Synthesis of Anion-Deficient Layered Perovskites, $ACa_2Nb_{3-x}M_xO_{10-x}$ (A = Rb, Cs; M = Al, Fe), Exhibiting Ion-Exchange and Intercalation. Evidence for the Formation of Layered Brownmillerites, $ACa_2Nb_2AlO_9$ (A = Cs, H)[‡]

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Anion-deficient layered perovskite oxides of the formula, $ACa_2Nb_{3-x}M_xO_{10-x}$ (A = Rb, Cs; M = Al, Fe) for $0 < x \leq 1.0$, possessing tetragonal structures similar to the parent $ACa_2Nb_3O_{10}$, have been synthesized. The interlayer A cations in these materials are readily exchanged with protons in aqueous HNO_3 to give the protonated derivatives, $HCa_2Nb_{3-x}M_xO_{10-x}$; the latter are solid Bronsted acids intercalating a number of organic amines including aniline ($pK_a = 4.63$). The distribution of acid sites in the interlayer region of $HCa_2Nb_2MO_9$ inferred from n-alkylamine intercalation suggests that oxygen vacancies and Nb/M atoms are disordered in the $ACa_2Nb_2MO_9$ samples prepared at 1100–1200 °C. Annealing a disordered sample of $CsCa_2Nb_2AlO_9$ for a long time at lower temperatures tends to order the Nb/Al atoms and oxygen vacancies to produce octahedral ($NbO_{6/2}$)–tetrahedral ($AlO_{4/2}$)–octahedral ($NbO_{6/2}$) layer sequence reminiscent of the brownmillerite structure.

Introduction

A variety of oxide materials of current interest are derived from the perovskite ($CaTiO_3$) structure.[1] For instance, the superconducting bismuthates,[2] $(K,Ba)BiO_3$ and $Ba(Pb,Bi)O_3$, the superconducting cuprates,[2,3] $La_{2-x}A_xCuO_4$ (A = Sr, Ba, Na, etc.) and $YBa_2Cu_3O_7$, the ferromagnetic[4] $SrRuO_3$ and $La_{1-x}Sr_xCoO_3$, and the ferroelectric[4] $BaTiO_3$ and $Bi_4Ti_3O_{12}$ are all perovskite-related materials. Besides the large number of stoichiometric (ABO_3) perovskites,[4a] several oxide materials that could be regarded as derivatives of the perovskite structure are known.[5,6] These perovskite derivatives may be grouped into two categories. The first category comprises nonstoichiometric compositions such as ABO_{3-x}, where the point defects are ordered in a specific manner to produce perovskite supersturcutres. Typical examples of this category would be the brownmillerite (Ca_2FeAlO_5) and the $YBa_2Cu_3O_7$ structures. In the brownmillerite structure,[7] oxygen vacancies are ordered along [110] of the cubic perovskite structure resulting in alternate sheets of $FeO_{6/2}$ octahedra (O) and $AlO_{4/2}$ tetrahedra (T) in the c direction. $YBa_2Cu_3O_7$ represents a unique oxygen-vacancy ordering in the perovskite structure,[2,3] where sheets of $CuO_{5/2}$ square-pyramids sandwich $CuO_{4/2}$ chains; the A-site atoms (yttrium and barium) are ordered as well in this structure. The second category of perovskite-derivative structures is represented by the Ruddlesden–Popper phases[8] and the Aurivillius phases.[9] These materials contain two-dimensional perovskite slabs of composition, $[A_{n-1}B_nO_{3n+1}]$, as one of the units building the layered structure. The perovskite slabs may be regarded as formed by slicing the three-dimensional perovskite structure along one of the cubic directions, the thickness of each slab being determined by the number (n) of BO_6 octahedra in the direction perpendicular to the slab. A series of layered oxides of the formula, $A'[A_{n-1}B_nO_{3n+1}]$ (A′ = K, Rb, Cs) discovered by Dion et al.[10] and extended by Jacobson et al.[11] and others[12] also contain such perovskite slabs. This series, of which $CsCa_2Nb_3O_{10}$ is a typical $n = 3$ member, has attracted considerable attention[13] in recent times in view

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of the possibility to carry out interesting interlayer chemistry between the perovskite slabs. Members of this series also exhibit visible light induced photocatalytic activity for hydrogen evolution reaction.[14]

We envisaged that it would be possible to create anion vacancies in the $[A_{n-1}B_nO_{3n+1}]$ perovskite slabs of the latter series by suitable chemical substitution and, if the vacancies were ordered to give rise to definite coordination polyhedra around B atoms, we would have made new anion-vacancy ordered layered perovskites. $La_2ACu_2O_6$ (A = Ca, Sr)[15] and $LaSr_3Fe_{3-x}Al_xO_9$[16] are two examples of such materials, derived respectively from the $n = 2$ and $n = 3$ members of the Ruddlesden-Popper series. To realize this possibility with the Dion–Jacobson series[10,11] of layered perovskites, we chose the oxides $ACa_2Nb_3O_{10}$ (A = Rb, Cs) and sought to replace Nb(V) by Al(III)/Fe(III), which would give the series $ACa_2Nb_{3-x}M_xO_{10-x}$ (M = Al, Fe). We could prepare such materials for the composition range $0 < x \leq 1.0$, for which the parent structure is retained at the gross level. The Al/Fe-substituted materials exhibit ion exchange and intercalation behavior similar to that of the parent $ACa_2Nb_3O_{10}$. Our results, which are reported in this paper, suggest that, while the anion vacancies are not ordered in the as-prepared samples of $ACa_2Nb_{3-x}M_xO_{10-x}$, ordering seems to occur in long-annealed samples of $ACa_2Nb_2AlO_9$ giving rise to octahedral $(NbO_{6/2})$–tetrahedral $(AlO_{4/2})$–octahedral $(NbO_{6/2})$ layer sequence. Accordingly, ordered $ACa_2Nb_2AlO_9$ could be regarded as layered analogs of the brownmillerite structure.

