Synthesis and Intercalation Chemistry of $K[Ca_2(Ca,Sr)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$ ($n = 4, 5$)

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A new series of layered perovskite oxides, $K[Ca_2(Ca,Sr)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$, has been prepared by the incorporation of $Ca(Sr)TiO_3$ perovskite slabs into $KCa_2Nb_3O_{10}$. With an increase in n, there is a progressive increase in unit cell parameters. Potassium atoms in these compounds can be exchanged by protons and these protonated forms do not show a doubled c axis. Proton-exchanged forms of these layered perovskite oxides are solid acids and react with organic bases such as n-hexylamine, forming n-$C_6H_{13}NH_3[Ca_2(Ca,Sr)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$, resulting in large layer separations. © 1991 Academic Press, Inc.

Introduction

Layered oxides having the general formula $M_m[A_{n-1}B_nO_{3n+1}]$ with $m = 2$, generally referred to as Ruddlesden–Popper phases, have corner-shared BO_6 octahedra in the layers with M atoms occupying the 9-coordinate sites between the perovskite layers (*1*). A schematic illustration of some of the members of the series is shown in Fig. 1. These oxides exhibit gradual changes in their electronic and magnetic properties with a progressive increase in n, and the lattice dimensionality changes from 2 to 3 as n increases from 2 to ∞ (*2–4*). These phases have two M atoms per formula unit in between the perovskite layers but do not show any interlayer chemistry (however, see below). A few years ago, Dion *et al.* (*5*) reported new layered perovskite oxides of the general formula $MCa_2Nb_3O_{10}$ (M = K, Rb, Cs, Tl; $n = 3$; $m = 1$). These oxides have a lower interlayer charge density and thereby exhibit interesting interlayer reaction chem-

istry. Following this, a series of oxides, $A[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ (A = K, Rb, Cs; $n = 3$–7), has been prepared and its interlayer reaction chemistry has been studied in detail (*6, 7*). The recent literature also contains reports on the synthesis and characterization of other related compounds such as $KLnNb_2O_7$ (Ln = La, Nd) (*8, 9*), $A_2Ln_2Ti_3O_{10}$ (A = Na, K, Rb; Ln = La, Nd, Sm, Gd, Dy) (*10, 11*), and $ABiNb_2O_7$ and $APb_2Nb_3O_{10}$ (A = Rb, Cs) (*12*). The commonality of all these oxides is that they readily exchange ions with the interlayer cation (*5–12*). Exchange has been observed in molten salts and by treatment with aqueous acid at ambient or elevated temperatures. Among the above compounds, the $A_2Ln_2Ti_3O_{10}$ family of oxides is the first example of layered oxides possessing a Ruddlesden–Popper structure with $m = 2$ and exhibiting interlayer chemistry. The protonated forms of these oxides, $H[A_{n-1}B_n O_{3n+1}]$, are solid acids and react with liquid or solid bases such as n-alkyl amines, yield-
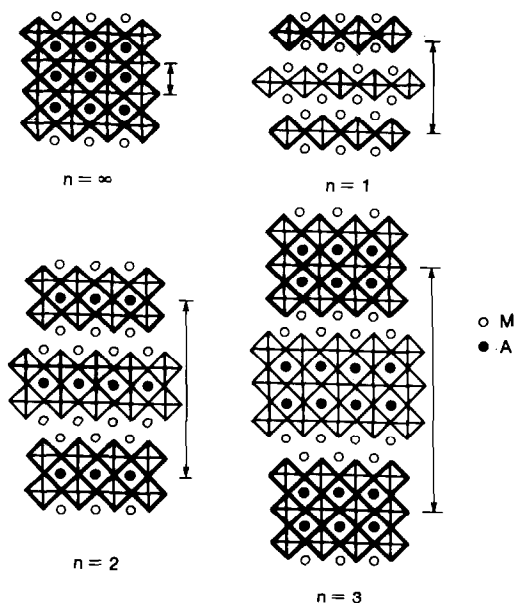
FIG. 1. Schematic illustration of some of the members of $M_m[A_{n-1}B_nO_{3n+1}]$ ($m = 2$; $n = 1, 2, 3$, and ∞).

ing products with large interlayer spacings. More recently, Treacy et al. (13) have been able to intercalate basic surfactant molecules into the phases, $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$, which result in the exfoliation of the layers into thin sheets.

