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$La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.85}$: a new oxide ion conductor

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Isovalent substitution of Mn(II) for Mg(II) in the oxide ion conductor, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$, yields a new oxide ion conductor which exhibits an ionic conductivity ($\sigma = 4.6 \times 10^{-2}$ S cm^{-1} at 800 °C) that is comparable to the conductivity of the Mg(II) analogue; interestingly, the Mn(II) oxide has a lower activation energy for conduction (E_a = 0.47 eV) than the Mg(II) oxide.

The strontium- and magnesium-substituted lanthanum gallate perovskite, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-z}$ **I**, first reported by Ishihara *et al.*[1] has turned out to be an excellent oxide ion conductor[2] that promises to replace yttria-stabilized zirconia (YSZ) in solid oxide fuel cells (SOFCs) operating at relatively low temperatures (600–800 °C).[3,4] Besides providing an optimal concentration of oxide ion vacancies, the exact role of strontium and magnesium toward the high oxide ion conductivity of phase **I** is unclear at present. While it is known[1,5] that substitution of other cations (such as Ca, Ba, lanthanides) for La/Sr adversely affects the ionic conductivity of **I**, the effect of other divalent cations substituting for Mg(II) in **I** has, to our knowledge, not been investigated.† We considered that Mn(II) would be an effective replacement for Mg(II) in **I**, in view of its size‡ and stability under reducing conditions. Also a Mn(II)-derivative of **I** is likely to have a better compatibility as electrolyte material in SOFCs using $La_{1-x}Sr_xMnO_3$ (LSM) as cathode material.[6] Accordingly, we investigated Mn(II)-substituted derivatives of **I** having the general formula, $La_{1-x}Sr_xGa_{1-y}Mn_yO_{3-z}$ **II**, for several values of x and y. Since Mn(II) is not stable under the normal synthetic conditions employed for the preparation of **I**, we developed a special route for the synthesis of members of **II** that involves preparation of a higher valent Mn perovskite first, followed by its subsequent reduction to the Mn(II) phase in hydrogen. Stabilization of lower/unusual oxidation states of transition metals under reducing conditions has been reported for several perovskite-related oxides.[7] Typical examples are stabilization of Ni(I) in $LaNiO_2$, $YSr_5Ni_3O_8$ and $LaSrCr_xNi_{1-x}O_{4-y}$.

Our results, which are reported here, show that the Mn(II)-derivative of **I** is indeed an excellent oxide ion conductor whose conductivity ($\sigma = 4.6 \times 10^{-2}$ S cm^{-1} at 800 °C) is comparable to that of **I**, but with a lower activation energy E_a for conduction (E_a = 0.47 eV).

$La_{1-x}Sr_xGa_{1-y}Mn_yO_z$ **II** oxides were prepared for various values of x and y between $0 < x, y \leqslant 0.2$ by reacting dry La_2O_3, $SrCO_3$, Ga_2O_3 and $MnC_2O_4{\cdot}2H_2O$ in the required proportions at 1100 °C (12 h), 1400 °C (12 h) and 1450 °C (36 h) in air, with intermittent grindings. At the last stage, the samples were made into pellets (0.9 cm diameter and *ca.* 0.2 cm height) suitable for electrical conductivity measurements. Powder X-ray diffraction (XRD) patterns (Siemens-D5005 X-ray diffractometer, Cu-Kα radiation) revealed formation of nearly single-phase perovskite-like materials for x = 0.1; y = 0.2 (**IIa**) (Fig. 1) and x = 0.2; y = 0.2 (**IIb**). All the major reflections could be indexed on a rhombohedral perovskite cell, excepting the weak ones at $d \approx$ 3.15 and 2.98 Å. These impurity reflections, which are likely due to La_4SrO_7, are weaker in **IIa** than in **IIb** indicating that the composition of **IIa** is closer to a single-phase perovskite than **IIb**. This observation is consistent with the formation of a single-phase perovskite in the Mg(II) system for the composition $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$.[1,8–10]

