

coefficient to those of the closer components and be chemically compatible with them.

SOFCS operate at high temperatures under either oxidising or reducing atmospheres over a long period of time. This can create different problems such as interface reactions which could promote the formation of insulating phases, limiting their long-term stability [1]. In light of this, the idea is to find new materials that are very stable at high temperatures and have the properties described above.

Here we report the investigation of the family of pyrochlores of general formula $A_2B_2O_7$ (where A is a trivalent ion, usually a rare earth, and B is a tetravalent ion) which are known to exhibit oxygen ion conductivities of the order of 10-2 S/cm at 1000 °C, making them promising candidates as electrolytes. Examples include: $Gd_2(Zr_{1-x}Sn_x)_2O_7$, [2], Ca-doped $Gd_2Ti_2O_7$ [3] and Ca-doped $Gd_2(Zr_{0.3}Ti_{0.7})_2O_7$ [4].

In particular we have focused on $Ln_2Zr_2O_7$ (Ln= Lanthanide) whose structure is mainly governed by the ion size difference between Ln^{3+} and Zr^{4+} [5]. These materials have the properties needed to be a good electrolyte (high melting point, high thermal expansion coefficient, low thermal conductivity, high thermal stability and high electrical conductivity) in SOFCs [6]. Among the rare earth zirconates, $Ce_2Zr_2O_7$ bears additional interest due to the catalytic application of the CeO_2 - ZrO_2 in several chemical processes in industry and automobiles [7].

We have study the stability in air of the solid solutions $La_{2-x}Ce_xZr_2O_7$ and $Gd_{2-x}Ce_xZr_2O_7$ and the effect of the Ce- doping on the conductivity. The X-ray diffraction studies show, that the La- series keeps the pyrochlore structure up to $x = 0.5$, while the Gd one adopts the fluorite structure. These results will be correlated to the conductive behavior of these materials.

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Crystal Structure and Diffusion Path of Mixed Conductors $PrBa_{1-x}Sr_xCo_2O_{5+}$ ($x = 0$ and 0.5)

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Mixed oxide-ionic and electronic conducting ceramics (MIECs) will become increasingly important for future environmentally friendly ("green") societies, because the MIECs are used as materials for oxygen separation membranes and cathodes of solid-oxide fuel cells (SOFCs). Oxygen is an important reactant in the industrial chemical processes and air is usually utilized as the oxygen source due to the cost problem. For lower temperature devices, novel MIECs with higher oxide-ion diffusivity are required. For this purpose, it is of vital importance to investigate the oxide-ion diffusion mechanism at an atomic scale. Recently, layered perovskite oxides such as $PrBaCo_2O_{5+}$, with cation order has been reported for cathode applications in the next generation of

intermediate temperature SOFCs operations [1]. $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ exhibits better cell performance [2]. Parfitt *et al.* suggested that cation order gives larger oxide-ion diffusivity and larger activation energy by molecular dynamics [3]. However, the structural origin, cation disorder and oxygen diffusion mechanism in $PrBa_{1-x}Sr_xCo_2O_{5+}$ is unclear.

In the present work, the crystal structures of $PrBaCo_2O_{5+}$ and $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ have been studied through neutron powder diffractometry at 1000 °C. The $PrBaCo_2O_{5+}$ and $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ were identified to be tetragonal $P4/mmm$ and $Pm\bar{3}m$, respectively. The diffraction data were analyzed by a combination of the Rietveld analysis, maximum-entropy method (MEM) and MEM-based pattern fitting (MPF). The refined interstitial oxygen concentration δ in $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ is larger than that in $PrBaCo_2O_{5+}$. The refined oxygen atomic displacement parameters of $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ are larger than those in $PrBaCo_2O_{5+}$. The oxygen atom exhibited a large anisotropic thermal motions perpendicular to the Co-O bond, $U_{22}(O)$ ($=U_{33}(O)$) $>$ $U_{11}(O)$. MEM nuclear-density distributions also indicated large anisotropic thermal motions of oxygen atoms perpendicular to the Co-O bond [4]. In the MEM nuclear density distributions, the oxygen diffusion paths in both of $PrBaCo_2O_{5+}$ and $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ were visualized.[5]

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Keywords: diffusion path, neutron powder diffraction, $PrBa_{1-x}Sr_xCo_2O_{5+}$

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In-situ high temperature powder diffraction study of T/P91 steel oxidation

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Low chromium ferritic steels have been extensively studied for applications in power generating plant life time. Formation of dense, thick, and adherent chromia (Cr_2O_3) layer on stainless steel, which is considered like a good way to increase the oxidation resistance, is closely related to many parameters such as chromium content, temperature, oxidizing atmosphere, cycles frequency and time of exposure [1-3]. For grades with 9%Cr such as T/P91, the chromium content is not enough to fulfil the protective action by creating a continuous chromia scale over 600°C. As a consequence, iron oxidation can occur, and lead to the total destruction of the material [2]. Corrosion mechanisms were proposed after several studies of post-mortem samples but no clear interpretation was found about oxide formation process before critic behaviour of the steel ("break away").

