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Structure and Electrical Conductivity of $La_{0.84}Sr_{0.16}MnO_3$

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X-Ray diffraction, density, and electrical conductivity measurements were performed on the perovskite-like mixed oxide $La_{0.84}Sr_{0.16}MnO_3$. A rhombohedral crystalline structure with lattice parameters $a = 3.893$ Å and $\alpha = 90°29'16''$ was assigned to the powder prepared by standard ceramic technique. Its theoretical density is therefore 6.576 g/cm³, while the experimental density was determined as 6.48 g/cm³. The conductivity measured at 1000°C is 133 Ω^{-1} cm^{-1}. The temperature dependence of the conductivity indicates that the charge carriers are small polarons. The activation energy of the mobility is 9.6 kJ/mole.

Introduction

Oxide perovskites of the general formula $LnMO_3$, where Ln = rare earth and M = chromium, cobalt, manganese, or nickel, are good electronic conductors and were tested in recent years for their suitability as air electrodes or interconnectors in a high-temperature fuel cell, HTFC (*1*). In order to increase their conductivities, alkaline earth metals are often added to them. For example, the Westinghouse group discussed the use of $La_{0.9}Sr_{0.1}MnO_3$ (*2*). Preliminary measurements by the BBC group (*3, 4*) on the composition $La_{0.84}Sr_{0.16}MnO_3$ (LS16MO) show that in addition to the good electronic conductivity, the material is chemically stable, is inert against stabilized zirconia, and adheres to the electrolyte during thermal cycling. It can be applied on the solid electrolyte by plasma spraying. It is also economically favorable to another good air electrode material, In_2O_3–3% SnO_2 (*2*). LS16MO is unstable under a reducing atmosphere as found on the fuel side of a HTFC. These properties make LS16MO a very interesting material for consideration as an air electrode in a HTFC.

While $LaMnO_3$ has been intensively investigated in the past years, $La_{1-x}Sr_xMnO_3$ has received much less attention. We report here on measurements on LS16MO of electrical conductivity in the temperature range 20–1100°C and of the density at room temperature. The conductivity at elevated temperatures and the density have not been measured yet, to our best knowledge, for the particular composition LS16MO nor for the related oxides $La_{1-x}Sr_xMnO_3$ $x > 0$. X-

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Ray measurements were used to determine the structure of LS16MO and for comparison with results reported on related oxides $La_{1-x}Sr_xMnO_3$ with $x = 0.14$ and 0.28.

Undoped $LaMnO_3$ is a p-type semiconductor (*5*). Its resistivity at 700°C was reported to vary between 0.06 (*6*) and 10 Ω cm (*5*). The variation is probably due to deviations from stoichiometry ($LaMnO_{3+y}$) in which Mn^{4+} ions create holes in the conduction band. The Mn^{4+} concentration can be increased by substituting a divalent cation such as Sr^{2+} for La^{3+} (*7*). Although the room temperature electrical conductivity of $La_{1-x}Sr_xMnO_3$ increases with the strontium content up to $x = 0.3$ (*8*), for the HTFC application, the concentration of Sr must be limited to $x \leq 0.16$. At higher values of x there is a significant reaction between the electrode and the doped ZrO_2 electrolyte at the operation temperature of the HTFC (*4*).

From structural analysis done previously by Harwood (*9*) on the related oxides $La_{1-x}Sr_xMnO_3$, with $x = 0.6$, 0.14, 0.28, . . . , one can infer that $La_{0.84}Sr_{0.16}MnO_3$ is a perovskite with a rhombohedral structure.

Experimental

$La_{0.84}Sr_{0.16}MnO_3$ (LS16MO) powder was prepared by a solid-state reaction of stoichiometric amounts of La_2O_3,[1] MnO_2,[1] and $Sr(OH)_2$[1] (with 10 wt% Bi_2O_3[1] as flux) as described by Rohr (*10*). The resulting compound was thoroughly ground, and served as the starting material for the experiments reported here.

X-Ray diffraction patterns of LS16MO powder were taken at room temperature (using Cu$K\alpha$ radiation) with a Philips type 1050 diffractometer.

The density of the powder was determined by the method of Archimedes with toluene.

Pellets of the LS16MO powder were prepared by standard ceramic methods.

The electrical conductivity of the samples in air in the temperature range $20°C \leq T \leq 1100°C$ was determined by the four-point technique of van der Pauw (*11*).

