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Topotactic Routes to Layered Calcium Cobalt Oxides

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Four Ca_xCoO_2 ($0.26 \leq x \leq 0.50$) oxides have been synthesized by the low-temperature ion exchange of layered Na_xCoO_2 oxides. The Ca_xCoO_2 structures all consist of $[CoO_2]_n$ sheets of edge-sharing octahedra with Ca^{2+} ions between layers in trigonal prismatic coordination. Different packing sequences of the close-packed oxygen layers can be obtained. $Ca_{0.50}CoO_2$ ($a = 4.881(2)$ Å, $b = 2.826(1)$ Å, $c = 5.654(3)$ Å, $\beta = 105.86(5)°$) and $Ca_{0.26}CoO_2$ ($a = 4.961(7)$ Å, $b = 2.805(3)$ Å, $c = 5.671(6)$ Å, $\beta = 106.7(1)°$) assume the monoclinic $P'3$ structure, while $Ca_{0.35}CoO_2$ ($a = 2.812(3)$ Å, $c = 10.872(2)$ Å) and $Ca_{0.27}CoO_2$ ($a = 2.812(1)$ Å, $c = 10.874(5)$ Å) take the hexagonal $P2$ structure. The structural relationships between the Ca_xCoO_2 products and their Na_xCoO_2 precursors are discussed, and the relationship between composition and $[CoO_2]_n$ layer-spacing in various A_xCoO_2 systems is illustrated. © 1998 Academic Press

INTRODUCTION

Low-temperature ion exchange reactions provide an important and simple route to metastable materials while allowing the manipulation of structural moieties and physical properties (1). Although multivalent-for-monovalent exchange reactions are far less utilized than monovalent-for-monovalent reactions, a sizeable body of examples exist to demonstrate the usefulness of such reactions. Divalent-for-monovalent ion exchange reactions have been observed in $H_2Ti_3O_7$ (2), HNb_3O_8 (3), $KFeS_2$ (4), β''-alumina (5), various zeolites (6), and numerous other systems (7–10), and in many cases they have led to new compounds or new structural phases of existing compounds. We are currently examining multivalent ion exchange as a method for augmenting the structures and consequently the properties of layered mixed-metal oxides (11, 12). Recently, we reported our initial examination of multivalent ion exchange into the Na_xCoO_2 system (11). Here, we expand and detail this investigation as we report the synthesis and characterization of several layered calcium cobalt oxides.

In this study, Na_xCoO_2 compounds with a variety of structure types are used as precursors for the ion exchange reactions. $NaCoO_2$, and to a greater extent $LiCoO_2$, have been investigated recently for their suitability as cathode materials in secondary batteries (12, 13). Stoichiometric $NaCoO_2$ and $LiCoO_2$ crystallize in the $O3$ structure type (α-$NaFeO_2$ structure; O is octahedral coordination of the alkali metal and 3 is number of layers in the repeat; see Fig. 1) (14). The structure consists of layers of CoO_6 edge-sharing octahedra. This rocksalt-related structure consists of cubic close-packed oxygen layers (*ABCABC*) with the cobalt and sodium occupying the octahedral sites of alternating layers. As sodium content decreases, a number of structural variations can occur, including the $P'3$ and $P2$ structures with *ABBCCA* and *ABBA* oxygen packing sequences, respectively (P is the trigonal prismatic coordination of alkali metal; prime ($'$) denotes a monoclinic distortion of the unit cell).

A_xCoO_2 compounds are known to readily undergo exchange of their alkali atoms with other monovalent ions. The ion exchange of $Na_{0.7}CoO_2$ with LiCl under reflux in methanol resulted in $LiCoO_2$ with a unique, metastable $O2$ structure type (15), and the exchange of $NaCoO_2$, $LiCoO_2$, or $Na_{0.7}CoO_2$ with $AgNO_3$ resulted in delafossite-type oxides (16, 17). Reports of divalent-for-monovalent ion exchange reactions in layered A_xMO_2 materials, however, are scarce. The only examples in the literature are the ion exchange of α-$NaFeO_2$ with molten magnesium and nickel salts, yielding spinel-like magnesium and nickel ferrites (18), and the exchange of $K_{0.23}NiO_2 \cdot nH_2O$ with Ca^{2+}, Sr^{2+}, and Ba^{2+} in aqueous solution (19). The choice of an aqueous system for the latter nickelate reactions is questionable given the poor crystallinity of the products and the tendency of some A_xNiO_2 compounds to hydrolyze to γ- and β-NiOOH upon contact with water (20–22). In any event, no other divalent-for-monovalent exchanges in the Na_xCoO_2 system have been reported to date.

