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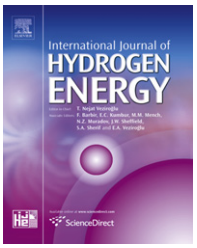

# Interstitial oxygen in the Ga-based melilite ion conductor: A neutron total scattering study

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ARTICLE INFO

*Article history:*
Received 30 June 2011
Received in revised form
20 September 2011
Accepted 30 September 2011
Available online 26 November 2011

*Keywords:*
Total scattering
Pair distribution function analysis
Ionic conductivity
Interstitial oxygen

ABSTRACT

In this paper we report a neutron total scattering experiment coupled to pair distribution function analysis (PDF) on a recently discovered Ga-based oxide-ion conductor characterized by interstitial oxygen migration. In particular, this study focuses on the short-range order analysis of the defect structure in $La_{1.50}Sr_{0.50}Ga_3O_{7.25}$ with the aim of shedding light on the position of the interstitial oxygen and on the distortion induced in the structure by the extra-oxygen. The data analysis reveals that the preferred position, at low-temperature, for the interstitial oxygen is within the pentagonal ring formed by the Ga1 and Ga2 atoms and shifted with respect to the centre of the pentagon.



## 1. Introduction

Significant efforts of the current research in the field of energy materials for solid oxide fuel cells (SOFC) are directed towards the discovery of new ion-conductors with optimal conductivity and chemical stability properties [1–4]. Over the last few years several new phases have appeared in the literature such as the oxide-ion conductors $La_2Mo_2O_9$ (LAMOX) [5–8], Ga-based oxides with tetrahedral units [9,10], apatites [11–14] and the proton conducting niobates [15–17]. The most recent material for which a high ionic conductivity has been reported is the $La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$ system [18].

The parent compound $LaSrGa_3O_7$ adopts the melilite structure, which consists of alternating cationic $(La/Sr)_2$ and corner-sharing tetrahedral anionic $Ga_3O_7$ layers. The structure is characterized by five-fold tunnels that accommodate the eight-coordinate La/Sr as chains of cations [18,19]. Fig. 1A and B reports a sketch of the structure along two axes.

In the tetragonal unit cell two distinct crystallographic sites are occupied by the Ga atoms (labelled Ga1 and Ga2), both in tetrahedral coordination, and three distinct crystallographic sites are occupied by the O atoms. The peculiarity of the $Ga2O_4$ units is the presence of non-bridging oxygen atoms, that is, oxygens that are not shared between Ga units. One interesting aspect of Ga-based melilite oxides is that the structure can accommodate interstitial oxygen by making the La/Sr ratio >1. This means that interstitial oxygen atoms are created according to:

$$2Sr_{Sr}^{\times} + La_2O_3 \rightarrow 2La_{Sr}^{\bullet} + O_{int}'' + 2SrO \quad (1)$$

Kuang and colleagues [18] found a very high purely ionic (oxide-ion) conductivity due to interstitial oxygen for the $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ oxide composition [18]. This resulted in a new class of electrolytes for SOFC where the oxygen does not move by a vacancy mechanism such as in yttria-stabilized zirconia [1] but through interstitial oxygen.

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0360-3199/$ – see front matter 
doi:10.1016/j.ijhydene.2011.09.157

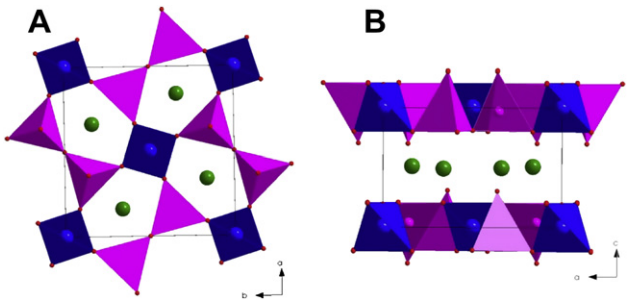


**Fig. 1 – Melilite structure of $LaSrGa_3O_7$: A) view along the *c* axis, showing the Ga tetrahedral units connected through bridging oxygens to form distorted pentagonal rings; B) view along the *b* axis, showing the layered nature of the structure with non-bridging oxygens pointing towards the La/Sr layer. Key: Ga1 (blue); Ga2 (pink); O (red); La/Sr (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)**

New materials characterized by interstitial defects require a good knowledge of the actual position of the interstitial atoms. Average structure probes such as diffraction are valuable in giving insights into these aspects; however, the possibility of using a local structure probe may further increase the level of knowledge of the defect positions and the local structure relaxations occurring around these defects. To this end we undertook a neutron total scattering investigation and pair distribution function (PDF) analysis on the $LaSrGa_3O_7$ and $La_{1.50}Sr_{0.50}Ga_3O_{7.25}$ samples. The use of total scattering methods for the investigation of energy materials is now well established [6,20–24] and has proved to be a successful way of getting information about the local structure and defect distribution in complex oxide systems.

