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A combinatorial approach to synthesis of the La$_{0.8}$Sr$_{0.2}$Co$_{1-y}$Mn$_y$O$_{3±δ}$ family of perovskite-type mixed conducting metal oxides and characterisation of the surface oxygen mobility

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Abstract

The mixed conducting perovskite-type La$_{0.8}$Sr$_{0.2}$Co$_{1-y}$Mn$_y$O$_{3±δ}$ family has been synthesised by a combinatorial method. This system including the two end member materials ($y=0$ and $1$) have been studied using temperature programmed methods in order to relate structure and composition to oxygen exchange under a hydrogen atmosphere. Oxygen is removed in two steps: firstly, labile surface oxygen from 350 to 450°C and then more strongly bound lattice oxygen. A relationship between the B-site manganese and cobalt content and ease of removal of lattice oxygen was demonstrated over the temperature range 600-820°C. Removal of labile surface oxygen was independent of the B-site composition but associated with A-site cations on the external surface of the crystallites.

Keywords: perovskite, La$_{0.8}$Sr$_{0.2}$Co$_{1-y}$Mn$_y$O$_{3±δ}$ family, temperature programmed, oxygen exchange, surface oxygen, lattice oxygen
Introduction

Over the last 40 years much effort has been focused on producing and evaluating mixed electronic-ionic conducting (MIEC) metal oxides for high temperature applications such as; oxygen sensors, cathodes for solid oxide fuel cells (SOFCs) and membranes for oxygen separation. The MIEC perovskite family, La_{0.8}Sr_{0.2}Co_{1-y}Mn_{y}O_{3±δ} (LSCM), has recently received attention with respect to bulk oxygen diffusion [1] and surface oxygen exchange [2] measurements by $^{18}$O/$^{16}$O isotope exchange diffusion profiling (IEDP). The family presents an interesting system to study as it can exhibit oxidative nonstoichiometry for high manganese content and nonstoichiometry for high cobalt content members. The defect chemistry has been described previously using Brouwer diagrams for La$_{1-y}$Sr$_y$BO$_{3±δ}$ perovskites as a function of oxygen partial pressure [3]. Five different regimes were postulated dependent on the B-site transition metal. With increasing oxygen partial pressure; (i) oxygen nonstoichiometry changes to oxidative stoichiometry, (ii) the electronic conductivity changes from p to n-type and (iii) the oxygen vacancy concentration changes from being proportional to $P_{O2}^{-1/n}$ to being approximately zero.

Relatively few studies have been undertaken to investigate the effect of B-site composition on oxygen transport. A combinatorial approach to accelerating materials discovery is of great value when attempting to correlate trends in physical properties of a candidate family. This approach has recently been launched to investigate the properties of the La$_{0.8}$Sr$_{0.2}$Co$_{1-y}$Mn$_y$O$_{3±δ}$ family for use as SOFC cathode materials [4-6]. It was found that increased cobalt doping in the LSCM family caused a non-linear decrease in the $a$ lattice parameter; ranging from 5.53Å ($y=1$) to 5.45 Å ($y=0$) but it maintains its hexagonal rhombohedral symmetry.
In this contribution a temperature programmed redox study has been carried out to complement information on the oxygen mobility and activity gained from IEDP measurements. The focus is on surface/near surface oxygen exchange and its relationship with the manganese and cobalt content.

**Experimental**

Two sets of LSCM pseudo-binary perovskites have been produced for this study for which high purity oxide and carbonate powders were used as sources for the metal cations: La$_2$(CO$_3$)$_3$, SrCO$_3$, MnCO$_3$ and Co$_3$O$_4$. The London University Search Instrument (LUSI), an aspirating-dispensing ink-drop printer work station (Modified ProSys 4510 manufactured by Cartesian Ltd., Huntingdon, Cambridge, U.K. [7]), was employed to deposit arrays of droplets. To produce the LSCM system, LUSI printed a series of 66 compositions of source powder mixtures on an alumina substrate. The mixtures were first dried in ambient air and then heated at 1250ºC to promote inter-diffusion and reaction to give the perovskite phase. To validate the synthesis another set of LSCM samples were produced from commercial La$_{0.8}$Sr$_{0.2}$MnO$_{3+δ}$ (LSM821) and La$_{0.8}$Sr$_{0.2}$CoO$_{3-δ}$ (LSC821) purchased from Praxair Ceramics Technologies Ltd. Composition and phase structure of all powders were analysed by X-ray diffraction (XRD) and Induction Coupled Plasma Mass Spectrometry (ICP-MS) respectively. ICP-MS was carried out using a Varian instrument VISTA PRO ICP-AES. XRD was carried out on a Phillips PW1710 automated powder diffractometer equipped with a secondary graphite crystal monochromator using CuKα radiation (λ=1.54178Å). Measurements were made relative to an external silicon standard. For standard phase identification analysis, samples were scanned in the region 20 = 20-90° using a step size of 0.04° s$^{-1}$. The oxygen stoichiometry in flowing air was measured by thermogravimetric analysis using a Netzsch STA 449C Jupiter simultaneous TG-DTA/DSC instrument. Two to four dots of each sample were ground to powders which were then measured from room temperature to 1040ºC at 9ºC min$^{-1}$. In
order to evaluate the oxygen stoichiometry we have assumed that initially $\delta = 0$ at 25°C in air; this is in accordance with the nonstoichiometry studies on La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ [8] and La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ [9] performed in varied oxygen partial pressures including 0.21 atm up to 1000°C. The system for notation of material composition used throughout this work is as follows; e.g., LSCM8255 corresponds to La$_{0.8}$Sr$_{0.2}$Co$_{0.5}$Mn$_{0.5}$O$_{3+\delta}$ and the end members are represented by; LSC821 (no manganese) and LSM821 (no cobalt).