EXPERIMENTAL

$NaCoO_2$ ($O3$)

$NaCoO_2$ was prepared by a variation of the literature method (23). Powdered cobalt metal (Aldrich, 99.8%, 2 μm)

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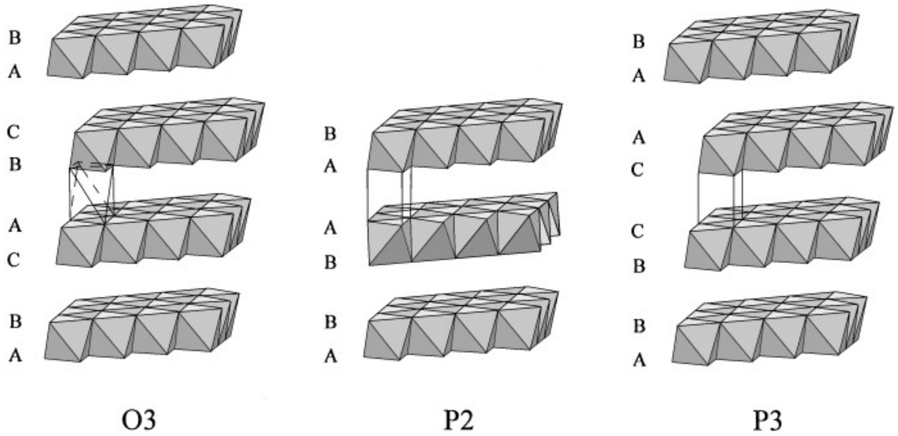

FIG. 1. The *O*3, *P*3, and *P*2 structures (O, octahedral coordination of the *A* cation; P, trigonal prismatic coordination of the *A* cation; 2, 3 are the number of layers in the repeat).

and anhydrous NaOH pellets (Aldrich, 99.99%) in 10% molar excess were ground together under inert atmosphere and placed in an alumina boat under flowing O_2 for approximately 5 days at 500°C with one intermittent grinding. The highly crystalline, dark violet product was stored and handled in an argon-filled dry box.

$Na_{0.7}CoO_2$ (*P*2)

$Na_{0.7}CoO_2$ was prepared by mixing stoichiometric amounts of NaOH and Co metal (24). The sample was heated in an alumina boat at 700°C for 6 days under flowing O_2 with frequent regrindings. Like $NaCoO_2$, the product is dark violet. Alternatively, Co metal and an excess of Na_2CO_3 may be heated at 850°C in air for one day, volatilizing off the unreacted carbonate as Na_2O and CO_2. Despite the lower temperature, product crystallinity is significantly better with the hydroxide method.

$Na_{0.5}CoO_2$ (*P′*3) *and* $Na_{0.5}CoO_2$ (*P*2)

Precursors with lower sodium contents, $Na_{0.5}CoO_2$ (*P′*3) and $Na_{0.5}CoO_2$ (*P*2), were prepared by oxidatively deintercalating sodium from $NaCoO_2$ (*O*3) and $Na_{0.7}CoO_2$ (*P*2), respectively. The samples were placed in a flask with a 100% molar excess of iodine dissolved in acetonitrile and stirred at room temperature under nitrogen for 2 days (25). The black products were collected by vacuum filtration and washed with anhydrous methanol with minimal air exposure, and then they were dried at 300°C under flowing O_2 to remove any residual moisture and/or iodine.

The literature contains accounts of the preparation of $Na_{0.6}CoO_2$ (*P′*3) and $Na_{0.5}CoO_2$ (*P*2) by direct reaction of the oxides at 500°C (23, 26). This was the preparative method used for $Na_{0.6}CoO_2$ in our initial report of the synthesis of Ca_xCoO_2 oxides (11). This method, however, was plagued by the consistent detection of trace quantities of Co_3O_4 in the XRD patterns, even with reaction times exceeding 2 weeks and regardless of the sodium source used (hydroxide, peroxide, or oxide). An alternate route to $Na_{0.5}CoO_2$ (*P′*3) by deintercalating $NaCoO_2$ with a bromine/acetonitrile solution has also been reported (25). We have found, however, that this reaction greatly reduces the crystallinity of the product and leads to X-ray reflections which cannot be indexed on the hexagonal unit cell.

Ion Exchange

$Ca_{0.50}CoO_2$ (*P′*3), $Ca_{0.35}CoO_2$ (*P*2), $Ca_{0.27}CoO_2$ (*P*2), and $Ca_{0.26}CoO_2$ (*P′*3) were easily synthesized by ion exchange of the appropriate precursor with a 10% stoichiometric excess of anhydrous $Ca(NO_3)_2$ (Aldrich, 99 + %):

$$Na_xCoO_2 + x/2\,Ca(NO_3)_2 \rightarrow Ca_{x/2}CoO_2 + x\,NaNO_3.$$

The reactants were ground together and compacted into 12-mm diameter pellets at ~11,000 psi. The pellets were placed in alumina boats and heated under flowing O_2 at 310°C for 2 days. The $NaNO_3$ byproduct and any unreacted NaOH or excess $Ca(NO_3)_2$ was removed by repeatedly grinding the products under distilled water. After washing, the products were dried at 120°C in air and stored in an argon-filled glove box.