Jacobson et al. (6) have prepared higher members of $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ ($n = 3-7$) by incorporating additional perovskite slabs of NbO_6 octahedra into the parent compound $KCa_2Nb_3O_{10}$. They have used $NaNbO_3$, a I–V perovskite oxide having a transition metal similar to that present in $KCa_2Nb_3O_{10}$, thus avoiding complexity. We thought that, by analogy, we should be able to incorporate other perovskite oxides such as $CaTiO_3$ and $SrTiO_3$ (II–IV perovskites) possessing different transition metal ions in different oxidation states than those of the parent compound (Ti^{4+} for Nb^{5+}), giving new oxides with higher layer thickness but preserving the interlayer cation chemistry of the parent compound, $KCa_2Nb_3O_{10}$, in-

tact. In this paper we report the synthesis of three new layered compounds of the general formula $K[Ca_2(Ca,Sr)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$.

We have been able to prepare $n = 4$ and $n = 5$ oxides by high-temperature reactions of $KCa_2Nb_3O_{10}$ with $CaTiO_3$ and only an $n = 4$ oxide in the case of $SrTiO_3$. It is interesting that the $n = 4$ oxide for the incorporation of $SrTiO_3$ into $KCa_2Nb_3O_{10}$ gives the expected layer thickness with only a half a mole of $SrTiO_3$, and additional amounts of $SrTiO_3$, if added, will be present as an impurity phase. Potassium ions in these compounds readily exchange for protons to give $H[Ca_2(Ca,Sr)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$ ($n = 4, 5$). These protonated oxides are solid acids and react with organic bases to give the respective alkylammonium derivatives. We have also been able to prepare an $n = 4$ compound with $CaTiO_3$ from a typical solid state reaction starting from individual oxides and exhibiting similar ion exchange properties.

Experimental

$KCa_2Nb_3O_{10}$ was prepared by firing stoichiometric amounts of $CaCO_3$ (Aldrich, 99 + %), K_2CO_3 (Aldrich, 99 + %), and Nb_2O_5 (Aldrich, 99.9%) at 1200°C in air, a procedure similar to that used by Dion et al. (5). $CaTiO_3$ and $SrTiO_3$ were prepared by heating stoichiometric amounts of $CaCO_3$/$SrCO_3$ (Aldrich, 99 + %/99.99%) and TiO_2 (Aldrich, 99.9%) at 1200°C for 3 days, with a subsequent annealing in O_2 for 12 hr at 900°C. Higher members of the $K[Ca_2Ca_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$ ($n = 4, 5$) were prepared by heating $KCa_2Nb_3O_{10}$ and $CaTiO_3$ in 1 : 1 and 1 : 2 molar ratios. Thoroughly mixed starting materials were heated at 1235 and 1300°C for 3 days. An $n = 4$ member of the $K[Ca_2Sr_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$ series was prepared by firing $KCa_2Nb_3O_{10}$ and 0.5 mole of $SrTiO_3$ at 1240°C for 2–3 days. $KCa_3Nb_3TiO_{13}$ ($n = 4$) was also prepared by heating stoichiometric amounts of K_2CO_3, $CaCO_3$, Nb_2O_5, and

TiO$_2$ at 1300°C for 3 days. An additional 20 mole% of K$_2$CO$_3$ was added in excess to avoid a possible loss of potassium due to volatilization. The product was washed thoroughly with distilled water to wash away the excess potassium ions and this was done by testing the filtrate for potassium ions. All the above firings were carried out with two intermittent grindings to ensure efficient mixing of the reactants so as to yield monophasic products. All final products were heated at 800°C for 12 hr in flowing oxygen to ensure proper oxygen stoichiometry. Potassium forms were converted to proton forms by refluxing with 6 N HCl at 60°C for 3 days, with the acid being replaced everyday. n-Hexylammonium [Ca$_2$ (Ca,Sr)$_{n-3}$Nb$_3$Ti$_{n-3}$O$_{3n+1}$] (n = 4, 5) phases were prepared by refluxing the protonated forms with n-hexylamine in water for 2–3 days at 60°C.

