	14·39(1)	$CsCa_2Nb_3O_{10}$
$HCaLaNb_2TiO_{10}$	3·855(6)	14·41(6)	$CsCa_2Nb_3O_{10}$
$HCa_{0·5}La_{1·5}Nb_{1·5}Ti_{1·5}O_{10}$	3·835(4)	14·39(6)	$CsCa_2Nb_3O_{10}$
$HLa_2Ti_2NbO_{10}$*	3·832(5)	14·52(5)	$CsCa_2Nb_3O_{10}$
$H_{1·5}La_2Ti_{2·5}Nb_{0·5}O_{10}$	3·832(6)	27·51(6)	$Sr_4Ti_3O_{10}$
$H_2La_2Ti_3O_{10}$	3·824(5)	27·40(6)	$Sr_4Ti_3O_{10}$
$H_2Ca_2Nb_2TiO_{10}$	3·844(6)	28·67(7)	$Sr_4Ti_3O_{10}$

*Anhydrous phase is unstable

and $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ ($0 \leqslant x \leqslant 1$), starting from the corresponding potassium or rubidium compounds by ion-exchange in aqueous HNO_3. In table 1 we list the compositions and lattice parameters and, in figure 1, the X-ray powder diffraction (XRD) patterns of a few representative members. These show that $H_yA_2B_3O_{10}$ oxides adopt two different structures: for $y \leqslant 1$ in $H_yA_2B_3O_{10}$($H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ and $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$), the structure is primitive tetragonal, similar to $CsCa_2Nb_3O_{10}$ and $HCa_2Nb_3O_{10}$ (Jacobson *et al* 1986), and for $1 < y \leqslant 2$ ($H_{2-x}La_2 Ti_{3-x}Nb_xO_{10}$), on the other hand, the structure is body-centred tetragonal (I4/mmm) similar to the structures of $Sr_4Ti_3O_{10}$ and $K_2La_2Ti_3O_{10}$. The difference between the two structures arises essentially from the stacking of the triple-perovskite $[A_2B_3O_{10}]$ layers in the *c*-direction. While the adjacent perovskite slabs are displaced by $(a + b/2)$ translation giving a body-centred tetragonal cell for $Sr_4Ti_3O_{10}$, there is no such displacement in the $CsCa_2Nb_3O_{10}$ structure (figure 2).

The difference in the structure of $H_yA_2B_3O_{10}$ oxides appears to have a profound influence on the Bronsted acidity, as revealed by intercalation of *n*-alkylamines and other bases. While the members of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ exhibit Bronsted acidity just as the parent $HCa_2Nb_3O_{10}$ (Jacobson *et al* 1987), intercalating several organic bases including pyridine (table 2), $H_2La_2Ti_3O_{10}$ and $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ for $0 < x \leqslant 0·75$ do not intercalate even strong bases such as piperidine ($pK_a = 11·2$) and guanidine ($pK_a = 12·5$) (Uma *et al* 1993). The lack of Bronsted acidity for the protons of $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$($0 \leqslant x \leqslant 0·75$) seems to be due to the special interlayer structure arising from the displacement of perovskite slabs in the $[1\,1\,0]$ direction (figure 2). It is significant that even the isostructural $H_2Ca_2Nb_2TiO_{10}$ (table 1) is exactly similar to $H_2La_2Ti_3O_{10}$ in its acidic behaviour, revealing that the lack of Bronsted acidity of these solids is structural in origin rather than due to the intrinsic acidity of the protons attached to TiO_6/NbO_6 octahedra.

