

## STRONTIUM-DOPED NEODYMIUM MANGANITE POWDERS OBTAINED BY THE SOLIDS MIXTURE TECHNIQUE

Reinaldo Azevedo Vargas<sup>1, a</sup>, Rubens Chiba<sup>1, b</sup>, Marco Andreoli<sup>1, c</sup> and  
Emília Satoshi Miyamaru Seo<sup>1, d</sup>

<sup>1</sup>Nuclear and Energy Research Institute – IPEN/CNEN-SP  
Materials Technology and Science Center – CCTM  
Components and Raw Materials SOFC Laboratory  
Av. Prof. Lineu Prestes, 2242 – Cidade Universitária (USP)  
CEP 05508-000 – São Paulo – Brazil

<sup>a</sup>ravargas@ipen.br, <sup>b</sup>rchiba@ipen.br, <sup>c</sup>mandreol@ipen.br, <sup>d</sup>esmiyseo@ipen.br

**Keywords:** Solid Oxide Fuel Cell, Cathode, Strontium-Doped Neodymium Manganite, Solids Mixture.

**Abstract.** Many ceramic materials are being studied for application as cathodes in Solid Oxide Fuel Cells (SOFCs), especially aiming to reduce the operating temperature. Several ceramic materials can act as cathodic components, including Strontium-Doped Neodymium Manganite ( $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ ). This work contributes to the aforementioned studies by analyzing the main physical, chemical and microstructural characteristics of  $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$  powders, where  $x = 0.10, 0.30,$  and  $0.50$ . These powders were obtained by the method of ceramic solids mixture. The homogeneity of the powder particles was found to be suitable for the preparation of suspensions, which can be evaluated rheologically and subsequently molded to the surface of the solid electrolyte.

### Introduction

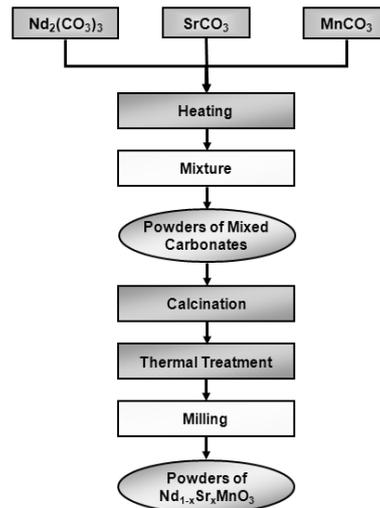
$\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$  (NSM) is an alternative ceramic material for application as a cathode in SOFCs (solid oxide fuel cells) operating between 500 and 800°C [1,2]. In recent years, the intense interest in cathodes has been due to characteristics such as good chemical and thermal stability. High catalytic activity for oxygen reduction, thermal expansion coefficient similar to that of electrolytes, and good electrical conductivity [3,4]. Doping neodymium manganite ( $\text{NdMnO}_3$ ) with strontium (Sr) improves the material's chemical stability and increases its electrical conductivity [1,2]. According to MINH [3,4], Sr is the preferred doping element because it improves thermal expansion and allows for greater electrical conductivity due to the formation of  $\text{Mn}^{4+}$  cations and the substitution of  $\text{Nd}^{3+}$  for  $\text{Sr}^{2+}$ . Studies aimed at obtaining NSM with a composition suitable for use as cathodes in SOFCs are therefore vitally important. The molar concentrations of Sr most exhaustively studied vary from  $0.05 \leq x \leq 0.50$  [1,2]. The literature presents different synthesization routes to obtain NSM, the main ones being solids mixtures, the citrate technique and combustion reaction [5].

In view of the above, this work consisted of a study of the synthesis of NSM cathode material using the solids mixture technique [2]. Our purpose is to contribute to the body of knowledge about the production of ceramic powders with characteristics suitable for application as cathodes in SOFCs by studying, principally, the influence of Sr dopant on the physical, chemical and microstructural characteristics of neodymium manganite.

### Materials and Methods

The starting materials used in the synthesis of NSM contained the following reagents: neodymium carbonate –  $\text{Nd}_2(\text{CO}_3)_3$ , 98.5% pure (Vetec); strontium carbonate –  $\text{SrCO}_3$ , 99.9% pure (Aldrich); manganese carbonate –  $\text{MnCO}_3$ , 99.9% pure (Aldrich); isopropyl alcohol –  $\text{C}_3\text{H}_8\text{O}$ , P.A. (Merck) and distilled water.

The powders were prepared by the solids mixture technique. The flowchart in Figure 1 illustrates the steps involved in the preparation of NSM.



