Rapid synthesis of colossal magnetoresistance manganites by microwave dielectric heating

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Colossal magnetoresistance manganites have been synthesised by the microwave dielectric heating of metal nitrates, which act both as effective microwave susceptors, and a ready source of oxidizing NO_2 to induce mixed valency.

The perovskite mixed-valent manganites of generic formula $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba; $0 \leqslant x \leqslant 1$), are currently the subject of intense enquiry in relation to the so-called 'colossal magnetoresistance' (CMR) effect.[1,2] The traditional ceramic (solid-state) synthesis of these CMR materials invariably requires conductive heating for extended periods at elevated temperatures; in some reported cases,[3] heating for 7 days at temperatures up to 1500 °C. Here, we illustrate the application of microwave dielectric heating to synthesise, in a period of minutes, a range of lanthanum alkaline-earth manganites exhibiting CMR. Importantly, we take advantage of the high intrinsic microwave susceptibility of component metal nitrate compounds [e.g. $Mn(NO_3)_2$] as compared to their moderately absorbing oxide counterparts (e.g. MnO_2, Mn_2O_3, etc.) in the synthesis of CMR materials. These findings are a clear illustration of the potential of microwave reaction selectivity—in this case via anion selectivity—in solid state chemical synthesis.

The microwave dielectric heating effect originates from the natural ability of certain substances to efficiently absorb, and then to transform electromagnetic (radiation) energy into heat. If sufficient heat can be generated at a local level, then chemical reactions may be initiated at a very rapid rate. More than a decade ago Mingos and co-workers carried out pioneering studies[4–6] of the use of microwave dielectric heating for the synthesis of advanced ceramic materials, most notably the high-temperature superconducting cuprates, $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$. The strong microwave absorbing properties of one of the reactant (constituent) oxides, CuO, leads to a rapid and highly effective synthetic pathway. In fact, CuO reaches a temperature of ca. 700 °C after only 30 s of irradiation in a commercially available microwave oven. By contrast, the binary oxide constituents of the ternary CMR perovskites, e.g. La_2O_3, MnO_2, etc. attain temperatures of only 107 and 321 °C, respectively, after 1800 s (30 min) in a similarly configured microwave oven, while $SrCO_3$ does not absorb microwaves to any significant degree.[6]

The addition of fine-grained, graphitic carbon (known to be an efficient microwave absorber), homogeneously distributed through the starting materials, achieves the desired effect of significantly increasing the temperature of the reaction mixture and results in compound formation. However, the presence of this reactive carbon at elevated temperatures results in highly reducing synthetic conditions and this adversely affects the formation of mixed-valent manganese (Mn^{3+}/Mn^{4+}), known to be essential for the CMR phenomenon in the perovskite manganite materials.[1,2]

We have directly measured the room temperature microwave reflection of a variety of constituent starting materials over the frequency range 1–6 GHz using a HP8722A network analyser in conjunction with a specially designed open-ended coaxial probe; a selection of the data are shown in Fig. 1.
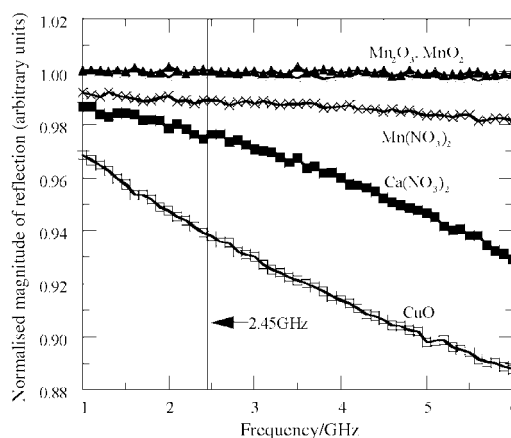

Fig. 1 Normalised magnitude of microwave reflection vs. frequency for various metal oxides and nitrates. The vertical line indicates the operating frequency of the microwave oven.

Whilst MnO_2 is frequently reported to be a good microwave susceptor,[5,7,8] we find that MnO_2 (and Mn_2O_3) are not as effective susceptors as compared with nitrate starting materials, e.g. $Ca(NO_3)_2$ and $Mn(NO_3)_3$. Moreover, there is another advantage in the use of nitrates; they decompose to yield highly oxidising NO_2 which facilitates the formation of the mixed Mn^{3+}/Mn^{4+} couple.

The manganites $La_{0.7}Sr_{0.3}MnO_{3+\delta}$, $La_{0.97}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_{3+\delta}$ were formed by first dissolving stoichiometric amounts of the constituent metal nitrates in distilled water. The resulting solution was then transferred to an open quartz tube, supported in a firebrick. A small piece of aluminium foil was placed over the end of the tube to prevent the mixture boiling over, whilst allowing NO_2 to escape. This assembly was then placed in the centre of the turntable of a domestic 950 W microwave oven, operating at 2.45 GHz, and irradiated for 5 min at the full power setting. Following the loss of H_2O and NO_2, the sample glowed bright orange and continued to do so until the microwave power was switched off. The sample was then left to cool at a natural rate in the microwave oven. The resulting black, well sintered fine powder was ground using a pestle and mortar before being subjected to a further 5 min of microwave irradiation.