The phase purity of the products was established by X-ray diffraction studies using a computer controlled Seifert Scintag PAD-II diffractometer equipped with Ni-filtered Cu$K\alpha$ radiation. The patterns were step scanned in steps of 0.02° for 10′ out to 60° 2θ. Data analysis was performed using computer programs specially developed for analyzing X-ray powder data (14). Lattice parameters were determined from the peak positions of reflections in the 2θ range 3°–60° by a least-squares fitting procedure. The water content as well as the stoichiometry of the hexylamine derivatives was established by thermogravimetric analysis done on a DuPont thermal analyst Model 2000 unit.

Results and Discussion

The unit cell parameters of K[Ca$_2$Ca$_{n-3}$ Nb$_3$Ti$_{n-3}$O$_{3n+1}$] (n = 4, 5) are listed in Table I. With an increase in n, the number of perovskite layers, there is a slight decrease in a and b parameters, but in the c-direction there is an increase in the layer thickness by 3.903 Å for n = 4 and 3.865 Å for n = 5,

TABLE I

LATTICE CONSTANTS OF
KCa$_2$(Ca,Sr)$_{n-3}$Nb$_3$Ti$_{n-3}$O$_{3n+1}$ (n = 3–5)

Compound	a (Å) ($\pm$0.002)	b (Å) ($\pm$0.002)	c (Å) ($\pm$0.01)
KCa$_2$Nb$_3$O$_{10}$	3.846	3.864	29.36
KCa$_3$Nb$_3$TiO$_{13}$	3.842	3.861	37.27
KCa$_4$Nb$_4$Ti$_2$O$_{16}$	3.833	3.856	45.00
KCa$_2$Sr$_{0.5}$Nb$_3$Ti$_{0.5}$O$_{11.5}$	3.863	3.878	37.39

suggesting an average increase of ~3.88 Å per additional layer added. A plot of layer thickness as a function of the number of perovskite layers is shown in Fig. 2. The interlayer separation (c/2) increases linearly with increasing n, and the slope calculated from Fig. 2 is 3.881 Å per each additional octahedron added, which is consistent with the structural model. The slight decrease in a and b parameters with an increase in n could be due to the elongation of the TiO$_6$ octahedra in the c-direction and shorter Ti–O–Ti bonds in the ab-plane. During the synthesis of these compounds the firing temperature was found to be very crucial, as even small changes resulted in multiphasic products. We were unsuccessful in preparing higher ($n \geq 6$) members of the series. Higher reaction temperatures (1300–1400°C) of preparation resulted in the formation of perovskite phases with smaller unit cells, in addition to very small amounts of phases corresponding to the lower members of the series. For example; in an attempt to prepare the n = 6 phase, KCa$_2$Nb$_3$O$_{10}$ and 3 mole of CaTiO$_3$ was heated between 1300–1400°C. The product gave an X-ray diffraction pattern showing low-intensity peaks corresponding to n = 4 and 5 phases, whereas the major phase corresponded to a CaTiO$_3$-related perovskite phase. Longer heating periods were also not of much help in preparing the higher members of the homologous series. We believe that part of the problem is volatilization of the alkali-metal
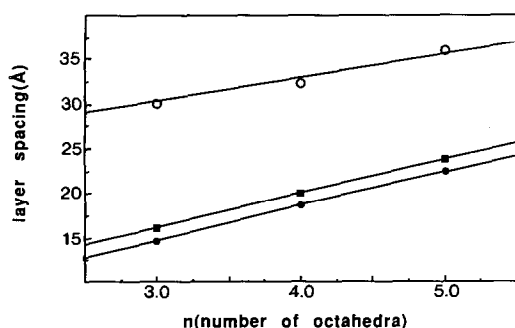
FIG. 2. Layer spacing of $MCa_2Ca_{n-3}Nb_3Ti_{n-3}O_{3n+1}$ ($n = 3–5$) as a function of the number of octahedra, n, for $M = K$ (closed circles), H_3O (closed squares), and $n\text{-}C_6H_{13}NH_3$ (open circles).