Recently, we prepared anion-deficient layered perovskites of the formula, $HCa_2 Nb_{3-x}M_xO_{10-x}$(M = Fe, Al) for $0 < x \leqslant 1·0$, possessing structure and properties similar to the parent $HCa_2Nb_3O_{10}$. Intercalation experiments suggest that while the oxygen vacancies in the perovskite slabs of the as-prepared materials are not ordered, the vacancies do seem to order in $ACa_2Nb_2AlO_9$(A = Cs, H) on long annealing of
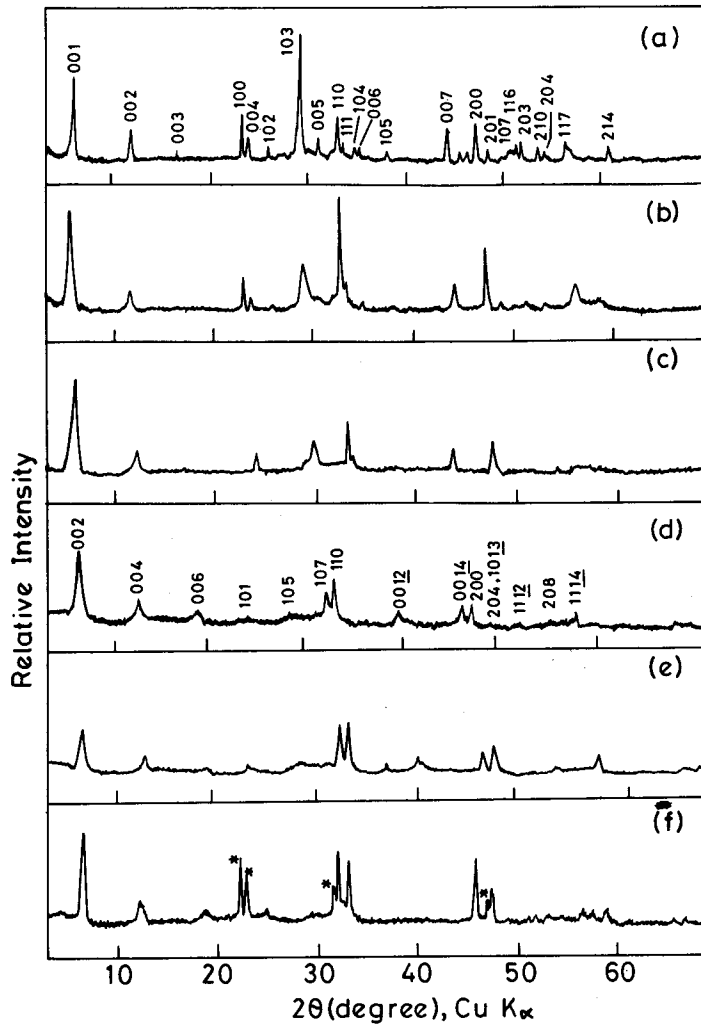
Figure 1. X-ray powder diffraction patterns of (a) $H_{0.5}La_{0.5}Ca_{1.5}Nb_3O_{10}$, (b) $HCaLaNb_2$ TiO_{10}, (c) $HLa_2NbTi_2O_{10}$, (d) $H_{1.5}La_2Ti_{2.5}Nb_{0.5}O_{10}$, (e) $H_2La_2Ti_3O_{10}$ and (f) H_2Ca_2 Nb_2TiO_{10}. In (f), asterisks denote impurity phase.

the parent at $1000°C$, giving rise to octahedral (NbO_6)–tetrahedral (AlO_4)–octahedral (NbO_6) layer sequence in the triple perovskite slabs. This layer sequence is reminiscent of the brownmillerite structure (Colville and Geller 1971). Accordingly, $ACa_2Nb_2AlO_9$ could be regarded the first examples of layered brownmillerites.

3.2 *Framework phosphates*

Phosphates of the formula, $A_xM_2(PO_4)_3$, consisting of $M_2(PO_4)_3$ framework formed by corner-sharing of MO_6 octahedra and PO_4 tetrahedra crystallize mainly in the NASICON $[Na_3Zr_2PSi_2O_{12}]$ (Hong 1976) and the langbeinite $[K_2Mg_2 (SO_4)_3]$ (Zemann and Zemann 1957) (figure 3) structures. The structure adopted by a given
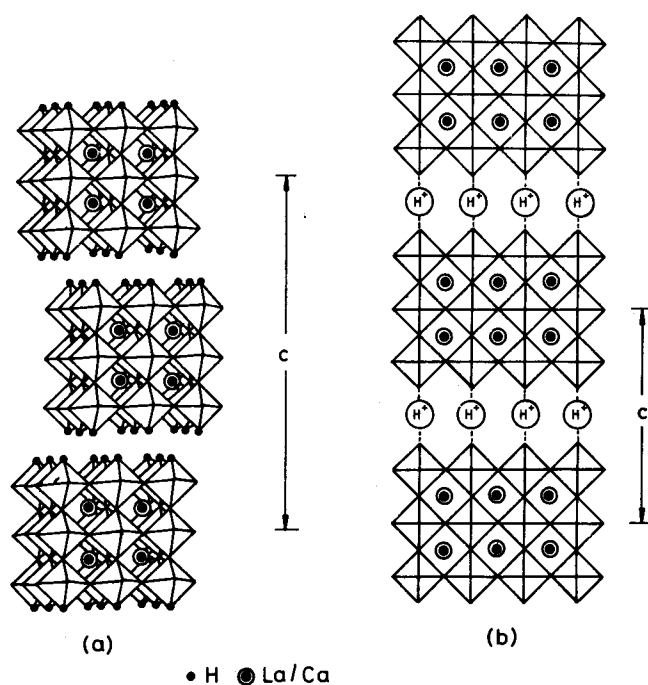
Figure 2. Idealized structures of (a) $H_2La_2Ti_3O_{10}$ and (b) $HCa_2Nb_3O_{10}$.

