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Synthesis of Layered Perovskite Oxides, $ACa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ (A = K, Rb, Cs), and Characterization of New Solid Acids, $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ ($0 < x \leqslant 2$), Exhibiting Variable Bronsted Acidity[†]

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Layered perovskite oxides of the formula $ACa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ (A = K, Rb, Cs and $0 < x \leqslant 2$) have been prepared. The members adopt the structures of the parent $ACa_2Nb_3O_{10}$. Interlayer alkali cations in the niobium–titanium oxide series can be ion-exchanged with Li^+, Na^+, NH_4^+, or H^+ to give new derivatives. Intercalation of the protonated derivatives with organic bases reveals that the Bronsted acidity of the solid solution series, $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$, depends on the titanium content. While the $x = 1$ member ($HCaLaNb_2TiO_{10}$) is nearly as acidic as the parent $HCa_2Nb_3O_{10}$, the $x = 2$ member ($HLa_2NbTi_2O_{10}$) is a weak acid hardly intercalating organic bases with $pK_a \sim 11.3$. The variation of acidity is probably due to an ordering of Nb/Ti atoms in the triple octahedral perovskite slabs, $[Ca_{2-x}La_xNb_{3-x}Ti_xO_{10}]$, such that protons are attached to NbO_6 octahedra in the $x = 1$ member and to TiO_6 octahedra in the $x = 2$ member.

Introduction

Metal oxides containing protons are attracting considerable attention in view of the potential application of such materials as solid acid catalysts[1] and proton conductors.[2] Protonated oxides possessing layered structures such as the smectite clays are well-known acid catalysts[1-3] for the synthesis of several industrially important organic chemicals. Understanding the factors that control the acidity of solid oxides is essential for rational design of acid catalysts for specific purposes.

Several protonated oxides of early transition metals are known to exhibit acidic properties, typical examples being heteropolyacids such as $H_3PMo_{12}O_{40}$[4] and the niobic ($HNb_3O_8{\cdot}H_2O$)[5] and titanic acids[6] ($H_2Ti_4O_9{\cdot}nH_2O$). A particularly attractive series of protonated oxides discovered recently are the layered perovskites of the formula, $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ ($n = 3$–7), which are derived from the parent compounds, $A[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ (A = K, Rb, Cs), by ion-exchange.[7-9] The structures of these[10] and related materials[11-13] consist of nMO_6(M = Nb, Ti) corner-sharing octahedra interleaved by A cations. Protonated phases of this family are novel Bronsted acids intercalating a variety of organic amines.[8,14] We envisaged that since the acidity of these materials is mainly related to the nature of the M atom, it should be possible to tune the acidity by changing the M atom. To investigate this hypothesis, we have chosen the $HCa_2Nb_3O_{10}$, $n = 3$, member of the above series, whose acidity has been well-characterized[14] by intercalation of organic amines. We have synthesized a series of phases, $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ ($0 < x \leqslant 2$), that are isostructural with $HCa_2Nb_3O_{10}$, and examined their acidity by intercalation of organic amines of different pK_a values. The results, which are reported in this paper, reveal an interesting variation of the Bronsted acidity with titanium content: while the $x = 1$ member ($HCaLaNb_2TiO_{10}$) is nearly as acidic as the parent $HCa_2Nb_3O_{10}$, the $x = 2$ member ($HLa_2NbTi_2O_{10}$) is a weak acid hardly intercalating organic bases with $pK_a \sim 11.3$. The results are explained on the basis of an ordering of niobium/titanium atoms in the triple octahedral perovskite slabs.

Experimental Section

Members of $ACa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ for A = K, Rb, and Cs and $0 < x \leqslant 2$ were prepared by reacting appropriate quantities of A_2CO_3, $CaCO_3$, La_2O_3, Nb_2O_5, and TiO_2 at 1100–1150 °C for 2 days with one grinding in between. Excess (25 mol %) of A_2CO_3 was added to compensate for the loss due to volatilization. After the reaction, the products were washed with distilled water and dried at 110 °C. The protonated derivatives, $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$, for $0 < x \leqslant 2$, were prepared from the corresponding potassium compounds by ion exchange in aqueous 6 N HNO_3 at 60 °C. The exchange was found to be complete in 2 days. Intercalation of various organic amines in $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ was investigated by refluxing the protonated solids with a 10% amine solution in *n*-heptane for several days. Exchange of K^+ in $KCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ for $0 < x \leqslant 2$ with Li^+, Na^+, and NH_4^+ was also investigated in molten nitrates of these cations.

