Opening a Perovskite to Valence Manipulation: Two-Step Topotactic Route to a New Mixed-Valence Titanate, Na$_{1-x+y}$Ca$_{x/2}$LaTiO$_4$

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Mixed-valence oxides with perovskite-related structures are known to exhibit a range of important properties including high-temperature superconductivity, colossal magnetoresistance, and catalytic activity.[1] While many of these materials are traditionally synthesized by direct reaction with aliovalent metal oxides at elevated temperatures, mild low-temperature routes are also desirable in that they may lead to new metastable materials with improved properties. Reductive intercalation with alkali metals is one topotactic method known to be effective in the low-temperature preparation of some select mixed-valence perovskites.[2−4] For this approach to be successful, however, the A-site in Ruddlesden−Popper perovskites, A$_2$[A$_{m-1}$B$_m$O$_{3m+1}$], (A = alkali, alkaline earth, and/or rare earth; B = transition metal; m = 1, 2, 3, or ∞) must be partially or completely vacant. Since most perovskites are stoichiometric with respect to A, methods that create vacancies on this site are appealing in that they would, when used in combination with reductive intercalation techniques, offer a significant new approach to the preparation of mixed-valence compounds.

We and others[5,6] have investigated the exchange of multivalent cations for monovalent ones in receptive hosts. When a multi-valent cation is exchanged into a compound, it is accompanied by the formation of one or more vacancies depending on the cation charge. The creation of these vacancies opens the host structure to further chemistry. In the case of reductive intercalation, it should be possible to insert alkali metal ions into the vacancies thereby producing mixed valency in the host. Herein we describe the use of this strategy in the manipulation of NaLaTiO$_4$.[7] This Ruddlesden−Popper phase (m = 1, K$_2$NiF$_4$ structure)[8] consists of LaTiO$_4{}^-$ layers separated by ion−exchangeable sodium ions.[9] Because the A-sites are fully occupied, direct reductive intercalation cannot occur. Initially NaLaTiO$_4$ is opened to intercalation by ion exchange with a divalent cation and then the interlayer vacancies created are utilized by alkali metal ions on intercalation. This simple two-step procedure readily results in a new mixed-valence titanate with a perovskite-related structure.

NaLaTiO$_4$ was prepared by literature methods.[8,10] Sodium ions were replaced in a two-for-one exchange by reacting stoichiometric amounts of anhydrous Ca(NO$_3$)$_2$ with NaLaTiO$_4$ in an evacuated, sealed Pyrex tube for 3 days at 350 °C.[11] The NaNO$_3$ byproduct, observed by X-ray powder diffraction, was readily removed with a water wash. The exchange product was then reacted with sodium metal vapor for several days at 300 °C.[12] During this time, the oxide turned from white to dark black. Relative amounts of sodium and calcium in both products were determined by spectroscopic methods.[13] Values were found to correspond to an 86% sodium exchange, x = 0.86 in Na$_{1-x}$Ca$_{x/2}$LaTiO$_4$, and an 88% sodium intercalation, y = 0.38 in Na$_{1-x+y}$Ca$_{x/2}$LaTiO$_4$.[14]

Compounds were characterized by both X-ray powder diffraction and magnetic susceptibility.[15] Figure 1 presents the powder patterns of the ion exchange and intercalated products in comparison to both the parent, NaLaTiO$_4$, and a simulated pattern for Na$_{0.51}$Ca$_{0.43}$LaTiO$_4$.[16] The NaLaTiO$_4$ structure is maintained in both products. The simulation, modeled after the parent[8a] with sodium and calcium ions statistically distributed over the same site, is in good agreement with the observed pattern of the intercalate.[17] Lattice parameters along with cell volumes are presented in Table 1. For the exchange material, a slight reduction in cell size is observed that is attributed to the smaller ionic radius of calcium (1.32 Å) versus that of sodium (1.38 Å).[18] A more dramatic variation in the cell is seen in the intercalated compound; the a parameter is found to expand by ∼0.1 Å while the c

