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$K_{1-x}La_xCa_{2-x}Nb_3O_{10}$, a Layered Perovskite Series with Variable Interlayer Cation Density, and $LaCaNb_3O_{10}$, a Novel Layered Perovskite Oxide with No Interlayer Cations*

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A series of layered perovskite oxides of the formula $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$ for $0 < x \leq 1.0$ have been prepared. All the members are isostructural, possessing the structure of $KCa_2Nb_3O_{10}$. The interlayer potassium ions in the new series can be ion-exchanged with protons to give $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$. The latter readily forms intercalation compounds of the formula $(C_nH_{2n+1}NH_3)_{1-x}La_xCa_{2-x}Nb_3O_{10}$, just as the parent solid acid $HCa_2Nb_3O_{10}$. The end member $LaCaNb_3O_{10}$ containing no interlayer cations is a novel layered perovskite oxide, being a $n = 3$ member of the series $A_{n-1}B_nX_{3n+1}$.

Introduction

Two series of layered oxides derived from the perovskite structure have attracted attention. One is the Ruddlesden–Popper series of the general formula $M_2[A_{n-1}B_nO_{3n+1}]$ of which Sr_2TiO_4 and $Sr_4Ti_3O_{10}$ are well-known $n = 1$ and $n = 3$ members (*1*). We have recently reported new $n = 3$ members of the formula $A_2Ln_2Ti_3O_{10}$ (A = K, Rb; Ln = La, Nd, Sm, Gd, Dy) (*2*). Another related series reported by Dion *et al.* (*3*) some years ago is of the formula $M[A_{n-1}B_nO_{3n+1}]$ of which $KCa_2Nb_3O_{10}$ is a typical $n = 3$ member. Subsequently Jacobson *et al.* (*4*) prepared $n = 3$–7 members of the series with the general formula $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ and we have prepared $n = 2$ members (*5*). Recently, Mohan Ram and Clearfield (*6*) have characterized additional $n = 4$ and 5 members of this series.

One of the reasons for the interest in oxides of this series is that they readily exchange the interlayer alkali cations with protons, forming the corresponding protonated derivatives, $H[A_{n-1}B_nO_{3n+1}]$; the latter are solid Brønsted acids, which react with organic bases to form intercalation compounds with large layer expansions (*4*, *7*). Recently, it has been shown that such intercalation compounds can be exfoliated into single layers (*8*) and can be "stuffed" with polyhydroxyaluminate species at the interlayer spacing, yielding novel molecular composites (*9*).

The existence of two different series of parent oxides with the same perovskite slab, $[A_{n-1}B_nO_{3n+1}]$, but with different interlayer cation density, led us to believe that layered

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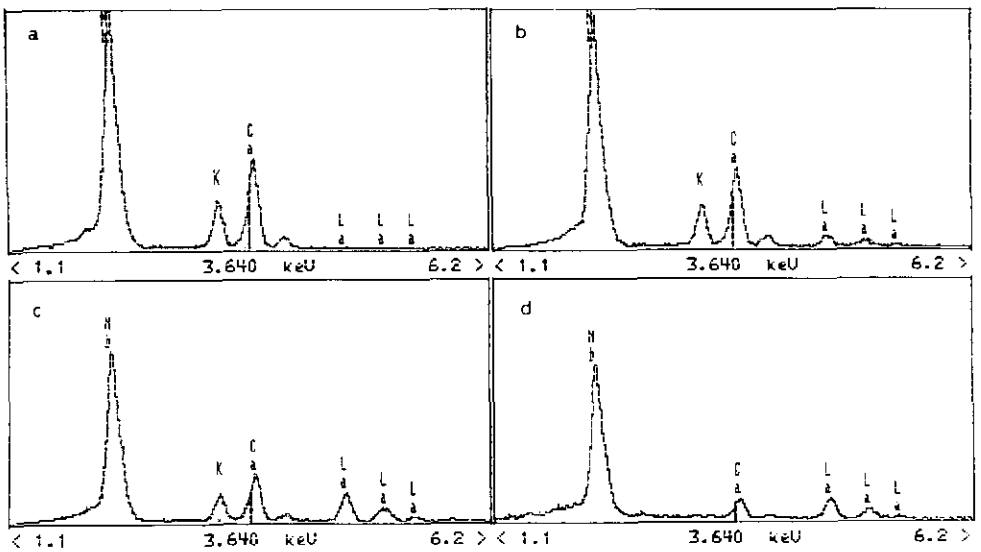

