

Pillaring Studies on Some Layered Oxides with Ruddlesden–Popper Related Structures

R. A. Mohan Ram* and A. Clearfield†

Department of Chemistry, Texas A&M University, College Station, Texas 77840

Received July 21, 1993; in revised form December 13, 1993; accepted December 14, 1993

Pillaring studies on four layered oxides, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, $\text{KCa}_3\text{Nb}_3\text{TiO}_{13}$, $\text{KCa}_4\text{Nb}_3\text{Ti}_2\text{O}_{16}$, and $\text{KCa}_2\text{Sr}_{0.5}\text{Nb}_3\text{Ti}_{0.5}\text{O}_{11.5}$, possessing Ruddlesden–Popper related structures have been carried out. The aluminum keggin ion, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, was used as the polymeric cation for the pillar. These samples were characterized by X-ray diffraction, thermogravimetric analysis, infrared spectroscopy, neutron activation analysis, and sorption studies. X-ray diffraction and other structural studies suggest that the polymeric cations were incorporated into the interlayer and upon calcination the layer thicknesses observed correspond to that expected for the formation of the dehydrated polymers in between the layers as a composite. BET surface area measurements and sorption experiments indicate that these products are nonporous oxides suggesting that the interlayer regions are stuffed rather than pillared. © 1994

Academic Press, Inc.

INTRODUCTION

Since the early sixties, zeolites have been used as fluid-cracking catalysts in oil refineries. Zeolites generally have small pore sizes or small external passageways leading into larger cavities. Thus, the gas–oil fraction of petroleum needs a large amount of nonselective precracking to reduce molecular sizes to fit the zeolites. Although theoretically suggested, researchers so far have not been able to synthesize large pore zeolites (16 to 20 rings) but 14- and 18-ring aluminum phosphates have recently been prepared [1]. As the search for alternatives to zeolites continued, a new class of porous materials was synthesized from smectite clay minerals [2]. This was accomplished by swelling the clays and inserting large species between the layers to keep them apart. Smectite clays are able to swell in water because of their low layer charge and, under this condition, easily intercalate organic guest molecules or large inorganic polymers [3]. Since the or-

ganically pillared structures are thermally unstable and the major motive for the preparation of these pillared materials is to provide new catalytically active large pore structures, robust pillars are necessary. Therefore, large inorganic polymeric cations such as the zirconium tetramer, $[\text{Zr}(\text{OH})_2 \cdot 4\text{H}_2\text{O}]_4^{8+}$, or the aluminum Keggin ion, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24} \cdot 12\text{H}_2\text{O}]^{7+}$, appeared to be good choices [4–7]. These inserted inorganic polymers arrange themselves so as to give large porosity for sorption and catalytic activity. However, similar methods cannot be employed for nonswelling clays or other nonsiliceous layered materials that do not swell in water. In this laboratory, we have established a method to pillar these nonswelling layered materials. The method involves first intercalating a larger amine between the layers, spreading the layers apart, and then exchanging the cationic pillar for the interlamellar alkylammonium ion. Several oxides and phosphates have been pillared in this way [8, 9a and 9b].

A decade ago, Dion *et al.* [10] reported on a series of perovskite-related compounds $M\text{Ca}_2\text{Nb}_3\text{O}_{10}$ ($M = \text{K}, \text{Rb}, \text{Cs}$) possessing only 50% of the cations occupying the interlayer spacing as compared to that of the other Ruddlesden–Popper oxides [11]. This work was followed up by the synthesis of several series of related oxides: KLnNb_2O_7 ($\text{Ln} = \text{La}, \text{Nd}$) [12, 13]; $\text{A}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}$ and $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}$) [14, 15]; ABiNb_2O_7 and $\text{APb}_2\text{Nb}_3\text{O}_{10}$ ($\text{A} = \text{Rb}, \text{Cs}$) [16]; $\text{K}[\text{Ca}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}]$ ($n = 3-7$) [17]; $\text{K}[\text{Ca}_2(\text{Ca}, \text{Sr})_{n-3}\text{Nb}_3\text{Ti}_{n-3}\text{O}_{3n+1}]$ ($n = 4, 5$) [18]; $\text{K}[\text{La}(\text{Ca}, \text{Sr})_{n-2}\text{Nb}_2\text{Ti}_{n-2}\text{O}_{3n+1}]$ ($n = 3-5$) [19]. A commonality in all these oxides is that they readily ion exchange the interlayer cations. Exchange has been observed in molten salts and by treatment with aqueous acid at ambient or elevated temperatures. The protonated forms of these oxides are solid acids and react with organic bases such as alkylamines, yielding products with large interlayer expansions [12–20]. We thought that these layered oxides are worth investigating for their pillaring chemistry as these oxides show extensive interlayer chemistry. Also, the layers are quite robust and would be expected to be stable at elevated temperatures. The

* Present address: Chemistry and Engineering Division, Southwest Research Institute, San Antonio, Texas 78228.

