Structural and high temperature electrical properties of $\text{La}_{y-x}\text{Sr}_x\text{MnO}_3$ perovskite materials

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ABSTRACT.

The phase constitution of $\text{La}_{y-x}\text{Sr}_x\text{MnO}_3$ perovskite materials with $0 \leq x \leq 0.4$ and $0.8 \leq y \leq 1$ prepared by wet chemical techniques has been determined. Single phase La-deficient materials have been obtained at $y=0.95$ and $x \geq 0.1$ as well as for $y \geq 0.8$ and $x \leq 0.1$. The observed variation of the lattice parameters leads to shrinking unit cell volume with Sr-content and with La-deficiency. Small polaron conduction has been observed for $x < 0.2$, while for $x \geq 0.2$ metallic-like behaviour is observed for La-deficient materials. The electrical conductivity of Sr-free materials at 950 °C approaches 100 S/cm. The activation energy for conduction changes strongly with sintering temperature and composition of the specimen.

1. INTRODUCTION.

The $(\text{La,Sr})\text{MnO}_3$ -perovskite materials are most promising candidates for the air electrode of the Solid Oxide Fuel Cell (SOFC), as they exhibit adequate thermal stability and electrical conductivity(1). However, stoichiometric $(\text{La,Sr})\text{MnO}_3$ perovskites react readily at $T \geq 1000$ °C with the zirconia-based electrolyte of SOFC forming $\text{La}_2\text{Zr}_2\text{O}_7$ and/or SrZrO_3 (2,3). These reaction products possess very low electrical conductivity (4) and might cause a severe performance degradation of a SOFC system. Therefore, a substantial improvement of the chemical compatibility between $(\text{La,Sr})\text{MnO}_3$ and zirconia is necessary for efficient long term operation of SOFC. One possibility for obtaining materials with adequate chemical compatibility might be offered by compositional modification of $(\text{La,Sr})\text{MnO}_3$ and, in fact, La-deficient perovskites show enhanced chemical inertness in reaction to yttria-stabilised zirconia, as has been recently demonstrated by systematic reactivity investigations (3). The present work reports on the synthesis, the phase constitution as well as on the structural and electrical properties of ABO_3 perovskite materials at various deficiencies in A-cation and/or Sr-substitution degrees.

2. EXPERIMENTAL PROCEDURES.

The perovskite powders have been prepared using nitrate salt solutions of desired cation content which were converted at 160-180 °C into fine powdered salt mixtures of high homogeneity using spray-drying or by the hot petroleum extraction technique (HPE). The dried salt mixtures were washed thoroughly before calcination with CCl_4 using a soxlet apparatus to reduce residual adhered hydrocarbons.

A complete characterisation of the dried products by XRD, TG/DTA and SEM techniques has been undertaken all the way through calcination. The formation of perovskite phase during calcination in air occurred at above 500 °C and was completed at 900 °C. The powders consisted of spherical grains with an average diameter of 5 μm and hollow spherical shells and had a BET-specific surface area of about 5 m^2/g . The cation and the impurity content of the powders after calcination has been

determined by chemical analysis using ICP-AES. The observed deviations from the intended composition were within the precision of the ICP-AES results, indicating the reliability of the used preparation methods. The major impurity of the HPE powders was carbon with $\leq 0.5\%$; spray-dried powders had a total impurity content of 800 ppm. Investigations on phase formation, phase constitution and determination of the lattice parameters were performed by X-ray powder diffraction analysis with a SIEMENS D5000 apparatus using $\text{Cu K}\alpha$ radiation. Initial investigations were performed with calcinated powders; for determination of the lattice parameters cold pressed pellets were used after annealing for 20 h at 1200 °C in air and quenching in water. The electrical conductivity was measured between 25 and 950 °C in air using the standard four point DC-technique. Rectangular bars of $20 \times 5 \times 4 \text{ mm}^3$ were cold pressed for this purpose and densified in air for 20 h at 1000–1500 °C. Same specimens were used for microstructural examinations and characterisation of the sintering behaviour of the materials. The electrical contacts on the specimens were facilitated by a Ag or Pt paste and thin Ag wires.