**Figure 1** – Experimental sequence of NSM powder preparation

The first step of the NSM synthesis consisted of oven-drying and subsequent premixing of the  $\text{Nd}_2(\text{CO}_3)_3$ ,  $\text{SrCO}_3$  and  $\text{MnCO}_3$  powders for each of the stoichiometries adopted. Mixing was carried out in a grinding mill in the presence of isopropyl alcohol in order to ensure the greatest possible homogenization of the material. After the mixing step, the powders of the various mixed carbonates were calcined and then heat-treated at  $1000^\circ\text{C}$  for 4 hours [8]. The synthesized material was then milled and the samples sieved to deagglomerate the powder particles prior to their physical, chemical and microstructural characterization.

The NSM powders were synthesized with different concentrations of strontium. The experiments were aimed at obtaining compounds with  $x$  equal to 10 (NSM10), 30 (NSM30) and 50 (NSM50) mol % of Sr.

## Results and Discussion

The NSM powders were characterized using the following techniques: infrared gas absorption, X-ray fluorescence spectrometry (XRF), laser scattering granulometry, gas helium picnometry, BET gas adsorption method, and calculation of average particle diameters, whose values are presented in Table 1.

**Table 1** – Results of the NSM powder characterizations

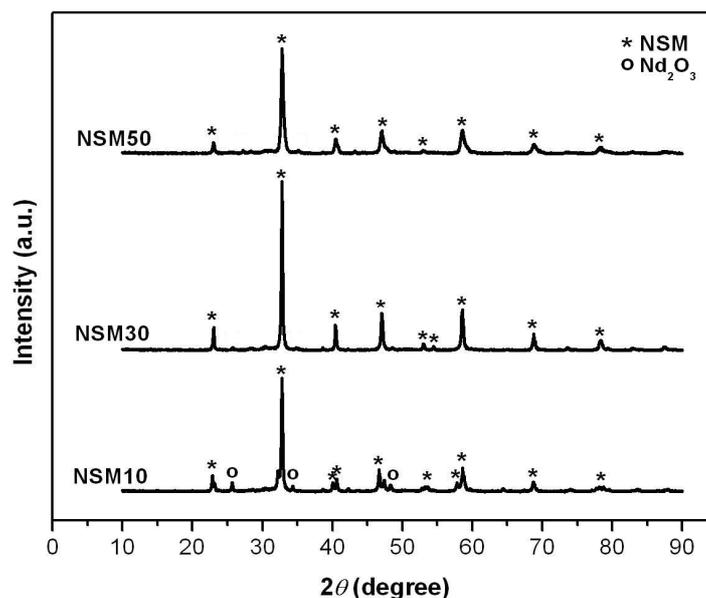
TECHNIQUE	RESULTS		
	NSM10	NSM30	NSM50
Infrared gas absorption	$0.0074 \pm 0.0001$ C %	$0.0020 \pm 0.0001$ C %	$0.0103 \pm 0.0001$ C %
X-ray fluorescence	$\text{Nd}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$	$\text{Nd}_{0.63}\text{Sr}_{0.37}\text{MnO}_3$	$\text{Nd}_{0.45}\text{Sr}_{0.55}\text{MnO}_3$
Laser scattering granulometry	$0.35 \mu\text{m}$	$0.35 \mu\text{m}$	$0.35 \mu\text{m}$
Gas helium picnometry	$6.200 \pm 0.004$ g/cm <sup>3</sup>	$6.180 \pm 0.007$ g/cm <sup>3</sup>	$5.850 \pm 0.007$ g/cm <sup>3</sup>
Gas adsorption	$10.1 \pm 0.1$ m <sup>2</sup> /g	$8.8 \pm 0.1$ m <sup>2</sup> /g	$7.9 \pm 0.1$ m <sup>2</sup> /g
Average particle diameter	$0.09 \mu\text{m}$	$0.10 \mu\text{m}$	$0.12 \mu\text{m}$

The XRD characterization of the NSM powders was based on the work of ARUNA et al. [6]. The neodymium (Nd) and strontium (Sr) concentrations used in this study were expected to result in an orthorhombic pseudo-perovskite structure. Table 2 presents the results revealed by X-ray diffraction.

**Table 2** – Crystalline structure and lattices of synthesized samples.

Sample	Crystalline Structure	Lattices [Å]		
		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 our results against those reported by KOSTOGLLOUDIS et al. [7] and SAKAKI et al. [1] confirmed the formation of an orthorhombic pseudo-perovskite structure and the presence of a small amount of neodymium oxide ( $\text{Nd}_2\text{O}_3$ ), as illustrated in Figure 1.