† To whom correspondence should be addressed.

alkylamine intercalated oxides could be used as starting materials for subsequent pillaring. Four compounds were selected for such a study: $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, one of the first oxides of this type prepared by Dion *et al.* [10], and $\text{KCa}_3\text{Nb}_3\text{TiO}_{13}$, $\text{KCa}_4\text{Nb}_3\text{Ti}_3\text{O}_{16}$, and $\text{KCa}_2\text{Sr}_{0.5}\text{Nb}_3\text{Ti}_{0.5}\text{O}_{11.5}$, prepared in this laboratory [18]. While this work was in progress, a paper by Hardin *et al.* [21], investigating the pillaring chemistry of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, came to our attention and will be discussed in the context of our results.

EXPERIMENTAL

$\text{KCa}_2\text{Nb}_3\text{O}_{10}$ 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.* [10]. Members of the $\text{K}[\text{Ca}_2\text{Ca}_{n-3}\text{Nb}_3\text{Ti}_{n-3}\text{O}_{3n+1}]$ series of oxides $n = 4, 5$ were prepared by heating stoichiometric amounts of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and CaTiO_3 (in 1 : 1 and 1 : 2 molar ratios). The thoroughly mixed starting materials were heated at 1235 and 1300°C for 3 days. A $n = 3.5$ member of the $\text{K}[\text{Ca}_2\text{Sr}_{n-3}\text{Nb}_3\text{Ti}_{n-3}\text{O}_{3n+1}]$ series was prepared by firing $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and 0.5 mol of SrTiO_3 at 1240°C for 2–3 days. 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 $[\text{Ca}_2(\text{Ca},\text{Sr})_{n-3}\text{Nb}_3\text{Ti}_{n-3}\text{O}_{3n+1}]$ ($n = 4, 5$) phases were prepared by refluxing the protonated forms with n -hexylamine aqueous solutions for 2–3 days at 60°C . Further experimental details and unit cell dimensions are provided in a recent paper [18]. $n\text{-C}_6\text{H}_{13}\text{NH}_3\text{-Ca}(\text{Sr})\text{-Nb}(\text{Ti})$ oxides were treated with 20–30 ml of 15% $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$ (aluminum chlorohydrol, Reheis Chemical Co.) at $50\text{--}60^\circ\text{C}$ for 1–3 days to get the pillared products. This $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$ solution, aged for 6 months, was found to contain predominantly the $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ species as reported in the literature and was confirmed by taking the NMR spectrum of the solution. In all cases, pillared products were cooled to room temperature, filtered, washed with water, and air-dried.

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 $\text{CuK}\alpha$ radiation. Some of the X-ray powder diffraction patterns were also recorded on a Rigaku RU200 rotating anode diffractometer using monochromatized $\text{CuK}\alpha$ radiation. The patterns were step scanned in steps of 0.02° for $10'$ out to $60^\circ 2\theta$. Data analysis was performed using computer programs specially developed for analyz-

ing X-ray powder data [22]. Lattice parameters were determined from the peak position of reflections in the 2θ range $3\text{--}60^\circ$ by a least-squares fitting procedure. The water content and the stoichiometry of the hexylamine and the pillared oxide derivatives were established by thermogravimetric analysis performed with a DuPont 951 thermogravimetric analyzer at a typical heating rate of $6^\circ\text{C}/\text{min}$ under flowing nitrogen. Metal analyses by neutron activation were performed at the Center for Chemical Characterization and Analysis in the Chemistry Department at Texas A&M University. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer (BioRad) under a N_2 atmosphere on pressed KBr pellets. BET surface areas were measured on a Quantachrome Autosorb-6 automated surface analysis instrument.