3. RESULTS AND DISCUSSION.

3.1 Phase constitution and crystal structure.

Fig.1 shows the results of XRD-analysis on the phase constitution of $\text{La}_{y-x}\text{Sr}_x\text{MnO}_3$ perovskite materials in a wide range of variation of composition; it includes also literature data (5,6,7), in accordance with the results of present investigation. In the range of compositions covered by present investigations, Fig.1 shows single phase perovskites for small La-deficiency, i.e. for $y=0.95$, irrespective of the Sr-substitution degree. At low Sr-contents the single phase region extends to higher La-deficiencies, i.e. up to $y=0.8$. Outside of the single phase region Mn_3O_4 has been identified (7) in small amounts in the specimens; it has been observed by standard ceramographic examinations to be precipitated at triple points of grain boundaries.

Fig.1: XRD results on phase constitution of stoichiometric and La-deficient $\text{La}_{y-x}\text{Sr}_x\text{MnO}_3$ perovskite materials. Closed (open) symbols denote single phase (two phase) materials. Squares denote the results of present work. Other data are taken from literature(5,6,7).

Fig. 2: Variation of unit cell volume of stoichiometric and La-deficient single phase $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskite materials with Sr-content and La-deficiency (after quenching from 1200 °C).

The $(\text{La},\text{Sr})\text{MnO}_3$ perovskite materials crystallize with orthorhombic or hexagonal symmetry depending on oxygen content, which is influenced by the preparation and calcination conditions. The orthorhombic unit cell symmetry was found for $x \leq 0.1$ for HPE powders; in the same composition range spray-dried powders crystallised with hexagonal symmetry. For $x > 0.1$ all materials crystallised with hexagonal symmetry, irrespective of preparation technique.

The lattice parameters of the stoichiometric $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ materials are in good agreement with the literature (8). The unit cell volume calculated thereof is shown in Fig.2, for both, the stoichiometric and the single phase La-deficient materials. The unit cell volume of the La-deficient perovskites decreases in the same manner with increasing Sr-content as for stoichiometric materials, see Fig.2. It is therefore reasonable to attribute this decrease to the smaller ionic radius of Mn^{4+} (8), whose concentration can be assumed to increase with increasing Sr-content in the specimen. The unit cell volume of the Sr-free compositions, see Fig.2, also decreases with increasing La-deficiency, approaching to a limiting value reached at $y \leq 0.9$. Combining both observations it might be concluded that the small systematic difference between the unit cell volumes of stoichiometric and La-deficient materials is caused by the La deficiency itself and might be related to the existence of vacancies on the A-site of the perovskite lattice (9).

3.2 Electrical conductivity.

No irreversible effects (7) have been observed in the electrical conductivity measurements which have a reproducibility of 10% within the whole composition and temperature range investigated. The data can be described according to a small polaron hopping mechanism. Thus, the conductivity, σ , which is mainly electronic (10), follows the expression

$$\sigma T = A \exp(-E_a/k_B T) \quad (1)$$

where T is the absolute temperature, k_B the Boltzmann constant and the preexponential factor A includes parameters like the number density, the jump distance and the fraction of sites occupied by charge carriers. Plots of $\ln(\sigma T)$ vs $1/T$ give straight lines allowing the determination of the activation energy, E_a , and the preexponential factor A , which is assumed to be temperature independent.

Well comparable sets of electrical conductivity data have been obtained with specimens prepared from HPE and spray-dried powders. The following discussion will

however be concerned with the results obtained by the HPE materials in order to exclude microstructural influences.

I. Sr-free specimen:

Electrical conductivities between 1 and 15 S/cm were obtained for the undoped La-deficient materials at 25 °C, with the best values corresponding to the specimen sintered at 1000-1200 °C and for $y \leq 0.9$. The observed values exceed greatly data (11) reported for LaMnO_3 at various oxygen contents; they indicate a significant oxygen excess in the specimens.

The dependence of $\ln(\sigma T)$ vs $1/T$ follows straight lines for all specimens, showing a gradual deviation from linearity above 600 °C to lower conductivity values. This deviation becomes more pronounced for specimens of higher porosity. In addition, a reversible jump in the electrical conductivity has been observed at above 450 °C, which can be clearly distinguished from the above deviation and should be related to a structural transition in these materials. The electrical conductivity at 950 °C ranges between 90-110 S/cm with the higher values obtained for La-deficient perovskites. Such high conductivities are adequate for application of these materials as air electrode of SOFC (12), and therefore, might put into question the necessity of the usually employed doping with Sr for improving the electrical conductivity of these materials.