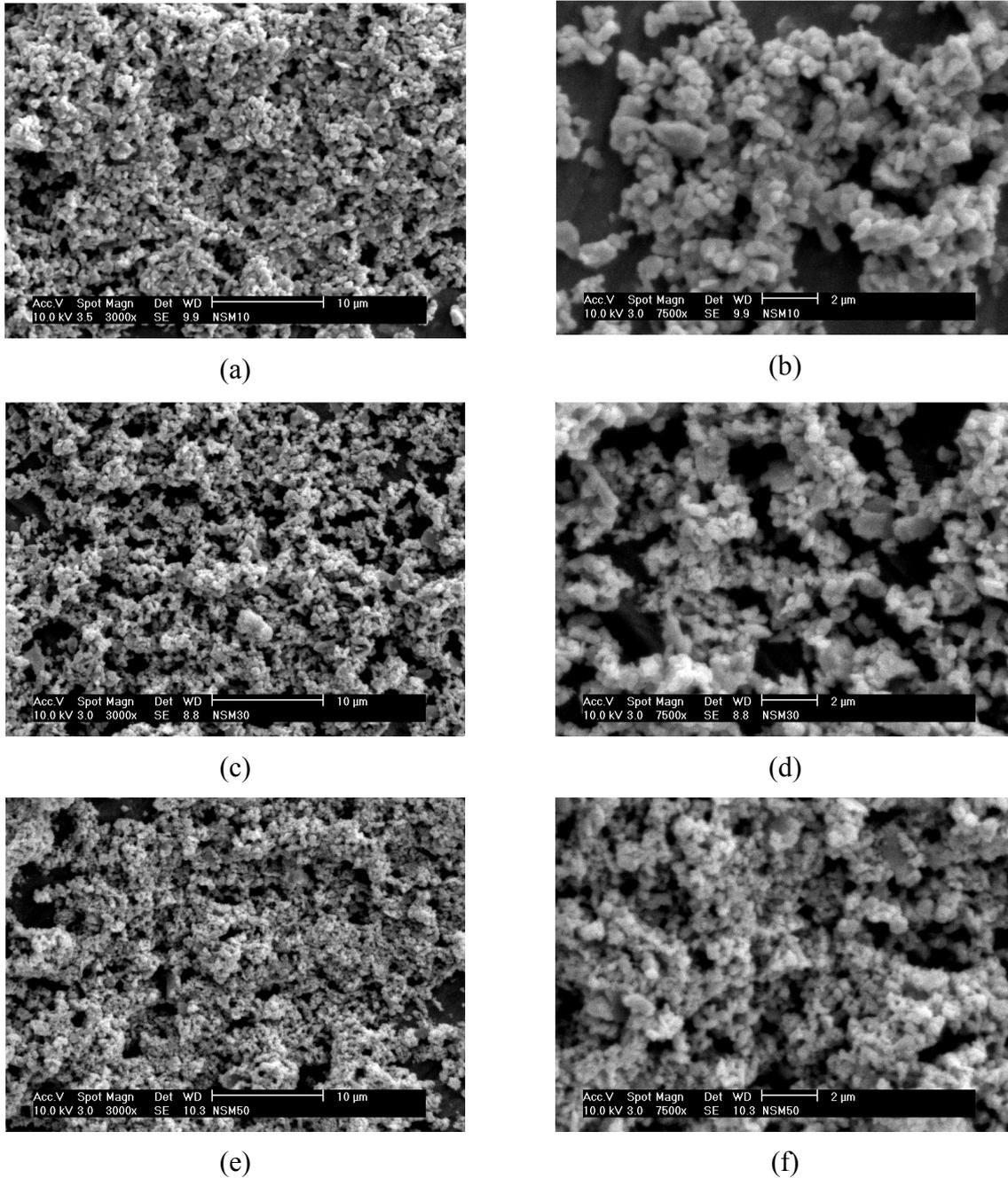
**Figure 1** – Diffractogram of the NSM powders

The lattice parameters were calculated with the help of the Crystallographica Search Match program, which enabled us to find the lattice parameters using the existing JCPDS database for these materials, with their respective crystalline structures and spatial groups. The CELREF program was used to calculate the refinement of the lattice parameters of samples NSM10, NSM30 and NSM50. The crystalline structure and its refined lattice parameters were identified visually and comparatively.