RESULTS

The n -hexylamine derivatives of $\text{H}[\text{Ca}_2\text{Ca}_{n-3}\text{Nb}_3\text{Ti}_{n-3}\text{O}_{3n+1}]$ ($n = 3, 4, 5$) and $\text{HCa}_2\text{Sr}_{0.5}\text{Nb}_3\text{Ti}_{0.5}\text{O}_{11.5}$ were treated with excess amounts of 15% aluminum chlorohydrol solution which had been aged for 6 months and found to contain $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ ion as the major species. The products were washed with water and dried at 45°C . Hereafter, the products obtained will be referred to as samples A, B, C, respectively, for the $n = 3, 4, 5$ members of the pillared $[\text{Ca}_2\text{Ca}_{n-3}\text{Nb}_3\text{Ti}_{n-3}\text{O}_{3n+1}]$ series of oxides and D for pillared $[\text{Ca}_2\text{Sr}_{0.5}\text{Nb}_3\text{Ti}_{0.5}\text{O}_{11.5}]$. The X-ray diffraction pattern as (a) pillared and (b) calcined products of sample A are shown in Fig. 1. These patterns are representative of all the other samples as they show a lot of common features. Some of the features as observed are discussed below. While only a few reflections were observed, they could be divided into two kinds: $(00l)$ and $(hk0)$ reflections. The (001) reflection was found to be very intense and broad while possible higher orders to (008) , marked with arrows in the figure, were very broad and of low intensity suggesting an oriented sample with some ordering in the c direction. All samples showed slightly weaker but narrower reflections at $3.84, 2.73, 1.93, \text{ and } 1.72 \text{ \AA}$ corresponding to the $(100), (110), (200), \text{ and } (120)$ reflections. While the d spacing of the $(00l)$ reflections varied for different samples depending on the number of perovskite slabs and temperature, the peaks corresponding to $(hk0)$ reflections remain unchanged suggesting that the perovskite slabs are robust and remain intact during pillaring. The observed changes were only in the interlayer spacings accounting for the changing layer thicknesses. A weak amorphous background was observed in the X-ray diffraction patterns, which was found to decrease as the thickness of the host layers increased, i.e., with increased values of n .

The major intense narrow reflections could be indexed, as shown above, on the basis of $a = b \cong 3.845 \text{ \AA}$. The

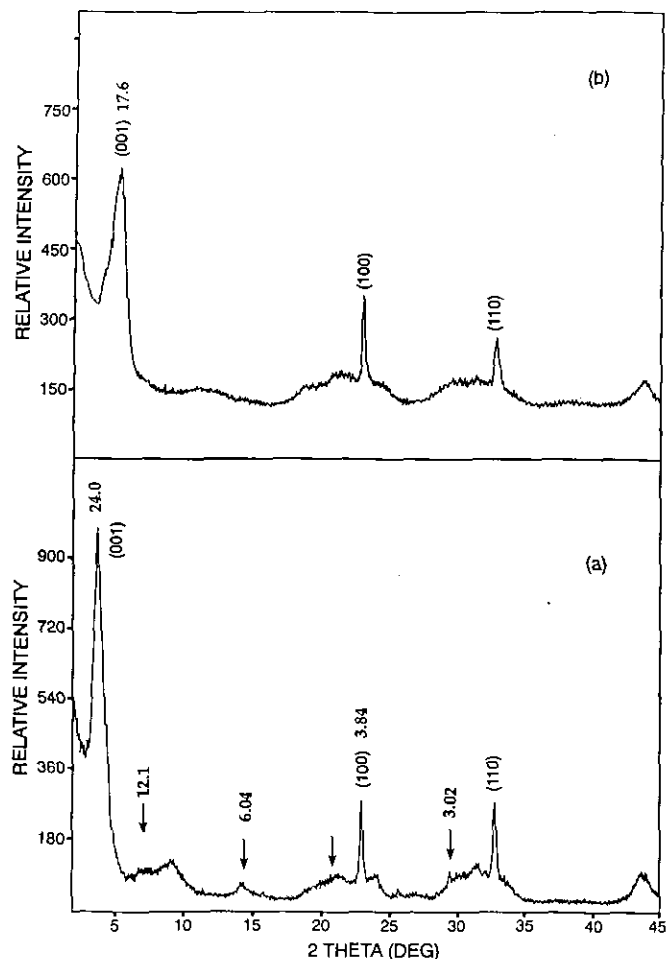


FIG. 1. Powder X-ray diffraction pattern of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]_{1/7}Ca_2Nb_3O_{10}$ as (a) pillared and (b) calcined at $200^\circ C$ for 24 hr. Possible higher order $00l$ reflections with l even buried in the amorphous background are shown as arrows.

indexing of these reflections in Ref. (21) is incorrect even if we assume that these axes are doubled. In general the pillared samples with higher values of n showed more order, as seen in Fig. 2 for sample B. This sample has a layered thickness of 16 \AA for four perovskite slabs as compared to a thickness of $\sim 12 \text{ \AA}$ for $Ca_2Nb_3O_{10}$ layers. In addition about twice the intensity was recorded for the reflections in this sample as for the one shown in Fig. 1 (under the same diffractometer operating conditions).

