Experimental report

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Proposal: 6-06-480 **Council:** 4/2017

Title: Local oxygen ordering in a new oxygen deficient perovskite, explored by atomic pair distribution function analysis

Research area: Chemistry

This proposal is a resubmission of 6-06-476

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Samples: Sr2ScGaO5

Instrument	Requested days	Allocated days	From	To
D4	3	3	23/10/2018	28/10/2018

Abstract:

Sr2SCGaO5, an oxygen deficient perovskite, is a new pure 3D oxygen electrolyte,particularly interesting in the intermediate temperature range. It crystalises in the cubic Pm-3m space group, showing 1/6 of all oxygen positions vacant.
Previuos neutron diffraction experiments as a funtion of the temperature, revealed a strong anharmonic displacements for the oxygen atoms, while a predominant formation of ScO6 octahedra and GaO4 tetrahedra is indicated by Raman spectroscopic studies, resulting in a complex oxygen defect structure with short range order. The cubic structure thus might consist on an average level on small Brownmillerite orthorhombic type domains with random orientation. The aim of the proposed experiment is thus to verify via a PDF analysis that a local oxygen defect ordering exists for the average cubic Sr2ScGaO5 phase. The results are also important to understand the underlying activation energy and diffusion pathways of the oxygen atoms by specific lattice dynamics in these systems

Local oxygen ordering in a new oxygen deficient perovskite, explored by atomic pair distribution function analysis

Oxygen ion conductors operating at moderate temperatures are materials of major interest for a series of application in the area of solid state ionics (Solid Oxide Fuel Cells (SOFC), batteries, electrodes, sensors, catalysts). Still today high operating temperatures above 800°C are generally required to obtain reasonable efficiency, limiting their application. In the search for improved oxygen ion conductors, oxygen deficient perovskite structures play an important role. In particular oxides with brownmillerite type structure ($A_2BB'O_5$), have attracted much attention, as they show oxygen ion mobility down to ambient temperature [1]. This unusual low-temperature oxygen mobility has been evidenced to rely on a phonon assisted diffusion mechanism, essentially based on large, dynamically activated displacements of the apical oxygen atoms of the BO_6 octahedra [2]. Oxygen diffusion at room temperature thus makes this class of compounds attractive for many technologically important applications in the field of solid state electrolytes and more specifically for membranes and pure electrolytes.
Sr_2ScGaO_5 is a special case as it shows pure oxygen ion conductivity related to the d^0/d^{10} electronic configuration of the B metals. Depending on the synthesis route, it adapts two polymorphs: the orthorhombic brownmillerite or an oxygen deficient Perovskite structure. Once synthesized, both phases are surprisingly kinetically stable up to 1400°C, rendering them as a model system to study oxygen diffusion mechanisms as a f(T). From $^{18}O/^{16}O$ oxygen isotope exchange reactions we proved that free oxygen mobility sets in at T = 530°C for both polymorphs.
Recently, we reported on Sr_2ScGaO_5 as a new brownmillerite phase, showing B-cation ordering of Sc^{3+} and Ga^{3+} on octahedral and tetrahedral sites respectively, adopting the *I2mb* space-group at ambient temperature [3]. We have extensively investigated this brownmillerite system by X-ray and neutron diffraction, inelastic neutron scattering, $^{17}O/^{45}Sr/^{71}Ga$-NMR, $^{18}O/^{16}O$-isotope exchange reactions, Raman spectroscopy and DFT lattice dynamical calculations with the aim to better understand the underlying diffusion mechanism, which we evidenced to be phonon assisted [3,6]. Neutron structure analysis indicates an order-disorder phase transition, establishing a dynamically disorder of the $(GaO_4)_\infty$-tetrahedral chains in the Brownmillerite phase above 500°C (order/disorder transition from *I2mb* to *Imma)*. DFT based lattice dynamical studies using Molecular Dynamics allowed also to correlate the set in of oxygen diffusion together with the switching dynamics of the $(GaO_4)_\infty$-tetrahedral chains above the order disorder phase transition.

Brownmillerite Sr_2ScGaO_5 shows a phase transition to the cubic perovskite structure completed at 1500°C, associated with improved oxygen ion conduction, probably related to the 3D perovskite framework and associated diffusion pathways [4]. Ionic conductivity investigated by impedance spectroscopy was found to be 10^{-4} S/cm at 600°C, and the activation energy of 0.67 eV for the cubic Sr_2ScGaO_5 is only half the value as reported for its brownmillerite counterpart, rendering this compound a good candidate for intermediate temperature electrolyte [5]. Structural studies, by powder and single crystal diffraction, showed large anisotropic disk shaped oxygen displacement factors in the cubic oxygen deficient Sr_2ScGaO_5 perovskite. This defect structure is, however, more complex as from ^{17}O-NMR and Raman studies; we evidenced some local ordering at ambient temperature.

The aim of the proposed experiment was to verify via a PDF analysis that a local oxygen defect ordering exists for the average cubic $Sr_2(ScGa)O_5$ phase. To this end we measured oxygen deficient Sr_2ScGaO_5 with cubic and orthorhombic structure, at different temperatures, from RT up to 800°C,

and also during cooling to check the reversibility of the process. Data have been collected on D4c with a wavelength of 0.5 Å, guarantying a neutron flux as high as 2.3×10^{7} $ncm^{-2}s^{-1}$ at a relatively high Q_{max}~23.5 $Å^{-1}$, which allows a robust Fourier Transform (FT) of the diffraction data, providing a PDF resolution of ~0.25 Å in *r*-space. The reduction and merging of the neutron data to obtain the pair distribution function, G(r), was done using the PDFgetN.

Results show that the cubic structure consists on an average level on small Brownmillerite type domains, as shown in figure 1. Thus, Sr_2ScGaO_5 is not comparable to the idealized perovskite framework, but shows an anionic sub-lattice with a complex distortion of the oxygen positions. Data refinements are still in progress for all the measured temperatures.

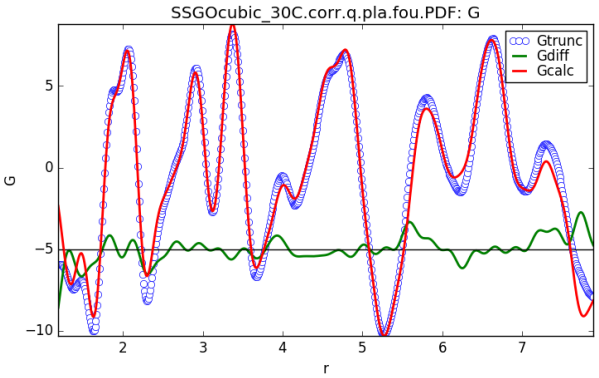

Figure 1: The explored -*r* region of the PDF of Sr_2ScGaO_5 and the fit using the orthorhombic *Imma* structure as a model.

References

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