oxide. Successful synthesis of an $n \geq 6$ member of the series may be achieved not only by use of high temperatures but also by using sealed platinum tubing to minimize the evaporation of the alkali-metal oxide. However, the unavailability of this facility at our laboratory limits our capability to synthesize higher members. The $K[Ca_2Ca_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$ ($n = 4, 5$) were found to gain ~1% of weight on heating. This may be due to the fact that these samples take up very small amounts of oxygen on heating.

Preparation of the strontium analogue was much more difficult. Equimolar amounts of $KCa_2Nb_3O_{10}$ and $SrTiO_3$ heated at 1240°C always yielded the desired $n = 4$ phase but with unutilized amounts of $SrTiO_3$ present. Neither longer annealing periods nor changes in firing temperature resulted in a monophasic $n = 4$ oxide. So, on the basis of the X-ray diffraction pattern, we calculated the approximate amount of $SrTiO_3$ present as an impurity. Based on this calculation, the amount of $SrTiO_3$ was decreased in the starting composition accordingly. The composition was calculated to be 1 : 0.7 and this was expected to give a monophasic $n = 4$ compound. However, this resulted only in a decrease in the amount of $SrTiO_3$ present as an impurity phase in the product. Further

calculations were made based on this new X-ray diffraction pattern and consequently a starting composition of 1 mole of $KCa_2Nb_3O_{10}$ and 0.5 mole of $SrTiO_3$ was found to give a clean $n = 4$ phase without the presence of any impurity phase (Fig. 3). The X-ray diffraction pattern showed an increase of ~3.96 Å in the layer thickness, which corresponds to the addition of one complete perovskite slab to the $n = 3$ compound. This increase is comparable to the added cubic perovskite, $SrTiO_3$, which as a unit cell dimension of $a = 3.905$ Å. The unit cell parameters of this compound as indexed on an orthorhombic unit cell are $a = 3.863$ Å (±0.002), $b = 3.878$ Å (±0.002), and $c = 37.39$ Å (±0.01). The increase in a and b parameters could possibly be the direct result of the insertion of the bigger strontium atom in place of calcium. Further reactions were attempted to investigate the possible stabilization of the $n = 4$ phase with lesser amounts of $SrTiO_3$. The addition of 0.3 mole of $SrTiO_3$ yielded the $n = 4$ phase (~18.8 Å, corresponding to the $\langle 002 \rangle$ reflection) together with a 16.4-Å phase. Our attempts to prepare a neat phase of this 16.4-Å phase were unsuccessful; a reaction of $KCa_2Nb_3O_{10}$ and 0.2 mole of $SrTiO_3$ at 1230°C for 3 days yielded ~80% of the 16.4-Å phase and ~10% each of the 18.8- and 14.8-Å phases. Efforts are underway to isolate this phase. The percentage yields reported above are based on the intensity of the $\langle 002 \rangle$ reflections for each phase (15). It is suspected that this 16.4-Å phase consists of alternate $n = 3$ and $n = 4$ perovskite layers. The formation of an $n = 4$ phase with only half a mole of $SrTiO_3$ is intriguing. There is no reason for us to believe that the final composition is different from the starting composition, $KCa_2Sr_{0.5}Nb_3Ti_{0.5}O_{11.5}$. A detailed X-ray Reitveld and electron diffraction analysis as well as high-resolution electron microscopic studies, which we have undertaken, should be of help in understanding the microstructure,
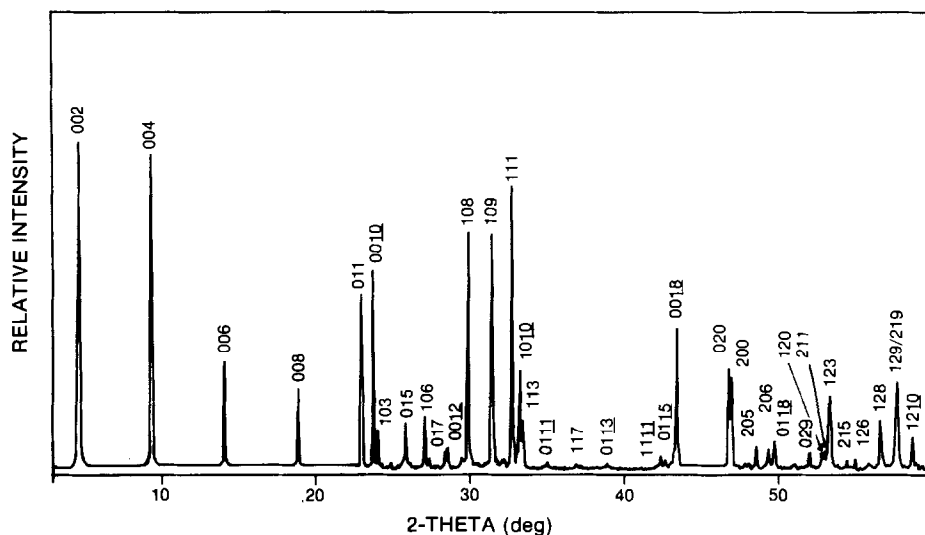
FIG. 3. X-ray diffraction pattern of $KCa_2Sr_{0.5}Nb_3Ti_{0.5}O_{11.5}$.