In Table 1 we have listed the layer thicknesses, expected and observed, for the amine intercalated, pillared, and calcined products of the several layered oxides under study together with that of $KLaNb_2O_7$ ($n = 2$) [23]. Sample A showed a layer spacing lower than that reported by Hardin *et al.* [21]. Two different pillaring experiments on sample B resulted in two different interlayer spacings. The changes in the layer spacings cannot be totally explained by the nature of the orientation of Keggin ion in between the layers and must in part be due to the extent of the polymer exchanged [23]. For example, one batch of pillared sample B and sample C yielded similar layer spacings of about $\sim 38.8 \text{ \AA}$ even though their layer thicknesses differ by about 3.9 \AA . However, on calcination a difference of about 3 \AA in their interlayer spacings was obtained. A plot of interlayer spacing after calcination as a function of the number of stacked perovskite units per layer is shown in Fig. 3. The first value, with $n = 2$, is taken from a lanthanum niobate [23]. Our value for $n = 3$, 17.6 \AA , is too small for a Keggin ion presence. Therefore, we used the value observed by Hardin *et al.* [21]. The slope of this line is 4.56 \AA per layer which should correspond to the increase in layer thickness. However, the value observed for the increase in layer thickness in the potassium salts is $3.9 \text{ \AA}/\text{layer}$ [18]. The larger than

TABLE 1
Layer Thickness of Several Amine Intercalated and Pillared Oxides of the Type $R[Ca_2(Ca)_{n-3}Nb_3Ti_{n-3}O_{3n+1}]$

Sample identity	No. of perovskite slabs, n , and layer thickness	Hexylamine intercalated oxide, \AA^a	Pillared oxide		Pillared and calcined ^c	Surface area, m^2/g
			Expected, \AA	Observed, \AA		
	2^b	25.4(100)	$\sim 17-20$	25.2	17.2	7
A	3(12.0)	28.6(80)	$\sim 21-24$	24.0(28.9) ^c	17.6(20.0) ^c	23
B	4(15.98)	32.3(80)	$\sim 24-27$	38.8(29.4) ^d	27.0(24.9) ^d	9
C	5(19.84)	35.9(65)	$\sim 28-31$	38.8	30.4	9
D	$4^*(16.0)$	29.5(60)	$\sim 24-27$	28.7	23.8	14

Note. $n = 4^*$ corresponds to $MCa_3Sr_{0.5}Nb_3Ti_{0.5}O_{11.5}$ as host.

^a Values in parentheses correspond to the extent of amine exchange in percentage.

^b Data for $KLaNb_2O_7$ from Ref. 23.

^c Data in parentheses from Hardin *et al.* [21].

^d Data in parentheses from a duplicate experiment.

^e Calcined between 200 and $350^\circ C$.

^f Allowed range is for the different orientations of the Keggin ion as per Ref. 24.