While $LaSr_3Fe_{3-x}Al_xO_9$[16] could be regarded as an anion-vacancy ordered derivative of the $n = 3$ Ruddlesden–Popper phase, $A_4B_3O_{10}$, $CsCa_2Nb_3O_{10}$,[10] may be thought of as an A-site-deficient derivative of $A_4B_3O_{10}$. $CsCa_2Nb_2AlO_9$ reported here represents a new derivative of $A_4B_3O_{10}$ where both ordered A-site vacancies as well as anion vacancies are present.

Experimental Section

Formation of $ACa_2Nb_{3-x}M_xO_{10-x}$ for A = K, Rb, Cs and M = Al or Fe was investigated by reacting appropriate quantities of A_2CO_3, $CaCO_3$, Nb_2O_5, and M_2O_3 at 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. The products were washed with distilled water and dried in air at 100 °C. Protonated derivatives, $HCa_2Nb_{3-x}M_xO_{10-x}$ for $0 < x \leq 1.0$, were prepared from the rubidium/cesium compounds by ion-exchange in aqueous 6 N HNO_3 at 60 °C. The exchange was found to be complete in 3 days. Intercalation of various amines in $HCa_2Nb_{3-x}M_xO_{10-x}$ was investigated by refluxing the protonated solids with a 10% solution of the amine in *n*-heptane for several days. Aniline intercalated into $HCa_2Nb_2AlO_9$ was polymerized by treating the aniline intercalate with an aqueous (0.4 M) solution of $(NH_4)_2S_2O_8$.

^{27}Al NMR spectra of $CsCa_2Nb_2AlO_9$ samples were recorded with a Bruker MSL-300 spectrometer operating at 78.21 MHz. A cylindrical rotor, with a spinning rate of 3–4 kHz was used to record the spectra. Chemical shift values are expressed relative to $Al(H_2O)_6^{3+}$. Other experimental procedures for the characterization of the solid oxides and their intercalates were the same as reported earlier.[13c,d]

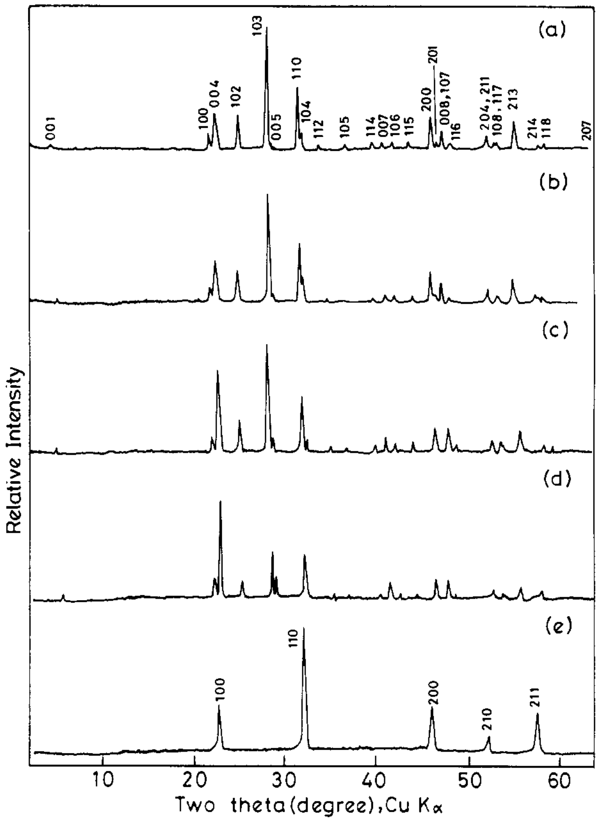

Figure 1. X-ray powder diffraction patterns of (a) $CsCa_2Nb_{2.5}Al_{0.5}O_{9.5}$, (b) $CsCa_2Nb_2AlO_9$, (c) $CsCa_2Nb_{2.5}Fe_{0.5}O_{9.5}$, (d) $CsCa_2Nb_2FeO_9$, and (e) $KCa_2Nb_2FeO_9$.

