Experimental Report

Proposal: **5-23-649** **Council:** 4/2012

Title: Oxygen defects and crystal structure of the n = 3 Ruddlesden Popper system LaSr3(Co,Fe,Ga)3O10-d

This proposal is a new proposal

Researh Area: Materials

Main proposer: **PRADO Fernando**

Experimental Team: PRADO Fernando

Local Contact: CUELLO Gabriel Julio

Samples:
LaSr3Fe1.5Co1.5O10
LaSr3Fe2GaO10
LaSr3Fe2.4Ga0.6O10
LaSr3Ga0.6Fe1.8Co0.6O10
LaSr3Ga0.3Fe1.35Co1.35O9.2
LaSr3Ga0.3Fe1.35Co1.35O10
LaSr3Ga0.6Fe1.8Co0.6O10
LaSr3Fe2.4Ga0.6O9.4
LaSrFe3O10

Instrument	Req. Days	All. Days	From	To
D2B	2	2	09/11/2012	11/11/2012

Abstract:

The crystal chemistry of the n = 3 Ruddlesden-Popper oxides LaSr3(Co,Fe,Ga)O10-delta will be studied. On one hand we are interested to determine the oxygen defect structure of the LaSr3Co1.5Fe1.5O10-delta phase in the temperature range 20 < T < 900 ºC in air. We expect to determine with accuracy both the position and the occupation number for the four oxygen atoms at high temperature to explain the mechanism for oxygen diffusion at high temperature.
On the other hand, we propose to study the structural transformation from tetragonal (I4/mmm)to orthorhombic (Fmmm)symmetry observed in the LaSr3(Co,Fe,Ga)O10-delta R-P phases when either Fe and Co are replaced by Ga or oxygen atoms are removed from de crystal structure.
We are asking for 2 days on D2B.

Experimental Report Ex N°: 5-23-649

Oxygen defects and crystal structure of the n = 3 Ruddlesden-Popper System $LaSr_3(Co,Fe,Ga)_3O_{10-\delta}$

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Introduction

Several studies have shown that $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ exhibits good structural stability and adequate values of oxide ion and electronic conductivity [1,2] for electrochemical applications. More recently, Lee and Manthiram [3] have found that the cathode performance of $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ in a SOFC is comparable to the perovskite phase $La_{0.6}Sr_{0.4}CoO_{3-\delta}$. In an attempt to increase the oxygen vacancy concentration and thereby improve the oxide ion conductivity and develop mixed conductors with lower TEC, Ga has been incorporated in the B site and the solid solutions $LaSr_3GaFe_{2-x}Co_xO_{10-\delta}$ [4] and $LaSr_3Fe_{1.5-x/2}Co_{1.5-x/2}Ga_xO_{10-\delta}$ with $0 \leq x \leq 0.8$ have been investigated [5]. The incorporation of Ga into the crystal lattice of $LaSr_3(Fe,Co)_3O_{10}$ causes: a) a structural transformation of the unit cell symmetry from tetragonal (S.G. I4/mmm) to orthorhombic (S. G. Fmmm) [4-6] affecting the mixed conducting properties [4], particularly oxygen permeation, although small variations were detected for the power density delivered by single cells [5], b) an increment of the oxygen vacancy concentration reducing the chemical contribution to the total thermal expansion and c) a reduction in the electrical conductivity. The crystal structure of the n = 3 R-P phases contains four non-equivalent oxygen crystal sites (see figure 1). Previous studies [7-9] have located the oxygen vacancies at the O(1) and O(4) sites, while fully occupancy was reported for the O(2) and O(3) crystal sites.