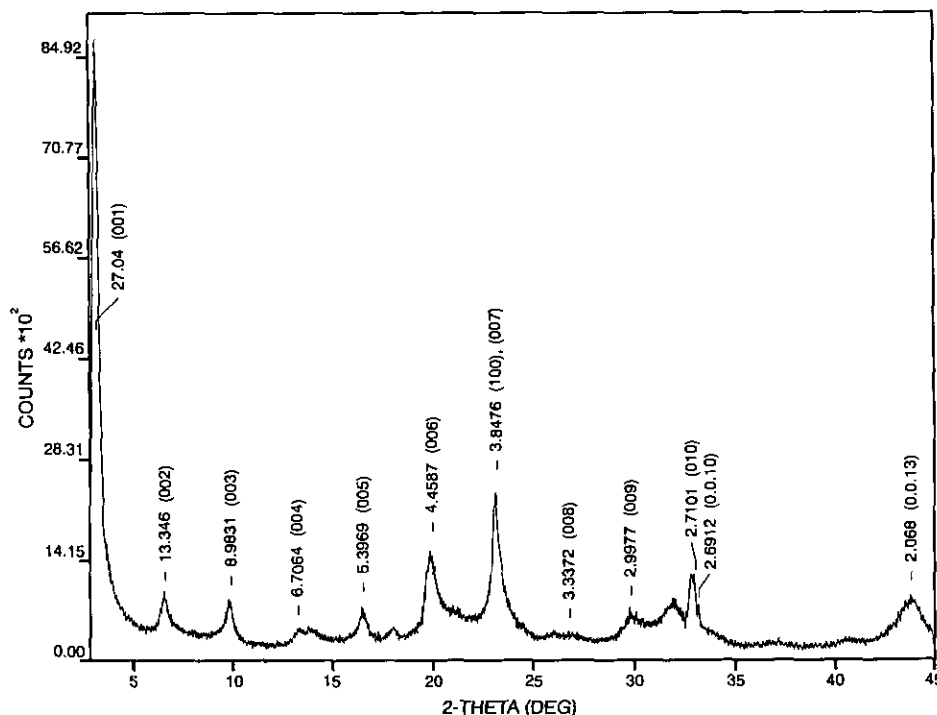


FIG. 2. Powder X-ray diffraction of sample B, aluminum pillared $[\text{Ca}_3\text{Nb}_3\text{TiO}_{13}]^-$, calcined at 200°C for 24 hr.

expected slope is due to the high interlayer spacing for sample C relative to the other samples, indicating incorporation of a larger than expected pillar. Two values were obtained for sample B. The open circle represents the analyzed sample where more than $\frac{1}{7}$ of a mole of Keggin ion was incorporated between the layers.

Elemental analyses for the uncalcined but air-dried Keggin ion exchanged phases are given in Table 2. The calculated values are based upon the assumption that one-seventh of a mole of Keggin ion is exchanged for the proton content of the solid perovskite phase. It is seen that

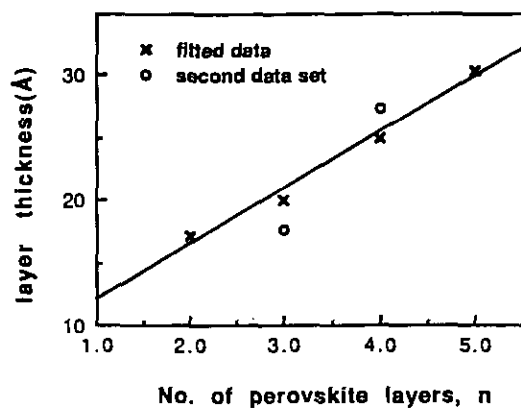


FIG. 3. Plot of layer thickness as a function of the number of perovskite layers in the aluminum pillared perovskites.

all samples except B contain considerably less aluminum than calculated. Thermogravimetric (TG) weight loss curves are shown in Fig. 4. The water loss is little more than might be expected to evolve from the Keggin ion present. For example, a reasonable formula for sample B is $[\text{Al}_{13}\text{O}_4(\text{OH})_{25.64}(\text{H}_2\text{O})_{10.36}^{15.36+}(\text{Ca}_3\text{Nb}_3\text{TiO}_{13}) \cdot 2\text{H}_2\text{O}]$. This formula ($FW = 884.79$) requires 7.48% Al, 13.73% Ca, 5.47% Ti, and 12.0% H_2O . The total measured water loss is 11.2% (TG analysis). The reduced charge on the aluminum polymer is required on the assumption that all of the aluminum is present as a somewhat more hydrolyzed Keggin ion. The water loss occurs in three stages whereas only two are apparent from the TGA curves. In the first stage both the interlamellar water (1.5 moles) and the water bonded to aluminum (1.94 moles) volatilized over a temperature range of $25\text{--}300^\circ\text{C}$ and amounts to 7.07%. The second stage involves condensation of the Keggin ion hydroxyl groups from about $300\text{--}450^\circ\text{C}$. This condensation also involves a transfer of sufficient protons from the Keggin ion to the layers to satisfy all the layer charges of one proton per $\text{Ca}_3\text{Nb}_3\text{TiO}_{13}$ unit. Thus, the amount of water released is 1.896 mol or 3.90%. Finally the protons released to the layers condense out a half mole of water (1.04%) at $500\text{--}600^\circ\text{C}$. In a separate experiment $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ was heated and it lost a half mole of water at 600°C to form $\text{Ca}_2\text{Nb}_3\text{O}_{9.5}$ or $\text{Ca}_4\text{Nb}_3\text{O}_{19}$. The nature of this class of dehydrated perovskites is under investigation, but it clearly shows that these layer protons in the