Characterization

X-ray powder diffraction (XRD) of the precursors and products were performed on a Philips X'Pert system or a Siemens D-5000 equipped with Cu*K*α radiation ($\lambda = 1.5418$ Å) and a graphite monochromator. Samples were scanned continuously over the range $5^\circ \leq 2\theta \leq 90^\circ$ at 0.1°/min. Tungsten (Alfa, 99.999%) or silicon (Aldrich, 99.999%) was used as an internal standard, and lattice parameters were refined with the program POLSQ (27). Moisture-sensitive samples were covered with polypropylene film or enclosed in a helium-purged Bühler HDK sample stage.

Thermogravimetric analyses (TGA) were performed on a TA Instruments Thermal Analyst 2000 system over the temperature range 25–1000°C with a ramp of 5°/min. Analyses were performed under an H_2 (8.5%)/He mixture flowing at ~25 mL/min. Reported values are the average of three runs.

Quantitative elemental analysis of sodium, calcium, and cobalt was performed on a Perkin–Elmer Plasma 40 Emission Spectrometer (ICP). Typically, about 100 mg of sample was digested in 10 mL concentrated HCl and diluted to 1000 mL, giving analyte concentrations between 10 and 60 μg/mL for each element.

RESULTS

Precursor Synthesis

Table 1 presents the composition and unit-cell values for the series of sodium cobalt oxide precursors. The composition/unit cell values for $NaCoO_2$ and $Na_{0.70}CoO_2$ are in good agreement with the literature (23, 24). The experimental composition of the $Na_{0.52}CoO_2$ ($P'3$) precursor reveals a slightly lower sodium content than the material prepared by Miyazaki *et al.* (28). This may, however, reflect differences in the reaction times of the deintercalation. The unit cell for $Na_{0.53}CoO_2$ ($P2$), prepared from the deintercalation of $Na_{0.70}CoO_2$, is large compared to that prepared by Jansen and Hoppe by direct reaction of oxides at 500°C (26).

Ion Exchange Products

The unit cell parameters for the Ca_xCoO_2 products are summarized in Table 1. The indexing of both $Ca_{0.50}CoO_2$ and $Ca_{0.35}CoO_2$ compounds is given in Table 2. $Ca_{0.50}CoO_2$ transforms to the $P'3$ structure. Vidyasagar *et al.* have previously reported the preparation of $Ca_{0.50}CoO_2$ by the decomposition of a carbonate precursor (29). The monoclinic unit cell of their product, however, was significantly larger than the one reported here, and it included several reflections not observed in our X-ray powder patterns. $Ca_{0.35}CoO_2$ ($P2$), $Ca_{0.27}CoO_2$ ($P2$), and $Ca_{0.26}CoO_2$ ($P'3$) each maintain the structure of their corresponding Na_xCoO_2 precursor. Evidence of a successful reaction is provided by the $NaNO_3$ byproduct, which is clearly discernible in the powder patterns of Ca_xCoO_2 before washing. Unlike the Na_xCoO_2 precursors, however, none of the Ca_xCoO_2 oxides appear to undergo structural changes as a result of air or moisture exposure, as determined by XRD. Figure 2 shows a comparison of X-ray powder patterns of the precursor, $Na_{0.52}CoO_2$, versus its exchange product, $Ca_{0.26}CoO_2$. Little or no line broadening is observed after reaction.

Quantitative elemental analysis was used to verify the stoichiometries of the products. In each case, the Ca^{2+}

TABLE 1
Summary of ICP and XRD Results for Na_xCoO_2 Precursors and Ca_xCoO_2 Exchange Products

Precursor[a]	Structure type	Unit cell (Å)	Literature values (Å)	Exchange product[a]	Structure type	Unit cell (Å)	Literature values (Å)
$NaCoO_2$	$O3$	Hexagonal $a = 2.886(4)$ $c = 15.600(6)$	Hexagonal (23) $a = 2.880$ $c = 15.58$	$Ca_{0.50}CoO_2$	$P'3$	Monoclinic $a = 4.881(2)$ $b = 2.826(1)$ $c = 5.654(3)$ $\beta = 105.86(5)^\circ$	Monoclinic (29)[d] $a = 11.50(2)$ $b = 5.73(1)$ $c = 4.74\ (1)$ $\beta = 109.2(2)^\circ$
$Na_{0.71}CoO_2$	$P2$	Hexagonal $a = 2.834(1)$ $c = 10.88(1)$	Hexagonal (24) $a = 2.833$ $c = 10.82$	$Ca_{0.35}CoO_2$	$P2$	Hexagonal $a = 2.812(3)$ $c = 10.872(2)$	this work
$Na_{0.53}CoO_2$	$P2$	Hexagonal $a = 2.820(1)$ $c = 11.057(1)$	Hexagonal (26)[b] $a = 2.84$ $c = 10.81$	$Ca_{0.27}CoO_2$	$P2$	Hexagonal $a = 2.812(1)$ $c = 10.874(5)$	this work
$Na_{0.52}CoO_2$	$P'3$	Monoclinic $a = 4.889(3)$ $b = 2.821(1)$ $c = 5.751(2)$ $\beta = 106.22(6)^\circ$	Monoclinic (24)[b,c] $a = 4.839$ $b = 2.831$ $c = 5.71$ $\beta = 106.3^\circ$	$Ca_{0.26}CoO_2$	$P'3$	Monoclinic $a = 4.961(7)$ $b = 2.805(3)$ $c = 5.671(6)$ $\beta = 106.7(1)^\circ$	this work