the ordering of the defects, and thereby the stability of the strontium analogue of the $n = 4$ phase with only half a mole of $SrTiO_3$, as well as the nature of the 16.4-Å phase.

The potassium forms were converted into protonated forms by refluxing with 6 N hydrochloric acid at 60°C. Thermogravimetric analysis of the $n = 4$ $CaTiO_3$ phase showed that 0.5 mole of water was lost up to 100°C and nearly a mole between 285 to 360°C. These losses correspond to the loss of interlayer water molecules and interlayer protons in the form of water, respectively (6). However, the $n = 5$ sample lost 1 mole of water around 100°C and 0.5 mole around 360°C (Fig. 4). This reversal in the order of water loss for the $n = 4$ phase is puzzling. Several sets of experiments under identical protonation conditions suggest that the amount of water loss may vary between the two steps but the total combined weight loss from both the steps always corresponds to ~1.5H_2O. However, this behavior seems to be unique for this compound ($n = 4$). The $SrTiO_3$ analogue of the $n = 4$ phase also showed similar thermogravimetric behavior

to the $n = 5$ $CaTiO_3$ phase, losing about 1 mole of water up to 100°C and nearly 0.5 mole between 300–370°C. Above 375°C both the $n = 5$ sample with $2CaTiO_3$ and the $n = 4$ sample with $0.5SrTiO_3$ lost around 0.36 and 0.16% of weight up to 600°C and gained back approximately the same amount up to 900°C. Although we are not
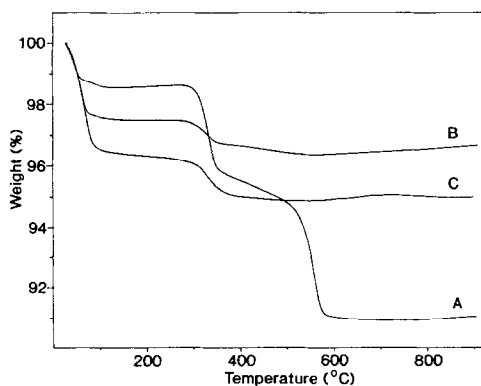

FIG. 4. Thermogravimetric curves for HCa_3Nb_3 $TiO_{13} \cdot xH_2O$ ($x = $ ~1.5) (curve A), $HCa_4Nb_3Ti_2O_{16} \cdot xH_2O$ ($x = $ ~1.0) (curve B), and $HCa_2Sr_{0.5}Nb_3Ti_{0.5}O_{11.5} \cdot xH_2O$ ($x = $ ~1.5) (curve C).

