

Strontium Dopant Concentrations Influence on $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ Structural and Electrical Conductivity

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Abstract. Many different types of ceramic materials are currently being studied as possible cathodes in Solid Oxide Fuel Cells (SOFC), in an attempt to reduce operating temperatures. Strontium-doped neodymium manganite ($\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$) was used as an intermediate temperature solid oxide fuel cell cathode. X-ray diffraction and electrical conductivity of the $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ system with a perovskite structure were studied in function of x equal to 0.10, 0.30 and 0.50. An orthorhombic pseudo-perovskite structure was assigned to all powder compositions prepared by standard ceramic technique. Electrical conductivity was described by the small polaron hopping conductivity model, as well as, increases due to regular increments of Sr content for all compositions. Electrical conductivity was measured at 25.2, 26.4 and 37.1 Scm^{-1} for x = 0.10, 0.30 and 0.50, respectively at 800°C.

Introduction

Intermediate temperature solid oxide fuel cells (ITSOFC); represent the basic building blocks for power generation in a variety of applications such as residential and commercial establishments, cogeneration systems and central utility power production stations.

These devices offer clean, pollution-free, high efficient technology that electrochemically convert gas fuels such as hydrogen, natural gas or gasified coal into electricity. These fuel cells are characterized by their efficiency, reliability, modularity, fuel adaptability and low NO_x and SO_x emission levels [1], [2], [3], [4] and [5].

In the ITSOFC operation, when an external load is applied to the fuel cell, oxygen from the air is reduced at specific reaction sites in the porous electrode which produce oxygen ions. At 1000°C, these oxygen ions migrate through a solid electrolyte from the cathode to the fuel cell electrode where the ions (fuel) are oxidized to release electrons to an external load.

The most promising cathode materials appear to be the mixed (electronic and ionic) conducting perovskite oxides of the ABO_3 structure, where A = rare earth and B = manganese, chromium, cobalt or nickel. Although these materials are good electronic conductors, alkaline earth metals such as Sr^{2+} or Ca^{2+} are often added in order to increase their conductivity [6, 7].

In general terms, the cubic structure of this class of material can create distortions of the structure. A cation is coordinated by twelve and B-site cation by six oxygen ions. Cations Sr^{2+} or Ca^{2+} (large ionic radii) substitute preferentially at A-sites and cations such as Co, Fe, Ni, Mn, Cr with small ionic radii occupy B-sites in the perovskite structure [8, 9].

$Nd_{1-x}Sr_xMnO_{3\pm\delta}$ is an alternative ceramic material for cathodes in ITSOFCs operating at temperatures between 500 and 800°C [10, 11]. In recent years, specific cathode characteristics as such good chemical and thermal stability has generated intense interest, as has high catalytic activity for oxygen reduction, thermal expansion coefficients similar to that of electrolytes and good electrical conductivity [1,12]. Doping neodymium manganite ($NdMnO_3$) with strontium (Sr) improves not only the chemical stability of the material but increases its electrical conductivity as well [10, 11]. According to Minh [1,12], Sr is the preferred doping element as it improves thermal expansion and allows for greater electrical conductivity due to Mn^{4+} cation formation and the substitution of Nd^{3+} for Sr^{2+} . Different synthesization routes to obtain NSM, the main ones being solid mixtures, the citrate technique and combustion reactions have been studied by different authors [13].

The purpose of this investigation was to evaluate the crystalline structure and electrical conductivity of a strontium-doped neodymium manganite ($Nd_{1-x}Sr_xMnO_{3\pm\delta}$, where $x=0.10, 0.30, 0.5$). The effects of Sr content on the properties of these oxides were also evaluated.

Experimental

The initial materials used in the synthesis of NSM contained the following reagents: $Nd_2(CO_3)_3$, 98.5% pure (Vetec); $SrCO_3$, 99.9% pure

(Aldrich); MnCO_3 , 99.9% pure (Aldrich) and $\text{C}_3\text{H}_8\text{O}$, P.A. (Merck). The powders were prepared by standard ceramic technique, consisting of oven-drying of the initial materials and subsequent mixing of the powders for 2h according to the adopted stoichiometry. Mixing was carried out in an attritor mill with isopropyl alcohol in order to attain the greatest possible homogenization of the material. The material was then synthesized by way of a solid reaction at 1000°C for 4h [7]. Next, the powder was calcinated in air at 1000°C for 4h to eliminate any residual carbon. The powder was then ground for 4h in an attritor mill and characterized by X-ray powder diffraction (XRD) on a Rigaku diffractometer using $\text{CuK}\alpha$ radiation. XRD patterns were obtained by continuous 0.02° 2θ , 20 - 80° 2θ , scanning rate. Wet milling with isopropyl alcohol was performed using zirconia balls. The milled products were dried and compacted into cylindrical pellets as 300MPa and 2500MPa, respectively. Compacting was undertaken in order to obtain NSM compositions of $x = 10$ (NSM10), 30 (NSM30) and 50 (NSM50) mol % of Sr and were then sintered as 1200°C for 4h. The electrical conductivity of the cylindrical pellets was measured by the four-probe DC method.

Results and discussion

The Nd and Sr concentrations used in this study were expected to result in an orthorhombic pseudo-perovskite structure [14]. Table 1 presents the obtained by X-ray diffraction results.

Table 1. Crystalline structures and synthesized powder lattices.