Emission spectroscopic analysis of the sintered pellets showed the following impurities: Bi: 0.8%; Al: 0.2%; Cr: 0.2%; Fe: 0.2%; Mg: 0.2%; Si: 0.2% and Sn: 0.1% wt.

Results and Discussions

X-Ray Diffraction and Density

The X-ray diffraction pattern of the LS16MO powder indicated the formation of a single-phase solid solution with perovskite-like structure, where the Sr^{2+} ions are expected to occupy La^{3+} sites. A rhombohedral symmetry was found; the lattice parameters were $a = 3983$ Å and $\alpha = 90°29'16''$. The weaker lines occurring between those that were indexed from the small unit cell just described could be accounted for by quadrupling the cell edges. In this way, the reflections were indexed satisfactorily.

The symmetry of the lattice agrees with that found by Harwood (*9*) for $La_{1-x}Sr_xMnO_3$, with $x = 0.14$, 0.28. However, our rhombohedral lattice parameter a is 0.3% larger than that which can be interpolated from his results for $x = 0.16$.

The substitution of Mn^{4+} ions for some Mn^{3+} ions in the ideal $LaMnO_3$ leads to distortion of the perovskite structure and to lattice shrinkage due to the smaller size of the Mn^{4+} ion. It is known that the stoichiometry and therefore the crystal structure of the pure $LaMnO_3$ is very sensitive to the preparation procedure (*12, 13*). Similarly, the number of the Mn^{4+} ions in the oxide $La_{1-x}Me_xMnO_3$ is fixed not only by the introduction of a certain amount of divalent cations Me^{2+}, such as Sr^{2+}, into the lattice, but also by the nonstoichiometry ($La_{1-x}Me_xMnO_{3+y}$) which depends on firing atmosphere, temperature, and time (*14*).

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[1] Merck, Darmstadt, Federal Republic of Germany.

No detailed data is available from the paper of Harwood (9) on the preparation conditions of his $La_{1-x}Sr_xMnO_3$ perovskites. The difference between ours and his cell dimensions for LS16MO can be due to a difference in the Mn^{4+} concentration and in the content of impurities.

From the above-mentioned lattice parameters, the crystallographic density of LS16MO was calculated to be 6.576 g/cm^3. This result is in good agreement with the Archimedes density of the powder, for which a value of 6.48 g/cm^3 is measured.

Sintering and Electrical Conductivity

Sintering of LS16MO was found to be difficult and many sintering conditions were tried. The procedure finally adopted led to an acceptable density of 80% of theoretical value (d_{th}). The pellets prepared by this procedure also had the highest electrical conductivity. The following steps were performed: (a) Fine-grain powder of size less than 2 μm was prepared by grinding the powder for 24 hr in a high-speed eccentric mill using a plastic jar and balls made of LS16MO. To remove the plastic debris the powder was heated for 1 hr at 450°C, then ground for another 15 min. (b) Pellets were prepared using a fairly high pressure of 900 MPa. (c) Pellets were sintered in an Al_2O_3 crucible at 1500°C for 24 hr.

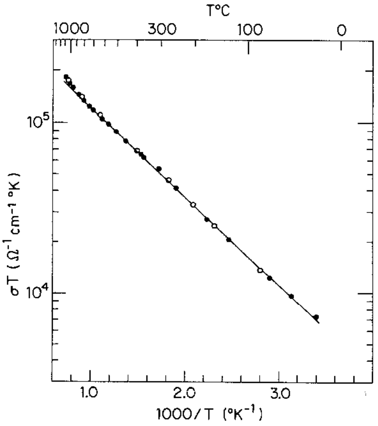

FIG. 1. The temperature dependence of the electrical conductivity for a sintered pellet of $La_{0.84}Sr_{0.16}MnO_3$.

Figure 1 shows the temperature dependence of the electrical conductivity, σ, of LS16MO. The $\ln(\sigma T)$ vs $1/T$ curve is a straight line over a wide temperature range. This is consistent with a small-polaron conduction mechanism (*15*). The activation energy is 9.6 kJ/mole. It is attributed to the thermally activated hopping mobility of the small polarons. The room temperature conductivity is 25.6 Ω^{-1} cm^{-1}, in good agreement with the data reported by Jonker for $La_{1-x}Sr_xMnO$, with $x \sim 0.16$ (*8*). This is higher than the value measured by Matsumoto *et al.* (*16*).