Considering that manganese in these oxides would be in a higher oxidation state, we investigated reduction of **IIa** and **IIb** in a thermogravimetric (TG) balance (Cahn TG-131 system) in flowing hydrogen (10 ml min^{-1}). Reduction occurs in two stages (*ca.* 250 and 500 °C) with weight losses of 0.30 and 0.15% respectively. These weight losses are consistent with the compositions $La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.92}$ for **IIa** and $La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.85}$ for **IIIa**, where the oxidation state of manganese is Mn(II). The reduced sample (**IIIa**) is oxidized in air back to the original stoichiometry in a single step around 200 °C. Accordingly, the average oxidation state of manganese in the precursor oxide **IIa** is 2.7+, which would correspond to the formula $La_{0.9}Sr_{0.1}Ga^{III}{}_{0.8}Mn^{III}{}_{0.14}Mn^{II}{}_{0.06}O_{2.92}$. Powder XRD patterns show that the reduced materials retain the rhombohedral perovskite structure,§ albeit with a slight increase in the unit cell parameters (Table 1), that is consistent with the reduction of Mn(III) to Mn(II).

Ionic conductivity of both as-prepared (**IIa** and **IIb**) and hydrogen-reduced samples (**IIIa** and **IIIb**) was measured on sintered pellets coated with gold paste. Impedance data were obtained in air (as-prepared samples) or in flowing argon (reduced samples) at 100 Hz–15 MHz and 60–800 °C employing a HP4194A Impedance/Gain-Phase Analyzer interfaced with an IBM-PC. For each sample, measurement was made for at least two heating and cooling cycles. Impedance plots at low temperatures could be resolved into two semicircles corresponding to the bulk and grain-boundary contribu-

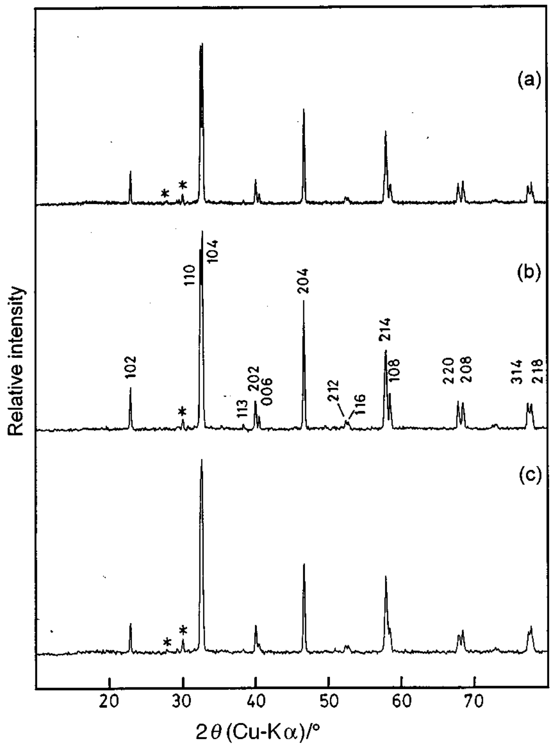

Fig. 1 Powder XRD patterns (Cu-Kα) of (a) $La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.92}$ **IIa**, (b) $La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.85}$ **IIIa** (reduction product of **IIa**) and (c) $La_{0.8}Sr_{0.2}Ga_{0.8}Mn_{0.2}O_{2.80}$ **IIIb**. Reflections due to impurity phase are marked by asterisks.

Table 1 Chemical composition, lattice parameters and ionic conductivity data for $La_{1-x}Sr_xGa_{1-y}Mn_yO_z$ perovskites[a]

Composition	Lattice parameters[b]				
	a/Å	c/Å	V/Å^3	$\sigma_{800\,°C}$/S cm^{-1}	E_a[c]/(eV)
$La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.85}$ (**IIIa**)	5.524(2)	13.360(7)	353.0(2)	4.60×10^{-2}	0.47
$La_{0.8}Sr_{0.2}Ga_{0.8}Mn_{0.2}O_{2.80}$ (**IIIb**)	5.525(1)	13.381(1)	353.7(1)	3.00×10^{-2}	0.57
$La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.92}$ (**IIa**)	5.518(1)	13.335(4)	351.6(2)	3.03×10^{-2}	0.38
$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (**I**)	[d]		358.14[e]	1.00×10^{-1}	1.07[f]

[a] For comparison, the data for $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ **I** are also included. [b] Rhombohedral lattice parameters are given for the hexagonal setting. [c] 60–800 °C. [d] The lattice parameters of **I** are a = 7.816, b = 5.539, c = 5.515 Å, β = 90.06° (ref. 10). [e] Equivalent volume. [f] Data taken from ref. 2.

tions to the resistivity. We have uniformly obtained the conductivity from the low-frequency intercept of the impedance plots, that includes both bulk and grain-boundary contributions. Accordingly, the values quoted here would correspond to a lower estimate of the actual conductivity of the samples.