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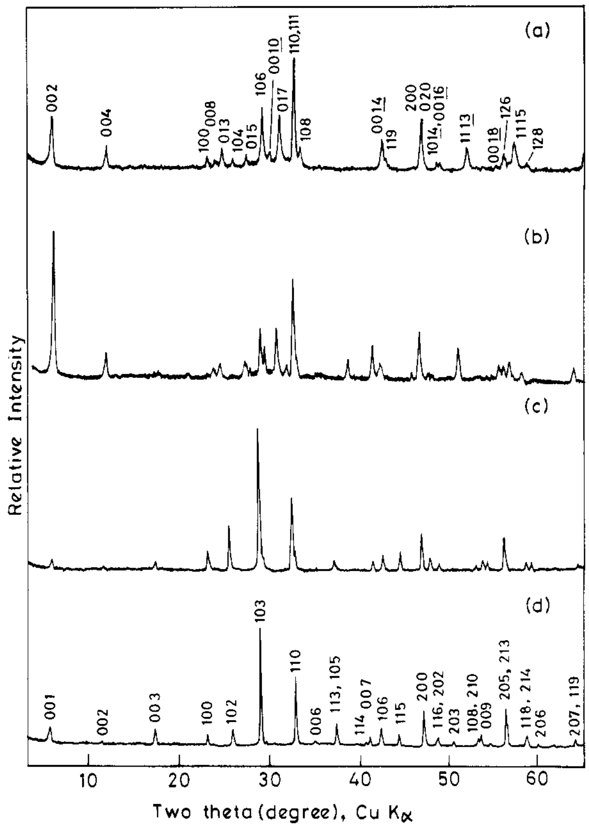

Figure 1. X-ray powder diffraction patterns of $ACa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ members: (a) $KCaLaNb_2TiO_{10}$, (b) $KLa_2NbTi_2O_{10}$, (c) $CsCaLaNb_2TiO_{10}$, and (d) $CsLa_2NbTi_2O_{10}$.

Elemental analysis of a few members of $KCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ was carried out by EDX method using a scanning electron microscope fitted with Link A-10 EDX analyzer. The solid phases were characterized by X-ray powder diffraction (JEOL JDX-8P X-ray powder diffractometer, Cu Kα radiation) and thermogravimetry (Cahn TG-131 system). Unit cell parameters were derived by least-squares refinement of X-ray powder diffraction data. Water of hydration and amine content of the protonated and intercalation compounds were determined from weight losses in thermogravimetric experiments.

Results and Discussion

Reaction of binary oxides and carbonates corresponding to the composition $ACa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ (A = K, Rb, Cs) in air at 1100 °C readily yields single-phase materials (as revealed by EDX analysis and X-ray diffraction) similar to $ACa_2Nb_3O_{10}$ phases[7] up to $x = 2.0$. From powder X-ray diffraction patterns (Figure 1), we find that the rubidium and cesium compounds crystallize in tetragonal structures with $a \simeq 3.85$ and $c \simeq 15.2$ Å, while the potassium analogues adopt orthorhombic structures with $a \simeq 3.87$, $b \simeq 3.86$, and $c \simeq 29.5$ Å. These structures are exactly similar to those of $ACa_2Nb_3O_{10}$ phases where the cesium compound[10] possesses a tetragonal structure with triple-octahedral perovskite-like $(Ca_2Nb_3O_{10})^-$ layers, stacked exactly one over the other, interleaved by cesium ions in between; the potassium analog adopts a similar structure with a doubled *c* axis due to the displacement of the alternate perovskite layers by half a unit cell.[8,9] The unit cell parameters of $ACa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ members are listed in Table I, and the indexed powder diffraction data for some of the typical members are given in Tables II and III.