Results and Discussion

We investigated the substitution of Al^{III}/Fe^{III} for Nb^V in $ACa_2Nb_3O_{10}$ (A = K, Rb, Cs) by reacting the alkali metal carbonates with the component oxides at 1100–1200 °C. Single-phase materials corresponding to the composition $ACa_2Nb_{3-x}M_xO_{10-x}$ were readily obtained for A = Rb and Cs in the range $0 < x \leq 1.0$. Energy-dispersive X-ray emission (EDX) analysis of the $x = 1$ members $CsCa_2Nb_2MO_9$ (M = Al, Fe), showed that the Cs:Ca:Nb:M ratio was 1:2:2:1 (within the experimental error) as expected for the formula. For example, the percentages of Cs, Ca, Nb and Al atoms in $CsCa_2Nb_2AlO_9$ were 14.5(7), 34.0(6), 34.4(3), and 17.0(5), respectively, while the corresponding calculated percentages are 16.67, 33.33, 33.33, and 16.67, respectively. Powder X-ray diffraction patterns (Figure 1) revealed that the phases possessed tetragonal structures similar to the parent $ACa_2Nb_3O_{10}$ (A = Rb, Cs).[10,13a] In Table 1, we give an indexing of the powder diffraction data for $CsCa_2Nb_2MO_9$ and, in Table 2, the lattice parameters of all the members of the series synthesized. The results show that it is indeed possible to substitute Al(III)/Fe(III) for Nb(V) in $ACa_2Nb_3O_{10}$ (A = Rb, Cs) retaining the layered perovskite structure of the parents. Interestingly, a similar substitution in $KCa_2Nb_3O_{10}$ did not occur; for instance, $KCa_2Nb_2FeO_9$ prepared by similar means adopted a cubic perovskite structure with $a = 3.932(4)$ Å (Figure 1e), instead of a layered structure.

It is known[11,13a] that layered $ACa_2Nb_3O_{10}$ readily exchange the interlayer A cations for protons in aqueous acids to give the corresponding protonated derivative,

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Table 1. X-ray Powder Diffraction Data for $CsCa_2Nb_2AlO_9$ and $CsCa_2Nb_2FeO_9$[a]

	$CsCa_2Nb_2AlO_9$			$CsCa_2Nb_2FeO_9$		
h k l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
0 0 1	15.24	15.11	3	15.11	15.14	5
1 0 0	3.867	3.873	13	3.883	3.876	15
0 0 4	3.770	3.778	38	3.778	3.785	100
1 0 2	3.447	3.446	29	3.447	3.450	13
1 0 3	3.069	3.070	100	3.079	3.074	45
0 0 5	3.023	3.022	7	3.023	3.028	20
1 1 0	2.743	2.738	54	2.743	2.740	43
1 0 4	2.710	2.704	22		2.708	
0 0 6	2.518	2.518	2	2.516	2.523	5
1 1 4	2.217	2.217	4	2.217	2.220	3
0 0 7	2.159	2.159	6	2.161	2.163	15
1 0 6	2.110	2.111	5	2.113	2.115	4
1 1 5	2.032	2.029	5		2.032	
2 0 0	1.937	1.937	26	1.937	1.938	18
2 0 1	1.922	1.920	6		1.922	
0 0 8		1.889			1.893	
	1.886		19	1.888		18
1 0 7		1.885			1.889	
1 1 6	1.852	1.854	4	1.855	1.856	3
2 0 4		1.723			1.725	
	1.723		11	1.723		7
2 1 1		1.720			1.722	
1 1 7	1.692	1.695	4	1.697	1.698	3
2 1 3	1.639	1.638	20	1.639	1.639	11
2 1 4	1.572	1.574	5	1.576	1.576	7
1 1 8	1.555	1.555	2		1.557	
0 0 11		1.374			1.376	
	1.370		4	1.370		5
2 2 0		1.369			1.370	
2 0 8		1.352			1.354	
	1.352		4	1.352		5
2 1 7		1.351			1.353	

[a] $a = 3.873(5)$; $c = 15.10(2)$ Å. $a = 3.876(8)$; $c = 15.14(3)$ Å.

Table 2. Lattice Parameters of $ACa_2Nb_{3-x}M_xO_{10-x}$ ($0 \leq x \leq 1.0$) (A = Rb, Cs; M = Al, Fe) and $KCa_2Nb_2FeO_9$

compound	*a* (Å)	*c* (Å)
$CsCa_2Nb_3O_{10}$	3.873(3)	15.08(1)
$CsCa_2Nb_{2.75}Al_{0.25}O_{9.75}$	3.866(3)	15.09(1)
$CsCa_2Nb_{2.50}Al_{0.50}O_{9.50}$	3.875(4)	15.13(2)
$CsCa_2Nb_{2.25}Al_{0.75}O_{9.25}$	3.873(5)	15.11(2)
$CsCa_2Nb_2AlO_9$	3.873(5)	15.10(2)
$CsCa_2Nb_{2.50}Fe_{0.50}O_{9.50}$	3.875(5)	15.06(2)
$CsCa_2Nb_2FeO_9$	3.876(8)	15.14(3)
$RbCa_2Nb_2AlO_9$	3.864(5)	14.94(2)
$RbCa_2Nb_2FeO_9$	3.885(7)	14.92(3)
$KCa_2Nb_2FeO_9$[a]	3.932(4)	

[a] Cubic perovskite structure.