FIG. 1. EDX spectra of (a) $KCa_2Nb_3O_{10}$, (b) $K_{0.75}La_{0.25}Ca_{1.75}Nb_3O_{10}$, (c) $K_{0.5}La_{0.5}Ca_{1.5}Nb_3O_{10}$, and (d) $LaCaNb_3O_{10}$.

perovskites with continuously variable interlayer cation density probably exist. Accordingly, we have synthesized a new series of layered perovskites of the formula $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$ ($0 < x \leq 1.0$), which are isostructural with $KCa_2Nb_3O_{10}$. The interlayer cation density in the series varies from 1 to 0 per formula unit. Formation of the end member $LaCaNb_3O_{10}$ with the same structure of $KCa_2Nb_3O_{10}$ shows that yet another homologous series of layered perovskites of the formula $[A_{n-1}B_nO_{3n+1}]$, where there are no interlayer cations, exists, of which $LaCaNb_3O_{10}$ is an $n = 3$ member. In this paper, we report the synthesis and characterization of $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$ members and their proton exchange and intercalation behavior.

Experimental

Members of $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$ for $0 < x \leq 1.0$ were prepared by reacting appropriate quantities of K_2CO_3, La_2O_3, $CaCO_3$, and Nb_2O_5 at 1150–1200°C for 2 days with one grinding in between. Excess (25 mole%) K_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 potassium in $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$ was exchanged with protons by refluxing the solids with continuous stirring in 6 *N* HNO_3 at 60°C. The exchange was complete in 2 days. *n*-Alkylamine intercalation compounds of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ were prepared by refluxing the protonated phases with a 10% amine solution in *n*-heptane around 90°C for several days until the reaction was complete.

Chemical analysis of the metals in the $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$ series was carried out by the EDX method using a scanning electron microscope fitted with a LINK A-10 EDX analyzer. The solid phases were characterized by X-ray powder diffraction (JEOL JDX-8P X-ray powder diffractometer, Cu$K\alpha$ radiation) and thermogravimetry (Cahn TG-131 system). Unit-cell

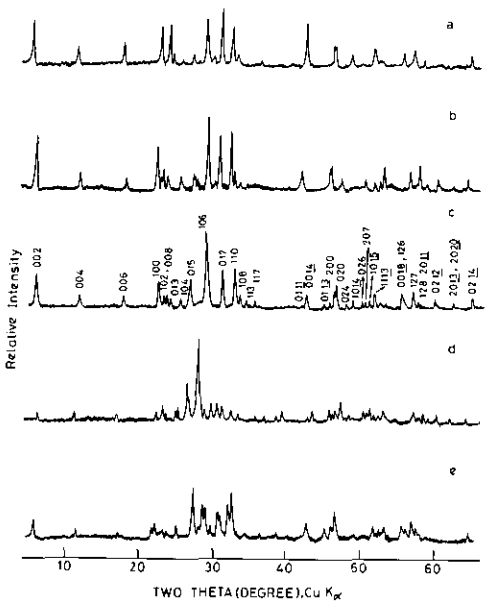

FIG. 2. X-ray powder diffraction patterns of $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$: (a) $x = 0.0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1.0$.

parameters were derived by least-squares refinement of the X-ray powder diffraction data. Water of hydration and amine contents of the protonated and intercalation compounds were determined from weight losses in thermogravimetric experiments.