Table I. Lattice Parameters of $ACa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ (A = K, Rb, Cs) and Their Derivatives

compound	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å)^3
$KCa_2Nb_3O_{10}$[a]	3.870 (2)	3.852 (2)	29.475 (8)	439
$KCa_{1.5}La_{0.5}Nb_{2.5}Ti_{0.5}O_{10}$	3.866 (8)	3.863 (8)	29.59 (7)	442
$KCaLaNb_2TiO_{10}$	3.873 (7)	3.868 (8)	29.81 (6)	447
$KCa_{0.5}La_{1.5}Nb_{1.5}Ti_{1.5}O_{10}$	3.864 (8)	3.855 (7)	29.91 (8)	446
$KLa_2NbTi_2O_{10}$	3.853 (7)	3.850 (6)	30.07 (8)	446
$RbCaLaNb_2TiO_{10}$	3.858 (4)		15.02 (2)	224
$RbLa_2NbTi_2O_{10}$	3.833 (3)		15.24 (2)	224
$CsCaLaNb_2TiO_{10}$	3.869 (4)		15.19 (2)	227
$CsLa_2NbTi_2O_{10}$	3.848 (1)		15.39 (1)	228
$LiLa_2NbTi_2O_{10}$[b]	3.839 (3)		28.42 (2)	419
$NaLa_2NbTi_2O_{10}$[b]	3.836 (2)		29.69 (2)	437
$NH_4La_2NbTi_2O_{10}$[b]	3.830 (2)		15.22 (2)	223

[a] Values for $KCa_2Nb_3O_{10}$ are taken from ref 9. [b] Phases obtained by ion exchange in molten nitrates starting from $KLa_2NbTi_2O_{10}$.

Table II. X-ray Powder Diffraction Data for $KCaLaNb_2TiO_{10}$[a]

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
002	15.10	14.905	51	119	2.110	2.110	11
004	7.50	7.453	21	200	1.937	1.936	45
100	3.875	3.873	12	020	1.935	1.934	45
008	3.731	3.726	9	024	1.871	1.872	9
013	3.612	3.604	19	10*14*	1.866	1.867	9
104	3.433	3.436	11	00*16*	1.863	1.863	9
015	3.249	3.244	13	11*13*	1.755	1.758	19
106	3.048	3.052	57	00*18*	1.658	1.656	4
00*10*	2.979	2.981	49	126	1.635	1.634	15
017	2.867	2.861	49	11*15*	1.603	1.606	25
110	2.730	2.737	100	128	1.570	1.569	6
111		2.725		02*14*	1.431	1.432	13
108	2.687	2.685	21	220	1.368	1.368	9
00*14*	2.127	2.129	26	02*16*	1.342	1.342	4

[a] *a* = 3.873 (7); *b* = 3.868 (8); *c* = 29.81 (6) Å.

Table III. X-ray Powder Diffraction Data for $KLa_2NbTi_2O_{10}$[a]

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
002	15.10	15.035	100	00*14*	2.146	2.148	21
004	7.43	7.518	19	119	2.110	2.111	10
006	5.009	5.012	6	200	1.927	1.926	31
102	3.722	3.731	7	020	1.924	1.925	31
013	3.600	3.592	10	00*16*	1.884	1.879	21
015	3.248	3.240	11	11*13*	1.765	1.763	21
106	3.053	3.054	33	126	1.631	1.629	11
00*10*	2.998	3.007	21	11*15*	1.616	1.614	9
017	2.870	2.864	33	217	1.598	1.599	12
110	2.714	2.720	67	128	1.567	1.566	5
111		2.712		02*14*	1.434	1.433	9
108	2.694	2.690	14	20*15*	1.400	1.388	3
019	2.524	2.520	4	00*22*	1.361	1.367	5
115	2.484	2.480	4	220		1.362	
117	2.301	2.300	13	02*16*	1.343	1.345	3

[a] *a* = 3.853 (7); *b* = 3.850 (6); *c* = 30.07 (8) Å.

Since it is known that the interlayer alkali cations are mobile in $ACa_2Nb_3O_{10}$ phases,[8,9,12] we have investigated the ion exchange of alkali cations of $KCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ series in molten nitrates of lithium, sodium and ammonium. X-ray powder diffraction patterns of the ion-exchanged products show that while the lithium and the sodium derivatives are tetragonal with $c \simeq 29.0$ Å, the ammonium compound adopts a tetragonal structure with $c \simeq 15.2$ Å (Table I). Accordingly, the structure of the ammonium derivative is likely to be similar to the structure[10] of $CsCa_2Nb_3O_{10}$.