$HCa_2Nb_3O_{10}$; the latter is a solid Bronsted acid exhibiting intracrystalline reactivity and intercalation behavior similar to clay minerals.[11,13b] We anticipated that layered $ACa_2Nb_{3-x}M_xO_{10-x}$ also would exhibit a similar reactivity. Accordingly, we could readily prepare protonated derivatives of $ACa_2Nb_{3-x}M_xO_{10-x}$ by ion exchange in aqueous HNO_3. Thermogravimetric analyses (Figure 2, Table 3) showed that the protonated derivatives were all hydrated, containing 0.6–1.4 molecules of water/formula unit of the oxide; the water molecules dehydrated around 80–100 °C. EDX analysis of the protonated materials revealed that the alkali ion was completely exchanged out and that the Ca:Nb:M ratio was not altered during the ion exchange. X-ray powder patterns (Figure 3) showed that the protonated materials were all isostructural with $HCa_2Nb_3O_{10}$ and $HCa_2Nb_3O_{10}\cdot1.5H_2O$,[13a] retaining the tetragonal structures of the parent materials (Table 3).

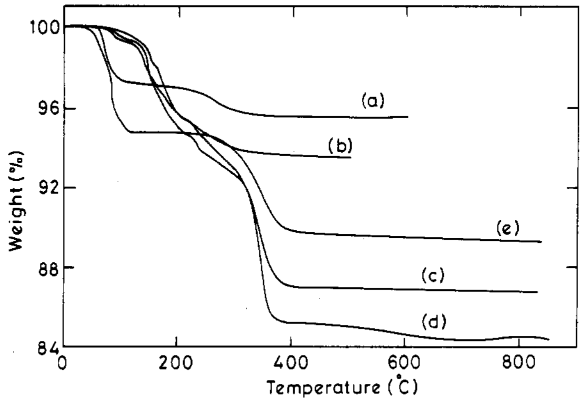

Figure 2. Thermogravimetric curves of (a) $HCa_2Nb_2AlO_9\cdot0.9H_2O$, (b) $HCa_2Nb_2AlO_9\cdot1.4H_2O$, (c) $(n\text{-}C_6H_{13}NH_3)_{0.6}\,H_{0.4}Ca_2Nb_2AlO_9$ (obtained from $HCa_2Nb_2AlO_9\cdot0.9H_2O$), (d) $(n\text{-}C_6H_{13}NH_3)_{0.8}\,H_{0.2}\text{-}Ca_2Nb_2AlO_9$ (obtained from $HCa_2Nb_2AlO_9\cdot1.4H_2O$), and (e) $C_6H_5\text{-}NH_3)_{0.5}H_{0.5}Ca_2Nb_2AlO_9$. Sample (a) was obtained by ion-exchange of as-prepared $CsCa_2Nb_2AlO_9$; sample (b) was obtained by ion-exchange of $CsCa_2Nb_2AlO_9$ annealed at 1000–950 °C for 4 weeks.

Table 3. Lattice Parameters of $HCa_2Nb_{3-x}M_xO_{10-x}$ ($0 \leq x \leq 1.0$) (M = Al, Fe) and Their Hydrates

compound	*a* (Å)	*c* (Å)
$HCa_2Nb_3O_{10}\cdot1.5H_2O$	3.854(4)	16.23(2)
$HCa_2Nb_3O_{10}$	3.850(6)	14.38(3)
$HCa_2Nb_{2.75}Al_{0.25}O_{9.75}\cdot1.1H_2O$	3.858(4)	16.27(2)
$HCa_2Nb_{2.75}Al_{0.25}O_{9.75}$	3.863(6)	14.43(2)
$HCa_2Nb_{2.50}Al_{0.50}O_{9.50}\cdot1.0H_2O$	3.856(4)	16.20(2)
$HCa_2Nb_{2.50}Al_{0.50}O_{9.50}$	3.859(7)	14.47(4)
$HCa_2Nb_{2.25}Al_{0.75}O_{9.25}\cdot1.0H_2O$	3.856(4)	16.26(2)
$HCa_2Nb_{2.25}Al_{0.75}O_{9.25}$	3.865(6)	14.42(5)
$HCa_2Nb_2AlO_9\cdot0.9H_2O$[a]	3.857(5)	16.22(2)
$HCa_2Nb_2AlO_9\cdot1.4H_2O$[b]	3.866(4)	16.27(3)
$HCa_2Nb_2AlO_9$	3.857(5)	14.41(2)
$HCa_2Nb_{2.75}Fe_{0.25}O_{9.75}\cdot1.1H_2O$	3.857(6)	16.27(3)
$HCa_2Nb_{2.75}Fe_{0.25}O_{9.75}$	3.862(8)	14.47(3)
$HCa_2Nb_{2.50}Fe_{0.50}O_{9.50}\cdot1.1H_2O$	3.853(6)	16.22(3)
$HCa_2Nb_{2.50}Fe_{0.50}O_{9.50}$	3.864(5)	14.42(2)
$HCa_2Nb_{2.25}Fe_{0.75}O_{9.25}\cdot1.0H_2O$	3.871(6)	16.26(5)
$HCa_2Nb_{2.25}Fe_{0.75}O_{9.25}$	3.871(7)	14.42(7)
$HCa_2Nb_2FeO_9\cdot0.6H_2O$	3.886(4)	16.25(5)
$HCa_2Nb_2FeO_9$	3.885(7)	14.43(4)

[a] Sample obtained by ion exchange of as-prepared $CsCa_2Nb_2AlO_9$. [b] Sample obtained by ion exchange of $CsCa_2Nb_2AlO_9$ annealed at 1000–950 °C for 4 weeks.