Compound	a (Å) (± 0.002)	c (Å) (± 0.01)
$HCa_2Nb_3O_{10}$[a]	3.849	16.21
$HCa_3Nb_3TiO_{13}$[a]	3.847	20.05
$HCa_4Nb_4Ti_2O_{16}$[a]	3.843	23.76
$HCa_2Sr_{0.5}Nb_3Ti_{0.5}O_{11.5}$[a]	3.846	20.00
$HA–Ca_2Nb_3O_{10}$[b]	3.854	30.16
$HA–Ca_3Nb_3TiO_{13}$[b]	3.849	32.31
$HA–Ca_4Nb_4Ti_2O_{16}$[b]	3.848	35.92
$HA–Ca_2Sr_{0.5}Nb_3Ti_{0.5}O_{11.5}$[b]	3.850	35.50

[a] Protonated forms possess ~1.5H_2O.

[b] HA– corresponds to n-hexylammonium.

certain, this weight gain may possibly be due to the change in oxygen concentration of the oxide with temperature. However, the TGA of the first batch of the $n = 4$ sample with $1CaTiO_3$ showed an additional step corresponding to a weight loss equivalent to that of 2 moles of water between 520–590°C (curve A of Fig. 4). We could not attribute this to the collapse of the structure as X-ray diffraction patterns of various protonated oxides taken after heating to 600°C showed no such collapse and the X-ray pattern could be indexed on the basis of a tetragonal unit cell with $a = b = 3.853$ Å and $c = 18.32$ Å. Also, other protonated oxides, an $n = 5$ oxide with $CaTiO_3$ and an $n = 4$ oxide with $SrTiO_3$, as well as other batches of the $n = 4$ oxide with $1CaTiO_3$, did not show any similar large weight loss at this temperature range. So, this weight loss seems to be unique for a particular batch of $HCa_3Nb_3TiO_{13} \cdot 1.5H_2O$. The protonated forms were found to crystallize in a tetragonal structure as opposed to those of the potassium which has an orthorhombic crystal structure (Table II). X-ray diffraction showed no evidence for a doubling of the c-axis, suggesting that the change from the potassium form to the proton form is accompanied by the translation of the adjacent perovskite layer.

The $H[Ca_2(Ca,Sr)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$ ($n = 4, 5$) phases are solid acids showing a Brönsted acidity similar to that of the protonated oxides, such as $HTiNbO_5$ and $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$, and react with organic amines (17, 18). Protonated compounds upon refluxing with n-hexylamine in water at 60°C give n-hexylammonium $[Ca_2(Ca,Sr)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$, resulting in large layer separations. The layer separations are larger than expected (see Table II) for a monolayer, suggesting a bilayer arrangement of organoammonium cations with inclined hydrocarbon chains (6). The stoichiometry of these reactions was determined by thermogravimetric analysis up to 1000°C. Observed and calculated weight changes for $[n\text{-}C_6H_{13}NH_3]_x[Ca_2(Ca)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$ were, for $n = 4$, 12.57 and 13.36%, respectively, and for $n = 5$, 7.4 and 11.33%, respectively, corresponding to $x = 0.94$ and $x = 0.65$ for $n = 4$ and $n = 5$ samples, respectively. Thermogravimetric analysis of $n\text{-}C_6H_{13}NH_3Ca_2Sr_{0.5}Nb_3Ti_{0.5}O_{13}$ suggested a 60% conversion of the proton form into the amine form. Data from the C, H, and N analyses of these oxides also confirm the above observations. In each case, however, X-ray patterns showed a single intercalated phase. A plot of the layer thickness of protonated as well as amine intercalated forms as a function of n, the number of perovskite layers, is shown in Fig. 2.