We have prepared the protonated phases, $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$, for $0 < x \leqslant 2$ by ion exchange in aqueous 6 N HNO_3 starting from the corresponding potassium compounds. Powder X-ray diffraction patterns (Figure 2) reveal that the protonated phases are exactly analogous to those of the corresponding hydrated niobium

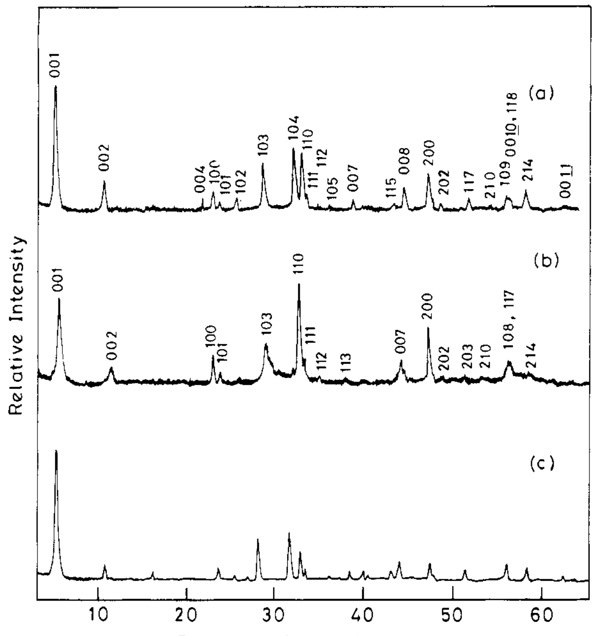

Figure 2. X-ray powder diffraction patterns of $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ and their hydrates: (a) $HCaLaNb_2TiO_{10}\cdot 1.5H_2O$, (b) $HCaLaNb_2TiO_{10}$, and (c) $HLa_2NbTi_2O_{10}\cdot 1.5H_2O$.

Table IV. Lattice Parameters of $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ and Their Hydrates

compound	*a* (Å)	*c* (Å)	*V* (Å)^3
$HCa_2Nb_3O_{10}\cdot 1.5H_2O$[a]	3.854 (4)	16.225 (2)	241
$HCa_2Nb_3O_{10}$[a]	3.850 (6)	14.379 (3)	213
$HCa_{1.5}La_{0.5}Nb_{2.5}Ti_{0.5}O_{10}\cdot 1.5H_2O$	3.852 (7)	16.24 (3)	241
$HCa_{1.5}La_{0.5}Nb_{2.5}Ti_{0.5}O_{10}$	3.860 (5)	14.39 (2)	214
$HCaLaNb_2TiO_{10}\cdot 1.5H_2O$	3.854 (6)	16.28 (3)	242
$HCaLaNb_2TiO_{10}$	3.855 (6)	14.41 (6)	214
$HCa_{0.5}La_{1.5}Nb_{1.5}Ti_{1.5}O_{10}\cdot 1.5H_2O$	3.844 (4)	16.35 (2)	242
$HCa_{0.5}La_{1.5}Nb_{1.5}Ti_{1.5}O_{10}$	3.835 (4)	14.39 (6)	212
$HLa_2NbTi_2O_{10}\cdot 1.5H_2O$	3.831 (5)	16.44 (2)	241

[a] Values for $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ and $HCa_2Nb_3O_{10}$ are taken from ref 9.

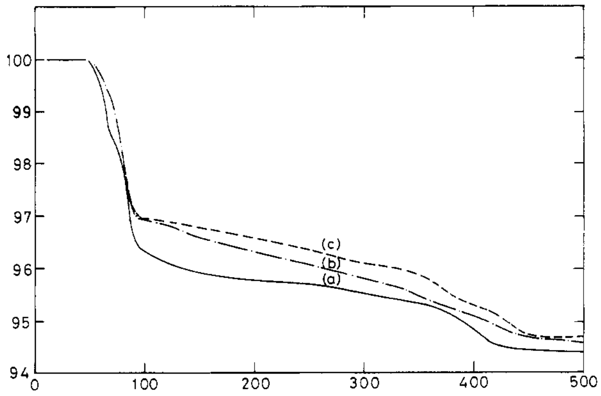

Figure 3. Thermogravimetric curves of hydrated $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$: (a) $HCaLaNb_2TiO_{10}\cdot 1.5H_2O$, (b) $HLa_2NbTi_2O_{10}\cdot 1.5H_2O$, and (c) $HCa_{0.5}La_{1.5}Nb_{1.5}Ti_{1.5}O_{10}\cdot 1.5H_2O$.