Results and Discussion

Chemical analysis by EDX (Fig. 1) and X-ray diffraction patterns (Fig. 2) of $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$ members show that single-phase materials isostructural with the parent $KCa_2Nb_3O_{10}$ are formed over the composition range $0 < x \leq 1.0$. The atomic ratio of K : La : Ca as determined from the EDX data (Fig. 1) varies as expected for the formula $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$. The unit-cell parameters and the potassium contents of $x = 0.0$, 0.25, 0.50, 0.75, and 1.0 members are listed in Table I, while the indexed powder diffraction data for the $x = 0.50$ and $x = 1.0$ members are given in Tables II and III. The results indicate that La^{3+} substitutes for Ca^{2+} in $KCa_2Nb_3O_{10}$, thereby decreasing the negative charge on the perovskite slab; charge balance is achieved by decreasing the potassium content in the interlayer space. There is a slight increase in the cell parameters and cell volume across the series, probably reflecting the replacement of smaller Ca^{2+} (radius of Ca^{2+} = 1.12 Å) by larger La^{3+} (radius of La^{3+} = 1.16 Å).

We could prepare single-phase end member $LaCaNb_3O_{10}$ by prolonged reaction at 1150°C. EDX analysis of the sample (Fig. 1) shows that the La : Ca ratio is 1 : 1, indicating clearly that $LaCaNb_3O_{10}$ is formed as a

TABLE I

UNIT-CELL PARAMETERS AND POTASSIUM CONTENT OF $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$

					Potassium content (%)	
x	a (Å)	b (Å)	c (Å)	V (Å^3)	Found	Calculated
0.00	3.866(3)	3.855(2)	29.46(1)	439	6.90	7.01
	(3.870)[a]	(3.852)	(29.475)			
0.25	3.881(4)	3.892(3)	29.62(2)	447	5.10	5.12
0.50	3.901(5)	3.901(4)	29.65(1)	451	3.20	3.33
0.75	3.913(3)	3.906(3)	29.74(1)	454	1.50	1.62
1.00	3.956(5)	3.886(6)	29.79(2)	458	—	—

[a] Values for $KCa_2Nb_3O_{10}$ given in parentheses are taken from Ref. (*12*).

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $K_{0.5}La_{0.5}Ca_{1.5}Nb_3O_{10}$

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
002	14.91	14.83	40	200	1.953	1.950	28
004	7.42	7.41	20	020	1.945	1.951	40
006	4.95	4.94	15	024	1.894	1.886	10
100	3.907	3.901	40	10$\underline{14}$	1.860	1.862	14
102	3.780	3.773	20	026	1.812	1.814	12
008	3.710	3.707	26	207	1.780	1.772	10
013	3.635	3.629	16	10$\underline{15}$	1.758	1.764	14
104	3.461	3.452	22	11$\underline{13}$		1.758	
015	3.268	3.260	20	00$\underline{18}$	1.645	1.647	22
106	3.072	3.063	100	126		1.645	
00$\underline{10}$	2.974	2.966	10	127	1.609	1.613	12
017	2.880	2.872	68	128	1.585	1.580	10
110	2.758	2.750	74	02$\underline{12}$	1.536	1.531	14
108	2.694	2.687	20	00$\underline{20}$	1.483	1.483	6
113	2.660	2.657	10	02$\underline{14}$	1.432	1.435	16
00$\underline{14}$	2.122	2.118	36	10$\underline{20}$	1.385	1.386	6
01$\underline{13}$	1.978	1.969	8	220	1.376	1.379	13