Table 2. Composition and lattice parameters of representative intercalation compounds of $H_yA_2B_3O_{10}$.

Host	Guest amine	Amine content	Lattice parameters (Å)	
			a	c
$H_{0.50}La_{0.50}Ca_{1.50}Nb_3O_{10}$	n-Decylamine	0·50	3·885(5)	34·00(1)
$H_{0.75}La_{0.25}Ca_{1.75}Nb_3O_{10}$	n-Decylamine	0·75	3·880(5)	34·28(1)
$HCa_2Nb_3O_{10}$	n-Decylamine	0·95	3·852(4)	34·57(7)
$HCa_2Nb_3O_{10}$	Aniline	0·90	3·871(5)	25·39(6)
$HCaLaNb_2TiO_{10}$	n-Decylamine	0·99	3·854(5)	34·73(6)
$HCaLaNb_2TiO_{10}$*	Piperidine	0·60	3·868(5)	23·69(5)
$HCaLaNb_2TiO_{10}$	Pyridine	0·60	3·858(4)	18·93(2)
$HCa_{0.50}La_{1.50}Nb_{1.50}Ti_{1.50}O_{10}$	n-Decylamine	0·48	3·848(7)	35·36(6)
$HLa_2Ti_2NbO_{10}$*	Piperidine	0·60	3·845(7)	23·86(5)
$HLa_2Ti_2NbO_{10}$*	Guanidine	0·50	3·850(2)	15·71(2)

*Amine compounds are hydrated

$A_xM_2(PO_4)_3$ depends on, among others, the size of the A cation and the value of x. Interestingly, the NASICON framework is stable even without the A cation, e.g. $Nb_2(PO_4)_3$ (Leclaire *et al* 1989).

We prepared several transition metal phosphates of the formula, $A_xM_2(PO_4)_3$ for A = Na or K and M = Ti and/or V, by a novel method involving hydrogen reduction
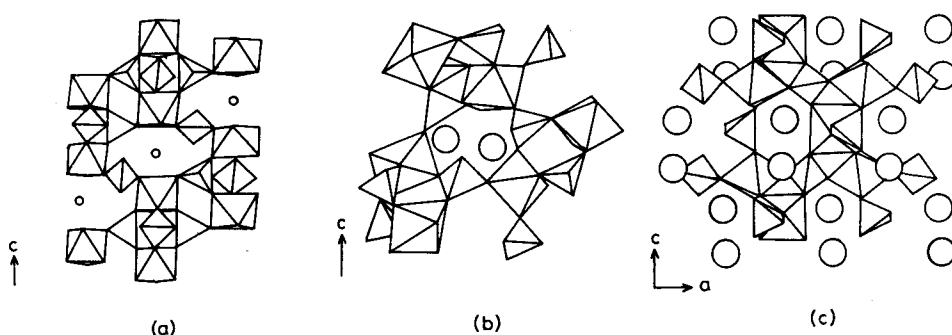
Figure 3. Framework structures of (a) NASICON, (b) langbeinite and (c) $KTiOPO_4$.

Table 3. Composition, colour and lattice parameters of $A_xM_2(PO_4)_3$.