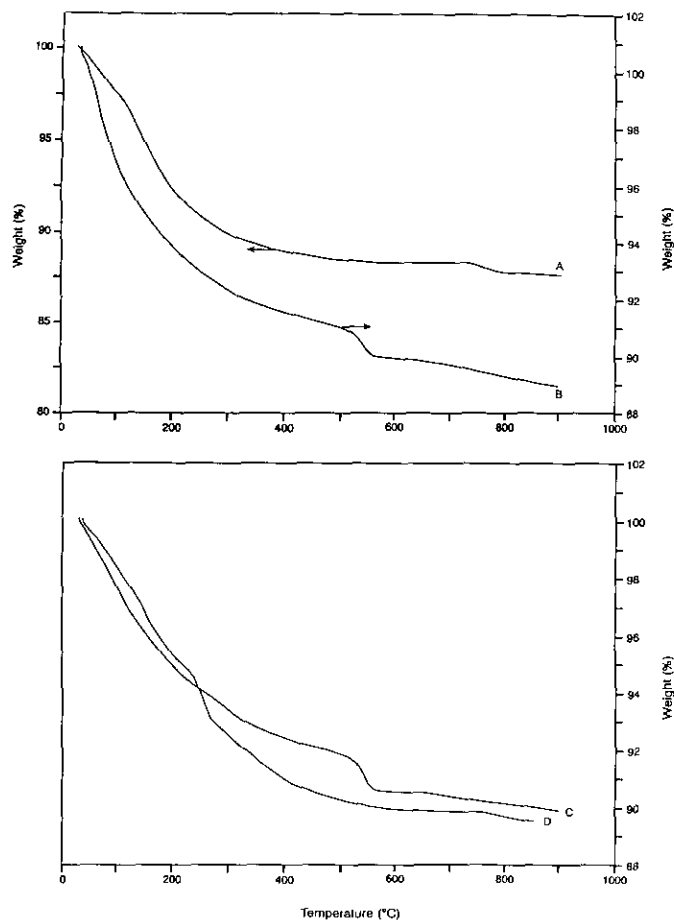


FIG. 4. Thermogravimetric curves of samples A-D.

unpillared niobate condense at approximately the temperature range observed in the present study.

BET surface areas were found to be low, of the order of 9–14 m²/g for the pillared samples suggesting nonporous materials instead of the desired porous pillared ones. Samples were degassed in vacuum at 200°C prior to surface area measurements. An ammonia sorption experiment

was carried out on one of these samples, $n = 4$, to help clarify the interlayer chemistry of these pillared but stuffed oxides: sample B was heated to 400°C, kept there for a few hours, and cooled to room temperature, and ammonia gas was passed over this solid for a period of 12 hr. Thermal analysis of the product showed a weight loss of only 0.84% corresponding to the loss of adsorbed ammonia. This is far less than the expected weight loss (2.215%) for 100% replacement of the protons in the interlayer formed during the calcination. Ammonia adsorption and desorption were also followed through the infrared N–H stretching/bending vibrations. The N–H vibrations observed for the ammonia-adsorbed samples started disappearing with increasing temperature immediately, showing that most of the sorbed NH₃ was physisorbed and loosely held. These experiments confirm that the product is one in which the interlayer region is filled (stuffed) rather than pillared without any interlayer pores. The strontium-containing compound with $n = 3.5$ had an interlayer spacing of 16 Å. This value indicates the presence of four perovskite slabs since this interlayer distance is the same as in KCa₃Nb₃TiO₁₃ [18]. Thus, defects of as yet unknown type must exist in the strontium compound. However, on pillaring it behaved like the second sample B recorded in Table 1, except that the aluminum-containing products were about an angstrom smaller in the interlayer spacing.

DISCUSSION

Both in the present study and in that of Hardin *et al.* [21] it was found that direct exchange of large polymeric cations into the interlayer space of the layered niobate perovskites was not possible. It is therefore necessary to first increase the interlayer distance to allow exchange to occur. This was first demonstrated by Clearfield and co-workers [8, 25] for α -zirconium phosphate into which butylamine was first intercalated and then exchanged out as an alkylammonium ion. In the present study somewhat

TABLE 2
Metal Analysis for Al₁₃ Pillared-Ca_{*n*-1}Nb₃Ti_{*n*-3}O_{3*n*+1} and
-Ca₂Sr_{0.5}Nb₃Ti_{0.5}O_{11.5} ($n = 3.5^*$)

Sample (<i>n</i>)	Aluminum (%)		Calcium (%)		Titanium (%)	
	Calculated*	Found	Calculated	Found	Calculated	Found
A 3	6.06	7.17	12.01	11.95	—	—
B 4	6.24	7.44	14.97	11.6	5.96	5.44
C 5	5.34	4.85	17.07	18.1	10.2	8.57
D 3.5*	6.61	6.06	10.56	10.44	3.16	3.41
			5.77 ^a	4.90 ^b		

Note. *a* and *b* are values for strontium in compound $n = 3.5^*$.

