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A Multistep Topotactic Route to the New Mixed-Valence Titanate, $Na_{2-x+y}Ca_{x/2}La_2Ti_3O_{10}$. Electron Localization Effects in a Triple-Layered Perovskite

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Mixed-valency can be introduced into mixed-metal oxides by traditional high-temperature methods[1] or by low-temperature topotactic routes.[2] Though the former has yielded an extensive number of compounds, the elevated temperatures required by these reactions do not always allow clear control of structure and stoichiometry. Our group is currently working to develop a series of reaction schemes for the routine low-temperature (≤500 °C) synthesis of new, potentially metastable, mixed-valence compounds. By utilizing such strategies, one can strive to manipulate electronic properties while maintaining salient structural features. Recently we described a simple two-step topotactic method for the preparation of a mixed-valence titanate with the K_2NiF_4 structure type.[3] This route consisted of aliovalent ion exchange of $NaLaTiO_4$ followed by alkali-metal intercalation. Here we expand this chemistry to the manipulation of the triple-layered perovskite, $K_2La_2Ti_3O_{10}$. A novel three-step procedure is used to prepare the mixed valence compound, $Na_{2-x+y}Ca_{x/2}La_2Ti_3O_{10}$ ($x = 1.22$, $y = 0.32$).

The synthetic route utilized in our approach relies on divalent ion exchange to open the host compound to reductive intercalation. For this step not to considerably disrupt the crystallinity of the host and to favor an extensive degree of exchange, there should be a close size match between exchanging cations such as that provided by sodium (1.38 Å) and calcium (1.32 Å).[4,5] Initially, $Na_2La_2Ti_3O_{10}$ was targeted as the starting compound to the triple-layered titanates, but we and others[6] have not been able to prepare single-phase samples, even by the methods of Toda *et al.*[7] An indirect route with sodium ion exchange of $K_2La_2Ti_3O_{10}$ was then used to access $Na_2La_2Ti_3O_{10}$.[8,9] Subsequently, divalent ion exchange with calcium nitrate was carried out to introduce cation vacancies,[10] and the resulting intermediate, $Na_{0.8}Ca_{0.6}La_2Ti_3O_{10}$, was then reduced by intercalation with sodium metal vapor.[11] The composition of the final product, $Na_{1.12}Ca_{0.61}La_{1.93}Ti_3O_{10}$, corresponds to a 100% monovalent cation exchange, ca. 60% divalent exchange, and ca. 55% intercalation into available cation vacancies.[12]

$Na_{1.12}Ca_{0.61}La_{1.93}Ti_3O_{10}$ was characterized by X-ray powder diffraction (XRD), magnetic susceptibility, and four-probe resistivity.[13] Diffraction patterns of $Na_2La_2Ti_3O_{10}$, the divalent exchange intermediate, and the intercalation product, along with a calculated pattern of the final product,[14] are shown in Figure 1. Though some loss of crystallinity would be expected in each of the synthetic steps, the broadening of diffraction lines is minimal. The lattice parameters and unit cell volumes for the parent, intermediates and final product are presented in Table 1. A slight overall cell contraction is observed on divalent exchange because

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(1) See, for example: (a) Sunstrom, J. E., IV; Kauzlarich, S. M.; Klavins, P. *Chem. Mater.* **1992**, *4*, 346. (b) Hamada, D.; Machida, M.; Sugahara, Y.; Kuroda, K. *J. Mater. Chem.* **1996**, *6*, 69. (c) MacEachern, M. J.; Dabkowska, J. D.; Garrett, J. D.; Amow, G.; Gong, W.; Liu, G.; Greedan, J. E. *Chem. Mater.* **1994**, *6*, 2092. (d) Edwards, P. P.; Ramakrishnan, T. V.; Rao, C. N. R. *J. Phys. Chem.* **1995**, *99*, 5228.

(2) Examples here include: (a) Poeppelmeier, K. R.; Leonowicz, M. E.; Longo, J. M. *J. Solid State Chem.* **1982**, *44*, 89. (b) Nadiri, A.; Le Flem, G.; Delmas, C. *J. Solid State Chem.* **1988**, *73*, 338. (c) Armstrong, A. R.; Anderson, P. A. *Inorg. Chem.* **1994**, *33*, 4366.

(3) McIntyre, R. A.; Falster, A. U.; Li, S.; Simmons, W. B.; O'Connor, C. J.; Wiley, J. B. *J. Am. Chem. Soc.* **1998**, *120*, 217.

(4) Ionic radii from Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(5) Mahler, C. H.; Cushing, B. L.; Lalena, J. N.; Wiley, J. B. *Mater. Res. Bull.* **1998**, *33*, in press. Cushing, B. L.; Wiley, J. B. *Mater. Res. Bull.* **1999**, *34*, in press.

(6) Wright, A. J.; Greaves, C. *J. Mater. Chem.* **1996**, *6*, 1823.

(7) Toda. K.; Kameo, Y.; Fujimoto, M.; Sato. M. *J. Ceram. Soc. Jpn.* **1994**, *102*, 735.