Composition	Colour	Reducing power of the sample		Lattice parameters (Å)		Structure type
		Found	Calcd.	a	c	
$Na_3V_2^{III}(PO_4)_3$	Green	3·99	4·00	8·68(2)	22·71(2)	NASICON
$V^{IV}V^V(PO_4)_3$	Brown	0·96	1·00	8·52(3)	22·02(4)	NASICON
$Li_3V_2^{III}(PO_4)_3$	Green	3·95	4·00	8·31(2)	22·50(2)	NASICON
$H_3V_2^{III}(PO_4)_3$	Greenish-black	3·96	4·00	8·57(3)	22·48(3)	NASICON
$Na_3Ti^{III}V^{III}(PO_4)_3$	Brown	3·00	3·00	8·759(3)	21·699(4)	NASICON
$NaTi^{IV}V^{IV}(PO_4)_3$	Green	0·96	1·00	8·460(5)	21·619(8)	NASICON
$K_2Ti^{IV}V^{III}(PO_4)_3$	Green	2·10	2·00	9·855(3)	—	Langbeinite
$Ba_{1·5}V_2^{III}(PO_4)_3$	Gray	3·96	4·00	9·884(3)	—	Langbeinite
$BaKV_2^{III}(PO_4)_3$	Greenish-yellow	3·94	4·00	9·873(2)	—	Langbeinite

of á preheated mixture of the constituents containing TiO_2/V_2O_5. We list, in table 3, the composition and lattice parameters and, in figure 4, the powder diffraction patterns of some of the new phosphates synthesized by us. We see that the sodium compounds, $Na_3V_2^{III}(PO_4)_3$ and $Na_3Ti^{III}V^{III}(PO_4)_3$, crystallize with the NASICON structure, while the potassium compound $K_2Ti^{IV}V^{III}(PO_4)_3$ adopts the langbeinite structure.

We anticipated that it would be possible to deintercalate sodium from the NASICON phosphates for the following reasons: It is known that sodium ions have a high mobility in the NASICON framework giving rise to fast sodium ion conductivity (Goodenough *et al* 1976). The presence of titanium and vanadium in the III oxidation state in $Na_3V_2(PO_4)_3$ and $Na_3TiV(PO_4)_3$ would permit oxidative deintercalation of sodium. Indeed we could deintercalate sodium completely from $Na_3V_2(PO_4)_3$ using Cl_2 in $CHCl_3$. The product of deintercalation is the new phosphate $V_2(PO_4)_3$, the reaction being
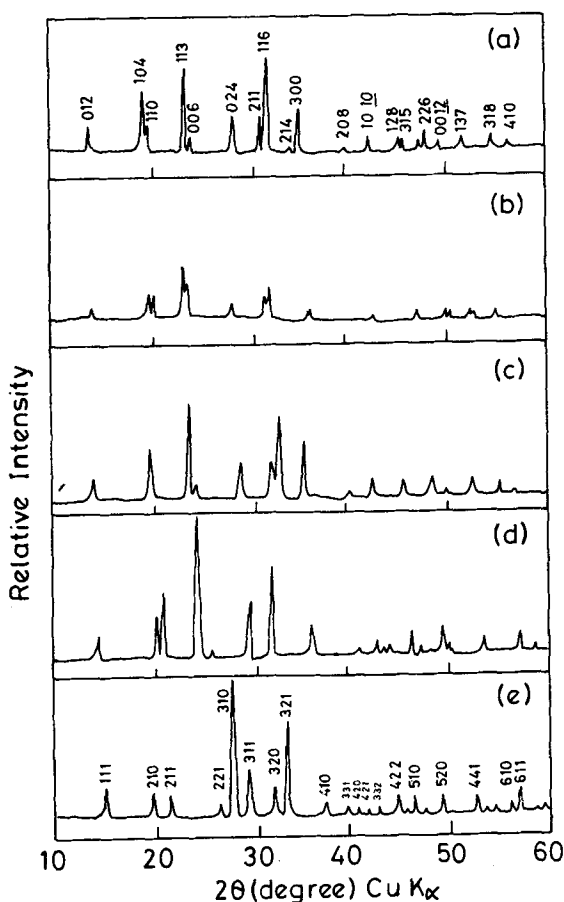
$$Na_3V_2(PO_4)_3 + \tfrac{3}{2}Cl_2 \rightarrow V^VV^{IV}(PO_4)_3 + 3\,NaCl.$$
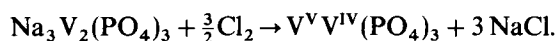
Figure 4. X-ray powder diffraction patterns of (a) $Na_3V_2(PO_4)_3$, (b) $V_2(PO_4)_3$, (c) Na_3TiV $(PO_4)_3$, (d) $NaTiV(PO_4)_3$ and (e) $K_2TiV(PO_4)_3$.

