Experimental report

05/09/2017

Proposal: 5-24-578 **Council:** 4/2016

Title: Localization of interstitial oxygen atoms in novel layered solid electrolytes with K2NiF4 structures, and study of its thermal evolution

Research area: Materials

This proposal is a new proposal

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Samples: La0.8Bi0.2SrInO4
La0.9Bi0.2Sr0.9InO4

Instrument	Requested days	Allocated days	From	To
D2B	3	3	07/10/2016	10/10/2016

Abstract:

Whereas most of solid electrolytes utilized in solid-oxide fuel cells (SOFC) commonly conduct oxide ions by a vacancy mechanism (e.g YSZ, GDC, LSGM), it has been recently demonstrated that the activation energy of O2- motion is lower for an interstitial mechanism in layered perovskites derived from LaSrInO4. These oxides exhibit the capability of inserting large amounts of oxygen interstitials. We have recently prepared novel electrolytes of composition Bi0.2La0.8SrInO4+delta and Bi0.2La0.9Sr0.9InO4+delta, where the presence of large Bi3+ ions expands the unit cell and improves the mobility of interstitial oxygens. Ionic conductivity in Bi0.2La0.8SrInO4 is higher by an order of magnitude, with a lower activation energy, compared with the pristine LaSrInO4 sample. In this experiment we aim to correlate the good performance of such materials with the structural features and to follow in situ their thermal evolution, unveiling, in particular, the influence of Bi3+ on the O contents, thermal displacements and evolution at the actual working conditions of the electrolyte in a SOFC.

The development of an intermediate temperature SOFC (working between 500 and 800 ºC) necessarily requires new electrolyte materials that are able to conduct O^{2-} ions with lower activation energies, so as to decrease the electrical resistance and to improve the electrochemical kinetics. Well-known fast O^{2-} ion conductors, such as YSZ, GDC and LSGM [1-3] are materials where the ionic conduction proceeds by an oxygen-vacancy mechanism. On the other hand, there are reports on layered perovskite-type compounds with the K_2NiF_4 structure that are well known to incorporate interstitial oxygen atoms inside their frameworks. In particular, layered perovskites like $LaSrInO_4$ [4,5]. The capability of inserting large amounts of oxygen interstitials is especially attractive for the use of these materials as electrolytes in SOFCs.

In previous works, we prepared and investigated as possible solid electrolytes a family of $La_{1+x}Sr_{1-x}InO_{4+\delta}$ (x= 0.1, 0.2) and $LaSrIn_{1-x}B_xO_{4+\delta}$ (B=Zr, Ti). By NPD data at RT we could identify by difference Fourier maps interstitial oxygen atoms in the NaCl layer of the K_2NiF_4 structure, observing a large excess oxygen contents and low activation energy values of 0.51 eV, significantly smaller than that of other electrolytes working with a vacancy mechanism, typically of 1 eV.

At present we have successfully explored the layered perovskites of composition $Bi_{0.2}La_{0.8}SrInO_4$ and $Bi_{0.2}La_{0.9}Sr_{0.9}InO_{4+\delta}$ prepared via a nitrate-citrate route. Fig. 1 shows the XRD patterns for two representative samples compared with the patron $LaSrInO_4$ sample. By Rietveld method (Fig. 2) we could see that the crystal structure incorporates Bi giving rise to dramatic variations of the unit-cell parameters. The electrical properties were assessed by means of *ac* impedance spectroscopy performed in the 400–800 °C temperature range. Fig. 3 illustrates the impedance diagrams in air at 500 ºC. The resistances increased with decreasing temperature, as expected. The Arrhenius plots (Fig. 4) show the temperature dependence of the conductivity (σT). It can be seen that the conductivity of these oxides is higher by an order of magnitude for $Bi_{0.2}La_{0.8}SrInO_4$, accompanied with a lower activation energy, compared with the parent $LaSrInO_4$ sample.

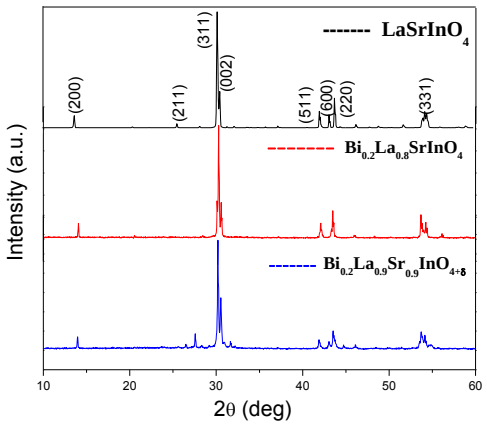

Fig. 1 XRD patterns indexed to an orthorhombic unit cell (space group Pbca).