$KCa_3Nb_3TiO_{13}$ ($n = 4$) was also prepared by heating the constituent oxides together (see under Experimental). The X-ray diffraction pattern showed a single phase but peaks were found to be slightly broader than those observed for the $n = 4$ oxide prepared by heating $KCa_2Nb_3O_{10}$ and $CaTiO_3$ together. The calcination temperature was also higher for this method of preparation. These observations are easily understandable and are the direct result of the different methods of preparation adopted: the former

method involves the insertion of a perovskite slab into an already existing basic structure and the latter is a typical solid state reaction to build the structural unit from scratch. However, the $n = 4$ oxide thus prepared by the solid state method was also found to undergo protonation and amination under identical conditions. Similar attempts to prepare higher members ($n \geq 5$) and the strontium analogue by the ceramic method were unsuccessful as this temperature range (1200–1400°C).

In conclusion, we have successfully incorporated II–IV perovskites into KCa$_2$Nb$_3$O$_{10}$, as illustrated by synthesizing the $n = 4$ and $n = 5$ members of the K[Ca$_2$ (Ca,Sr)$_{n-3}$Nb$_3$Ti$_{n-3}$O$_{3n+1}$] series in the case of CaTiO$_3$ but only $n = 4$ with SrTiO$_3$. All the potassium forms undergo ion exchange to give proton forms. In turn these proton forms which are solid acids react with bases such as n-hexylamine to give large layer separations. A detailed electron microscopic study is underway to understand the microstructure of these compounds. We are also investigating the pillaring chemistry of these oxides. Our efforts to synthesize higher members of the above series of oxides as well as initial experiments to incorporate LaAlO$_3$, a III–III perovskite, were unsuccessful. Further experiments to incorporate LaAlO$_3$ and other perovskites are underway.

Acknowledgments

References

1. S. N. Ruddlesden and P. Popper, *Acta Crystallogr.* **10**, 538 (1957); **11**, 54 (1958).
2. R. A. Mohan Ram, L. Ganapathi, P. Ganguly, and C. N. R. Rao, *J. Solid State Chem.* **63**, 139 (1986).
3. R. A. Mohan Ram, P. Ganguly, and C. N. R. Rao, *J. Solid State Chem.* **70**, 82 (1987).
4. C. N. R. Rao, P. Ganguly, K. K. Singh, and R. A. Mohan Ram, *J. Solid State Chem.* **72**, 14 (1988).
5. M. Dion, M. Ganne, and M. Tournoux, *Mater. Res. Bull.* **16**, 1429 (1981); M. Dion, M. Ganne, M. Tournoux, and J. Ravez, *Rev. Chim. Miner.* **21**, 92 (1984).
6. A. J. Jacobson, J. W. Johnson, and J. T. Lewandowski, *Inorg. Chem.* **24**, 3727 (1985).
7. A. J. Jacobson, J. T. Lewandowski, and J. W. Johnson, *J. Less-Common Met.* **116**, 137 (1986).
8. M. Dion, M. Ganne, and M. Tournoux, *Rev. Chim. Miner.* **23**, 61 (1986).
9. J. Gopalakrishnan and V. Bhat, *Mater. Res. Bull.* **22**, 413 (1987).
10. M. Gondrand and J. C. Joubert, *Rev. Chim. Miner.* **24**, 33 (1987).
11. J. Gopalakrishnan and V. Bhat, *Inorg. Chem.* **26**, 4299 (1987).
12. M. A. Subramaninan, J. Gopalakrishnan, and A. W. Sleight, *Mater. Res. Bull.* **23**, 837 (1988).
13. M. M. J. Treacy, S. B. Rice, A. J. Jacobson, and J. T. Lewandowski, *Chem. Mater.* **2**, 279 (1990).
14. P. R. Rudolf, "The Graph System of Powder Programs," Chemistry Department, Texas A&M University, College Station, TX (1988).
15. R. A. Mohan Ram, A. Clearfield, P. S. Kobiela and W. P. Kiok, *Physica C* **166**, 125 (1990).
16. A. Grandin, M. M. Borel, and B. Raveau, *J. Solid State Chem.* **60**, 366 (1985).
17. H. Rebbah, G. Desgardin, and B. Raveau, *Mater. Res. Bull.* **14**, 1125 (1979).
18. A. J. Jacobson, J. W. Johnson, and J. T. Lewandowski, *Mater. Res. Bull.* **22**, 45 (1987).