The activation energies determined by fitting the linear part of the $\ln(\sigma T)$ vs $1/T$ plots change with La-deficiency. For certain La-deficiency a strong smooth increase with sintering temperature has been observed. For example, for $\text{La}_{0.95}\text{MnO}_3$, the activation energy lies between 0.15 and 0.30 eV for specimens sintered at 1000 °C and 1400 °C, respectively.

II. Sr-containing specimen.

Several perovskite materials with partial substitution of Sr for La exhibited small polaron conduction regardless of La deficiency. By changing the composition, the electrical conductivity increases with Sr-content and its magnitude is apparently

Fig.3: Temperature dependence of the electrical conductivity of $\text{La}_{0.55}\text{Sr}_{0.4}\text{MnO}_3$ after sintering for 20 h at the temperatures indicated in the figure. The data have not been corrected for the porosity of the specimens.

not influenced by the second phase (Mn_3O_4) in the two-phase materials, see Fig.1.

However, for several La-deficient materials with Sr-content $x \geq 0.2$, the predominance of semiconducting behaviour breaks gradually down and the temperature dependence of the electrical conductivity resembles metallic behaviour as shown in Fig.3 for $\text{La}_{0.55}\text{Sr}_{0.4}\text{MnO}_3$. Perovskites with metallic-like conductivity behaviour exhibit the best conductivity approaching 250-300 S/cm at 950 °C, see Fig.3. Below 200 °C the electrical conductivity of these materials increases strongly reaching 1000 S/cm at 25 °C and 5000 S/cm at liquid nitrogen temperature.

Metallic-like conductivity has been observed for $x \geq 0.4$ in stoichiometric $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ compositions. In La-deficient materials, the transition from the semiconducting to the metallic behaviour shifts to lower Sr-contents, i.e. up to $x=0.2$, indicating a remarkable sensitivity on La-deficiency. As depicted in Fig.5 not only the composition but also the sintering conditions play an important role. Apparently, the defect configuration affecting the transition in the conductivity behaviour is aided by vacant La sites (and the concomitant distortion of the perovskite lattice) and by oxygen content as well.

Fig.4 shows plots of $\ln(\sigma T)$ vs inverse temperature for semiconducting $\text{La}_{0.85}\text{Sr}_{0.1}\text{MnO}_3$ specimens after sintering at 1000-1300 °C. The main features depicted by Fig.4 are the change of the activation energy with sintering temperature and the deviation of the data from linearity at high temperatures. Both these features have been observed for all semiconducting compositions investigated and should be related to changes of the oxygen content in the specimens. Particularly for the deviation of the electrical conductivity from linearity a decrease of the oxygen content of the specimens during the measurement might be responsible. In this case a composition dependent amount of oxygen (and Mn^{4+}) in excess of that caused by Sr-doping has to be assumed. Further, a fast diffusion of oxygen is necessary for a reasonable interpretation of these effects.

Fig.4: Linearity between $\ln(\sigma T)$ and $1/T$ for $\text{La}_{0.85}\text{Sr}_{0.1}\text{MnO}_3$ specimens after sintering at the temperatures indicated in the figure. Notice the change in the activation energy with sintering temperature.

The activation energy for perovskites with $0 < x \leq 0.1$ increases with the temperature

used for sintering of the specimen. This may be caused by release of oxygen during sintering and the corresponding reduction of the amount of Mn^{4+} as specimens are subjected to sintering at increasingly higher temperatures.

In contrast to that, the activation energy of metallic-like specimens, i.e. for $x \geq 0.2$, shows different behaviour. It first decreases smoothly with increasing sintering temperature of the specimen as shown in Fig.5 for several compositions and then remains approximately constant. The lowest values obtained agree with data reported (6,7) for neighboring compositions.

Fig.5: Variation of the activation energy of the electrical conductivity with sintering temperature for La-deficient materials of different compositions.

4. CONCLUSIONS.

La-deficient materials of the formula $La_{1-x}Sr_xMnO_3$ are single phase perovskites for $y=0.95$ and $0 \leq x \leq 0.4$, showing similar crystal structure as stoichiometric compounds. These materials are semiconductors at low Sr-content and exhibit metallic-like conduction for $x \geq 0.2$ and $y < 1$. The activation energy has been observed to depend on the composition and to be greatly influenced by the thermal history of the specimens. This observation indicates the importance of oxygen content for the electrical behaviour of this type of materials.

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