$V_2(PO_4)_3$ retains the NASICON framework of the parent $Na_3V_2(PO_4)_3$, showing that the deintercalation is a topochemical reaction. It should be mentioned that, unlike $Nb_2(PO_4)_3$ which could be prepared by a direct solid state reaction (Leclaire *et al* 1989), $V_2(PO_4)_3$ could not be prepared by a direct method. $V_2(PO_4)_3$, a mixed-valent phosphate having vanadium in the V and IV states in an 'empty' NASICON framework, is an excellent host material for reductive insertion of electropositive species such as hydrogen and lithium. In table 3, we list the characteristics of $Li_3V_2(PO_4)_3$ and $H_3V_2(PO_4)_3$ prepared by soft-chemical means starting from $V_2(PO_4)_3$ (Gopalakrishnan and Rangan 1992).

Interestingly, a similar deintercalation of sodium from $Na_3TiV(PO_4)_3$ by chlorine in $CHCl_3$ proceeds to the extent of removal of two-thirds of the sodium atoms giving $NaTiV(PO_4)_3$. Chemical analysis and magnetic susceptibility establish the formula of the deintercalation product to be $NaTi^{IV}V^{IV}(PO_4)_3$.

Most importantly, we could not deintercalate potassium from the langbeinite $K_2TiV(PO_4)_3$ under similar conditions. Even prolonged reaction with chlorine did not result in a significant deintercalation. The lack of deintercalation reactivity of

this phase in contrast to the facile deintercalation of sodium from $Na_3V_2(PO_4)_3$ and $Na_3TiV(PO_4)_3$ is presumably related to the structure. Langbeinite being a true cage structure with small windows connecting the cages does not permit mobility of potassium ions through the $K_2TiV(PO_4)_3$ framework, while NASICON being a skeletal structure with an interconnected interstitial space permits facile mobility of sodium ions through the framework resulting in deintercalation, provided appropriate transition metal atoms such as Ti(III) and V(III), which can undergo oxidation, is incorporated in the framework.

$KTiOPO_4$(KTP) is another framework phosphate containing one-dimensional channels parallel to [0 0 1] where the potassium atoms reside (figure 3) (Tordjman et al 1974). Since it is known that this structure also allows mobility of potassium ions through the channels resulting in ion-exchange and ionic conductivity (Jarman 1989), we expected that it would be possible to oxidatively deintercalate potassium from this structure by incorporating appropriate transition metal atom in the framework. More importantly, since KTP is an unique nonlinear optical (NLO)
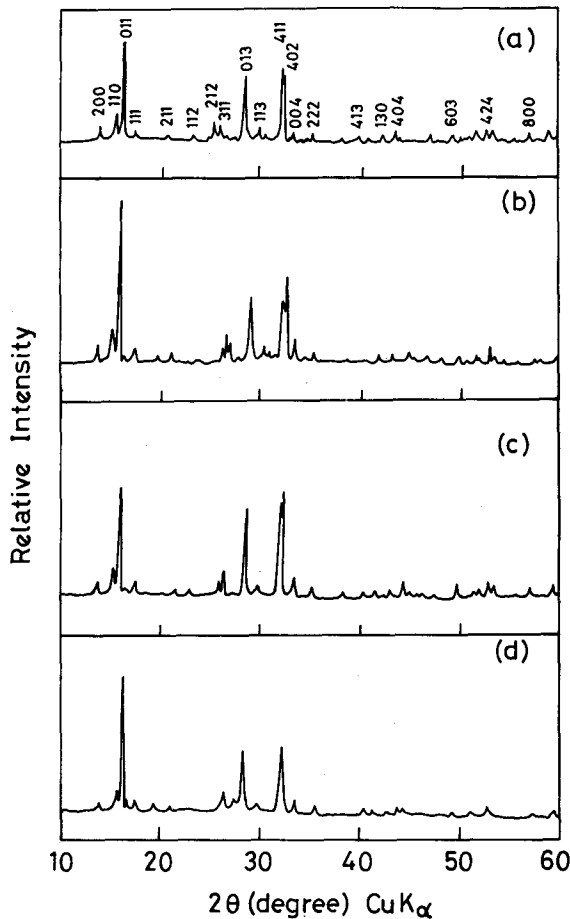

Figure 5. X-ray powder diffraction patterns of (a) $KNb_{0.5}Ti_{0.5}OPO_4$, (b) $K_{0.5}Nb_{0.5}Ti_{0.5}OPO_4$, (c) $KNb_{0.5}V_{0.5}OPO_4$ and (d) $K_{0.5}Nb_{0.5}V_{0.5}OPO_4$.