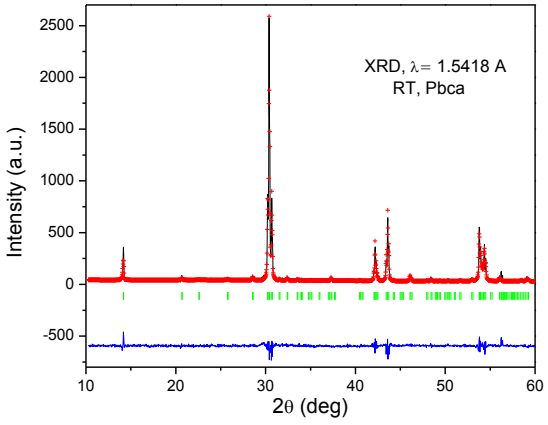

Fig. 2. Rietveld plot (XRD) for $Bi_{0.2}La_{0.8}SrInO_4$ at RT

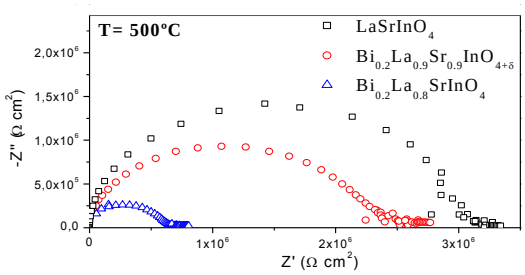

Fig. 3. *ac* impedance spectra of $Bi_xLa_{1-x}SrInO_4$ (x= 0.0, 0.2) and $Bi_{0.2}La_{0.9}Sr_{0.9}InO_{4+\delta}$, with Pt electrode at 500 °C in air.

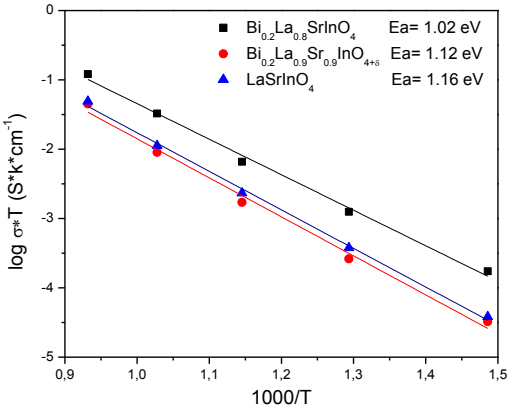

Fig. 4. Arrhenius plot for $Bi_xLa_{1-x}SrInO_4$ (x= 0.0, 0.2) and $Bi_{0.2}La_{0.9}Sr_{0.9}InO_{4+\delta}$

In this experiment, neutron powder diffraction (NPD) data were collected in the diffractometer D2B for the mentioned $Bi_{0.2}La_{0.8}SrInO_4$ and $Bi_{0.2}La_{0.9}Sr_{0.9}InO_{4+\delta}$ layered perovskites. The high intensity mode ($\Delta d/d \approx 5 \cdot 10^{-4}$) was selected, with a neutron wavelength λ= 1.594 Å within the angular 2θ range from 8° to 150°. The collection time was of 3 h per pattern. Additionally, the related compound $La_{1.2}Sr_{0.8}$-xBaxInO4 was studied at increasing temperaturas (200, 400, 600, 800 ºC) in order to evaluate the evolution of the oxygen interstitials with temperature.

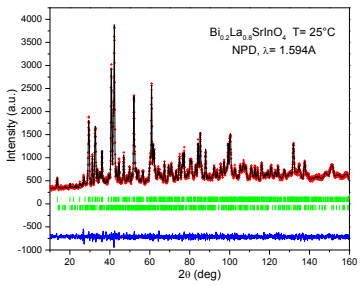

Fig. 5. NPD profile for $Bi_{0.2}La_{0.8}SrInO_4$ at 25 °C in air, refined in the Pbca space group. The vertical markers correspond to the allowed Bragg reflections for the main phase; the second series of markers correspond to the Sr_3La4O_9 minor impurity phase.

As an example of the quality of the Rietveld refinements, we illustrate the case of $Bi_{0.2}La_{0.8}SrInO_4$ perovskite, for which the crystal structure can be defined in the P*bca* space group at room temperature (Fig. 5).

Fig. 6 shows a view of the orthorhombic crystal structure, consisting of layers of rotated InO_6 octahedra alternating with (La/Sr)–O layers with the NaCl structure

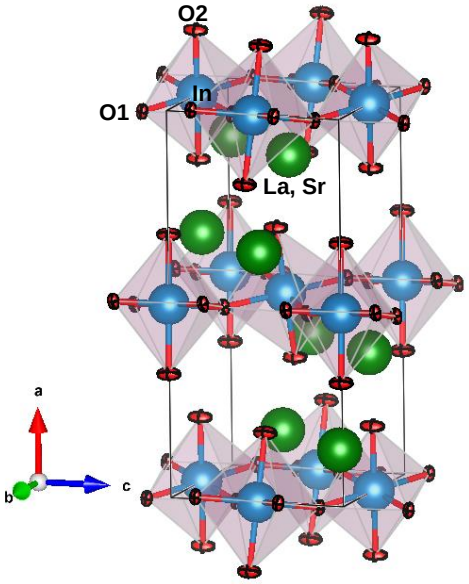

Fig. 6. Crystal structure along the c direction of $Bi_{0.2}La_{0.8}SrInO_4$ showing sheets of tilted InO_6 octahedra alternating with (La,Sr)–O layers. Anisotropic ellipsoids for O1 and O2 oxygen atoms are also shown.

We found the presence of oxygen vacancies at the octahedral lattice, determining that the stoichiometric formula was $Bi_{0.2}La_{0.8}SrInO_{3.96}$. However, By Difference Fourier maps no interstitial oxygen was identified.

References

[1] S.P.S. Badwal, Solid State Ionics 52 (1992) 23–32.
[2] T. Takahashi, H. Iwahara, Energy Convers. 11 (1971) 105–111.
[3] B.C.H. Steele, Solid State Ionics 129 (2000) 95–110.
[4] L. Troncoso, J. A. Alonso, A. Aguadero, J. Mater. Chem. A, 3 (2015) 17797–17803
[5] L. Troncoso, J. A. Alonso, M.T. Fernández-Díaz, A. Aguadero, Solid State Ionics 282 (2015) 82–87