Experimental Report

27/05/2014

Proposal: **5-22-720** **Council:** 10/2012

Title: Tailoring electrical properties ofdouble perovskites
as material components for SOFCs.

This proposal is resubmission of: 5-23-646

Researh Area: Materials

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Samples: La2-x-y+CexSryMTiO6-δ (M=Co, Ni; 0=<y=<0.3, 0.1=<x=<0.2)

Instrument	Req. Days	All. Days	From	To
D2B	3	2	05/07/2013	07/07/2013

Abstract:

Perovskites derived from La2-x-yCexSry(VAC)zMTiO6-d (M=Co, Ni; VAC=vacancies) by doping with Sr and Ce, (0<=y<=0.3, 0.1<=x<=0.2, 0<=z<=0.2), prepared in air are promising materials for electrodes or electrolytes in SOFCs due to their high electrical conductivity. The actual conductivity values and charge-carriers are different: significant n-type, p-type conductivity (or both) depending on the

ambient conditions (dry air or dry H2/Ar). Different explanations for these results arise, related to the presence of oxygen vacancies in the material and therefore, possible ionic conductivity. Neutron diffraction will help us to determine which is the operating mechanism working for a given composition.

Tailoring electrical properties of double perovskites in the system $La_{2-x-y+\square}Ce_xSr_yMTiO_{6-\delta}$ (M=Co, Ni; $0\leq y\leq0.2$, $0.1\leq x\leq0.2$, $0\leq\square\leq0.3$) for energy production in Solid State Fuel Cells (SOFCs)

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The aim of the proposal was to understand the mechanism(s) involved in electrical conduction in the materials of the series $La_{2-x-y+\square}Ce_xSr_yMTiO_{6-\delta}$ (M=Co, Ni; $0\leq y\leq0.2$; $0.1\leq x\leq0.2$; and $0\leq\square\leq0.3$) by combining NPD performed at ILL and SXRD measured at ESRF. In these materials we combine the presence of anionic vacancies and cations in high oxidation states (such as Co^{3+}) with Ce^{4+} which is easily reduced. As a result, a given composition shows a specific electrical behavior depending on the balance of all these species, allowing a fine tune of their properties making them potentially useful for different applications. To fully determine the mechanisms involved in the electrical properties the use of several techniques is mandatory, In particular NPD gives information about oxygen substructure and ordering of Ti and Co(Ni); these two structural features cannot be studied by X-ray diffraction making the use of neutron mandatory.

In the experimental proposal we intend to study the following samples:

(1) $La_{1.6}Ce_{0.1}Sr_{0.3}MTiO_{5.90}$ (M=Co and Ni) prepared in air (two patterns).
(2) $La_{1.4}Ce_{0.2}Sr_{0.2}MTiO_{5.70}$ (M=Co and Ni) prepared in air (two patterns).
(3) $La_{1.3}Ce_{0.2}Sr_{0.2}MTiO_{5.55}$ (M=Co and Ni) prepared in air (two patterns).
(4) A part of the above samples will be treated under a reducing atmosphere of a dry H_2/Ar mixture to simulate SOFC operating conditions, (six more patterns).

Due to beam-time limitations we finally decided to perform the experiments described in the two first items. Besides, we determined that samples with large A-site under-stoichiometry, $La_{1.3}Ce_{0.2}Sr_{0.2}MTiO_{5.55}$, are not single-phase.
Therefore, the patterns of selected samples were recorded without any problem with a very high quality.

Now we are working on the simultaneous fitting of NPD and SXRD data; we have being waited for the synchrotron data since they are absolutely necessarily. Indeed, the title perovskites could be of orthorhombic (Pnma) or monoclinic ($P2_1/n$) symmetry depending on subtle structural features. Although NPD gives more information about some aspects, peak-to-peak resolution is much better in SXRD data making them suitable for symmetry determination.
Thus, Fig. 1 shows graphic result of the fitting of RT NPD pattern of sample with nominal composition $La_{1.6}Ce_{0.1}Sr_{0.3}NiTiO_{5.90}$, to the model depicted in the inset. Several important points have been determined. First, the actual composition agrees with the nominal one, though some NiO (ca. 2% w) is observed as impurity phase; Ni and Ti ions are partially ordered among the B-sites, some oxygen vacancies are confirmed to exist, Ce ions are exclusively located in A-sites.

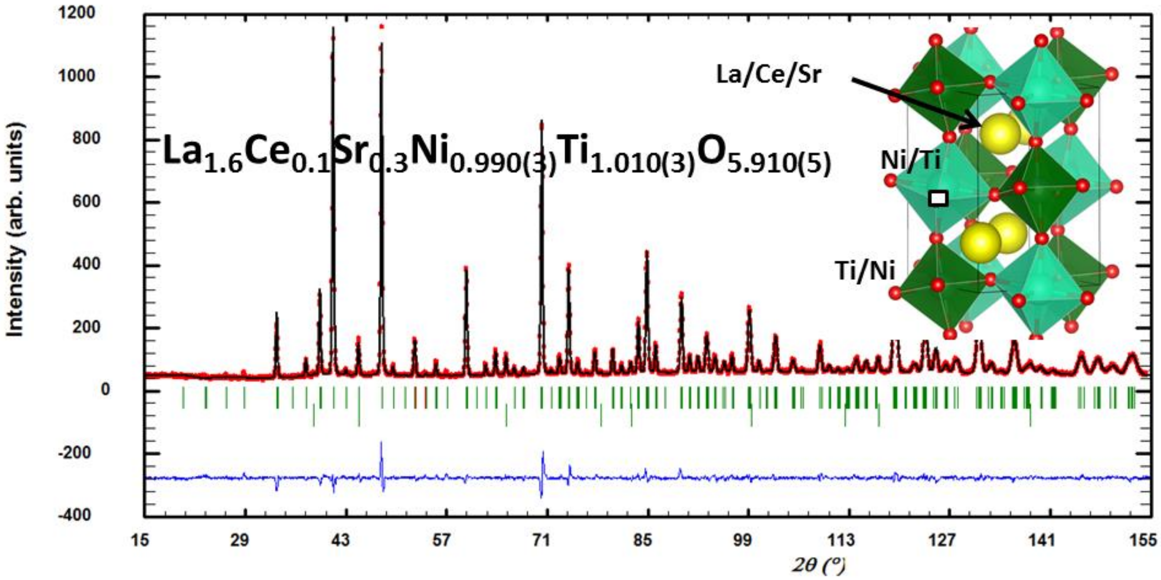

Figure 1: NPD pattern at RT for $La_{1.6}Ce_{0.1}Sr_{0.3}NiTiO_{5.90}$.

On the other hand, the similar sample of nominal composition with A-site sub-stoichiometry $La_{1.4}Ce_{0.2}Sr_{0.2}NiTiO_{5.70}$ seems to present an actual composition far from the nominal one, with segregation of noticeable amounts of NiO and re-adjusted metals contents. Besides, this material is orthorhombic with no B-ions order.

Interestingly, for similar compounds containing cobalt instead of nickel present the actual compositions correspond to the nominal ones. No segregation of cobalt oxide was detected. This seems to be related the ability of Co^{2+} to be oxidized into $Co3^{+}$ in such a way that the effect of A-site doping and/or vacancies is the oxidation of cobalt. Therefore, no compositional re-adjustment is observed in these materials.