Temperature programmed (TP) experiments on LSCM powder samples were performed using a fully automated and programmable gas supply-microreactor-gas analysis system (CATLAB, Hiden Analytical, UK). The outlet from the microreactor fed into a soft ionisation quadrupole mass spectrometer via a heated capillary line providing continuous online analysis. Calibration was achieved using a standard comprising; 2% H$_2$, 2% O$_2$, 2% CO and 2% CO$_2$ with helium as balance gas. Water calibration was achieved by feeding in water using helium as carrier via a water saturator unit directly into the mass spectrometer at a known partial pressure, measured independently by hygrometer. All flow rates are quoted at standard temperature and pressure (STP) and all gases used were 99.9995% pure (BOC, UK) with helium as balance. The same temperature programmed oxidation-desorption-reduction (TPO-TPD-TPR) sequence was applied to each sample. For TPO 20% O$_2$/He was used, for TPD 100% He and for the TPR 5% H$_2$/He, total inlet gas flow rates were 100 ml min$^{-1}$. A standard heating rate of $\beta = 10^\circ$C min$^{-1}$ was used for all TP experiments. This rate was used to facilitate rapid screening of all ten samples to obtain possible trends in redox events quickly over the four cycles and to enable comparison with TGA data. The cooling rate in all cases was approximately $\beta = 10^\circ$C min$^{-1}$ over the range 1000 to ca 300°C, below this the heating rate was not controllable and was slower. TPO and TPD included a one hour dwell time before cooling. A flush out period of three hours at 40°C before the TPD was employed to remove gas phase oxygen from the microreactor and gas lines. The TPO-TPD-TPR experiment is represented schematically in Fig. 1a, four cycles were used; at the end of
each cycle there was a three hour flush out period with helium before the next TPO-TPD-TPR sequence. Approximately 14 mg of each sample was used but insufficient quantities of LSCM8228 were produced for use in these TP studies. The peak positions are given to the nearest 5 or 10°C.

**Results and Discussion**

*Sample characterisation*

From the XRD patterns (not shown) a rhombohedral unit cell was found for all the compositions. A weak signal for Co$_3$O$_4$ (JCPDS card 42-1467) was detected for LSCM8237 and traces of La$_2$SrO$_x$, and La$_2$CoO$_4$ were detected for LSCM8219. Aluminium was not detected by ICP-MS or by XRD suggesting that significant contamination by the sample substrate had not occurred.

*Oxygen exchange studies*

The aim of the TPO step (not shown) was to provide a standard method to clean the sample crystallite surfaces and to ensure complete re-oxygenation to prepare the sample for subsequent TPD and TPR analysis. The first of the four TPO-TPD-TPR cycles revealed carbon dioxide and water removal during TPO, the subsequent three TPOs revealed no more removal for all samples.

TPD (not shown) indicated that no oxygen desorption took place when exposed to pure helium; this may be a consequence of the experimental conditions such as the small amount of sample used reducing sensitivity. In other work three oxygen desorption peaks have been previously observed for LaCoO$_3$; two low temperature peaks around 300°C and 500°C which have been assigned to surface oxygen species (α oxygen) and one peak at higher temperature between 600 and 800°C associated with lattice oxygen (β oxygen) removal [10].
For brevity, only TPR data for the LSM821 and LSC821 end members and LSCM8255 and LSCM8282 are presented (Fig 1b-e), the discussion includes all data however. It was found that exposure to hydrogen under the imposed conditions removed oxygen from the samples producing only water. We observed, in general, two main reduction peaks; one in the range _ca_ 345 to 465°C assigned to labile surface oxygen (α oxygen), and the second in the range _ca_ 540°C to 820°C assigned to lattice oxygen (β oxygen). The peaks were often asymmetric or appeared to have unresolved shoulders. Each sample had reached steady state at the second cycle i.e., the second, third and fourth was very similar, only data from the first and fourth cycles are presented for clarity. The origins of this change from first to subsequent cycles may lie in a combination of sintering of the sample and compositional changes during the first redox cycle. Apart from the two end members the materials in this work contain two redox active centres which may complicate interpretation as the TPR may show a superposition of the redox activity from the cobalt and manganese.