Table 4. Composition and Lattice Parameters of *n*-Hexylamine Intercalation Compounds of $HCa_2Nb_{3-x}M_xO_{10-x}$ ($0 \leq x \leq 1.0$) (M = Al, Fe)

		lattice parameters (Å)	
host	amine content	*a*	*c*
$HCa_2Nb_3O_{10}$	1.00	3.856(4)	28.36(2)
$HCa_2Nb_{2.75}Al_{0.25}O_{9.75}$	0.80	3.860(6)	28.18(2)
$HCa_2Nb_{2.50}Al_{0.50}O_{9.50}$	0.75	3.858(4)	28.68(5)
$HCa_2Nb_{2.25}Al_{0.75}O_{9.25}$	0.70	3.866(7)	28.60(7)
$HCa_2Nb_2AlO_9$[a]	0.60	3.851(7)	28.24(6)
$HCa_2Nb_2AlO_9$[b]	0.80	3.862(4)	28.48(5)
$HCa_2Nb_{2.50}Fe_{0.50}O_{9.50}$	0.76	3.870(5)	28.39(7)
$HCa_2Nb_{2.25}Fe_{0.75}O_{9.25}$	0.70	3.885(6)	28.24(8)
$HCa_2Nb_2FeO_9$	0.60	3.880(7)	28.28(6)

[a] Sample obtained by ion exchange of as-prepared $CsCa_2Nb_2AlO_9$. [b] Sample obtained by ion exchange of $CsCa_2Nb_2AlO_9$ annealed at 1000–950 °C for 4 weeks.

The protonated materials, $HCa_2Nb_{3-x}M_xO_{10-x}$, are solid Bronsted acids, as is the parent $HCa_2Nb_3O_{10}$,[13b] readily intercalating *n*-alkylamines to form *n*-alkylammonium derivatives, $(n\text{-}C_nH_{2n+1}NH_3)_zH_{1-z}[Ca_2Nb_{3-x}M_xO_{10-x}]$. In Figure 4, we show the X-ray diffraction patterns of a few typical intercalation compounds and in Tables 4 and 5, we list the composition and lattice parameters of all the

Table 5. Composition and Lattice Parameters of Intercalation Compounds of $HCa_2Nb_2MO_9$ (M = Al, Fe)

	$HCa_2Nb_2AlO_9$			$HCa_2Nb_2FeO_9$		
		lattice parameters (Å)			lattice parameters (Å)	
amine	intercalated amine content	*a*	*c*	intercalated amine content	*a*	*c*
n-hexylamine	0.60	3.851(7)	28.24(6)	0.60	3.880(7)	28.28(6)
n-heptylamine	0.60	3.860(7)	30.39(4)	0.50	3.878(6)	30.50(4)
n-octylamine	0.60	3.859(5)	31.86(6)	0.50	3.886(5)	31.75(4)
n-nonylamine	0.60	3.856(6)	33.30(7)	0.50	3.887(6)	33.26(5)
n-decylamine	0.62	3.862(4)	34.61(5)	0.50	3.887(4)	34.72(4)
n-dodecylamine	0.58	3.860(5)	44.75(5)	0.50	3.887(7)	44.80(6)
n-dodecylamine[a]	0.50	3.861(4)	37.90(5)	0.50	3.885(4)	37.94(7)
n-hexadecylamine	0.63	3.857(6)	52.89(7)	0.60	3.886(4)	52.94(6)
n-hexadecylamine[a]	0.60	3.857(5)	44.63(4)	0.60	3.880(6)	44.65(4)
n-octadecylamine	0.50	3.855(7)	57.42(6)	0.44	3.879(7)	57.52(4)
pyridine	0.30	3.851(6)	18.39(7)	0.25	3.878(7)	18.41(7)
aniline	0.50	3.87(5)	25.42(6)	0.50	3.880(6)	25.46(7)

[a] Samples annealed around 100 °C.