(8) Gopalakrishnan, J.; Bhat, V. *Inorg. Chem.* **1987**, *26*, 4299.

(9) $K_2La_2Ti_3O_{10}$ was prepared as in ref 8 from La_2O_3 (Alfa, 99.99%) and TiO_2 (Alfa, 99.99%) with a 30% excess of $K_2CO_3{\cdot}1.5H_2O$ (Alfa, 99.5%). Samples were heated in alumina crucibles at 1000 °C for 2 days with one regrinding. The product was washed with copious amounts of water and then heated at 500 °C for 24 h. The compound readily forms a hydrate, so it was stored in an argon-filled drybox. Sodium ion exchange was carried out at 360 °C in air in an alumina crucible for 2 weeks with a 10-fold excess by weight of $NaNO_3$ (EM Science, ACS Reagent). The sample was then washed thoroughly with hot distilled water to remove the KNO_3 byproduct and excess $NaNO_3$. $Na_2La_2Ti_3O_{10}$ does not form a hydrate and was stored in air.

(10) Aliovalent ion exchange on $Na_2La_2Ti_3O_{10}$ was carried out with a 4-fold molar excess of anhydrous calcium nitrate (Aldrich, 99%) in a sealed, evacuated Pyrex tube at 350 °C for 4 days. The product was thoroughly washed with hot distilled water and dried at 140 °C overnight. The white powder is air stable. Efforts to exchange $K_2La_2Ti_3O_{10}$ directly with $Ca(NO_3)_2$ produced a poorly crystalline material with a limited degree of exchange.

(11) Reductive intercalation was performed by heating the divalent exchange product with an equal mass of sodium metal (Alfa, 99.95%) in an evacuated Pyrex tube at 320 °C for 3 days. Excess sodium metal was removed by placing the tube in a temperature gradient (25 → 320 °C). The dark gray product showed slight air sensitivity so all samples were stored in an argon-filled drybox and any air exposure minimized. **Caution:** *Sodium metal can react explosively with water. Excess sodium should be safely disposed of by reacting it with an alcohol.*

(12) Ratios of exchange cations were determined by electron microprobe, direct current plasma (DCP), and/or inductively coupled plasma (ICP) spectroscopy. The cation ratios (Na, Ca, La, and Ti) of the final product were determined commercially by ICP. The low value for lanthanum (1.93 versus 2.00) is attributed to the error in the ICP measurements, which can be several percent due to matrix effects; an error of less than 2% in both titanium and lanthanum would account for this difference. Samples for DCP and ICP were digested in a 10% HCl solution.

(13) X-ray diffraction data were collected in step-scanning mode between 10 and 95° 2 θ with a 0.02° step width and 10 s count time on a Philips X'pert-MPD system (Cu Kα radiation, $\lambda = 1.5418$ Å) equipped with a graphite monochromator. Cell parameters were refined by a least-squares method. Magnetic susceptibility measurements were made on a Quantum Design MPMS-5S SQUID susceptometer between 2 and 300 K at 50 G (zero-field cooled) on polycrystalline samples before and after reductive intercalation. DC conductivity measurements of the reduced phase were taken between 2 and 300 K by the four-point probe method on a small rectangular unsintered pressed pellet; platinum leads were connected with silver paste.

(14) The powder pattern was calculated from a model based on $Na_2La_2Ti_3O_{10}$ (ref 6) with the FORTRAN program *LAZY-PULVERIX*; Yvon, K.; Jeitschko, W.; Parthe, E. Laboratoire de Crystallographie aux Rayon-X, University Geneve: Geneva, Switzerland, 1977.

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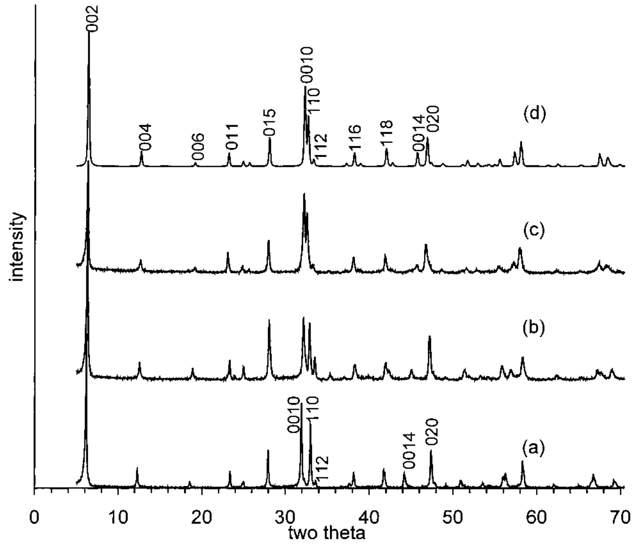

Figure 1. X-ray powder diffraction patterns of the (a) monovalent exchange, (b) divalent exchange, and (c) intercalation products and (d) a simulated pattern of the intercalation product.[14] Miller indices are indicated for selected reflections.