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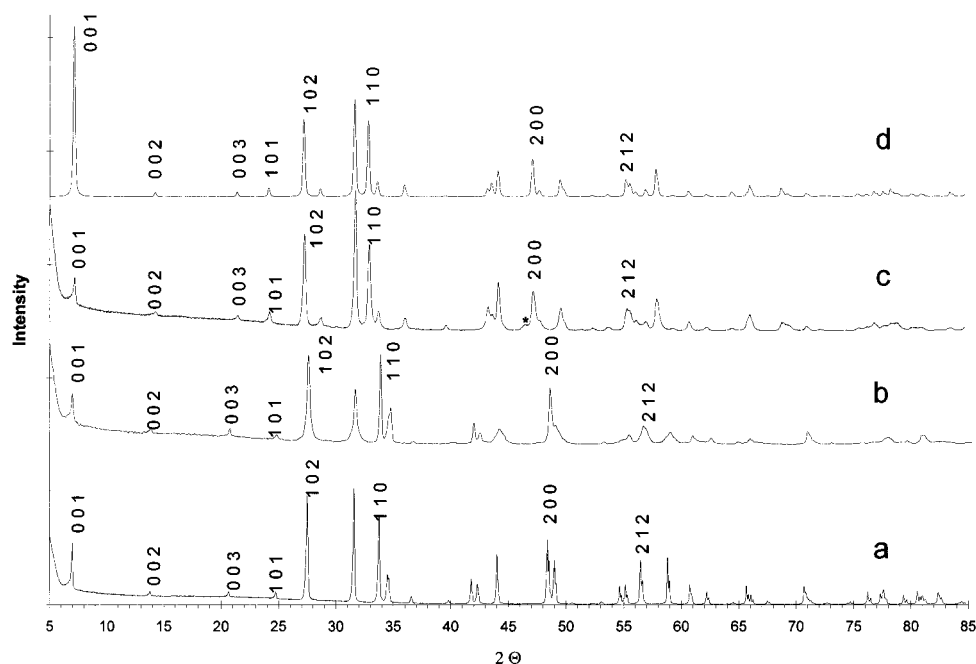(7) Blasse, G. *J. Inorg. Nucl. Chem.* **1968**, *30*, 656.

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(10) Stoichiometric amounts of La$_2$O$_3$ (Aldrich, 99.99%) and TiO$_2$ (Aldrich, 99.99%) and a 30% excess of Na$_2$CO$_3$ (Aldrich, 99.99%) were heated in an alumina crucible in air at 930 °C for 72 h. Interstitial grindings were performed every 24 h with the addition of a further 30% excess of Na$_2$CO$_3$. The resultant white powder was thoroughly washed with distilled water and dried at 160 °C. The unit cell parameters are in good agreement with the literature (Table 1).
(11) Typically a stoichiometric amount of the nitrate (Aldrich, 99%) was combined with 1.57 g (5.7 mmol) of NaLaTiO$_4$ in a tube (12 mm od). The product was white in color.
(12) An excess of sodium metal (0.3 g, 13.0 mmol, Aldrich, 99.999%) was weighed out on a piece of Pyrex tubing (6 mm od) for ease of handling, the combination was placed in a Pyrex tube (12 mm od) along with 0.3 g (1.1 mmol) of sample, and the tube was sealed under vacuum. The excess sodium partly compensated the loss due to reaction with the glass; unreacted sodium was distilled away from the product by heating the sample tube in a temperature gradient. The intercalation reagents and products were all handled in an argon-filled drybox. *Caution: Sodium metal can explosively react with water. Excess sodium should be safely disposed of by reacting it with an alcohol.* The intercalation product degrades very slowly on exposure to air.
(13) Calcium and sodium contents were determined commercially by inductively coupled plasma spectrometry (ICP) and atomic absorption (AA), respectively.
(14) This formulation does not account for the possibility of oxygen nonstoichiometry.
(15) Digitized X-ray diffraction patterns were collected on a Philips-Norelco diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator. Cell parameters were refined by a least-squares method. Room-temperature susceptibility measurements were performed on a Quantum Design MPMS-5S SQUID susceptometer.
(16) The pattern of Na$_{0.51}$Ca$_{0.43}$LaTiO$_4$ was calculated with the *LAZY-PULVERIX* FORTRAN program (Yvon, K.; Jeitschko, W.; Parthe, E. Laboratoire de Crystallographie Aux Rayon-X; University of Geneve: Geneva, Switzerland, 1977.