[a] Compositions determined by ICP.

[b] Unit cell corresponds to material prepared by direct reaction of oxides.

[c] Unit cell corresponds to compound with the composition $Na_{0.6}CoO_2$.

[d] Sample was prepared by decomposition of a carbonate precursor.

TABLE 2
XRD Results for $Ca_{0.50}CoO_2$ ($P'3$) and $Ca_{0.35}CoO_2$ ($P2$)

$Ca_{0.50}CoO_2$				$Ca_{0.35}CoO_2$[a]			
d_{obs} [Å]	d_{calc} [Å]	$h\ k\ l$	I/Io	d_{obs} [Å]	d_{calc} [Å]	$h\ k\ l$	I/Io
5.4431	5.4384	0 0 1	100	5.4325	5.4362	0 0 2	100
2.7146	2.7192	0 0 2	25	2.7184	2.7181	0 0 4	26
2.4234	2.4213	1 1 0	10	2.4352	2.4355	1 0 0	14
2.3437	2.3474	− 1 1 1	15	2.2222	2.2227	1 0 2	31
2.1035	2.1045	1 1 1	4	2.0216	2.0215	1 0 3	16
1.9696	1.9684	2 0 1	15	1.8139	1.8139	1 0 4	29
1.9489	1.9500	− 1 1 2	27	1.4543	1.4538	1 0 6	19
1.8150	1.8128	0 0 3	4	1.4062	1.4062	1 1 0	12
1.6905	1.6936	1 1 2	7	1.3608	1.3614	1 1 2	6
1.6735	1.6729	− 2 0 3, − 2 1 2	6	1.2492	1.2489	1 1 4	3
1.4136	1.4131	0 2 0, − 1 0 4	9	1.2179	1.2178	2 0 0	9
1.3818	1.3869	− 3 0 3	3	1.1879	1.1883	2 0 2	3
1.3582	1.3596	0 0 4	7	1.1545	1.1543	2 0 3	1
1.2588	1.2583	3 1 1, 0 2 2	3	1.1116	1.1113	2 0 4	1
1.2202	1.2199	1 0 4, 3 0 2	3				
1.2098	1.2107	− 2 2 0	3				
1.1481	1.1479	2 2 1	4				
1.1073	1.1077	− 4 1 2	3				
1.0882	1.0876	4 0 1, 0 0 5	3				
1.0801	1.0795	− 2 2 3	3				

[a] Two or three minor ($\ll 1$), broad reflections sometimes appeared in $Ca_{0.35}CoO_2$ and $Ca_{0.26}CoO_2$ at $d = 4.02$, 3.78, and 3.23 Å.These reflections could not be indexed on the respective cells or assigned to any known impurity.

content of the ion exchange products was equal to exactly one-half the Na^+ content of its precursor and no sodium was detectable in the Ca_xCoO_2 products, indicating 100% exchange. Attempts to exchange fractional amounts of sodium from $NaCoO_2$, forming $Na_{1-x}Ca_{x/2}CoO_2$ solid solutions, resulted in mixtures of $Ca_{0.5}CoO_2$ and unreacted $NaCoO_2$.

The oxygen content of the Ca_xCoO_2 products was verified by TGA (Table 3). Reduction under dilute hydrogen resulted in a residue of xCaO + Co metal. With decomposition events occurring simultaneously, the thermograms were not simple (Fig. 3). Consequently, samples were analyzed by total mass loss and no attempts were made to characterize the decomposition pathways. In the instances of $Ca_{0.35}CoO_2$ ($P2$) and $Ca_{0.27}CoO_2$ ($P2$), which are both derived from the $Na_{0.7}CoO_2$ ($P2$) precursor, we considered the possibility of oxygen nonstoichiometry since some accounts of the synthesis of $Na_{0.7}CoO_2$ report oxygen deficiency (30–32). The TGA results of the Ca_xCoO_2 products, however, showed no evidence of weight gain when analyzed under flowing oxygen.