$a = 3.901(5)$, $b = 3.901(4)$, $c = 29.65(1)$ Å

distinct phase. The powder diffraction pattern of the sample (Fig. 2e) could be indexed on an orthorhombic cell ($a = 3.956$, $b = 3.886$, and $c = 29.79$ Å) (Table III) which is similar to that of $KCa_2Nb_3O_{10}$. Formation of $LaCaNb_3O_{10}$ consisting of charge-neutral perovskite slabs held together by weak dipolar and van der Waals forces reveals the possibility of yet another series of layered perovskites of the formula $[A_{n-1}B_nX_{3n+1}]$ of which $LaCaNb_3O_{10}$ is the only known $n = 3$ member. $n = 1$ and $n = 2$ members of this series, which would have the formulas BX_4 and AB_2X_7, respectively, do not exist among metal oxides. SnF_4 (*10*) and $SmZrF_7$ (*11*) consisting of perovskite (ReO_3)-like single and double octahedral sheets could, however, be regarded as $n = 1$ and $n = 2$ members of this series. MoO_3 consisting of charge-neutral edge-shared MoO_6-octahedral slabs (*10*) held together by weak van der Waals and dipolar forces is another layered oxide similar to $LaCaNb_3O_{10}$. Structures of the $[A_{n-1}B_nX_{3n+1}]$ layered perovskites are shown schematically in Fig. 3.

We have investigated the proton-exchange and intercalation chemistry of $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$ members with a view to comparing their behavior with that of $KCa_2Nb_3O_{10}$. Protonated phases of the formula $H_{1-x}La_xCa_{2-x}Nb_3O_{10} \cdot yH_2O$ ($y \sim 1.0$) are readily obtained by ion exchange of potassium in aqueous acids, similar to the formation of $HCa_2Nb_3O_{10}$ from $KCa_2Nb_3O_{10}$ (*12*). Powder X-ray diffraction patterns (Fig. 4) and thermogravimetry (Fig. 5) show that the protonated phases are hydrated just as the parent $HCa_2Nb_3O_{10}$ (*12*). The anhydrous $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ for x up to 0.5 are readily obtained by dehydration around 100°C. The anhydrous product of the $x = 0.75$ phase, $H_{0.25}La_{0.75}Ca_{1.25}Nb_3O_{10}$, is however thermally unstable, continuously decomposing beyond 150°C. The total weight loss in all the cases corresponds to the reaction

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR $LaCaNb_3O_{10}$

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
002	14.90	14.89	45	108	2.702	2.709	23
004	7.46	7.45	23	117	2.330	2.322	20
006	4.97	4.96	20	$00\bar{1}4$	2.127	2.128	35
100	3.967	3.956	33	$10\bar{1}3$	1.990	1.983	30
011	3.861	3.854	40	200	1.971	1.978	33
102	3.830	3.824	18	020	1.947	1.943	50
008	3.730	3.723	26	211	1.762	1.760	30
013	3.619	3.619	23	213	1.737	1.736	26
014	3.439	3.445	35	122		1.732	
015	3.260	3.254	100	028	1.718	1.720	30
106	3.099	3.092	70	126	1.643	1.645	30
016	3.052	3.059	73	217	1.631	1.629	28
$00\bar{1}0$	2.986	2.979	40	$02\bar{1}0$		1.627	
107	2.890	2.896	43	$11\bar{1}5$	1.609	1.614	30
017	2.866	2.870	50	$20\bar{1}1$	1.598	1.597	23
110	2.770	2.772	70	$02\bar{1}4$	1.435	1.435	20
112	2.725	2.729	73	220	1.382	1.386	15
				222		1.380	

$a = 3.956(5)$, $b = 3.886(6)$, $c = 29.79(2)$ Å

$$H_{1-x}La_xCa_{2-x}Nb_3O_{10} \cdot 1H_2O \rightarrow La_xCa_{2-x}Nb_3O_{10-[(1-x)/2]} + 1 + [(1 - x)/2]H_2O.$$

The X-ray diffraction patterns of the hydrated and anhydrous $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ (Fig. 4) are similar to those of $HCa_2Nb_3O_{10} \cdot 1.5H_2O$ and $HCa_2Nb_3O_{10}$ (*12*), indicating that the structures are tetragonal with one formula unit per cell. The halving of the *c* parameter of the protonated phases (Table IV) as compared to the parent potassium-containing phases indicates that ion exchange produces a relative translation of the perovskite slabs as in the case of $HCa_2Nb_3O_{10}$. The layers are stacked exactly one over the other in the protonated phases, whereas they are displaced by *a*/2 relative to each other in the potassium-containing phases (*4*, *12*).