* Calculated on the assumption that the Al₁₃ species has a charge of +7.

less than $\frac{1}{7}$ of a mole of the aluminum Keggin ion was exchanged per formula weight of perovskite except in the case of sample B.

The XRD data and electron micrographs indicate, in concert with the results of Hardin and co-workers [21], that the perovskite layers remain intact. However, the X-ray pattern (Fig. 1) for the aluminum-exchanged $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ shows that a high degree of disorder is present and that some amorphous material may also be present. As the value of n increases the X-ray patterns exhibit less disorder (see Fig. 2) and less evidence of an amorphous background. The broadness of some of the $(00l)$ reflections however may indicate a fair amount of turbostratic disorder. From this evidence we construct a model in which the perovskite layers are held apart by the aluminum Keggin ions. The presence of a high charge (close to $7+$) on the Keggin ion and some disorder in their arrangement in the interlayer space result in stresses on the layers. These stresses could take the form of layer curvature [21], rotation of the layers in a turbostratic manner, and some amorphatization of the composite which forms. The thicker the layers, the better able are they to remain undeformed by the induced stresses and yield better quality X-ray patterns.

The surface areas of all the samples were low indicating that nonporous materials were produced. This result is not surprising given the high layer charge of the perovskites. A single charge is contained within an area of $(3.85 \text{ \AA})^2$, i.e., the $a \times b$ unit cell dimensions. Seven such units are required to accommodate the charge of an $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ species. Each Keggin ion unit requires about twice 110 \AA^2 of surface area being about 10.5 \AA in diameter [24]. However, the space available is 104 \AA^2 or about 94.5% of that required. Thus, on the assumption that the $7+$ charge is retained by the Keggin ion no more than 0.135 mol can be exchanged per mole of host compound. Samples C and D are slightly below this value (0.130 and 0.1331, respectively) and 0.137 for sample A. The values for these three samples are close enough to the limiting value to indicate that the entire interlamellar region is filled with the aluminum species. Even after calcination there would only be 2–3 \AA of free space between pillars.

Sample B contains 0.187 mol of the Al_{13} species which is 1.38 times the maximum allowed on a size basis. The air-dried product has an interlayer spacing of 38.8 \AA , which is $\sim 22.8 \text{ \AA}$ larger than the layer thickness ($\sim 16 \text{ \AA}$) [18]. This increase in interlayer distance indicates that a double stack of Keggin ions is present. Since there is a 38% excess of Keggin ions more than $\frac{1}{3}$ of the pillars could be constituted as a double stack. At the same time the charge per Al_{13} unit would have to be reduced to a maximum of 5.36. One can construct a model on this basis in which somewhat more than one-third of the pillars are of double height while the remainder are one Keggin ion high, leav-

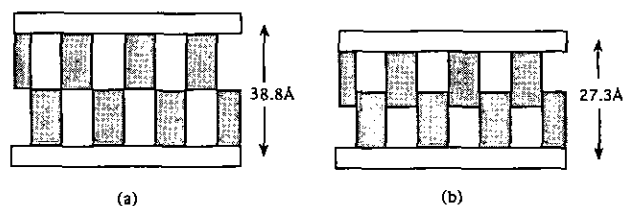


FIG. 5. Schematic illustration of the interlayer after exchange intercalation of the Al_{13} Keggin ion in the case where a double stack of Keggin ions is required to explain the interlayer spacing (a) before calcination and (b) filling in of the empty spaces on calcination. The interlayer will reduce up to the point where the adjacent pillars fuse by condensation of hydroxyl groups to split out water.

ing gaps of empty space between the taller pillars. Upon calcination the interlayer distance shrinks to a value of 27.0 \AA which represents a gallery height or a distance between perovskite layers of 11.0 \AA . This distance was arrived at by subtracting the thickness of the layers in $\text{KCa}_3\text{Nb}_3\text{TiO}_{13}$ [18] from the observed value of the Al_{13} pillared product. This difference is about 3 \AA larger than the final interlayer increase ($\sim 8 \text{ \AA}$) of the other perovskite layered compounds after calcination in which a single stack of Keggin ions was present. Thus, the double stack of pillars must crumble to fill a portion of the open space already present and additional space created by the dehydration process.