DISCUSSION

The ion exchange routes described here provide an effective method of synthesizing layered Ca_xCoO_2 oxides. Furthermore, this low-temperature route probably represents the best means of retaining the layer structures of the Na_xCoO_2 precursors. TGA of the Ca_xCoO_2 compounds run under flowing O_2 indicated an onset of decomposition near 450°C. Thus, a direct reaction of, for instance, $3\,Ca(NO_3)_2 + 2\,Co_3O_4 \rightarrow 6\,Ca_{0.50}CoO_2$ would not produce $Ca_{0.50}CoO_2$ ($P'3$) since this reaction would likely require temperatures exceeding 500°C. This may explain the differing XRD results of Vidyasagar *et al.*, who prepared $Ca_{0.5}CoO_2$ by decomposing a carbonate precursor at 620°C (29).

The transformation from octahedral to trigonal prismatic coordination as $NaCoO_2$ is converted to $Ca_{0.5}CoO_2$ is a simple matter of $[CoO_2]_n$ planes shifting, a commonly observed behavior in A_xMO_2 compounds. Delmas has suggested that as the spacing between adjacent cobalt layers increases (from increased ionic radius of the **A** cation or decreased occupation in the alkali layer), trigonal prismatic coordination tends to predominate due to its enhanced thermal stability over octahedrally coordinated systems (33). The literature contains evidence to support this. $NaCoO_2$ ($O3$) has been reported to transform to the $P'3$ structure near the composition $Na_{0.7}CoO_2$ as sodium is removed electrochemically (34) or to the $P2$ structure if $NaCoO_2$ is heated at 700°C for prolonged periods (13). Miyazaki et al. have estimated a 3.7 kcal/mol difference in the free energies of the $O3$ and $P3$ phases of Na_xCoO_2 (28).

At stoichiometries below $x = 0.5$, the A_xMO_2 (A = Li, Na; M = first-row transition metal) systems tend to exhibit structural deformations and a general loss of crystallinity (35–38). In some systems, particularly the vanadium oxides, this may be the result of transition-metal migration into the alkali layer (39–41). Little data is available for the Na_xCoO_2 system, however, and although the Li_xCoO_2 has been extensively studied, the literature contains conflicting accounts of its structural behavior. Most reports of the chemical and electrochemical deintercalation of $LiCoO_2$ maintain that the system begins to lose reversibility (the ability to fully reintercalate lithium) just below $x = 0.5$ due to structural deformations (35, 36). Conceivably, this is the effect observed in attempting the bromine/acetonitrile preparation of $Na_{0.5}CoO_2$ which led to X-ray reflections unattributable to the product on a hexagonal unit cell. Notwithstanding, our XRD studies indicate that Ca_xCoO_2 compounds do not suffer any such adverse structural consequences for $0.3 \leq x \leq 0.5$. This supports the contention of Thomas *et al.* that the instability in A_xCoO_2 systems below $x = 0.5$ is more the result of high concentrations of highly oxidized cobalt than an excessive number of vacancies in the alkali layer (42). In $Ca_{0.26}CoO_2$, for instance, x is significantly lower than 0.5, but the Co^{IV} concentration is only approximately equal to that of $Na_{0.52}CoO_2$ and hence no structural deformations are observed. The increased electrostatic interactions between Ca^{2+} and O^{2-} (relative to those of Li^+