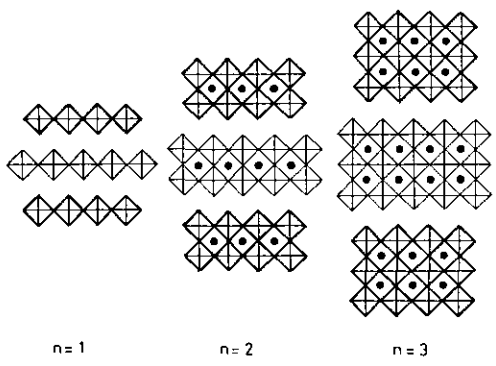

FIG. 3. Schematic representation of the structures of the $A_{n-1}B_nX_{3n+1}$ (X = F or O) series of layered perovskites.

Members of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ exhibit Brønsted acidity, forming intercalation compounds with organic amines just as the parent $HCa_2Nb_3O_{10}$ (*7*). We have prepared intercalation compounds of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ for $x = 0.75$, 0.50, and 0.25 with *n*-hexylamine, *n*-decylamine, and *n*-dodecylamine. The intercalation compounds are readily formed, with all three amines producing large expansions in the *c* parameter

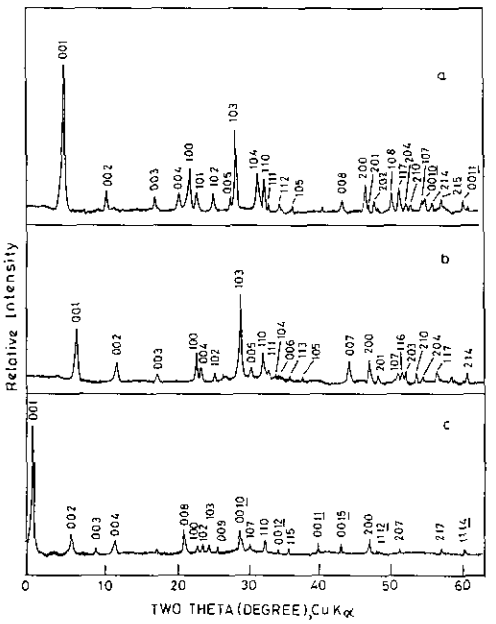

FIG. 4. X-Ray powder diffraction patterns of (a) $H_{0.5}La_{0.5}Ca_{1.5}Nb_3O_{10} \cdot 1H_2O$, (b) $H_{0.5}La_{0.5}Ca_{1.5}Nb_3O_{10}$, and (c) $(C_6H_{13}NH_3)_{0.5}La_{0.5}Ca_{1.5}Nb_3O_{10}$.

(Fig. 4). The compositions of the intercalation compounds determined by thermogravimetry correspond to the expected formula $[C_nH_{2n+1}NH_3]_{1-x}La_xCa_{2-x}Nb_3O_{10}$ (n = 6, 10 and 12) for all values of x investigated (Table V), indicating complete intercalation of the protonated phase.

The intercalation behavior of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ is similar to that of $HCa_2Nb_3O_{10}$ although the proton content is less than one in the former series. Thus, the c parameters of the n-hexyl-, n-decyl-, and n-dodecylamine intercalation compounds of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ are nearly the same as those of the corresponding amine intercalation compounds of $HCa_2Nb_3O_{10}$ (*7*), revealing that the n-alkylammonium cations form bilayer arrangements between the inorganic slabs. The n-alkylamine intercalation compounds of $HCa_2Nb_3O_{10}$ are divided into four distinct groups depending on the c-axis