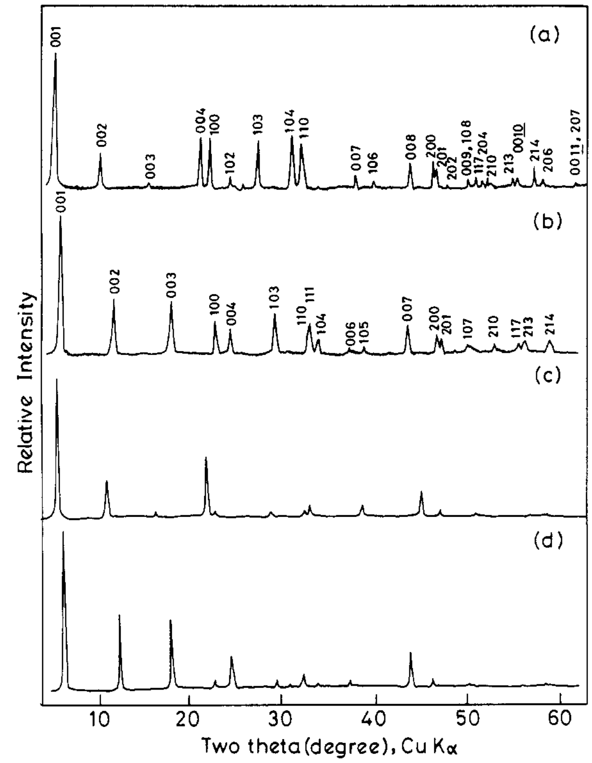

Figure 3. X-ray powder diffraction patterns of $HCa_2Nb_{3-x}M_xO_{10-x}$ and their hydrates: (a) $HCa_2Nb_2AlO_9{\cdot}1.4H_2O$, (b) $HCa_2Nb_2AlO_9$, (c) $HCa_2Nb_2FeO_9{\cdot}0.6H_2O$, and (d) $HCa_2Nb_2FeO_9$.

intercalation compounds of $HCa_2Nb_{3-x}M_xO_{10-x}$. Besides *n*-alkylamines, we could also intercalate pyridine (pK_a = 5.25) and aniline (pK_a = 4.63) in $HCa_2Nb_2MO_9$, revealing that the Bronsted acidity of these materials is nearly the same as $HCa_2Nb_3O_{10}$. The latter intercalates pyridine but not 3-bromopyridine (pK_a = 2.8).[13b] Interestingly, we could polymerize the monomer aniline intercalated into $HCa_2Nb_2MO_9$ by oxidation[17] with $(NH_4)_2S_2O_8$ giving novel polyaniline/$Ca_2Nb_2MO_9$ composites.[18]

The *n*-alkylamine intercalation compounds of $HCa_2Nb_{3-x}M_xO_{10-x}$ show large expansions of the *c*-parameter (Tables 4 and 5), the values being nearly the same as those of $HCa_2Nb_3O_{10}$.[13b] Accordingly, a plot of the *c* parameters of the intercalation compounds of $HCa_2Nb_2MO_9$ (M = Al, Fe) against the number of carbon atoms in the *n*-alkylamines (Figure 5) shows two linear regions, one for C_6–C_{16} amines and the other for C_{12}–C_{18} amines. The alkyl chain orientation angles, α, derived from the slopes of the plots are 39.6° and 58° for the two regions. The corresponding angles are 40.5° and 62.3° for the *n*-alkylamine intercalation compounds[13b] of $HCa_2Nb_3O_{10}$. The results clearly show that the Bronsted acidity and intercalation behavior of $HCa_2Nb_{3-x}M_xO_{10-x}$ members closely resembles the behavior of $HCa_2Nb_3O_{10}$. There is however one significant difference, namely the quantity of the amine intercalated. The data given in Tables 4 and 5 reveal that the quantity of amine intercalated in $HCa_2Nb_{3-x}M_xO_{10-x}$ decreases with *x* and that the average amine content of

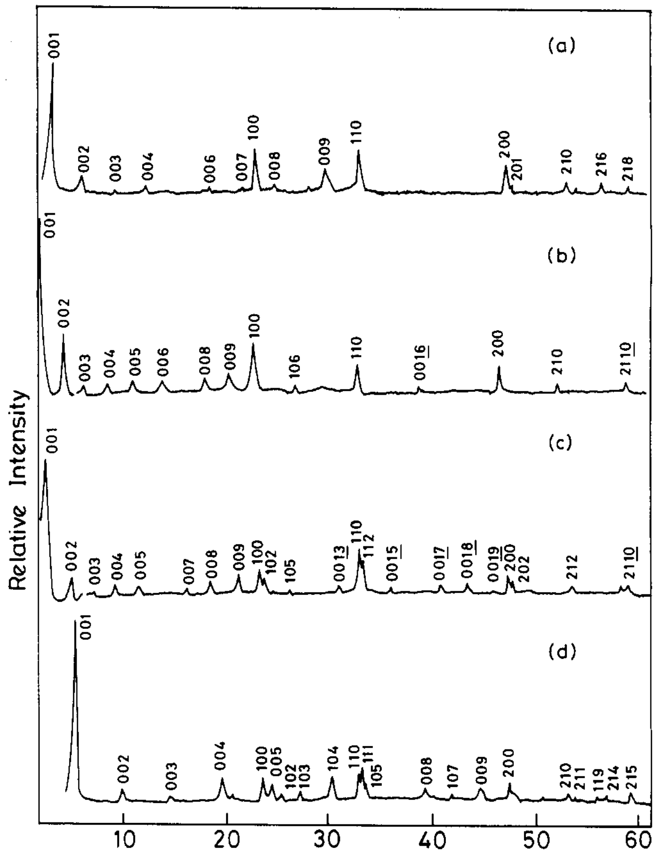

Figure 4. X-ray powder diffraction patterns of typical intercalation compounds of $HCa_2Nb_{3-x}M_xO_{10-x}$: (a) $(n\text{-}C_6H_{13}NH_3)_{0.75}H_{0.25}Ca_2Nb_{2.5}Al_{0.5}O_{9.5}$, (b) $n\text{-}C_{10}H_{21}NH_3)_{0.62}H_{0.38}Ca_2Nb_2AlO_9$, (c) $(n\text{-}C_{12}H_{25}NH_3)_{0.50}H_{0.50}Ca_2Nb_2FeO_9$, and (d) $(C_5H_5NH)_{0.25}H_{0.75}Ca_2Nb_2FeO_9$.