Sample NSM10 showed the presence of a small amount of  $\text{Nd}_2\text{O}_3$  (JCPDS no. 000-86-1531) resulting from the incomplete solid state reaction with the segregated  $\text{Nd}^{3+}$  ions. The crystalline structure, lattice parameters and presence of  $\text{Nd}_2\text{O}_3$  are consistent with the values presented by SAKAKI et al. [1].

The presence of  $\text{Nd}^{3+}$  in the form of  $\text{Nd}_2\text{O}_3$  is influenced by the ionic radius of the ion. The  $\text{Nd}^{3+}$  ion has an ionic radius of 1.08 Å, while the ionic radius of the  $\text{Sr}^{2+}$  ion is 1.13 Å [2]. Because the ionic radius of the  $\text{Sr}^{2+}$  ion is larger than that of the  $\text{Nd}^{3+}$  ion, there is a limitation and substitution of Nd for Sr in the  $\text{NdMnO}_3$  structure [1,2].

The morphology of the powder particles after synthesis was examined by scanning electron microscopy (SEM). The micrographs in Figure 2 show the homogeneity of the particle agglomerates and indicate that the mean size of many of these agglomerates is less than 1  $\mu\text{m}$ .



**Figure 2** – SEM micrograph of NSM10 (a,b), NSM30 (c,d) and NSM50 (e,f)

An analysis of the micrographs and a comparison of the mean particle diameters found in the particle size distribution confirm the formation of a large quantity of very homogeneous agglomerates in the three synthesized materials.

The SEM analysis revealed NSM powders with particle sizes of less than 0.50 μm. The morphologies of the samples were very similar to those obtained by the sol-gel process in the work of GAUDON et al. [10].

### Conclusions

The solids mixture used in this work allowed for the synthesis of neodymium manganite powders doped with strontium concentrations of 10, 30 and 50 mol %.

The XRF analyses confirmed that the synthesis effectively led to NSM compositions with values close to the calculated stoichiometric ones.

The SEM micrographs revealed that the sizes of the particles, which appeared in an agglomerate morphology, were less than 1  $\mu\text{m}$ . This finding was confirmed by the laser scattering granulometry analysis ( $< 0.5 \mu\text{m}$ ).

The powders were also examined by XRD, which revealed the formation of NSM as the main phase NSM and the formation of a minor amount of secondary phase  $\text{Nd}_2\text{O}_3$ . The crystalline structure of NSM powders was orthorhombic.

The findings of this work are expected to contribute to the body of knowledge about cathodic material for the manufacture of SOFCs.

### Acknowledgements

The authors thank CNPq (*Conselho Nacional de Desenvolvimento Científico e Tecnológico*) for its financial support, and their friends and colleagues at IPEN's CCTM (*Centro de Ciência e Tecnologia de Materiais*) and CQMA (*Centro de Química e Meio Ambiente*) for their generous help and invaluable contributions to this work.

### References

- [1] Y. Sakaki, Y. Takeda, A. Kato, N. Imanishi, O. Yamamoto, M. Hattori, M. Lio and Y. Esaki: *Solid State. Ion.* Vol. 118 (1999), p. 187.
- [2] T.L. Wen, H. Tu, Z. Xu and O. Yamamoto: *Solid State. Ion.* Vol. 121 (1999), p. 25.
- [3] N.Q. Minh: *J. Am. Ceram. Soc.* Vol. 76 (3) (1993), p. 563.
- [4] N.Q. Minh: *Solid State. Ion.* Vol. 174 (1-4) (2004), p. 271.
- [5] S.T. Aruna, M. Muthuraman and P.C. Kashinarh. *J. Mat. Chem.* Vol. 7 (12) (1997), p. 2499.
- [6] S.T. Aruna, M. Muthuraman and P.C. Kashinarh: *Solid State. Ion.* Vol. 120 (1999), p. 275.
- [7] G.Ch. Kostogloudis, N. Vasilakos and J. Ftikos: *J. Europ. Ceram. Soc.* Vol. 17 (12) (1997), p. 1513.
- [8] Y. Takeda, Y. Sakaki, T. Ichikawa, N. Imanishi, O. Yamamoto, M. Mori, N. Mori and T. Abe: *Solid State. Ion.* Vol. 72 (1994), p. 257.
- [9] M. Gaudon, C. Laberty-Robert, F. Ansart, P. Stevens and A. Rousset: *Solid State Sci.* 4 (2002), p. 125-.

## **Advanced Powder Technology VII**

doi:10.4028/www.scientific.net/MSF.660-661

## **Strontium-Doped Neodymium Manganite Powder Obtained by the Solids Mixture Technique**

doi:10.4028/www.scientific.net/MSF.660-661.1113