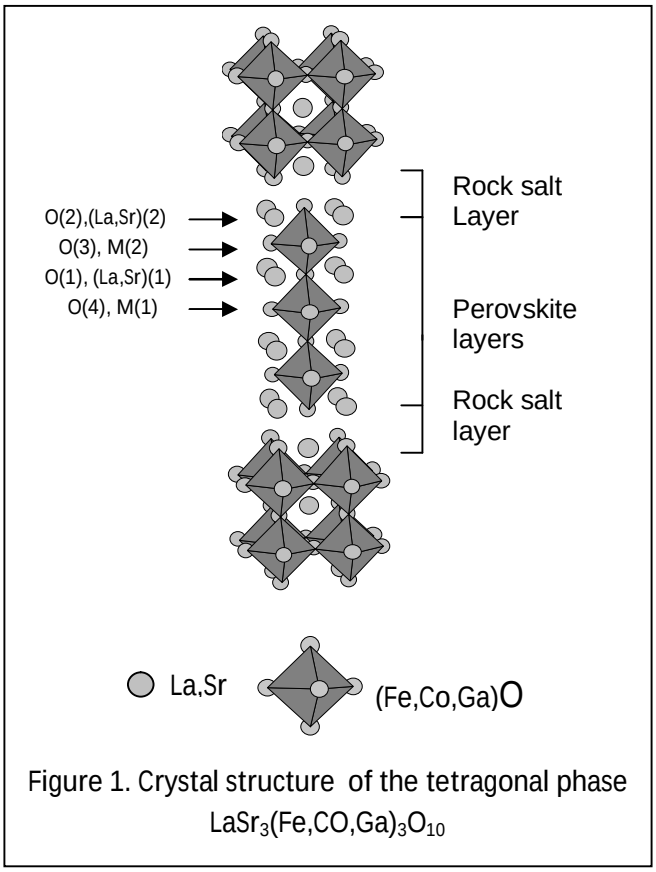

Figure 1. Crystal structure of the tetragonal phase $LaSr_3(Fe,CO,Ga)_3O_{10}$

In this work, we have investigated the variations of the crystal chemistry of the n = 3 R-P phases belonging to the system $LaSr_3(Fe,Co,Ga)_3O_{10-\delta}$ by NPD. We have determined the oxygen defect structure of the $LaSr_3Co_{1.5}Fe_{1.5}O_{10-\delta}$ phase at the working temperatures of the electrochemical applications in the temperature range $20 < T < 900$ ºC, in air. We are studying the structural transformation from tetragonal (I4/mmm) to orthorhombic (Fmmm) symmetry observed in the $LaSr_3(Co,Fe,Ga)_3O_{10-\delta}$ R-P phases when either Fe and Co are replaced by Ga or oxygen atoms are removed from de crystal structure.

Experimental

Samples of $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ (FP01),$LaSr_3Fe_2GaO_{10}$ (FP08), $LaSr_3Fe_{2.4}Ga_{0.6}O_{10}$ (FP09), $LaSr_3Ga_{0.6}Co_{0.6}Fe_{1.8}O_{10}$ (FP10) and $LaSr_3Ga_{0.3}Co_{1.35}Fe_{1.35}O_{10}$ (FP18) were prepared by solid state reaction. After the synthesis, the samples were slowly cooled at a rate of 1°C/min in air. Figure 2 shows the location of the samples in a phase diagram of the system $LaSr_3(Fe,Co,Ga)_3O_{10-\delta}$ [1,4-7]. Furthermore, samples were prepared with different oxygen content values subject to the following conditions:

a) Sample FP01 y FP08 were prepared under pure O2 at a pressure and temperatura of P = 100 *atm* and T = 500 °*C* during 6 h.

b) Samples FP09, FP10 and FP18 were reduced at T = 900 °*C* during 24 h a $pO_2 = 1\times10^{-5}$ *atm* and then fast quenched at room temperature.

c) Samples FP01 and FP10 were reduced at T = 900 °*C* during 24 *h* under a $pO_2 = 1.6\times10^{-2}$ *atm* and then fast quenched .

Neutron Powder Difraction measurements were performed at room temperatura using a Vanadium sample holder. For the compound $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ (FP01), we have recorded data at T = 250, 500, 700 y 900 °C, in air using a quartz simpleholder. The measurements were performed using a wavelenght of λ = 1.594 Å at the D2B line at the ILL.

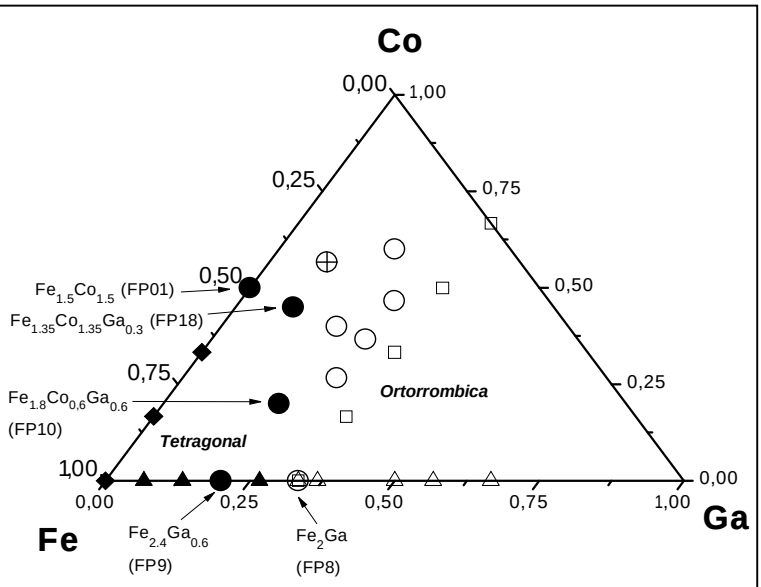

Figure 2. Location of the samples in the phase diagram of the system $LaSr_3(Fe,Co,Ga)_3O_{10-\delta}$.

Preliminary Results

The NPD data obtained for the compound $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ at T = 20, 250, 500, 700 and 900 °C have been analyzed using the Rietveld method with Fullprof [10].The crystal structure was refined systematically on the basis of the tetragonal space group I4/mmm. This analysis combined with titration iodometry allowed us to determine with accuracy the absolute oxygen content of the samples, the occupancy of the oxygen crystal sites O(1) to O(4) and also the coordinates of the oxygen atoms in the unit cell as a function of temperature.