Table 4. Composition, colour, lattice parameters and SHG intensity of KTP-like phosphates.

Composition	Colour	Reducing power of the sample		Lattice parameters (Å)			SHG intensity*
		Found	Calcd.	a	b	c	
$KNb_{0.5}Ti_{0.5}OPO_4$	Dark blue	0·45	0·50	12·976(5)	6·488(4)	10·773(6)	—
$K_{0.5}Nb_{0.5}Ti_{0.5}OPO_4$	Light blue	—	—	12·879(9)	6·402(7)	10·659(4)	0·9
$KNb_{0.5}V_{0.5}OPO_4$	Brown	0·98	1·00	12·949(6)	6·431(8)	10·686(4)	—
$K_{0.5}Nb_{0.5}V_{0.5}OPO_4$	Green	0·52	0·50	12·801(6)	6·357(4)	10·569(5)	0·5
$KTa_{0.5}V_{0.5}OPO_4$	Grey	0·98	1·00	12·985(4)	6·442(3)	10·696(4)	—
$K_{0.5}Ta_{0.5}V_{0.5}OPO_4$	Yellow	0·53	0·50	12·819(5)	6·367(4)	10·615(5)	0·4

*Normalized with respect to that of $KTiOPO_4$ which is taken as unity

material showing second harmonic generation (SHG) of the 1064 nm radiation, we envisaged that it would be possible to synthesize new NLO materials by deintercalation. To realize this possibility, we prepared new KTP-analogues, $KM_{0.5}M'_{0.5}OPO_4$ ($M = Nb^V, Ta^V; M' = Ti^{III}, V^{III}$) and investigated oxidative deintercalation of potassium using Cl_2 (figure 5). Deintercalation proceeds according to the following typical example

$$KNb_{0.5}^V Ti_{0.5}^{III} OPO_4 + (1/4)Cl_2 \rightarrow K_{0.5}Nb_{0.5}^V Ti_{0.5}^{IV} OPO_4 + (1/2)KCl,$$
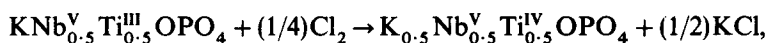
giving new KTP-analogues, $K_{0.5}M_{0.5}M'_{0.5}OPO_4$ (table 4). While the parent materials do not show an SHG response to 1064 nm radiation, the deintercalated materials, $K_{0.5}M_{0.5}M'_{0.5}OPO_4$, do show an SHG response. Both $K_{0.5}Nb_{0.5}^V Ti_{0.5}^{IV} OPO_4$ and $K_{0.5}Ta_{0.5}^V Ti_{0.5}^{IV} OPO_4$ prepared by this route show a powder SHG intensity comparable to that of KTP. The synthesis of these new KTP analogues reveals the importance of d^0 and d^1 cations in determining the NLO property of KTP and related materials.

3.3 Layered and three-dimensional vanadium-tungsten oxide hydrates related to α-MoO₃ and WO₃·1/3H₂O

We prepared two new vanadium-tungsten oxide hydrates of the general formula, $H_x V_x W_{1-x} O_3 \cdot yH_2O$ for $x = 0.125$; $y = 1.5$ and $x = 0.33$; $y = 0.33$ by *acid-leaching* of $LiVWO_6$ in aqueous HNO_3/HCl (table 5). $H_{0.125}V_{0.125}W_{0.875}O_3 \cdot 1.5 H_2O$(I), obtained by leaching $LiVWO_6$ in dilute HNO_3/HCl, crystallizes in a layered, α-MoO_3-like structure. I dehydrates around 130°C to give a hexagonal phase similar to the one reported by Feist and Davies (1991), $H_{0.33}V_{0.33}W_{0.67}O_3 \cdot 1/3 H_2O$(II) is another new hydrate obtained by refluxing $LiVWO_6$ with concentrated HNO_3. II is iso-structural with $WO_3 \cdot 1/3H_2O$ (Gerand *et al* 1981). II dehydrates topochemically around 330°C to give hexagonal-WO_3-like (Gerand *et al* 1979) $H_{0.33}V_{0.33}W_{0.67}O_3$ (III). A schematic representation of the structures of the hydrates and their dehydration products is given in figure 6.

