Experimental report

06/12/2021

Proposal: 6-06-490 **Council:** 10/2019

Title: Impact of the local distortions onproton transfer in triple conducting materials for high temperature electrochemical devices.

Research area: Materials

This proposal is a new proposal

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Samples: La0.9Sr0.1Sc0.9Co0.1O3-d (saturated with H2O, D2O and dry)
La0.9Sr0.1Sc0.95Co0.05O3-d (saturated with H2O, D2O and dry)
La0.9Sr0.1ScO3-d (saturated with H2O, D2O and dry)

Instrument	Requested days	Allocated days	From	To
D4	4	4	24/08/2020	28/08/2020

Abstract:

La0.9Sr0.1ScO3-d (LSS) perovskites are promising electrolyte materials for various electrochemical devices such as gas sensors, hydrogen pumps, membrane reactors and protonic-ceramic fuel cells. By doping LSS with transition metals (Me) of variable valance into the Sc sublattice, we create perovskites of the composition La0.9Sr0.1Sc1-xMexO3-d. These triple conducting materials, capable to conduct protons, oxygen ions and electronic holes, are perfect candidates for electrode materials and hydrogen separation membranes. However, there is no understanding yet available of the impact of transition metals onto structural distortions, changes in the proton sites and dynamics. With this proposal, we want to perform neutron pair distribution function (PDF) measurements on Cobalt-doped LSS, due to its superiority of total conductivity at high oxygen partial pressures. Experiments on dried, hydrated and deuterated samples of three different Co concentrations (x = 0, 0.05 and 0.1) will allow us understand the influence of transition metals on local distortions, proton positions and dynamics in perovskite-like oxide systems.

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Introduction

Proton-conducting oxides are intensively studied due to their applications in renewable and green energy as essential parts of protonic-ceramic fuel cells (PCFCs), electrolyzers (PCEs) for hydrogen generation, or membrane reactors [1–3]. Variously doped oxides based on $LaScO_3$ were previously investigated and identified to have competitive conductivity as well as good chemical and thermal stability with the most promising composition being $La_{0.9}Sr_{0.1}ScO_{3-\delta}$[4–6].

The transport properties of oxide electrolytes are determined by point defects, which produce a short-range disorder. Moreover, the mobility of protonic defects is sensitive to the type of acceptor dopant and its influence on the lattice [7]. Hence, to understand the functional properties of triple-conducting oxides it is essential to know where point defects are located, how they interact with each other and affect the lattice around them. In this experiment, we study the local and defect structure of triple-conducting oxides $La_{0.9}Sr_{0.1}Sc_{1-x}Co_xO_{3-\delta}$ (x = 0; 0.05; 0.1).

Results

From the small-box refinement of neutron PDFs (see Fig. 1) the stoichiometric formula of the saturated samples are determined as follows: LSS – $La_{0.9}Sr_{0.1}ScO_3D_{0.08}$; LSSCo5 – $La_{0.9}Sr_{0.1}Sc_{0.95}Co_{0.05}O_3D_{0.1}$; LSSCo10 – $La_{0.9}Sr_{0.1}Sc_{0.9}Co_{0.1}O_3D_{0.02}$. Since the structure contains two symmetrically different oxygens, for the refinement two separate deuterium atoms were introduced – one for each oxygen. The proton incorporation occurs through oxygen vacancies, we supposed that D would be preferably found around the oxygen 8d position, which contains more vacancies. However, from the several repeated refinements, we observed more or less equal distribution in D occupation between those two positions.

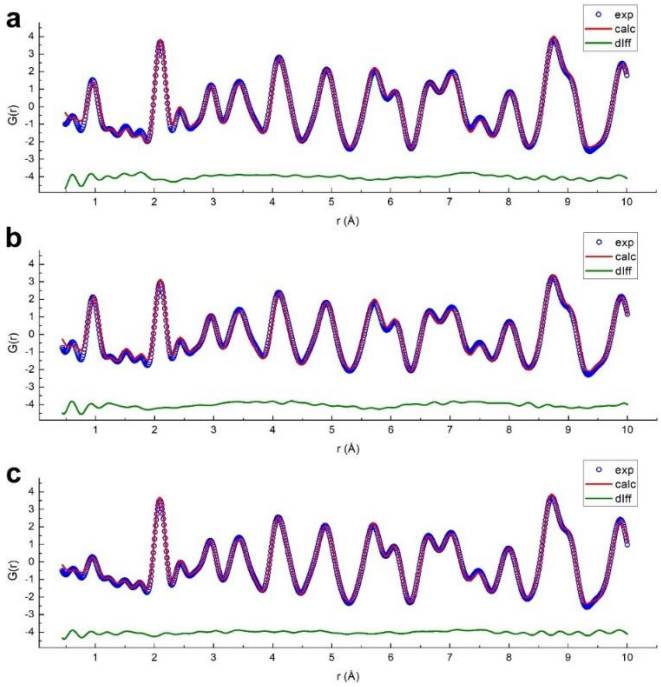

Fig. 1. Fits of neutron PDFs of saturated with D_2O; **a –** $La_{0.9}Sr_{0.1}ScO_{3-\delta}$ (LSS), **b –** $La_{0.9}Sr_{0.1}Sc_{0.95}Co_{0.05}O_{3-\delta}$ (LSSCo5), **c –** $La_{0.9}Sr_{0.1}Sc_{0.9}Co_{0.1}O_{3-\delta}$ (LSSCo10) with perovskite structure in Pnma space group.

In order to model defect distribution, big-box modeling methods were used. The model of the crystal structure and corresponding PDFs of dried and saturated samples are obtained using the Molecular Dynamics (MD) simulations along with Reverse Monte Carlo (RMC) modeling technique (Fig. 2). The distribution of point defects and proton dynamics are studied. It is established that point defects of opposite charges form clusters, which potentially could decrease the performance of the material.

These results are combined with non-constant force field MD to study possible proton trapping. A manuscript is currently being written and shortly before submission.

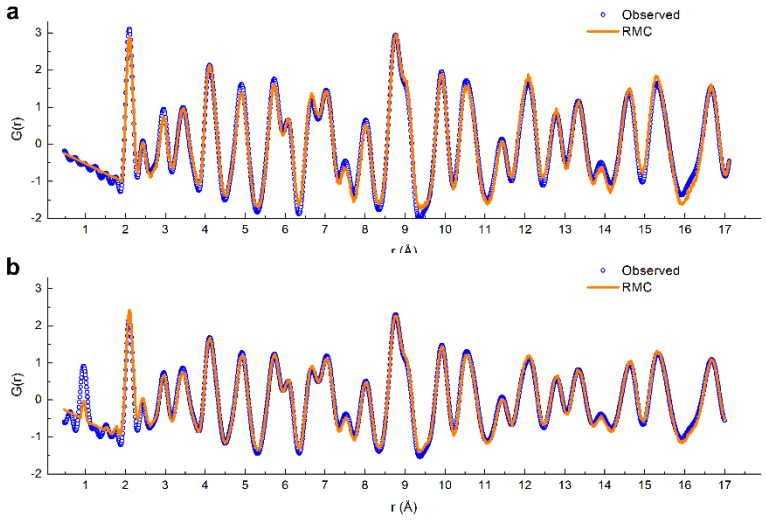

Fig. 2. Experimental and modeled by RMS-MD neutron PDFs of dried $La_{0.9}Sr_{0.1}Sc_{0.9}Co_{0.1}O_{3-\delta}$ – **a** and saturated with D_2O – **b**.

References

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