TABLE IV

UNIT-CELL PARAMETERS OF HYDRATED AND ANHYDROUS $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$

Compound	a (Å)	c (Å)	V (Å^3)
$HCa_2Nb_3O_{10} \cdot 1.5H_2O$[a]	3.854(4)	16.23(1)	241
$HCa_2Nb_3O_{10}$[a]	3.854(7)	14.37(1)	213
$H_{0.75}La_{0.25}Ca_{1.75}Nb_3O_{10} \cdot 1H_2O$	3.884(8)	16.38(1)	247
$H_{0.75}La_{0.25}Ca_{1.75}Nb_3O_{10}$	3.880(8)	14.41(1)	217
$H_{0.50}La_{0.50}Ca_{1.50}Nb_3O_{10} \cdot 1H_2O$	3.882(2)	16.38(2)	246
$H_{0.50}La_{0.50}Ca_{1.50}Nb_3O_{10}$	3.881(5)	14.39(1)	216
$H_{0.25}La_{0.75}Ca_{1.25}Nb_3O_{10} \cdot 1H_2O$	3.888(2)	16.40(1)	247

[a] Values taken from Ref. (*12*).

expansion (*7*). Amines with 6 to 16 carbon atoms belong to group III where the angle α which the organic chains make with the layer surface is 40.5°. The c parameters of the intercalation compounds of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ with C_{10} and C_{12} amines coincide with the corresponding amine intercalation compounds of $HCa_2Nb_3O_{10}$, revealing that the orientation of the organic chain is exactly the same as with the group III intercalation compounds of $HCa_2Nb_3O_{10}$. The c parameters of n-hexylamine intercalation compounds of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ are slightly larger (31.5 and 29.4 Å) than the value for the n-hexylamine intercalation

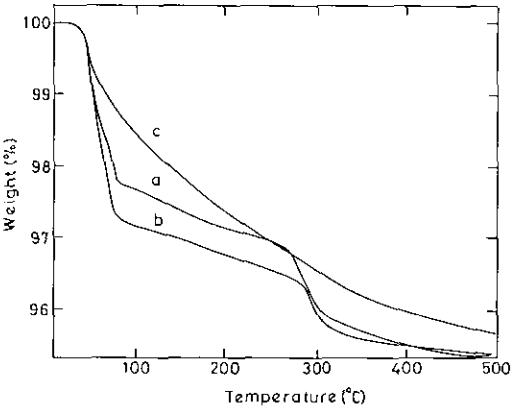

FIG. 5. Thermogravimetric curves of $H_{1-x}La_xCa_{2-x}Nb_3O_{10} \cdot yH_2O$ recorded in air: (a) x = 0.25, (b) x = 0.50, and (c) x = 0.75.

compound of $HCa_2Nb_3O_{10}$ (28.32 Å), revealing that the former compounds probably belong to group II (rather than group III), making a higher chain angle α.

With *n*-dodecylamine, we obtain two different sets of intercalation compounds, one with a large c parameter ($c \sim 44.5$ Å) and the other with a small c parameter ($c \sim 37.6$ Å). The compounds with the large c are obtained by drying the sample at room temperature, whereas those with the small c are obtained by annealing the samples at 100°C. Exactly the same behavior was reported by Jacobson *et al.* (*7*) for C_{12}–C_{16} amine intercalation compounds of $HCa_2Nb_3O_{10}$. The changes in c parameter for these phases have been attributed to rearrangement in the packing of the hydrocarbon chains during high-temperature annealing. On the basis of layer expansion systematics of intercalation compounds of $HCa_2Nb_3O_{10}$, Jacobson *et al.* (*7*) have suggested that in general the bilayer organic amine chains are likely to exist in *gauche* blocks (*13*) or 6_1 helices (*14*) rather than linear all-*trans* chains. We believe that the amine configurations of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ intercalation compounds are most likely the same as those of $HCa_2Nb_3O_{10}$ intercalation compounds.

