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Communications

Subcritical Hydrothermal Synthesis of Perovskite Manganites: A Direct and Rapid Route to Complex Transition-Metal Oxides

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Soft chemical methods for the synthesis of inorganic solids, such as the use of sol–gel precursors or molten salts as reaction media, have been studied for a number of years now.¹ The hydrothermal method, widely used to prepare zeolites and other microporous solids, is attractive for studying as a route to multinary oxide phases since it offers the possibility of one-step synthesis under very mild conditions (typically <300 °C). Some attention has already been given to the synthesis of technologically important transition-metal oxides by the hydrothermal route,² for example, barium titanate for multilayer capacitors,³ substituted ceria for solid oxide-ion conductors,⁴ and lithium manganese oxides for

battery cathode materials.⁵ The method has great scope for extension into more complex oxide systems.

We have investigated the hydrothermal synthesis of mixed-metal manganites of composition $A_{1-x}A'_xMnO_{3+\delta}$, where A is a rare-earth metal and A' an alkali-earth metal. Such oxides have been widely studied for their magnetic and magnetoresistive properties,^{6,7} for their use as catalysts,⁸ and for application as cathodes in solid-oxide fuel cells.⁹ We have found that we can reproducibly synthesize $La_{0.5}Ba_{0.5}MnO_{3+\delta}$ from standardized solutions of $MnCl_2$, $KMnO_4$, $Ba(OH)_2$, and $La(NO_3)_3$ (molar ratio 1.4:0.6:1.0 Mn^{II} : Mn^{VII} : La : Ba) mixed with saturated KOH solution and heated at 240 °C for 24 h in a Teflon-lined hydrothermal autoclave (~50% fill). The average manganese oxidation state in this mixture is 3.5, as required in the product. After the solution is cooled and washed with deionized water, the black product is highly crystalline, as evidenced by the powder X-ray pattern, Figure 1. Note that these data were collected from material as isolated from the hydrothermal autoclave with no subsequent calcination or annealing. A small (<1%) amount of $BaMnO_3$ is indicated by the diffraction data, but it should be noted that even by the solid-state synthetic route, this impurity is commonly observed in similar amounts.¹⁰

Iodometric titration¹¹ shows that the value of δ is zero within experimental error. Thermogravimetric analysis, performed from room temperature to 900 °C, shows that

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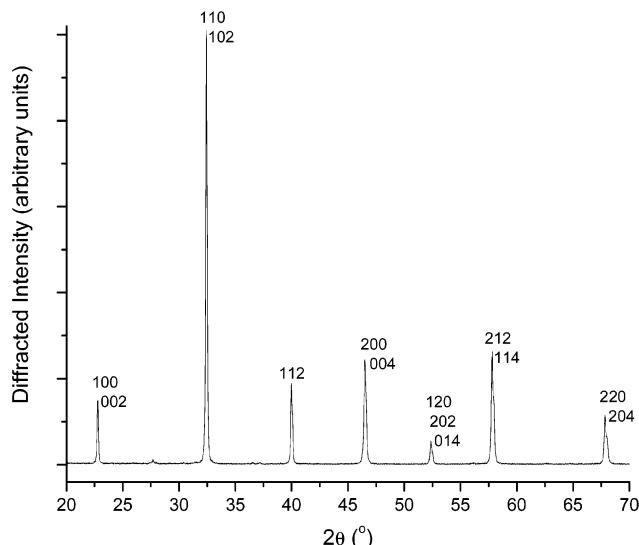


Figure 1. Powder X-ray diffraction data collected from $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ ($\text{Cu K}\alpha$, $\lambda_{\text{av}} = 1.5418 \text{ \AA}$, Bruker D8 diffractometer). The Miller indices are assigned on the basis of a tetragonal cell, $a = 3.9128(16) \text{ \AA}$, $c = 7.8074(3) \text{ \AA}$ (see text).