## 2. Material and methods

Samples of composition $LaSrGa_3O_7$ and $La_{1.50}Sr_{0.50}Ga_3O_{7.25}$ were prepared by solid-state reaction starting from $La_2O_3$, $Ga_2O_3$ and $SrCO_3$ (Aldrich). Following the procedure described in Ref. [18], in order to compensate for the Ga volatilization at high temperature, an excess of $Ga_2O_3$ has been used (1 wt% for $LaSrGa_3O_7$ and 3.05 wt% for $La_{1.50}Sr_{0.50}Ga_3O_{7.25}$). A first thermal treatment was performed at 1200 °C for 20 h, followed by a thermal treatment at 1200 °C for 15 h and a final treatment at 1400 °C for 8 h. Each step was preceded by careful grinding and isostatic pressing of the samples to improve physical contact between particles. After each thermal treatment the samples have been slowly cooled down to room temperature.

Neutron powder diffraction (NPD) measurements at 15 K were carried out on the NPDF diffractometer at the Lujan Center at Los Alamos National Laboratory in a cylindrical vanadium tube (diameter 0.6 cm). Total acquisition time was approximately 8 h for each sample. Data from an empty container were also collected to subtract the container scattering. The corrected total scattering structure function, S(Q), was obtained with the program PDFGETN [25]. Finally, the PDF was obtained by Fourier transformation of S(Q). A $Q_{max} = 35.0$ Å$^{-1}$ was used. Refinement of the experimental PDF data was carried out with the aid of PDFGUI and PDFFfit2 software [26]. Refinement of the average structure was carried out with the GSAS package [27]. Three data banks were used for Rietveld and four for PDF analysis.

## 3. Results and discussion

On the two samples investigated we first refined, by means of the Rietveld method, the neutron diffraction patterns at 15 K in order to get the average structure parameters that were used as the starting model of the PDF analysis. The starting average structure model used to refine the neutron diffraction patterns were taken from Ref. [18]. The Rietveld-refined patterns are reported in Fig. 2A for $LaSrGa_3O_7$ and Fig. 2B for $La_{1.50}Sr_{0.50}Ga_3O_{7.25}$ (one bank reported) while the structural parameters obtained from the refinement are shown in Tables 1 and 2 for $LaSrGa_3O_7$ and $La_{1.50}Sr_{0.50}Ga_3O_{7.25}$, respectively. Table 3 reports selected distances for the two compositions as

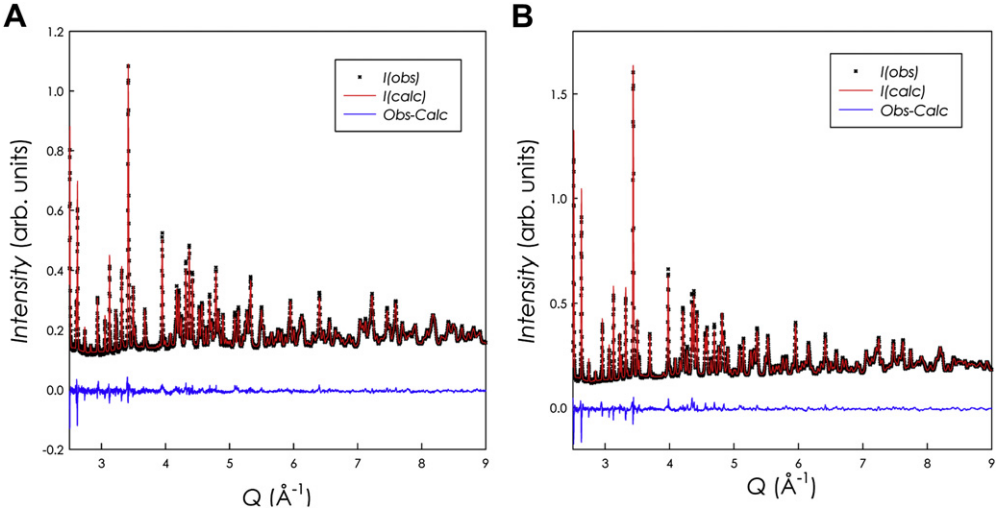


**Fig. 2 – Rietveld refinement of neutron data at 15 K for $LaSrGa_3O_7$ (A) and $La_{1.50}Sr_{0.50}Ga_3O_{7.25}$ (B).**