A significant difference between $HCa_2Nb_3O_{10}$ and $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ is in the exchange site density. The exchange site density of $HCa_2Nb_3O_{10}$ is quite high, there being one site per 14.8 Å^2 (*7*). The site density obviously decreases with x in the series $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$. Thus, there would be one site per ~30 Å^2 for the $x = 0.5$ phase, and the approximate area per site would be 60 Å^2 for the $x = 0.75$ phase. What is remarkable is that even with such a low density of protons, facile intercalation of alkylamines occurs in the series $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$, with nearly the same lattice expansion as with the parent compound $HCa_2Nb_3O_{10}$. Obviously, the chains do not seem to fold to fill the void volume as x increases nor does the solid intercalate additional amine molecules. In this respect, the intercalation behavior of $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$ is different from that of clays (*15*) but comparable to that of $Ag_6Mo_{10}O_{33}$ (*15, 16*), where even with a low packing density of amines (area/chain > 50 Å^2), *gauche*-block structures are stabilized. It has been suggested that if the host layers are rigid enough, a few pillars on a large area can pry apart the layers, maintaining a regular distance between them (*15*). The thick

TABLE V

COMPOSITION AND UNIT-CELL PARAMETERS OF *n*-ALKYLAMINE INTERCALATION COMPOUNDS OF $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$

Composition	Lattice parameter (Å)		Weight loss (%)	
	a	*c*	Found	Calculated
$(C_6H_{13}NH_3)_{0.75}La_{0.25}Ca_{1.75}Nb_3O_{10}$	3.882(5)	31.68(2)	13.50	13.76
$(C_6H_{13}NH_3)_{0.50}La_{0.50}Ca_{1.50}Nb_3O_{10}$	3.884(4)	31.56(2)	8.67	8.88
$(C_6H_{13}NH_3)_{0.25}La_{0.75}Ca_{1.25}Nb_3O_{10}$	3.885(6)	29.44(2)	4.30	4.45
$(C_{10}H_{21}NH_3)_{0.75}La_{0.25}Ca_{1.75}Nb_3O_{10}$	3.880(5)	34.28(1)	18.65	18.80
$(C_{10}H_{21}NH_3)_{0.50}La_{0.50}Ca_{1.50}Nb_3O_{10}$	3.885(5)	34.00(1)	12.70	12.82
$(C_{10}H_{21}NH_3)_{0.25}La_{0.75}Ca_{1.25}Nb_3O_{10}$	3.884(6)	34.01(2)	6.30	6.46
$(C_{12}H_{25}NH_3)_{0.75}La_{0.25}Ca_{1.75}Nb_3O_{10}$	3.870(5)	44.42(2)	21.10	21.30
$(C_{12}H_{25}NH_3)_{0.75}La_{0.25}Ca_{1.75}Nb_3O_{10}$[a]	3.874(6)	37.81(1)	20.80	21.30
$(C_{12}H_{25}NH_3)_{0.50}La_{0.50}Ca_{1.50}Nb_3O_{10}$	3.867(4)	44.61(2)	14.50	14.67
$(C_{12}H_{25}NH_3)_{0.50}La_{0.50}Ca_{1.50}Nb_3O_{10}$[a]	3.862(7)	37.55(1)	14.15	14.67

[a] Samples annealed at 100°C.

perovskite-like niobate layers ($La_xCa_{2-x}Nb_3O_{10}$) are apparently quite rigid just like the molybdenum–oxygen layers of $Ag_6Mo_{10}O_{33}$ exhibiting this unusual intercalation behavior. Further investigations of the intercalation of the layered perovskites with other organic bases are in progress.

In summary, we have prepared a new series of layered perovskites of the formula $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$, possessing the structure of $KCa_2Nb_3O_{10}$. The interlayer potassium ions in this series can be exchanged with protons giving the Brønsted acids, $H_{1-x}La_xCa_{2-x}Nb_3O_{10}$, that readily intercalate alkylamines. The end member $LaCaNb_3O_{10}$, isotypic with $KCa_2Nb_3O_{10}$ but containing no interlayer cations, is a novel layered perovskite oxide synthesized for the first time.

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