Table 1. Tetragonal Unit Cell Parameters of the Parent, Intermediates, and Final Product

cmpd[12]	unit cell (Å)	cell vol. (Å^3)	lit. cell (Å)
$K_2La_2Ti_3O_{10}$	$a = 3.869(1)$ $c = 29.77(2)$	445.6	$a = 3.871(2)$ $c = 29.78(2)$[8]
$Na_2La_2Ti_3O_{10}$	$a = 3.8330(1)$ $c = 28.662(1)$	421.10	$a = 3.834(7)$ $c = 28.65(6)$[8]
$Na_{0.8}Ca_{0.6}La_2Ti_3O_{10}$	$a = 3.8334(2)$ $c = 28.385(2)$	417.12	this work
$Na_{1.12}Ca_{0.61}La_{1.93}Ti_3O_{10}$	$a = 3.8778(2)$ $c = 27.813(2)$	418.23	this work

of the smaller size of Ca^{2+} versus Na^+. On intercalation, the *a* parameter expands while the *c* contracts, this is ascribed to the size increase of titanium upon reduction and the greater electrostatic attraction between the perovskite sheets and the interlayer cations, respectively.[3,15] The magnetic data (Figure 2), corrected for diamagnetism, shows predominately temperature independent paramagnetism (χ_{TIP}) down to ca. 50 K and Curie−Weiss behavior at lower temperatures.[16] Resistivity measurements from 2 K (Figure 2, inset) reveal semiconductive behavior ($\rho_{300K} = 4.7 \times 10^4$ Ω cm); however, plots of log ρ vs T^{-1} were nonlinear. The dramatic rise in resistivity at low temperatures is indicative of weakly localized states;[17] low-temperature data ($T < 10$ K) exhibit a $T^{-1/4}$ response attributed to a variable range hopping mechanism.[17,18] The extensive TIP component, the low-temperature Curie−Weiss behavior, and variable range hopping have been associated with Anderson localization effects in semiconductors.[19] Such a response, possibly in combination with small polarons, is not unreasonable in a layered system that contains a random distribution of monovalent and divalent cations as well as vacancies in its interlayer. The observation of metallic behavior above 25 K in the structurally related oxygen-deficient calcium titanate,[20] even at *d*-electron counts approaching zero, further suggests that localization effects are at work in $Na_{1.12}Ca_{0.61}La_{1.93}Ti_3O_{10}$.

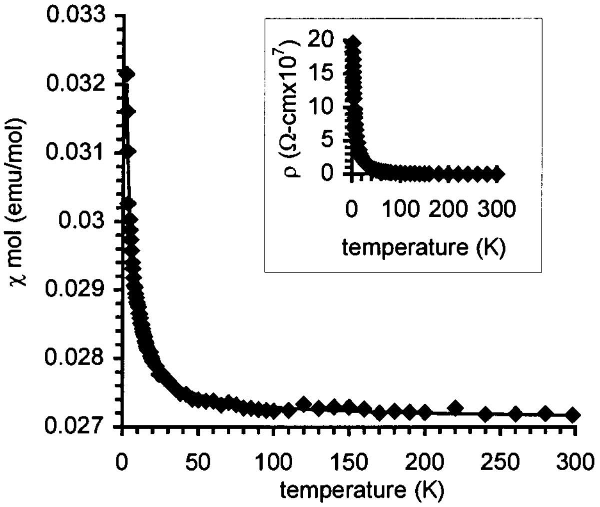

Figure 2. Molar susceptibility versus temperature for $Na_{1.12}Ca_{0.61}La_{1.93}Ti_3O_{10}$. The solid line represents the fit to $\chi = [C/(T\ \theta)] + \chi_{TIP}$.[16] The inset is a plot of resistivity versus temperature.

The multistep processing presented here allows the introduction of mixed valency into the triple-layered perovskite, $K_2La_2Ti_3O_{10}$. Initial results indicate that divalent exchange levels in excess of 90% are possible and that comparable degrees of intercalation should follow. If the bottom of the conduction band for these compounds is localized on the inner transition metal oxide layer as has been suggested,[21] it is then expected that higher electron counts will overcome the influence of the localization effects such that the Fermi energy will cross the mobility edge to result in metallic behavior. By careful selection of reaction pathways in other Ruddlesden−Popper, or even Dion-Jacobson, type perovskites that contain exchangeable cations, one should be able to consciously direct their electronic properties while maintaining specific structural details. Such strategies, however, are not necessarily limited to those pathways outlined above.

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(16) Magnetic data were fit to the equation $\chi = [C/(T - \theta)] + \chi_{TIP}$. The χ_{TIP} is 0.027 emu/mol while the Weiss constant (θ) and Curie constant (C) are −1.8 K and 0.019 cm^3 K/mol, respectively. The correlation coefficient (r) was 0.998. The compound is diamagnetic before reductive intercalation.

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(18) Data below 10 K (log ρ vs $T^{-1/4}$) were fit to a linear function with a correlation coefficient of 0.993.

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