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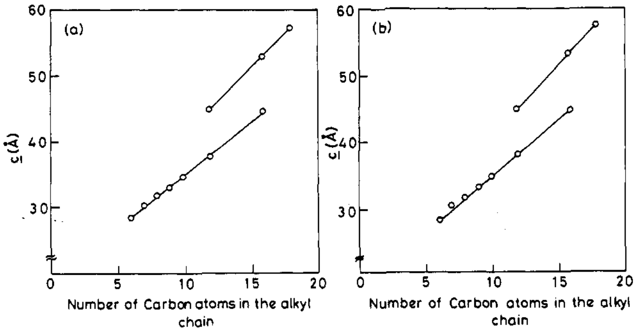

Figure 5. Plots of *c* parameter versus the number of carbon atoms in (a) $(n\text{-}C_nH_{2n+1}NH_3)_xH_{1-x}Ca_2Nb_2AlO_9$ and (b) $(n\text{-}C_nH_{2n+1}NH_3)_xH_{1-x}Ca_2Nb_2FeO_9$.

$HCa_2Nb_2MO_9$ intercalates is around 0.6 mol of amine/formula unit of the host solid. $HCa_2Nb_3O_{10}$, on the other hand, takes up 1 mol of amine/formula unit of the host solid,[13b] corresponding to the transformation of all the interlayer protons to *n*-alkylammonium ions.

The intercalation of less than 1 mol of amine/formula unit of the host most likely implies that, unlike in $HCa_2Nb_3O_{10}$, all the interlayer protons of $HCa_2Nb_2MO_9$ (M = Al, Fe) do not have the same acidity. The differential acidity of the protons in $HCa_2Nb_2MO_9$ would in turn imply that the Nb and M atoms (as well as the oxygen vacancies) in the perovskite slabs are not ordered. Assuming a statistical distribution of Nb and M atoms in the triple-perovskite slabs, $[Ca_2Nb_2MO_9]$, one would expect that Nb atoms occupy two-thirds of the octahedral sites and Al atoms, one-third of the octahedral sites in every sheet. The oxygen vacancies are most likely distributed around the M atoms converting their octahedra into square pyramids. It is possible to visualize several models for the disordered structure of $ACa_2Nb_2MO_9$. Two such models, which are speculative, are shown in Figure 6a,b.

The implication of such a disordered structure toward the acidity of $HCa_2Nb_2MO_9$ is that there are three different kinds of protons in the interlayer region, viz., NbO···H···ONb (I), NbO···H···OM (II), and MO···H···OM (III), their relative proportion being approximately 44.5%, 44.5%, and 11%, respectively. Presumably, the acid strength of these sites would vary in the order I > II > III. Intercalation of about 0.50–0.60 mol of amine in $HCa_2Nb_2MO_9$ (Table 5) is qualitatively in agreement with the above model, indicating that the most acidic sites I and part of acid sites II are probably involved in intercalation of *n*-alkylamines.

As mentioned in the Introduction, the primary motivation for the present work was to prepare anion-vacancy ordered layered perovskites of the type $ACa_2Nb_2MO_9$ (M = Al, Fe). Since the materials of this composition prepared at 1100–1200 °C turned out to be disordered, containing most likely a statistical distribution of Nb/M atoms as well as oxygen vacancies in the perovskite slabs, we explored the possibility of ordering the atoms/vacancies by annealing the samples for long periods. By trial and error, we found that ordering occurs on annealing the as-prepared $CsCa_2Nb_2AlO_9$ at 1000–950 °C. A sample of $CsCa_2Nb_2AlO_9$ annealed for 4 weeks yielded a $HCa_2Nb_2AlO_9$ that intercalated 0.80 mol of *n*-hexylamine/mol of the solid (Table 4). More importantly, another sample of $CsCa_2Nb_2AlO_9$ annealed for 8 weeks at 1000 °C and slowly cooled (1 °C/min) to 600 °C yielded a $HCa_2Nb_2AlO_9$ that intercalated ~0.90 mol of *n*-hexylamine/mol of the oxide.