compound, $HCa_2Nb_3O_{10}\cdot 1.5H_2O$, having tetragonal cells with $a \simeq 3.85$ Å and $c \simeq 16.3$ Å. The lattice parameters of the hydrated and anhydrous compounds of the series $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ for $0 < x \leq 2$ are collected in Table IV. Thermogravimetric experiments (Figure 3) confirm that the protonated compounds are hydrated with 1.5 H_2O. The water of hydration is lost around 60–70 °C. The anhydrous phases are obtained by drying the samples around 100 °C, except for the $x = 2.0$ member, $HLa_2NbTi_2O_{10}$, for which the anhydrous phase is not stable.

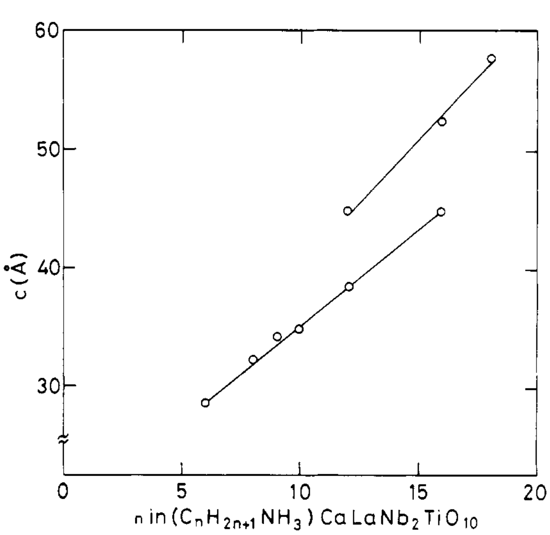

Figure 4. *c* axis spacing versus the number of carbon atoms in alkyl chain for the *n*-alkylammonium intercalation compounds of $HCaLaNb_2TiO_{10}$.

Jacobson et al.[14] have shown that $HCa_2Nb_3O_{10}$ is a strong Bronsted acid intercalating several organic bases including pyridine, which has a pK_a value of 5.3. We have investigated the Bronsted acidity of $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ for $0 < x \leq 2$ members by intercalation with a variety of organic bases having different pK_a values. The unit cell parameters and the compositions of the products as determined by thermogravimetry are listed in Table V. The results reveal that the $x = 1$ member ($HCaLaNb_2TiO_{10}$) intercalates a wide variety of organic amines including *n*-alkylamines of pK_a values ranging from 5.3 (pyridine) to 11.30 (piperidine) (Figure 5), indicating that $HCaLaNb_2TiO_{10}$ is nearly as acidic as $HCa_2Nb_3O_{10}$. The layer expansions as determined from the *c* parameters for the various *n*-alkylamine intercalation compounds of $HCaLaNb_2TiO_{10}$ are approximately the same as those of $HCa_2Nb_3O_{10}$, indicating the presence of bilayer gauche–block organic chains between the inorganic oxide layers.[14]

A plot of the *c* parameter with the number of carbon atoms of the *n*-alkylammonium intercalation compounds, $(n\text{-}C_nH_{2n+1}NH_3)CaLaNb_2TiO_{10}$, shows that all these compounds are similar to the type III (C_6–C_{16}) and type IV (C_{12}–C_{18}) intercalation compounds[14] of $HCa_2Nb_3O_{10}$ (Figure 4). A least-squares fit of the data for the region C_6–C_{16} gives

$$c = 1.67n + 18.525\ \text{Å};\quad \alpha = 41.0°$$

where α is the mean angle which the organic chains make with the inorganic layer surface. In the case of C_{12} and C_{16} amine intercalation, phases with two different *c* parameters are obtained (Table V). Phases with a larger *c* are obtained by drying the samples at room temperature, while those with a smaller *c* are formed by annealing the samples at 100 °C. The changes in *c* parameter in similar phases of $HCa_2Nb_3O_{10}$ have been attributed[14] to a rearrangement in the packing of the hydrocarbon chains during annealing.