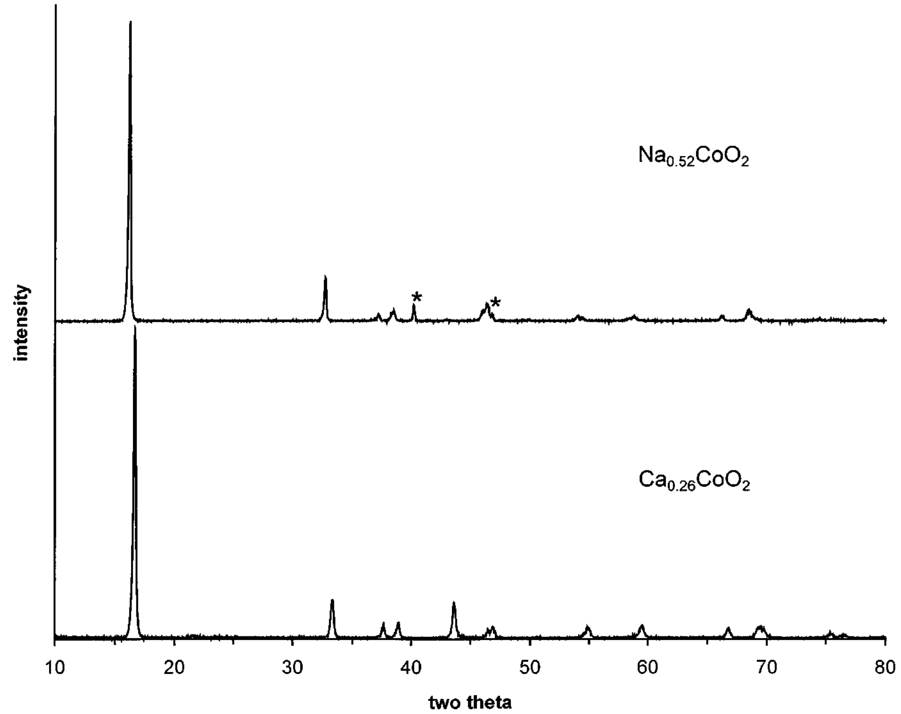

FIG. 2. X-ray powder diffraction patterns of the precursor, $Na_{0.52}CoO_2$ ($P'3$), versus its exchange product, $Ca_{0.26}CoO_2$ ($P'3$). Peaks marked with asterisk (*) are due to the platinum sample holder.

or Na^+) and strong repulsions between Ca^{2+} and Co^{III}/Co^{IV}, however, certainly contribute to the relative stability of the $[CoO_2]_n$ layers of the Ca_xCoO_2 system, making a direct comparison to the Na_xCoO_2 and Li_xCoO_2 systems somewhat inappropriate. The effects of substituting divalent cations into the **A** sites of A_xCoO_2 is illustrated by examining the distances between adjacent $[CoO_2]_n$ layers in the various systems (Table 4). In the progression from $NaCoO_2$ to $Na_{0.52}CoO_2$, the spacing between $[CoO_2]_n$ layers expands ~0.07 Å for every 0.1 equivalents of Na^+ removed. Even Li_xCoO_2 shows an expansion of ~0.02 Å per 0.1 equivalents of removed Li^+ (note, however, that when $x < 0.5$ this trend becomes erratic, and by some accounts reverses) (41, 43, 44). In Ca_xCoO_2, however, the spacing between adjacent $[CoO_2]_n$ layers shows essentially no variation over the composition range studied, indicating that the greater electrostatic interaction provided by the Ca^{2+} is enough to overcome the repulsive forces between the negatively charged layers.

TABLE 3
Summary of TGA Results for Reduction of the Ca_xCoO_2 Series

Ca_xCoO_2 composition	Experimental mass loss (wt%)[a]	Theoretical mass loss (wt%)
$Ca_{0.50}CoO_2$ ($P'3$)	21.57(5)	21.63
$Ca_{0.35}CoO_2$($P2$)	25.18(4)	25.15
$Ca_{0.27}CoO_2$($P2$)	27.69(9)	27.34
$Ca_{0.26}CoO_2$ ($P'3$)	27.33(5)	27.47

[a] Estimated standard deviations based on three runs are shown in parentheses.

The relationship between $[CoO_2]_n$ layer-spacing and composition in Table 4 leads to a few other deductions. The $Na_{0.5}CoO_2$ reported by Jansen and Hoppe in 1974, which was prepared by direct reaction, has a hexagonal unit cell of $a = 2.84(3)$ Å and $c = 10.81(1)$ Å, giving a spacing of ~5.41 Å between adjacent $[CoO_2]_n$ layers (26). We, however, calculated an interlayer spacing of 5.53 Å for $Na_{0.53}CoO_2$, and Kikkawa *et al.* reported a distance of 5.56 Å for $NaCoO_2$ deintercalated to $Na_{0.5}CoO_2$ (25). Given the near-linear relationship between composition and interlayer spacing for the Na_xCoO_2 system, the actual composition of the Jansen and Hoppe material should lie near $Na_{0.7}CoO_2$, suggesting a problem with the authors' quantitative analysis, which may explain our difficulty in reproducing the synthesis.

We have indexed the $P'3$ structure on a monoclinic unit cell, although the original report of $P'3$ $Na_{0.6}CoO_2$ by Fouassier *et al.* (23) and a subsequent report by Kikkawa *et al.* (25) both indexed the material on a slightly distorted orthorhombic cell with parameters very similar to those of