Figure 1. X-ray powder diffraction patterns of (a) $NaLaTiO_4$, (b) the calcium ion exchange product, (c) the intercalation product, and (d) a simulated pattern of intercalation product with composition, $Na_{0.51}Ca_{0.43}LaTiO_4$. Miller indices are indicated for select reflections. Unindexed reflection (*).[17]

Table 1. Tetragonal Cell Parameters for the Parent, $NaLaTiO_4$, and the Exchange and Intercalation Products

cmpd	unit cell (Å)	cell vol. (Å³)	lit. cell (Å)
$NaLaTiO_4$	$a = 3.7731(6)$	185.37	$a = 3.7759(1)$
	$c = 13.021(2)$		$c = 13.022(1)$[9a]
$Na_{0.13}Ca_{0.43}LaTiO_4$[13]	$a = 3.764(2)$	183.40	this work
	$c = 12.945(6)$		
$Na_{0.51}Ca_{0.43}LaTiO_4$[13]	$a = 3.8627(4)$	186.27	this work
	$c = 12.484(2)$		

parameter contracts by $\sim$0.46 Å. These lattice changes in a and c are attributed to the larger size of Ti^{3+} (0.81 Å) versus that of Ti^{4+} (0.75 Å)[18] and the greater electrostatic attraction between the more highly charged perovskite sheets and the interlayer cations, respectively. Comparable behavior has been observed after reductive intercalation of other layered perovskites such as those with the Dion–Jacobson structure type, $A[A_{m-1}B_mO_{3m+1}]$.[19] Room-temperature magnetic measurements are consistent with the formation of Ti^{3+}; a positive susceptibility (1.8μ_B), greater than the theoretical value of 1.0μ_B (spin only, 38% Ti^{3+}), is observed. Variable-temperature magnetic and electronic studies as a function of composition will be reported elsewhere.

Initial results indicate that control over the extent of mixed-valency is best exercised in the ion exchange step. By simply using less than stoichiometric amounts of $Ca(NO_3)_2$, lower values of x in $Na_{1-x}Ca_{x/2}LaTiO_4$ and correspondingly fewer vacancies can be introduced into the host, whereby on subsequent intercala-

tion a smaller fraction of the titanium is reduced. Controlling valency by lowering the amount of sodium metal available for intercalation appears less effective in that the resulting product will sometimes contain unreacted starting material.

$Na_{1-x+y}Ca_{x/2}LaTiO_4$ represents a new mixed-valence titanate[20] with a perovskite-related structure. The combination of multivalent ion exchange and reductive intercalation used in its preparation offers an effective strategy for valence manipulation. Because many mixed metal oxides[5d–f,6,21] and nonoxides[22] are known to undergo, or are likely to undergo, ion exchange with multivalent cations, it should be possible to extend this two-step approach to a variety of compounds. The ability to carry out such successive reactions on a host, especially at relatively low temperatures, then becomes especially significant in that it may result in a greater degree of control over structure and properties than afforded by more traditional single-step high-temperature processing. Molecular chemists routinely draw from their reaction libraries to direct the construction of a targeted molecule by the sequential, multistep manipulation of some parent. Similar abilities for solid-state chemists could result in a more routine approach to the rational design and construction of new nonmolecular materials. Two-step strategies such as that presented here should serve in the development of such methods.

(17) A small, broad reflection (<3%) is observed at 46.3° 2θ. This is attributed to a minor impurity that forms on intercalation. The phase is likely an intercalated, defect perovskite, $Na_xLa_{1-y}TiO_3$ (0.33 ≤ y ≤ 0.5, x ≤ y). Though it is thought that this perovskite is initially present as an amorphous impurity in the parent compound, the possiblity it is a decomposition product has not yet been ruled out. Note however, that the small amount of this impurity does not increase if the intercalation step is carried out for longer times or at higher temperatures; this would not be expected if the impurity was from decompostion.

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