In a separate experiment a second sample B was prepared ($n = 4$) which yielded a 29.4- \AA interlayer spacing. On calcination this distance was reduced to 24.9 \AA or an interlayer alumina region of 8.9 \AA in height, a value expected from pillars composed of a single layer of Keggin ions. Conversely, sample C contained 0.13 mol of Keggin ion but still produced a layer spacing large enough to be considered a double stack of Al_{13} ions ($\sim 19 \text{ \AA}$ expansion). If all the pillars were of this height, the product should be pillared and porous. However the double stack may take the forms pictured in Figs. 5a and 5b, which on calcination fill most of the void space. The final increase in interlayer spacing of 10.5 \AA is still larger than normal but would only leave small voids between pillars.

It is clear from this study and also that of Hardin *et al.* [21] that new strategies for producing pillared porous materials with the layered Ruddlesden–Popper phases are necessary. These include partial intercalation of Keggin ions, use of narrower pillars such as chromium polymers, and further reduction of the layer charge. It may thus be possible to produce porous materials with very robust layers for high-temperature catalysis.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant DMR 8801283 for which grateful acknowledgment is made.

REFERENCES

1. M. E. Davis, C. Saldarriaga, C. Montes, J. M. Garces, and C. Crowder, *Nature* **331**, 698 (1988).
2. D. E. W. Vaughan, R. J. Lussier, and J. S. McGee, U.S. Patent 41766090, 1979.
3. T. J. Pinnavia, *Science (Washington, DC)* **220**, 365 (1983).
4. N. Lahav, V. Shani, and J. Shabtai, *Clays Clay Miner.* **26**, 107 (1978).
5. G. W. Brindley and R. E. Semples, *Clays Clay Miner.* **25**, 229 (1977).
6. R. Burch (Ed), *Catal. Today* **2** (1988).
7. D. E. W. Vaughan and R. J. Lussier, in "5th International Conference Zeolites, Naples, Italy. Heyden, London, 19.
8. A. Clearfield, and B. D. Roberts, *Inorg. Chem.* **27**, 3237 (1988).
9. (a) S. Cheng and T.-C. Wang, *Inorg. Chem.* **28**, 1429 (1989); (b) A. Clearfield, M. Kuchenmeister, J.-D. Wang, and K. Wade, in "Zeolite Chemistry and Catalysis" (P. A. Jacobs, Ed.), p. 485. Elsevier, Amsterdam, 1991.
10. 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).
11. S. N. Ruddlesden and P. Popper, *Acta Crystallogr.* **10**, 538 (1957); **11**, 54 (1958).
12. M. Dion, M. Ganne, M. Tournoux, and J. Ravez, *Rev. Chim. Miner.* **23**, 61 (1986).
13. J. Gopalakrishnan, V. Bhat, and B. Raveau, *Mater. Res. Bull.* **22**, 413 (1987).
14. M. Gondrand and J. C. Joubert, *Rev. Chim. Miner.* **24**, 33 (1987).
15. J. Gopalakrishnan and V. Bhat, *Inorg. Chem.* **26**, 4299 (1987).
16. M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, *Mater. Res. Bull.* **23**, 837 (1988).
17. A. J. Jacobson, J. W. Johnson, and J. T. Lewandowski, *Inorg. Chem.* **24**, 3727 (1985); A. J. Jacobson, J. T. Lewandowski, and J. W. Johnson, *J. Less Common Metals* **116**, 137 (1986).
18. R. A. Mohan Ram and A. Clearfield, *J. Solid State Chem.* **94**, 45 (1991).
19. R. A. Mohan Ram and A. Clearfield, unpublished results.
20. A. J. Jacobson, J. W. Johnson, and J. T. Lewandowski, *Mater. Res. Bull.* **22**, 45 (1987).
21. S. Hardin, D. Hay, M. Mullikan, J. V. Sanders, and T. W. Turney, *Chem. Mater.* **3**, 977 (1991).
22. P. R. Rudolf, "The Graph System." Department of Chemistry, Texas A&M University, College Station, TX.
23. R. A. Mohan Ram, and A. Clearfield, manuscript in preparation.
24. Susan Bradley, Ph.D. Thesis. Department of Chemistry, University of Calgary, Canada, Nov. 1991.
25. A. Clearfield and R. M. Tindwa, *Inorg. Nucl. Chem. Lett.* **15**, 251 (1979).