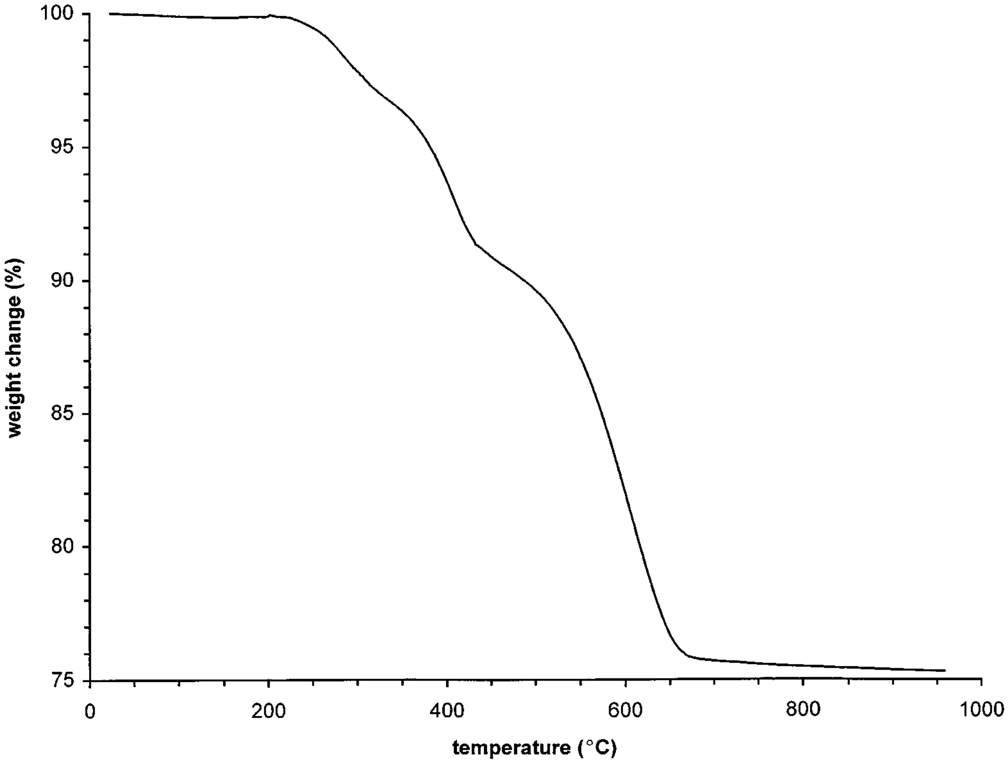

FIG. 3. TGA of Ca_xCoO_2 in dilute hydrogen. Reduction products are CaO and cobalt metal.

$NaCoO_2$ (*O*3). A later report indexed the material on a significantly smaller monoclinic cell similar to ours (24). Since no single-crystal work has been reported for the *P*′3 structure, a degree of uncertainty remains as to which unit cell is correct. The *P*′3 $Ca_{0.50}CoO_2$ and $Ca_{0.29}CoO_2$ reported here will satisfactorily index in either geometry. The monoclinic unit cell was chosen based on its smaller volume.

TABLE 4
Distance between Adjacent $[CoO_2]_n$ Layers for Various A_xCoO_2

A_xCoO_2 composition	$[CoO_2]_n$ separation (Å)
$LiCoO_2$	4.70^a
$Li_{0.74}CoO_2$	4.74^a
$Li_{0.49}CoO_2$	4.81^a
$NaCoO_2$	5.200(2)
$Na_{0.71}CoO_2$	5.44(1)
$Na_{0.53}CoO_2$	5.529(1)
$Ca_{0.50}CoO_2$	5.438(2)
$Ca_{0.35}CoO_2$	5.436(1)
$Ca_{0.27}CoO_2$	5.437(3)
$Ca_{0.26}CoO_2$	5.432(4)

[a] Values calculated from unit cells reported in Ref. (38).

CONCLUSIONS

A series of layered calcium cobalt oxides with both the *P*2 and *P*′3 structure types have been prepared by low-temperature ion exchange routes. The introduction of divalent cations appears to essentially fix the $[CoO_2]_n$ layer spacing as a function of composition (x in Ca_xCoO_2), at least over the range $0.26 \leq x \leq 0.50$. It will be of interest to gauge the effect of this on the electrochemical intercalation of alkali metal cations—such studies are currently under way.

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REFERENCES

1. A. Clearfield, *Chem. Rev.* **88,** 125 (1988).
2. H. Izawa, S. Kikkawa, and M. Koizumi, *J. Solid State Chem.* **69,** 336 (1987).
3. R. Nedjar, M. M. Borel, and B. Raveau, *Ann. Chim.* (*Paris*) **13,** 155 (1988).