Considering firstly the TPR peak positions; work on LSM821 (Fig 1d) by Buciuman et al. [11-12] revealed two unresolved low temperature peaks centred at 334 and 440°C and a high temperature peak at 790°C with a low intensity shoulder at lower temperature. In comparison we observe a broad average for the two low temperature peaks centred at 400°C and a variation in the high temperature β oxygen peak _ca_ 30°C either side of the high temperature peak reported by Buciuman et al.

In Fig 2 the variation of the α and β peak position as a function of B-site composition for the first and fourth cycles is shown. The α peak falls within 350-450°C with no clear trend, suggesting that B-site substitution does not have a direct effect upon this oxygen. Previous studies using Low Energy Ion Scattering (LEIS) and X-ray Photoelectron Spectroscopy (XPS) have revealed the depletion of B-site cations at the surface of a number of these perovskite-type mixed metal oxides. For the material La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3}, LEIS measurements revealed the presence of mainly lanthanum, strontium, and oxygen at the
surface [13]. Similarly, for the Sm$_{1-x}$Sr$_x$CoO$_3$ system, strontium, samarium and oxygen are dominant at the surface, with strong preferential strontium segregation noted for the higher strontium contents [14]. XPS studies on La$_2$NiO$_{4+\delta}$ and LaNiO$_3$ showed a preference for lanthanum and oxygen in the outer surface layers [15]. These studies suggest that the surfaces of these oxides are dominated by the A-O termination of the perovskite lattice and that A-site rare earth and/or strontium cations determine the surface properties of these materials. Thus we suggest that the $\alpha$ reduction peak presented here is associated with surface A-site cations in the LSCM family. The authors, however also note a recent XANES study on a SrCoO$_{3-\delta}$ perovskite family with $(3-\delta)_{\text{average}}$ over the range 2.5 to 2.82 that has indicated another possible contribution for the surface $\alpha$ peak observed in this work; the reduction of octahedral coordinated cobalt at the surface of the crystal to four and five-coordinated cations [16]. However if this were the source of the $\alpha$ oxygen then we might expect to observe a stronger dependence upon the cobalt content of the LSCM materials. In contrast we observe that the $\beta$ peak position tends to lower temperature with increasing cobalt in a fairly smooth manner with the rate of change being lower for cobalt contents $\sim >40\%$. In broad terms, this loss can be explained by the weaker Co-O bond compared to the Mn-O bond making reduction easier. The detailed shape of the temperature variation is interesting and it is relevant to consider some further observations. The TGA data presented in Fig 3, although recorded in air, shows that the loss of oxygen at a temperature of 1040°C increases with cobalt content to a maximum of $\delta=-0.13$ for LSC821. The shape of the TGA curve shows that the LSCM system does not release oxygen to an appreciable degree, in air, until the cobalt content is $>40\%$. Similar features have been seen in measurements of the kinetic data for oxygen isotopic exchange for the LSCM system [1] where it was observed that, for 20% strontium substitution, the mobility of the lattice oxygen is very low until $\sim >30\%$ of the manganese has been replaced by cobalt. These observations, together with our TPR
data would imply that the lattice oxygen stoichiometry and transport properties of these perovskite solid solutions become much more favourable for practical applications at between 30 to 40% cobalt substitution.

Conclusions

The perovskite-type La$_{0.8}$Sr$_{0.2}$Co$_{1-y}$Mn$_y$O$_{3\pm\delta}$ family has been synthesised by a combinatorial method. Temperature programmed reduction under hydrogen showed that oxygen is removed in two steps; firstly, labile surface oxygen and then more strongly bound lattice oxygen is removed. A relationship between the B-site manganese/cobalt content and ease of removal of lattice oxygen was also demonstrated. Removal of labile surface oxygen was independent of the B-site composition indicating the dominance of the A-site cations on the external surface of the crystallites. The cobalt/manganese content influenced the trend in the ease of removal of lattice oxygen.

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References


Figure captions

Fig. 1a Representation of the TPO-TPD-TPR experiment indicating salient experimental parameters. Also shown are example TPR data showing water production for the end members LSM821 (1b) and LSC821 (1e) and the family members LSCM8255 (1c) and LSCM8282 (1d); (—) represents first cycle data and (—―) represents the fourth cycle data. Peak temperatures and sample weights are also indicated. The rate of water production is normalised to the sample mass. $F=100 \text{ ml min}^{-1}$ and $\beta=10^\circ \text{C min}^{-1}$.

Fig. 2 Plot of $\alpha$ and $\beta$ oxygen peak positions as a function of B-site manganese and cobalt content for the LSCM family and LSM821 and LSC821 end members.

Fig. 3 Oxygen non stoichiometry determined in flowing air measured by TGA at a heating rate of $9^\circ \text{C min}^{-1}$ to the final set point temperature of 1040$^\circ \text{C}$.
Fig 1.

![Graph showing peak temperature vs. y_{Mn} for different cycles.](image)

Fig. 2
Fig. 3