The key to a successful development of T/P91 steel grade lies in a better understanding of the material reactivity at high temperature through the observation and characterization of the germination and growth of the surface oxide layers occurring within the first oxidation instants. Three oxides can mainly be formed under oxidation conditions: Cr_2O_3 , Fe_2O_3 and Fe_3O_4 . If the first one has a protective action against corrosion, the appearance and growth of the other two oxides can lead to the catastrophic behaviour.

In order to better understand the oxidation mechanisms of T/P91 steel, an in-situ diffraction experiment was performed at the ID31 High

Resolution Powder Diffraction beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The study was performed at two different temperatures (750°C and 850°C), during 60 hours under 200 mbar of oxygen. Data analysis was done using Topas program (Bruker AXS).

A complex oxide structure was identified, with five different oxides forming in three steps during the high-temperature oxidation treatment. The phase growing during the first oxidation stages was identified and the time when detrimental oxides appear was measured at both temperatures. In parallel, the quantitative analysis of the in-situ powder diffraction patterns brought information about the reaction kinetics.

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Structural properties of AFeO_{3-δ} perovskites. Effect of A-site parameters

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The structural properties for the AFeO_{3-δ} perovskite materials can be changed using the size and charge of the A sites cations (A = Ln_{1-x}M_x) [1]. The A-size can be evaluated through the mean A-cation radius, <r_A>, and the size variance or size disorder, σ²(r_A), which describes the mismatch in ionic radii of the cations at the A-site [2].

The AFeO₃ system has been chosen due to the potential properties and stability of these materials as cathodes for Solid Oxide Fuel Cells [3].

This work summarises the independent studies on the separate effects of x <r_A> [4] and σ²(r_A) [5] in the structural properties of AFeO₃ perovskites. In order to separate their contribution to the changes in the structural properties, perovskites with general formula Ln_{1-x}M_xFeO_{3-δ} (Ln = La, Pr and/or Nd; M = Sr, Ca and/or Ba) with 0.2 ≤ x ≤ 0.8; 1.21 ≤ <r_A> ≤ 1.25 Å and 0.0021 ≤ σ²(r_A) ≤ 0.0155 Å² have been synthesised by conventional ceramic solid state reaction under identical synthetic conditions. The samples have been characterised by X-ray powder and neutron powder diffraction and Rietveld analysis. For each series, one parameter has been varied independently keeping the other two constant.

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Investigations of LiMn₂O₄ nanocrystalline electrode materials

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Lithium manganese oxide (LiMn₂O₄) is a potential candidate for cathode material in Li-ion batteries (LIBs) due to its low cost, low toxicity and high safety. These make LiMn₂O₄ a material promising for use in large scale batteries for powering electric vehicles (EV) or hybrid electric vehicles (HEV) [1]. The high energy density lithium ion batteries need cathode materials with both large volumetric capacity and high density. Nanocrystalline lithium manganese oxide (LiMn₂O₄) material of spinel structure was synthesized by modified sol-gel method using citric acid as a first chelating agent. As the second agent was used glycol ethylene, glycolic acid or acetic acid [2]. The calcination temperature was 450-700°C for a few hours in air. The obtained samples were characterized by the following methods: scanning electron microscopy (SEM/EDX), X-ray photoelectron spectroscopy (XPS), SQUID magnetometry and EPR. Chemical composition, oxidation state of manganese and magnetic properties were examined.

The SEM images show different size of the grains depending on the synthesis process (the example image is shown below). Some contaminations with sodium, potassium or fluor were coming from the starting materials or technological processes. The XPS the complex Mn3p lines were deconvoluted to find the intensity of the Li 1s line and its content in the examined compounds was determined. The ratio of Mn³⁺/Mn⁴⁺ depended on the synthesis process. The C1s lines of the measured samples were intense and complex due to not well-chosen calcination time and temperature. The results were referred to the magnetic measurements results and ESR showing a presence of some extra magnetic phases.

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Probing 'breathing' mechanisms of ZIFs with high pressure

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Porous materials have attracted a wide scope of interest within the scientific community for a range of possible uses based primarily upon their large surface areas. Metal-organic frameworks (MOFs) are forming an increasingly attractive sub-section of porous materials due