The Arrhenius plots of the conductivity of the **III**-series of oxides are shown in Fig. 2. The conductivity (σ) at 800 °C and the activation energy (E_a) values obtained from the Arrhenius plots are given in Table 1. We see that among the samples investigated, sample **IIIa**, which is the Mn(II) analog of the well known oxide ion conductor, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$, shows the highest conductivity of 4.6×10^{-2} S cm^{-1} at 800 °C. The corresponding conductivity for the Mg(II) oxide[2] is *ca.* 1.0×10^{-1} S cm^{-1} at 800 °C. The E_a value for the Mn(II) derivative (0.47 eV) is however significantly lower than the corresponding E_a for the Mg(II) oxide[2] (1.07 eV). Accordingly, we see that isovalent substitution of Mn(II) for Mg(II) in the oxide ion conductor, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85,}$ produces a new oxide ion conductor whose conductivity is of the same order of magnitude as the Mg(II) parent oxide, but lowers the activation energy E_a. Interestingly, as-prepared samples (**IIa** and **IIb**) where manganese occurs in a mixed-valent state [Mn(II)/(III)] also exhibit considerable conductivity. Both ionic as well as electronic contributions to the conductivity most likely exist in these phases.

We have investigated the oxygen partial pressure dependence of the conductivity of the sample **IIIa**. The results show a slight increase in the conductivity at higher oxygen pressures [$p(O_2) > 10^{-8}$ atm], indicating the appearance of a p-type electronic contribution. We therefore believe that the conduction of the Mn(II) oxide reported here would be purely ionic only at low oxygen partial pressures [$p(O_2) < 10^{-10}$ atm].

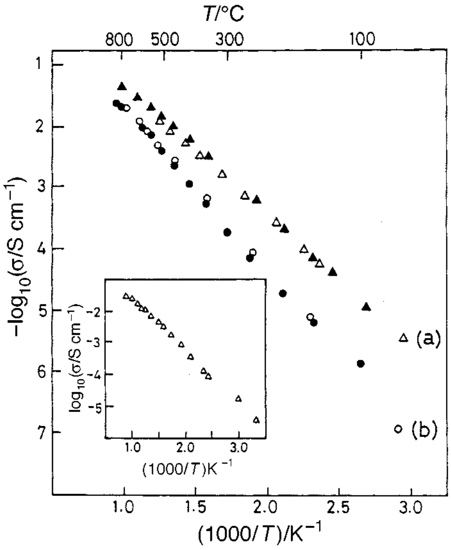

Fig. 2 Arrhenius plots for the electrical conductivity of (a) $La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.85}$ **IIIa** and (b) $La_{0.8}Sr_{0.2}Ga_{0.8}Mn_{0.2}O_{2.80}$ **IIIb**. Closed and open data points correspond to second heating and cooling cycles respectively. The data for sample **IIa** are shown in the insert.

In conclusion, we have shown that isovalent substitution of Mn(II) for Mg(II) in 'the most promising oxide ion conductor', $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ **I** yields a new oxide ion conductor exhibiting a comparable conductivity with a lower activation energy. The present work suggests that substitution of other divalent cations such as Co(II), Ni(II), Zn(II) and Cd(II) in **I** is worthy of exploration, especially to understand the role of ionic radius and electronic configuration in determining σ and E_a.

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Notes and references

† After the present work was completed, we came to know that the Fe- and Cr-substituted derivatives of **I** have recently been investigated: R. T. Baker, B. Gharbage and F. M. B. Marques, *J. Eur. Ceram. Soc.*, 1998, **18**, 105.

‡ The effective ionic radii of Mn(II) and Mg(II) in octahedral coordination are 0.83 and 0.72 Å respectively. Mn(II), like Mg(II), is known to accept octahedral coordination in oxides; see R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

§ Unlike the Mg(II) oxide **I**, which crystallizes in an orthorhombic[7] (*Pnma*) perovskite structure [with a slight distortion to monoclinic (*I*2/*a*) symmetry[9]], the Mn(II) analog reported here adopts a rhombohedral ($R\bar{3}m$) perovskite structure.

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