The highest value of the conductivity at 1000°C was 133 Ω^{-1} cm^{-1}. This was reached for a sample whose apparent density was 80% d_{th}. To estimate the theoretical conductivity at 1000°C, σ_{th}, for a completely dense material we consider σ for the same material prepared with different densities and extrapolate to $d = d_{th}$. This is not plausible since the electrical conductivity depends both on porosity and pore shape (*17*). However, all our samples were fired at 1500°C for 12–36 hr. The difference in density was mainly due to difference in powder grain size, pressure, and the addition of Bi_2O_3 as flux (which eventually evaporates at the sintering temperature). As a result the contact between grains was good, i.e., the neck size was comparable to the grain size though the samples were porous. Scanning electron microscopy showed that the pores in our samples were interconnected. We therefore expect no abrupt change in σ as d is varied, and assume $\sigma \propto d^\beta$. Figure 2 shows that this assumption holds quite well in the range of densities measured $50\% \leq d \leq 80\%$, with $\beta \sim 2.1$. Extrapolation to $d = d_{th}$ yields $\sigma_{th} = 220\ \Omega^{-1}$ cm^{-1}. This might be slightly too high, since for $d \gtrsim 0.9\ d_{th}$ the pores should be isolated and σ should vary linearly with d (*17*). This is corrected by the

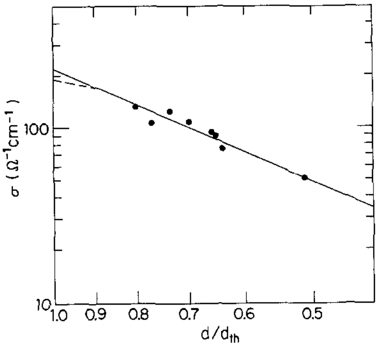

FIG. 2. A log–log presentation of σ at 1000°C vs d/d_{th}.

dashed curve in Fig. 2. The final estimate for σ_{th} is 190 Ω^{-1} cm^{-1}. The mobility calculated from this conductivity, assuming that the concentration of the holes equals that of Sr^{2+}, is 0.4 cm^2/V sec.

Attempts to sinter at a higher temperature of 1720°C resulted in a liquid-phase reaction with the Al_2O_3 sample holder. Pellets pressed at 900 MPa and fired beforehand at 1500°C for 24 hr were used. Analysis of the reacted samples showed that a few weight percent Al_2O_3 improved somewhat the density of LS16MO to 85% d_{th}. However, the room temperature conductivity dropped to 5 Ω^{-1} cm^{-1}. The degradation of the conductivity with the addition of Al^{3+} ions to LS16MO is expected on the grounds of the conduction model of Goodenough for rare earth perovskites (*18, 19*) and the study of Anderson *et al.* (*20*) on aluminum-doped $LaCrO_3$.

Summary

The crystallographic structure and electrical transport properties were measured for $La_{0.84}Sr_{0.16}MnO_3$ (LS16MO) perovskite, which seems to be a promising air electrode material for high-temperature fuel cells.

X-Ray diffraction of LS16MO powder shows that the material has a rhombohedral crystalline structure with a = 3.893 Å and α = 90°29′16″. Its theoretical density is 6.576 g/cm^3, while the experimental value found for the powder is 6.48 g/cm^3.

LS16MO was sintered to a density of 80% d_{th}. Reaction of the material with a few weight percent Al_2O_3 at 1720°C increased the density to 85%, but had an adverse effect on the electrical conductivity.

Electrical conductivity measurements gave a value of 133 Ω^{-1} cm^{-1} at 1000°C for a sample of 80% d_{th}, from which we estimate 190 Ω^{-1} cm^{-1} for a completely dense material. The temperature dependence of the conductivity is that expected for small-polaron hopping. The activation energy of the mobility is 9.6 kJ/mole. The mobility at 1000°C is 0.4 cm^2/V sec.

The value of σ_{th} = 190 Ω^{-1} cm^{-1} is acceptable for HTFC air electrodes (*21*). In addition, it was previously found that LS16MO is compatible with stabilized zirconia regarding thermal expansion and chemical stability (*4*). It seems that LS16MO is indeed an attractive air electrode material for HTFC.

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