the material undergoes negligible mass change; this is consistent with the formulation $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ and also indicates that the solid contains no surface-bound water or hydroxyl groups. All peaks of the X-ray pattern can apparently be indexed using a primitive cubic cell, $a = 3.9076(2) \text{ \AA}$. It has previously been shown, however, that $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ exists in two polymorphs: in the first, lanthanum and barium are disordered over the A sites of a cubic perovskite structure ($a = 3.906 \text{ \AA}$), and in the second, lanthanum and barium are ordered in layers so that a tetragonal cell with $c \approx 2a$ is required to describe the structure ($a = 3.916 \text{ \AA}$, $c = 7.805 \text{ \AA}$).¹⁰ Since La^{3+} and Ba^{2+} are isoelectronic, the difference between the two polymorphs is extremely difficult to detect by X-ray diffraction, particularly when using laboratory powder diffraction and when there is some peak broadening due to small particle size. The magnetic properties of the two polymorphs do, however, differ, and this provides a means of distinguishing the two forms of the solids. Figure 2 shows the temperature dependence of the magnetization of hydrothermal $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ from 5 to 400 K. Analysis of these data shows that the material is ferromagnetic with a Curie temperature of 330 K; this shows the material to be the ordered, tetragonal polymorph of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ ($T_c = 330 \text{ K}$) since the disordered polymorph has a considerably lower Curie temperature (270 K).¹⁰ The previously described synthetic route to tetragonal $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ was lengthy: solid-state reaction of appropriate quantities of La_2O_3 , MnO_2 , and BaCO_3 at 1500 °C in an Ar/O_2 flow followed by slow cooling to 800 °C in the same atmosphere and finally cooling slowly to room temperature in an oxidizing atmosphere to optimize the oxygen content of the sample.¹⁰

Scanning electron microscopy of hydrothermal $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ reveals that the material consists of well-formed, cube-shaped crystallites of dimension $\sim 0.5 \mu\text{m}$, with a narrow particle-size distribution, Figure 3a. In

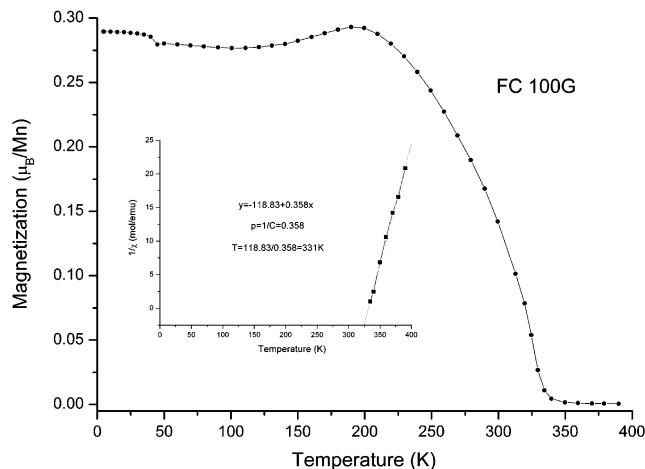


Figure 2. Magnetization as a function of temperature for hydrothermal $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$. The inset shows the calculation of T_c . Data were collected on a Quantum Design MPMS-5 SQUID magnetometer.

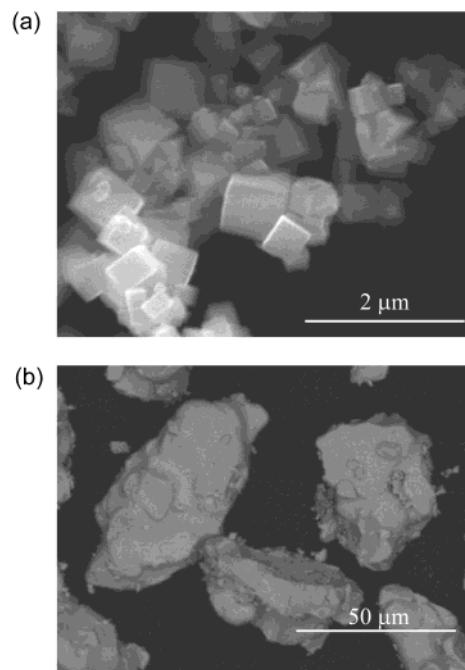


Figure 3. Scanning electron micrographs of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$: (a) prepared hydrothermally at 240 °C and (b) prepared by the conventional solid-state route at 1500 °C.

contrast, the material produced by the solid-state route (as described above) is made up of large ($\sim 50 \mu\text{m}$) particles that have no definite form, Figure 3b.