In contrast to the intercalation behavior of the $x = 1.0$ phase ($HCaLaNb_2TiO_{10}$), the $x = 2$ member ($HLa_2NbTi_2O_{10}\cdot 1.5H_2O$) does not intercalate *n*-alkylamines (C_6–C_{16}) at all, even after prolonged reaction with the amine solution in *n*-heptane. This lack of intracrystalline

Table V. Composition and Lattice Parameters of Intercalation Compounds of $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ with Organic Bases

solid acid	organic base	pK_a of the organic base	intercalated amine content	lattice param (Å) *a*	lattice param (Å) *c*
$HCaLaNb_2TiO_{10}$	*n*-hexylamine	10.64	0.98	3.853 (5)	28.78 (7)
$HCaLaNb_2TiO_{10}$	*n*-octylamine	10.65	0.96	3.854 (5)	32.32 (7)
$HCaLaNb_2TiO_{10}$	*n*-nonylamine	10.64	0.94	3.854 (4)	34.32 (2)
$HCaLaNb_2TiO_{10}$	*n*-decylamine	10.64	0.99	3.854 (5)	34.73 (6)
$HCaLaNb_2TiO_{10}$	*n*-dodecylamine	10.63	1.01	3.854 (6)	44.86 (7)
$HCaLaNb_2TiO_{10}$	*n*-dodecylamine[a]	10.63	0.97	3.854 (2)	37.98 (6)
$HCaLaNb_2TiO_{10}$	*n*-hexadecylamine	10.61	1.00	3.854 (3)	52.63 (4)
$HCaLaNb_2TiO_{10}$	*n*-hexadecylamine[a]	10.61	0.96	3.854 (5)	44.76 (5)
$HCaLaNb_2TiO_{10}$	*n*-octadecylamine	10.61	1.00	3.854 (5)	56.65 (5)
$HCaLaNb_2TiO_{10}$	piperidine[b]	11.30	0.60	3.868 (5)	23.69 (5)
$HCaLaNb_2Ti_{10}$	pyridine	5.30	0.60	3.858 (4)	18.93 (2)
$HCa_{0.5}La_{1.5}Nb_{1.5}Ti_{1.5}O_{10}$	*n*-hexylamine	10.64	0.53	3.851 (6)	28.96 (6)
$HCa_{0.5}La_{1.5}Nb_{1.5}Ti_{1.5}O_{10}$	*n*-decylamine	10.64	0.48	3.848 (7)	35.36 (6)
$HLa_2NbTi_2O_{10}{\cdot}1.5H_2O$	piperidine[b]	11.30	0.60	3.845 (7)	23.86 (5)
$HCa_2Nb_3O_{10}$	piperidine[b]	11.30	0.62	3.868 (5)	23.69 (5)

[a] Samples annealed at 100 °C. [b] Amine compounds are hydrated with $1.5H_2O$.