Powder	Crystalline Structure	Lattices ($\text{\AA}$)		
		a	b	c
NSM10	Orthorhombic	5.4599	5.4600	7.7110
NSM30	Orthorhombic	5.4494	5.4547	7.9640
NSM50	Orthorhombic	5.4310	5.4700	7.6250

A comparison of the results against those reported by Kostogloudis et al [9] and Sasaki et al [10] confirmed the formation of an orthorhombic structure, as well as , the presence of a small amount of neodymium oxide (Nd_2O_3) for Sr content equal to 10% mol, (Fig. 1).

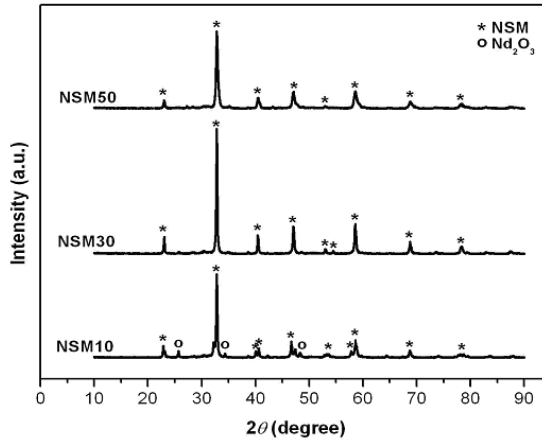


Figure 1. XRD NSM powder patterns.

The lattice parameters were calculated using a Crystallographica Search Match program, enabling the calculation of the lattice parameters using the existing JCPDS database for these materials, with their respective crystalline structures and spatial groups. A CELREF program was used to calculate the lattice refinement parameters of the NSM10, NSM30 and NSM50 samples. The crystalline structure and its refined lattice parameters were identified visually and comparatively. The NSM10 sample showed the presence of a small amount of Nd_2O_3 (JCPDS n^o. 000-86-1531) resulting from an incomplete solid state reaction with the segregated Nd^{3+} ions. The crystalline structure, lattice parameters and presence of Nd_2O_3 are consistent with values presented by Sasaki et al [10]. The presence of Nd^{3+} in the form of Nd_2O_3 is influenced by the ionic radius of the ion. The Nd^{3+} ion has an ionic radius of $1.08\text{\AA}$, while the radius of the Sr^{2+} ion is $1.13\text{\AA}$ [11]. As the ionic radius of the Sr^{2+} ion is larger than the Nd^{3+} ion, there is a limitation and substitution of Nd for Sr in the NdMnO_3 [10, 11].

The electrical conductivity logarithm, $\log \sigma$ of NSM10, NSM30 and NSM50 sintered at 1200°C in air is plotted as a function of temperature in Fig. 2. The $\log(\sigma T)$ versus the $1/T$ curve is a straight line over a wide temperature range, characteristic of the polaron hopping transport mechanism for which conductivity can be represented by the function $\sigma = (A/T)\exp(-E_a/kT)$ [1, 15], where A is the pre-exponential factor, k, the Boltzmann constant, T, the absolute temperature and E, the activation energy. For the $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ system, the temperature dependent conductivity can be described by the small polaron hopping

activity model. According to Minh [1], the Mn-based perovskite oxide LnMnO_3 electronic charge is carried by a small polaron conduction mechanism. Fig. 2 presents the increases in relation to temperature for all compositions ($x= 0.10$ to 0.50). The electrical conductivity for NSM50 was higher than that of NSM10 and NSM30, which revealed that the Nd deficiency was effective in increasing the conductivity of the stoichiometric NSM cathode. At 650°C , electrical conductivity is 22.7 , 24.0 and 34.6Scm^{-1} for $x=0.10$, 0.30 and 0.50 , respectively. At 800°C , electrical conductivity is respectively, 25.2 , 26.4 and 37.1Scm^{-1} for $x=0.10$, 0.30 and 0.50 .

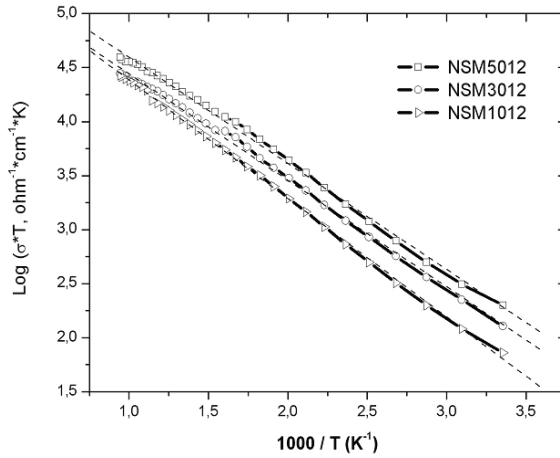


Figure 2. Log σ versus $1000/T$ for NSM10, NSM30 AND NSM50 sintered pellets.

Conclusion

X-ray diffraction of all studied powder compositions shows that the material has an orthorhombic structure. A lower Sr content (10% mol) is evidenced by the presence of a small amount of the neodymium oxide (Nd_2O_3), showing an ineffective synthesis reaction.

Electrical conductivity can be described by the small polaron hopping conductivity model and the increase with regular increments of Sr content for all compositions. At 800°C , electrical conductivity is 25.2 , 26.4 and 37.1Scm^{-1} for $x=0.10$, 0.30 and 0.50 .

The crystallographic structure and electrical transport properties were measured for NSM50 perovskite, which seems to an interesting air electrode material ITSOFC use.

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