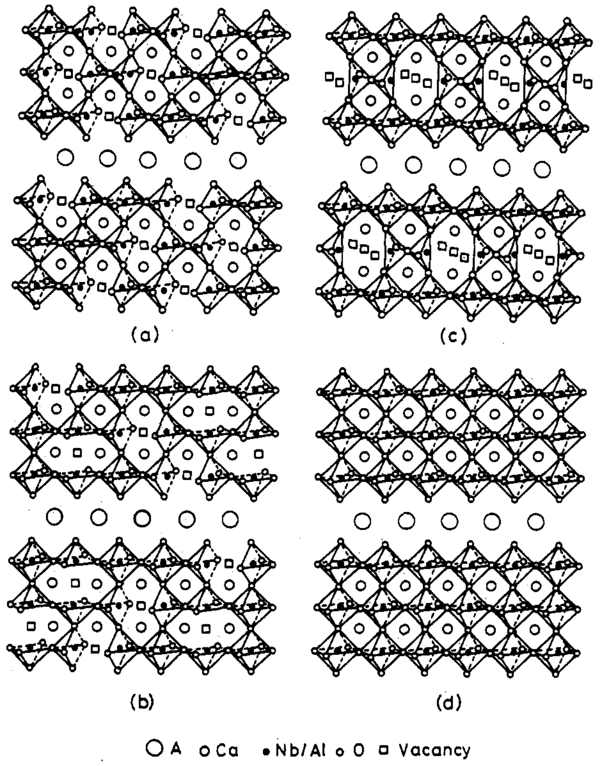

Figure 6. Possible models for the structure of $ACa_2Nb_2AlO_9$ (A = Rb, Cs): (a) and (b) disordered structures for as-prepared samples; (c) ordered structure for sample annealed for long time. In (d), the structure of $ACa_2Nb_3O_{10}$ is shown for comparison.

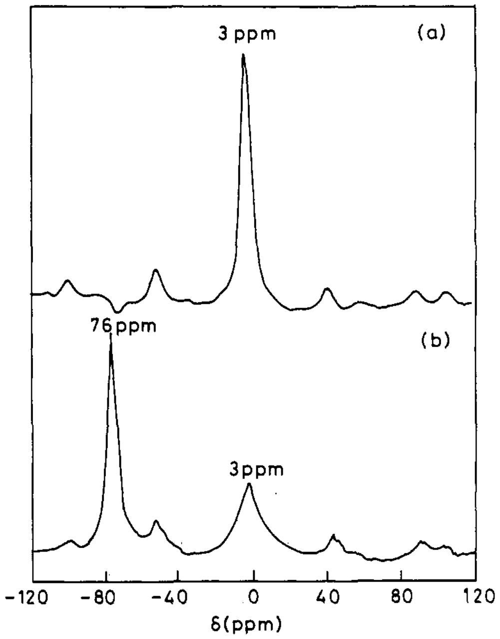

Figure 7. ^{27}Al NMR spectra of (a) $CsCa_2Nb_2AlO_9$ prepared at 1150 °C and (b) $CsCa_2Nb_2AlO_9$ annealed at 1000–950 °C for 8 weeks.

Accordingly, we believe that, on long-annealing, $CsCa_2Nb_2AlO_9$ orders into a structure consisting of octahedral $(NbO_{6/2})$–tetrahedral $(AlO_{4/2})$–octahedral $(NbO_{6/2})$ layer sequence in the $[Ca_2Nb_2AlO_9]$ slabs (Figure 6c). Such a structure would be a two-dimensional analog of the brownmillerite structure, in the same way as $ACa_2Nb_3O_{10}$ (Figure 6d) is a two-dimensional analog of the perovskite structure. A similar octahedral–tetrahedral–octahedral, brownmillerite–like, layered structure has recently been proposed for $LaSr_3Fe_2AlO_9$, and evidence toward such an ordering was indeed found for the composition, $LaSr_3(Fe_{0.8}Al_{0.2})_3O_{8.95}$, from a single-crystal X-ray and neutron powder diffraction study.[16] Confirmation of the ordered structure proposed for $ACa_2Nb_2AlO_9$ (A = Cs, H) in this work must await a crystal structure determination.

In an attempt to provide further support to the formation of an ordered $CsCa_2Nb_2AlO_9$ on annealing, we recorded ^{27}Al NMR spectra of the as-prepared and long-annealed samples. The spectrum of the as-prepared sample (Figure 7a) shows a single resonance with a chemical shift of ~3 ppm relative to $Al(H_2O)_6^{3+}$. Such a resonance is characteristic of octahedral/near-octahedral coordination of Al(III) in oxides.[19-21] In contrast, the annealed sample shows a sharp resonance at 76 ppm that has grown at the expense of the resonance at 3 ppm (Figure 7b). The resonance at 76 ppm is most likely due to tetrahedrally[22] coordinated Al(III). ^{27}Al NMR experiments therefore indicate that ordering of Al(III) indeed occurs in the long-annealed samples of $CsCa_2Nb_2AlO_9$ giving tetrahedral coordination to Al(III) and thus supporting the ordered structure suggested in Figure 6c.

In summary, we have shown that it is possible to substitute Al(III)/Fe(III) for Nb(V) in $ACa_2Nb_3O_{10}$ (A = Rb, Cs) giving $ACa_2Nb_{3-x}M_xO_{10-x}$ ($0 < x \leq 1.0$) that retain the layered structure of the parent materials. Interlayer A cations in the Al(III)/Fe(III)-substituted materials are readily exchanged with protons in aqueous HNO_3 to give the corresponding protonated derivatives, $HCa_2Nb_{3-x}M_xO_{10-x}$. The latter are solid Bronsted acids intercalating *n*-alkylamines and aniline. From the quantity of *n*-alkylamine intercalated into the $x = 1$ member, $HCa_2Nb_2MO_9$, we inferred that the oxygen vacancies as well as the Nb and M atoms are not ordered in the as-prepared samples. On annealing the as-prepared $CsCa_2Nb_2AlO_9$ for long periods, ordering seems to occur to give rise to octahedral (NbO_6)–tetrahedral (AlO_4)–octahedral (NbO_6) layer sequence, reminiscent of the brownmillerite structure.

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