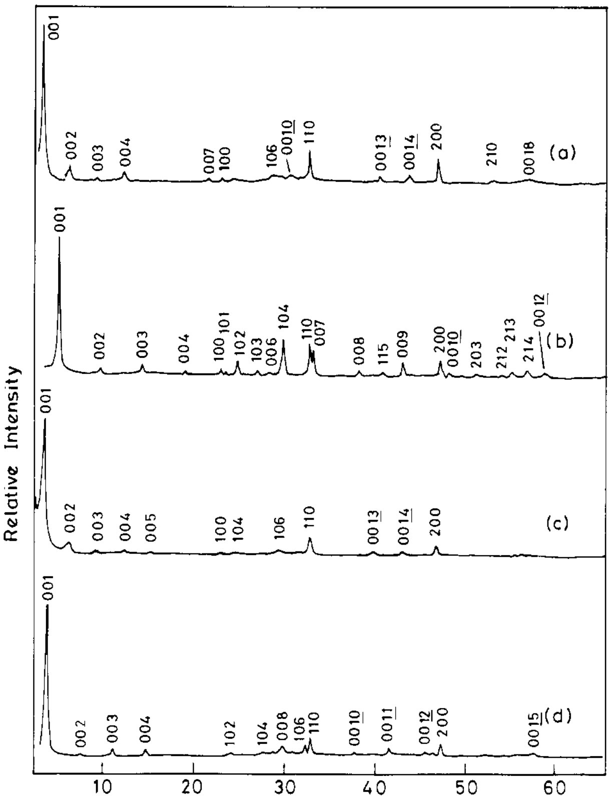

Figure 5. X-ray powder diffraction patterns of some intercalation compounds of $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$: (a) $(C_5H_5NH)_{0.6}H_{0.4}$-$CaLaNb_2TiO_{10}$, (b) $(C_6H_{13}NH_3)_{1.0}CaLaNb_2TiO_{10}$, (c) $(C_6H_{13}NH_3)_{0.53}H_{0.47}Ca_{0.5}La_{1.5}Nb_{1.5}Ti_{1.5}O_{10}$, and (d) $(C_5H_{10}NH_2)_{0.6}H_{0.4}La_2NbTi_2O_{10}{\cdot}1.5H_2O$.

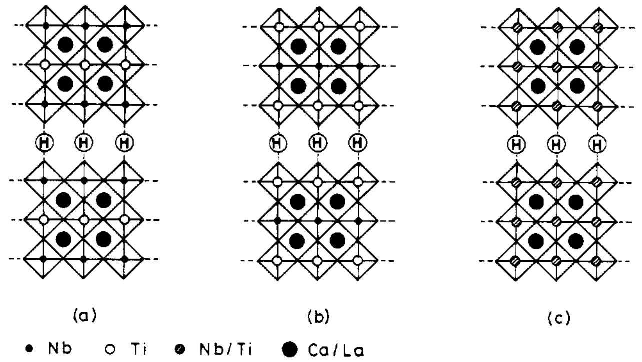

Figure 6. Idealized structures of $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ showing ordering of Nb and Ti atoms: (a) $x = 1.0$, (b) $x = 2$, and (c) $x = 1.5$.

reactivity of $HLa_2NbTi_2O_{10}{\cdot}1.5H_2O$ stands in marked contrast with the facile reactivity of $HCaLaNb_2TiO_{10}$. The only intercalation that we observed for $HLa_2NbTi_2O_{10}{\cdot}1.5H_2O$ was that with piperidine (pK_a = 11.3), after prolonged (1 week) reaction (Figure 5). The intercalation product with piperidine has the composition $(C_5H_{10}NH_2)_{0.6}H_{0.4}La_2NbTi_2O_{10}{\cdot}1.5H_2O$ showing incomplete intercalation.

The remarkable change in the acidity of the series, $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$, as *x* increases may be explained as follows: In $HCaLaNb_2TiO_{10}$, niobium and titanium atoms are most likely ordered in the triple-octahedral perovskite slabs such that titanium atoms occur in the middle octahedra flanked by niobium atoms on both the outer octahedra (Figure 6a). Such an ordering would result in protons attached to NbO_6 octahedra as in the case of $HCa_2Nb_3O_{10}$. Accordingly, the acidity of $HCaLaNb_2TiO_{10}$ is roughly the same as that of $HCa_2Nb_3O_{10}$. With $HLa_2NbTi_2O_{10}{\cdot}1.5H_2O$, the ordering of niobium and titanium atoms in the perovskite slabs is probably reversed (Figure 6b); the niobium atoms are in the middle octahedra flanked by titanium atoms on the outer octahedra. Accordingly, the protons of $HLa_2NbTi_2O_{10}$ would be attached to TiO_6 octahedra. The dramatic decrease of acidity on going from the $x = 1$ to the $x = 2$ member in the series $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ can thus be explained by such an ordering if we assume that the protons attached to TiO_6 octahedra are less acidic than those attached to NbO_6 octahedra. This assumption is consistent with literature reports that protonated niobium oxides (e.g., $HNb_3O_8{\cdot}H_2O$)[5] are more acidic than protonated niobium–titanium oxides (e.g., $HTiNbO_5$)[15] which in turn are more acidic than protonated titanium oxides (e.g. $H_2Ti_4O_9$).[14,16] The weak acidity of $HLa_2NbTi_2O_{10}{\cdot}1.5H_2O$ is comparable to that of $H_2La_2Ti_3O_{10}$, a layered perovskite possessing a similar structure but with twice the interlayer proton density.[17] $H_2La_2Ti_3O_{10}$ where the protons are attached to TiO_6 octahedra does not intercalate alkylamines, just as $HLa_2NbTi_2O_{10}{\cdot}1.5H_2O$.