Both I and III, which could be regarded as functionalized derivatives of α-MoO_3 and hexagonal WO_3 structures, exhibit redox and acid-base intercalation/insertion reactivity characteristic of layered and tunnel structures. Thus, I readily intercalates

Table 5. Composition and lattice parameters of vanadium-tungsten oxide hydrates and their derivatives.

Composition	Lattice parameters (Å)		
	a	b	c
$H_{0.125}V_{0.125}W_{0.875}O_3 \cdot 1.5H_2O(I)$	7.77(3)	13.87(6)	7.44(3)
$H_{0.33}V_{0.33}W_{0.6}O_3 \cdot 1/3H_2O(II)$	7.22(3)	12.54(7)	7.66(4)
$H_{0.33}V_{0.33}W_{0.6}O_3(III)$	7.25(4)	—	3.87(2)
$K_{0.18}[H_{0.125}V_{0.125}W_{0.875}O_3 \cdot 1.5H_2O]$	7.63(3)	13.74(7)	7.41(3)
$(NH_4)_{0.125}V_{0.125}W_{0.875}O_3 \cdot 1.5H_2O$	7.88(3)	24.70(9)	7.17(2)
$(n\text{-}C_6H_{13}NH_2)_{0.58}H_{0.125}V_{0.125}W_{0.875}O_3 \cdot 1.5H_2O$	7.73(4)	38.4(2)	7.43(4)
$(n\text{-}C_{10}H_{21}NH_2)_{0.61}H_{0.125}V_{0.125}W_{0.875}O_3 \cdot 1.5H_2O$	7.78(9)	58.0(6)	7.55(9)
$H_{0.90}[H_{0.33}V_{0.33}W_{0.67}O_3]$	7.26(2)	—	3.87(2)
$K_{0.33}[H_{0.33}V_{0.33}W_{0.67}O_3]$	7.25(4)	—	3.87(3)
$(NH_4)_{0.30}H_{0.03}V_{0.33}W_{0.67}O_3$	7.24(2)	—	3.86(1)

(a)

(b)
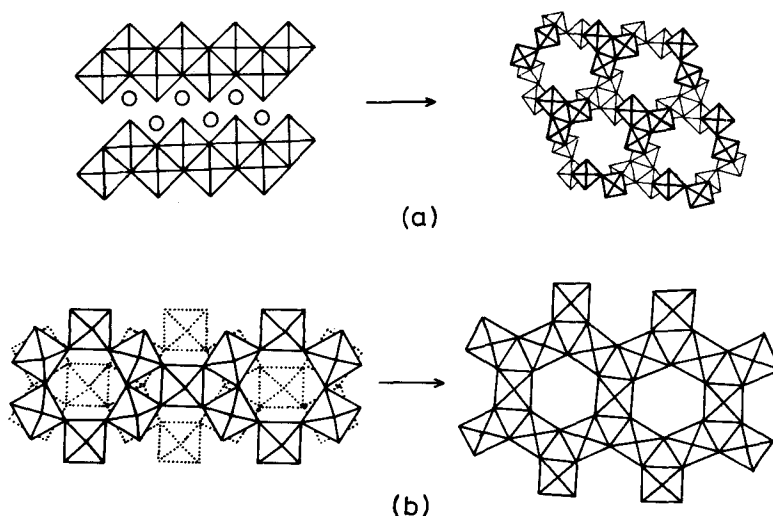
Figure 6. Schematic representation of the structural changes accompanying dehydration of (a) $H_{0.125}V_{0.125}W_{0.875}O_3 \cdot 1.5H_2O$ and (b) $H_{0.33}V_{0.33}W_{0.67}O_3 \cdot 1/3H_2O$.

n-alkylamines resulting in large layer expansions characteristic of layered structures (table 5). Especially significant is the insertion of ammonia molecules into the hexagonal tunnels of III through an acid–base reaction involving the acidic protons.

In summary, the foregoing examples of synthesis of oxide materials show that imaginative routes to synthesis of solids can be developed based on a knowledge of crystal chemistry and chemical reactivity combined with painstaking efforts at the laboratory bench.

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