For instance, Figure 3 shows the variation of the total oxygen content of $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ as a function of temperature, while Figure 4 exhibits the evolution of the occupancy of the oxygen crystal sites O(1) and O(4) with temperature. The total oxygen content decreases with temperature until the oxygen vacancy concentration reaches a value of 5% at T = 900 °C in air. We have determined the presence of oxygen vacancies mainly in the O(4) crystal sites located at the $(FeCo)O_2$ plane at the center of the perovskite block. The oxygen vacancy concentration reaches 25% at this crystal site at 900 °C. Moreover, a small concentration of oxygen vacancies, around 2%, was detected at the O(1) crystal sites located at the (La/Sr)O next to the $(Fe/Co)O_2$ planes containing the O(4) crystal sites. Finally no oxygen vacancies were

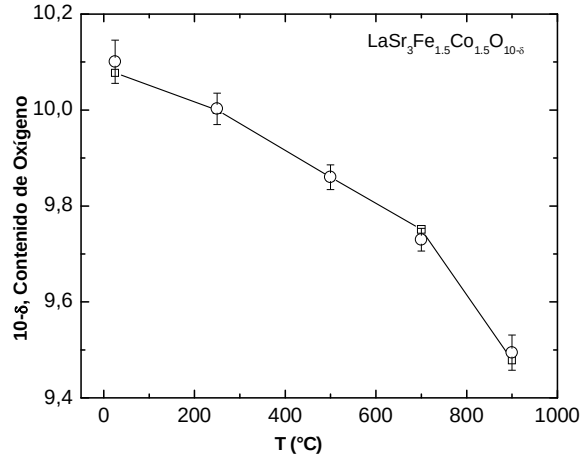

Figure 3. Variation of the oxygen content with temperature for $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$

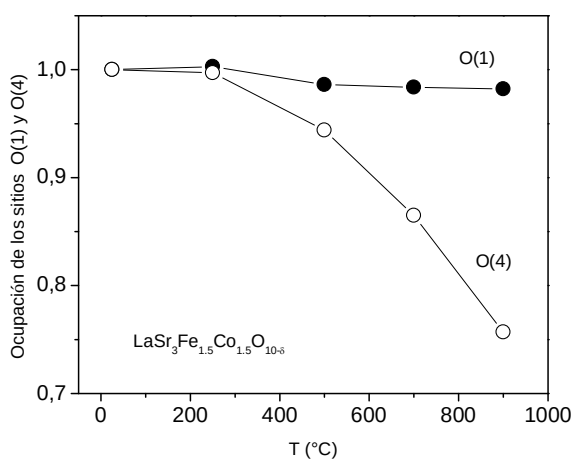

Figure 4. Variation of the occupancy for crystal sites O(1) and O(4) of $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$.

detected at the other two crystal sites O(2) and O(3).

Furthermore, we have evaluated the behavior of the crystal structure of this Ruddlesden-Popper phase with temperature. Basically, we have monitored the effects of temperature on the expansion of the rock salt and the perovskite layers. We have found that the rock salt layer thickness remains almost constant with varying temperature and oxygen content, while the perovskite layer is strongly affected by the oxygen atom removal from the crystal structure. The relative movements of the atoms is a consequence of the electrostatic repulsion between cations due to the elimination of oxygen atoms in the middle of the perovskite layer. Similar behavior was also observed for the $Sr_3(Fe,Co)_2O_7$ compound, which is another Ruddlesden-Popper phase with two perovskite layers instead of 3 as is the case of $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$.

The NPD data recorded at room temperature for samples containing Ga, $LaSr_3Fe_2GaO_{10}$ (FP08), $LaSr_3Fe_{2.4}Ga_{0.6}O_{10}$ (FP09), $LaSr_3Ga_{0.6}Co_{0.6}Fe_{1.8}O_{10}$ (FP10) and $LaSr_3Ga_{0.3}Co_{1.35}Fe_{1.35}O_{10}$ (FP18) are currently being analized with the intention to explain the reasons for the structural transformation from tetragonal to orthorhombic symmetry when the oxygen content of the simple is modified. We expect to correlate this structural information with the behavior of the physical properties such as the electrical conductivity and the electrochemical behavior as cathode for SOFC.

Summary

NPD data were collected at the D2B line during two days at room temperature on samples belonging to the system $LaSr_3(Fe,Co,Ga)_3O_{10-\delta}$ and as a function of temperature (T = 250, 500, 700 y 900 °C) in air for the sample $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$. The analysis of the NPD data allowed us to determine the evolution of the defect structure at high temperature of $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ by determining the occupancy of the different oxygen crystal sites. We have found the oxygen vacancies locates mainly at the O(4) crystal sites, a little fraction locates at the O(1) crystal site, while the cristal sites O(2) and O(3) remains fully occupy. Furthermore we have determined the expansion behavior of the crystal structure as a function of temperature. NPD data corresponding to samples containing Ga, system $LaSr_3(Fe,Co,Ga)_3O_{10-\delta}$, are still under analysis.

Referencias

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