In an attempt to provide further support to the proposed ordering of niobium/titanium atoms for the $x = 1$ and *x*

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= 2 members of $ACa_{2-x}La_xNb_{3-x}Ti_xO_{10}$, we have calculated the intensities of 00*l* reflections on the basis of the structural model[10] of $CsCa_2Nb_3O_{10}$. Although there is a qualitative agreement between the calculated and experimental intensities of 00*l* reflections in the sense that both vary in the order $CsCa_2Nb_3O_{10} \lesssim CsCaLaNb_2TiO_{10} < CsLa_2NbTi_2O_{10}$, an unambiguous distinction between the ordered and disordered structures could not be made, because the experimental intensities of 00*l* reflections of these phases as obtained from powder X-ray diffraction data are affected considerably by preferred orientation.[9]

We have investigated the intercalation of *n*-alkylamines in the $x = 1.5$ member, $HCa_{0.5}La_{1.5}Nb_{1.5}Ti_{1.5}O_{10}$, to provide additional support to the ordering of niobium/titanium atoms in the series. Three different orderings of niobium and titanium atoms are possible for this compound: (1) The middle octahedral layer of the trioctahedral perovskite slab is occupied by niobium, leaving $(Nb_{0.25}Ti_{0.75})$ atoms on the average in each of the outer octahedral sheets; (2) the middle octahedral layer is occupied by titanium, leaving $(Nb_{0.75}Ti_{0.25})$ atoms on the average in each of the outer octahedral sheets, and (3) there is a statistical distribution of niobium and titanium atoms, which would result in an average distribution of $(Nb_{0.5}Ti_{0.5})$ atoms in every octahedral sheet. Only partial intercalation of *n*-hexyl- and *n*-decylamines is observed (Table V), which is consistent with a statistical distribution of niobium and titanium atoms in this material. Thus intercalation experiments with $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ reveal a unique variation of acidity across the series that appears to be related to the ordering of niobium–titanium atoms in the triple perovskite slabs. Although it is generally known that protonated niobium oxides[5,18] are more acidic than niobium–titanium[15,19] and titanium oxides,[14,16] what is significant in the present work is that, in an isostructural series of oxides containing both niobium and titanium, we have shown how the Bronsted acidity varies across the series in an unique manner that depends on the ordering of niobium–titanium atoms.

In the three-dimensional perovskite oxides, it is known[20] that ordering of octahedral-site cations occurs when there is a significant difference in the size and/or the charge. In the present series of layered perovskites, the sizes of Nb^{5+} and Ti^{4+} are nearly the same and the charge difference is not much. The ordering model proposed on the basis of intercalation experiments for the $x = 1$ and $x = 2$ members of the $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ series requires further confirmation by structural investigation.

Conclusion

In this paper, we have described the synthesis of a new series of protonated layered perovskites of the formula, $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$, from the corresponding potassium compounds by ion exchange. The protonated compounds are isostructural with the parent $HCa_2Nb_3O_{10}$, which has been reported in the literature to be a strong Bronsted acid. Investigation of the Bronsted acidity of $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ series for $0 < x \leq 2.0$ by intercalation of a variety of organic bases has shown that the acidity varies in an interesting manner. The $x = 1$ member ($HCaLaNb_2TiO_{10}$) is nearly as acidic as $HCa_2Nb_3O_{10}$, while the $x = 2$ member ($HLa_2NbTi_2O_{10}\cdot 1.5H_2O$) is a weak Bronsted acid just being able to intercalate piperidine ($pK_a = 11.3$). The protons attached to NbO_6 octahedra are expected to be more acidic than the protons attached to TiO_6 octahedra. Accordingly, the variation of the Bronsted acidity across the series is probably due to an ordering of niobium–titanium atoms in the triple octahedral perovskite slabs, $[Ca_{2-x}La_xNb_{3-x}Ti_xO_{10}]$, which results in protons being attached to NbO_6 octahedra in the $x = 1$ member and to TiO_6 octahedra in the $x = 2$ member. The present work implies that substitution of tungsten–molybdenum for niobium in a similar series would produce phases of much higher Bronsted acidity.

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