X-Ray powder diffraction patterns (Fig. 2) were collected using a Siemens D5000 system (Cu-Kα_1 radiation) and these clearly show the presence of the desired phases, but the diffraction peaks are consistently broader than those generally
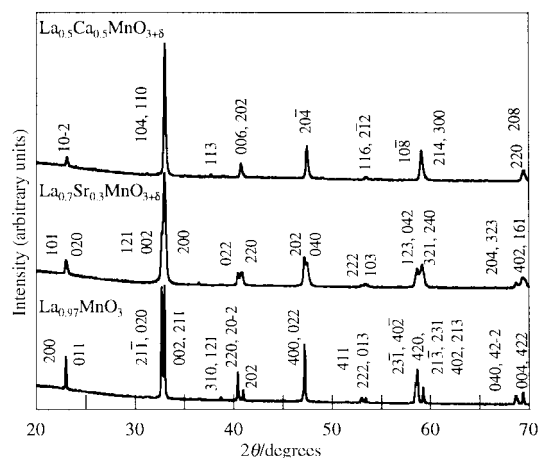
Fig. 2 X-Ray powder diffraction patterns for three manganites prepared using microwave dielectric heating.
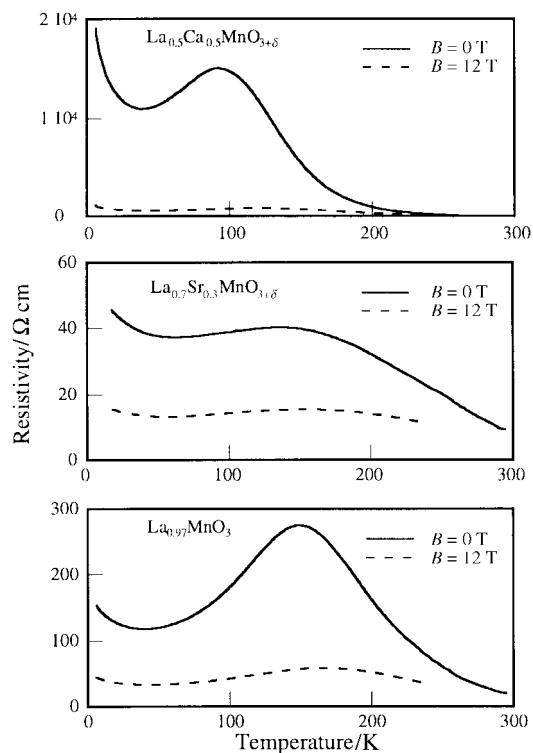

Fig. 3 Temperature variation of the electrical resistivity in magnetic fields (*B*) of 0 and 12 T for manganites produced using microwave dielectric heating.

produced by conventional solid state techniques.[9] This difference probably arises because microwave synthesis is somewhat akin to combustion synthesis in producing samples with small particle size.[10] The Rietveld method was applied to the refinement of crystal structures using the GSAS suite of programs.[11] The material $La_{0.7}Sr_{0.3}MnO_{3+\delta}$ is orthorhombic, $a = 5.4640(4)$, $b = 7.7277(6)$, $c = 5.5285(4)$ Å, space group *Pnma*; $La_{0.97}MnO_3$ is monoclinic, $a = 7.7970(4)$, $b = 5.5271(3)$, $c = 5.4842(3)$ Å, $\beta = 90.8(2)°$, space group *I2/a*; $La_{0.5}Ca_{0.5}MnO_{3+\delta}$ is rhombohedral, $a = 5.4763(5)$, $c = 13.379(1)$ Å, space group $R\bar{3}c$. These Rietveld refinements, combined with thermogravimetric analyses, indicated that these materials were fully oxygenated, with δ *ca.* zero.

The CMR properties of sintered pellets of the above materials were examined using a four-point resistivity probe in magnetic fields of 0 and 12 T. All three samples were found to exhibit CMR and the data are shown in Fig. 3. Whilst these samples show a very clear CMR effect, $La_{0.7}Sr_{0.3}MnO_{3+\delta}$ shows rather different CMR behaviour to materials produced by the conventional ceramic route.[12] This may be due to the orthorhombic symmetry of this sample resulting in reduced transfer of e_g electrons when compared with rhombohedral or pseudocubic phases.[13] The structural and CMR properties of the $La_{1-\delta}MnO_3$ system are extremely sensitive to synthesis conditions. For instance, the orthorhombic form shows no CMR properties at all.[14] Our sample of $La_{1-\delta}MnO_3$ adopts the less common monoclinic form and exhibits good CMR behaviour.[14] $La_{0.5}Ca_{0.5}MnO_{3+\delta}$ shows CMR comparable with previous literature reports.[12] Thermogravimetric analyses of these materials indicated no oxygen stoichiometry. Recently we have extended the microwave synthesis procedure to include the spinel manganates such as the battery material $LiMn_2O_4$ *etc.*

In summary, we have illustrated that dielectric heating represents a rapid and effective route to the synthesis of CMR manganites. Moreover, the direct measurement of microwave-reflecting properties (Fig. 1) greatly aids the choice of constituent starting materials.

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