We have also investigated the formation of related manganites. For example, $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ can be synthesized under analogous hydrothermal conditions using solutions of KMnO_4 , MnCl_2 , SrSO_4 , and $\text{La}(\text{NO}_3)_3$ as starting materials and heating for a period of 24 h at 240 °C. SEM again reveals the sample to be made up of $\sim 1 \mu\text{m}$ dimension cube-shaped crystallites. Previous studies of the synthesis of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ required precisely controlled temperatures ($> 1400 \text{ }^\circ\text{C}$, close to the melting point of the reaction mixture) with lengthy annealing cycles at a number of different temperatures.¹² Powder X-ray diffraction of hydrothermal $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ reveals a simple X-ray pattern that apparently may be indexed with a primitive cubic cell ($a = 3.8419(4) \text{ \AA}$). This polymorph of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is iso-

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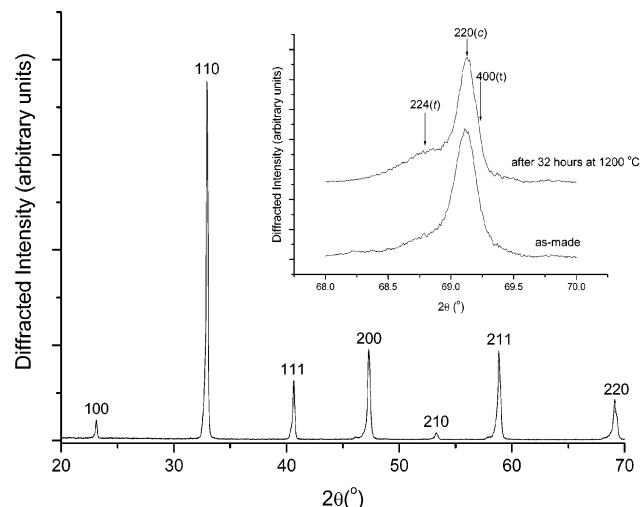


Figure 4. Powder X-ray diffraction data collected from $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($\text{Cu K}\alpha$, $\lambda_{\text{av}} = 1.5418 \text{ \AA}$, Bruker D8 diffractometer). Inset is the effect of annealing at $1200 \text{ }^\circ\text{C}$ on the sample, indicating the transformation from cubic (*c*) to tetragonal (*t*) polymorph.

structural with the disordered $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ mentioned above, that is, with no ordering of the A-site substituents. This is noteworthy since Woodward et al. have previously shown that when using a ceramic synthesis route, a two-polymorph mixture of orthorhombic and tetragonal $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ was produced.¹² To test the possibility that our material is a metastable phase, formed only due to the mild reaction conditions used, a sample was heated in air at $1200 \text{ }^\circ\text{C}$ for 32 h. Figure 4 shows the powder X-ray pattern of the result-

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ing material in the region $68\text{--}70 \text{ }^\circ\text{2}\theta$ (after removal of the $\text{Cu K}\alpha_2$ contribution). A splitting of the 220 peak into several components is clearly observed. Although these peaks are not completely resolved, this splitting is entirely consistent with the presence of the tetragonal polymorph ($I4/mcm$, $a = 5.440 \text{ \AA}$, $c = 7.766 \text{ \AA}$), as indicated in Figure 4. The material prepared after annealing for this short time is a mixture of the cubic and lower symmetry forms of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. Simulation of the XRD data shows that the as-prepared sample contains 80% of the cubic polymorph and 20% of the tetragonal polymorph, and after heat treatment the amount of cubic polymorph is reduced to 65%.

Our one-step hydrothermal route to mixed-metal manganites may be contrasted to other *chimie douce* routes to the solids, such as the sol–gel method, which although allow rapid mixing of reagents at close to room temperature, require a subsequent firing step using temperatures in excess of $1000 \text{ }^\circ\text{C}$.¹³ The hydrothermal method offers potential for both control of polymorph produced, including access to metastable phases not seen at high temperatures, and of particle morphology. This will be of the utmost importance in advances in the practical application of these materials, for example, in the preparation of high surface-area catalysts or the preparation of fine-grained ceramics for electronic applications.

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Supporting Information Available: Figures showing neutron diffraction and powder XRD data of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, respectively (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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