and our indexing involves the use of a smaller monoclinic unit cell (Table 1).

As would be expected from the topotactic nature of ion-exchange reactions, a strong correlation exists between the structures of the precursors and the products. For $Ca_{0.3}CoO_2$ ($P'3$) and $Ca_{0.35}CoO_2$ ($P2$), the products are isostructural with the precursors. In the case of $Ca_{0.5}CoO_2$ ($P'3$), $NaCoO_2$ (O3) does not have the same structure type, but the $P'3$ orientation is readily obtained by a simple shift of the $CoO_2{}^{-}$ layers. A similar transformation occurs as a function of sodium composition in both the electrochemical deintercalation of $NaCoO_2$, where the $P'3$ structure is observed after the removal of approximately 20% of the sodium,[6] and in the direct synthesis of the $x = 1.0$ (O3) *vs.* the $x = 0.60$ ($P'3$) members of the Na_xCoO_2 system.[2] In contrast, the orientation of the layers remains essentially constant ($O3$), except for slight monoclinic distortions, on deintercalation of a similar amount of the smaller lithium ion from $LiCoO_2$.[7] The size of the interlayer cation should have a significant influence on the relative orientation of $CoO_2{}^{x-}$ layers. Because calcium and sodium have nearly equivalent ionic radii,[8] it is therefore not surprising that the behaviour of the calcium materials more closely parallels that of Na_xCoO_2.

A number of investigators have examined multivalent cation-exchange reactions.[9–11] Though the bulk of this work has been carried out in aqueous solution,[9] this can be problematic when dealing with moisture-sensitive materials.[12] Anhydrous molten salts provide an effective alternate route.[10] In the reactions reported here, the moisture sensitivity of the Na_xCoO_2 reactants is precluded with the use of anhydrous calcium nitrate, while the low-melting $NaNO_3$ byproduct (308 °C)[13] is expected to enhance the diffusion of calcium ions to the reaction interface. Synthetic approaches such as this will continue to be effective in the preparation of new materials. Preliminary results already indicate that other alkaline- earth-cation transition-metal compounds, as well as materials with lower cation loadings, are accessible by this route.

The Ca_xCoO_2 compounds described here may hold some significance as battery cathode materials. It has been observed that the diffusivity of cations through adjacent trigonal-prismatic sites can be greater than between octahedral sites.[6] Though calcium with its divalent charge is not expected to be particularly mobile, the interlayer vacancies adjacent to the calciums may be receptive to the introduction of other cations. The placement of mobile cations into these vacancies could result in an effective cathode material, possibly expanding the reversibility window of the cathode while minimizing the need for special circuitry to prevent overcharge. We are currently investigating the utility of such systems.

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Footnotes

† Precursors were prepared by literature methods.[2] All samples were handled in an argon-filled drybox. The Na_xCoO_2 precursors are dark violet and are moisture sensitive, while the black Ca_xCoO_2 products show no sign of moisture sensitivity.

‡ Digitized X-ray powder diffraction data were collected on a Philips-Norelco diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å) and a graphite monochromator. Silicon or tungsten were used as internal standards. Elemental analysis was performed on an ARL SEMQ electron microprobe.

§ The model for the $P'3$ structure was derived from that proposed by Delmas *et al.*[1] and the model for the $P2$ structure came from the single-crystal structure determination reported by Jansen and Hoppe.[3] Rietveld analysis is to begin shortly.

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