4. H. Boller, *Monat. Chem.* **109,** 975 (1978).
5. S. Sattar, B. Ghosal, M. L. Underwood, H. Mertwoy, M. A. Saltzberg, W. S. Grydrych, G. S. Rohrer, and G. C. Farrington, *J. Solid State Chem.* **65,** 231 (1986).
6. A. K. Cheetham and P. Day, "Solid State Chemistry: Compounds," Clarendon, Oxford, 1992, and references therein.
7. (a) A. Grandin, M. M. Borel, and B. Raveau, *Ann. Chim.* (*Paris*) **13,** 51 (1988). (b) R. Nedjar, M. M. Borel, A. Leclaire, and B. Raveau, *Mater. Res. Bull.* **23,** 497 (1988).
8. O. Kalogirou, *J. Solid State Chem.* **102,** 318 (1993).
9. A. Grandin, M. M. Borel, and B. Raveau, *Mater. Res. Bull.* **20,** 129 (1985).
10. B. L. Cushing, A. U. Falster, W. B. Simmons, Jr., and J. B. Wiley, *J. Chem. Soc. Chem. Commun.* 2635 (1996).
11. R. A. McIntyre, A. U. Falster, S. Li, W. B. Simmons, Jr., C. J. O'Connor, and J. B. Wiley, *J. Am. Chem. Soc.* **120,** 217 (1998).
12. R. Koksbang, J. Barker, H. Shi, and M. Y. Saïdi, *Solid State Ionics* **84,** 1 (1996).
13. L. W. Shacklette, T. R. Jow, and L. Townsend, *J. Electrochem. Soc.* **135,** 2669 (1988).
14. C. Delmas, C. Fouassier, and P. Hagenmuller, *Physica B* **99,** 81 (1980).
15. C. Delmas, J. Braconnier, and P. Hagenmuller, *Mater. Res. Bull.* **17,** 117 (1982).
16. R. D. Shannon, D. B. Rogers, and C. T. Prewitt, *Inorg. Chem.* **10,** 713 (1971).
17. Y.-J. Shin, J.-H. Kwak, and S. Yoon, *Bull. Korean Chem. Soc.* **18,** 775 (1997).
18. (a) M. C. Blesa, U. Amador, E. Morán, N. Menéndez, J. D. Ternero, and J. Rodríguez-Carvajal, *Solid State Ionics* **63,** 429 (1993). (b) M. C. Blesa, E. Morán, U. Amador, and N. H. Anderson, *J. Solid State Chem.* **129,** 123 (1997).
19. P. N. Bityutskii and V. I. Khitrova, *Sov. Phys. Crystallogr.* **29,** 270 (1984).
20. J. J. Braconnier, C. Delmas, C. Fouassier, M. Figlarz, B. Beaudouin, and P. Hagenmuller, *Rev. Chim. Miner.* **21,** 496 (1984).
21. C. Delmas, *Mater. Res. Soc. Symp. Proc.* **210,** 335 (1991).
22. O. Glemser and J. Einerhand, *Z. Anorg. Allg. Chem.* **26,** 261 (1950).
23. C. Fouassier, G. Matejka, J.-M. Reau, and P. Hagenmuller, *J. Solid State Chem.* **6,** 532 (1973).
24. C. Delmas, C. Fouassier, and P. Hagenmuller, "Inorganic Syntheses," Wiley, New York, 1983.
25. S. Kikkawa, S. Miyazaki, and M. Koizumi, *J. Solid State Chem.* **62,** 35 (1986).
26. M. Jansen and R. Hoppe, *Z. Anorg. Allg. Chem.* **408,** 104 (1974).
27. D. A. Keszler and J. A. Ibers, "Modified POLSQ," Dept. of Chemistry, Northwestern Univ., Evanston, IL, 1983.
28. S. Miyazaki, S. Kikkawa, and M. Koizumi, *Synth. Met.* **6,** 211 (1983).
29. K. Vidyasagar, J. Gopalakrishnan, and C. N. R. Rao, *Inorg. Chem.* **23,** 1206 (1984).
30. C. Delmas, J. J. Braconnier, C. Fouassier, and P. Hagenmuller, *Solid State Ionics* **3,** 165 (1981).
31. J. Molenda, C. Delmas, P. Dordor, and A. Stokłosa, *Solid State Ionics* **12,** 473 (1984).
32. R. J. Balsys and R. L. Davis, *Solid State Ionics* **69,** 69 (1994).
33. C. Delmas, *Mater. Sci. Eng. B* **3,** 97 (1989).
34. S. Kikkawa, S. Miyazaki, and M. Koizumi, *J. Power Sources* **14,** 231 (1985).
35. J. Desilvestro and O. Haas, *J. Electrochem. Soc.* **137,** 5C (1990).
36. K. Ozawa, *Solid State Ionics* **69,** 212 (1994).
37. G. G. Amatucci, J. M. Tarascon, and L. C. Klein, *Solid State Ionics* **83,** 167 (1996).
38. K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, *Mater. Res. Bull.* **15,** 783 (1980).
39. R. Brec, E. Prouzet, and G. Ouvrard, *J. Power Sources* **43,** 277 (1993).
40. L. A. de Picciotto, M. M. Thackeray, and W. I. F. David, *Mater. Res. Bull.* **19,** 1497 (1984).
41. C. Delmas, *Mater. Sci. Eng. B* **3,** 97 (1989).
42. M. G. S. R. Thomas, W. I. F. David, J. B. Goodenough, and P. Groves, *Mater. Res. Bull.* **20,** 1137 (1985).
43. T. Ohzuku and A. Ueda, *J. Electrochem. Soc.* **141,** 2972 (1994).
44. G. G. Amatucci, J. M. Tarascon, and L. C. Klein, *J. Electrochem. Soc.* **143,** 1114 (1996).