Experimental report

27/09/2024

Proposal:	**5-23-793**	**Council:**	4/2023
Title:	Neutron diffraction study of the mixed oxide ion and proton conductorSr3-xCaxV2O8		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:
$Sr_{2.85}Ca_{0.15}V_2O_8$
$Sr_3V_2O_8$
$Sr_{2.8}Ca_{0.2}V_2O_8$
$Sr_{2.9}Ca_{0.1}V_2O_8$

Instrument	Requested days	Allocated days	From	To
D2B	3	3	01/09/2023	04/09/2023

Abstract:

$Sr_3V_2O_8$ crystallises in the palmierite structure and is the first compound with this structure to exhibit significant oxide ion and proton conductivity. It is important to investigate new materials for application in next generation hydrogen fuel cells. In order to further investigate the mechanism of ionic conductivity in palmierites and to tune the conductivity, the series $Sr_{3-x}Ca_xV_2O_8$ has been synthesised (x = 0.00, 0.10, 0.15, 0.20). Impedance spectroscopy results show an enhancement of both the oxide ion and proton conductivity by almost an order of magnitude upon increasing x from 0 - 0.2. In order to determine the exact position of the oxygen atoms in of $Sr_{3-x}Ca_xV_2O_8$, and to reveal the presence (or absence) of any thermal rearrangement of the oxygen sites, we propose to perform a neutron diffraction study on the D2B diffractometer at both 25 °C and 600°C. The palmierite structure is a new crystal system to display oxide ion and proton conductivity. This significant study will give us more important information for understanding the relationship behind the ionic conductivity and the structural disorder in palmierites.

Experiment 5-23-793

Neutron diffraction study of the mixed oxide ion and proton conductor $Sr_{3-x}Ca_xV_2O_8$

Oxide ion conductors are technologically important materials with application as electrolytes in Solid Oxide Fuel Cells (SOFCs). A high operating temperature is generally required to achieve the high oxide conductivity required for devices ($\sigma > 10^{-2}$ S/cm) which is typically 700 °C for yttria stabilised zirconia (YSZ). [1] In order to reduce system costs it is highly desirable to find new materials which exhibit significant ionic conductivity at lower temperatures (450-600 °C). [2] We have recently discovered a new oxide ion and proton conductor, $Sr_3V_2O_8$ [3]. $Sr_3V_2O_8$ crystallises in the palmierite structure which contains isolated tetrahedra (Fig. 1). Impedance spectroscopy results show that $Sr_3V_2O_8$presents prevalent ionic conduction, with a large protonic component under humidified air ($t_H \sim 0.6-0.8$) and high protonic mobility. In particular, the total proton conductivity of $Sr_3V_2O_8$ is 2.0×10^{-5} S cm^{-1} at 800 °C, which is competitive with the best proton conductors constituted by isolated tetrahedral units [3]. In order to further investigate the mechanism of ionic conductivity in palmierites and to tune the conductivity, the series $Sr_{3-x}Ca_xV_2O_8$ has been synthesised (x = 0.00, 0.10, 0.15, 0.20).

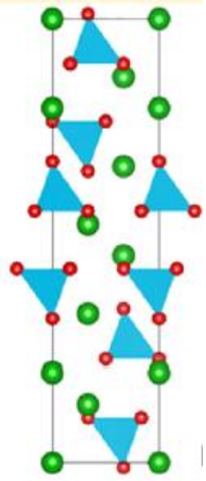

Figure 1 Average crystal structure of the palmierite $Sr_{3-x}Ca_xV_2O_8$. Colours: green spheres, Ba; blue, V tetrahedra; red spheres, O.

Impedance spectroscopy results show that upon increasing x in the series $Sr_{3-x}Ca_xV_2O_8$ there is a significant increase in both the oxide ion and proton conductivity. There is nearly an order of magnitude increase in both the total oxide ion and proton conductivity as x increases from 0 – 0.2. In order to gain further understanding of why the ionic conductivity is enhanced with Ca doping, a neutron diffraction experiment was performed on D2B at both 25 °C and 600°C on $Sr_{3-x}Ca_xV_2O_8$ (x = 0 – 0.2).

As previously reported [3], $Sr_3V_2O_8$ crystallises in the $R\bar{3}m$ space group at both temperatures as confirmed by Rietveld analysis. Initial refinements with the $Sr_{2.95}Ca_{0.05}V_2O_8$ 20 °C data were performed with the $R\bar{3}m$ space group as an excellent fit to this model was obtained from the XRD data. However, a poor fit to the $R\bar{3}m$ space group was observed from the neutron diffraction data. There is a clear intensity mismatch between the model and the data for certain peaks such as 72.65 and 77.15 ° 2θ (Figure 2). Subsequent refinements were attempted with the $C2/c$ space group as it is a subgroup of $R\bar{3}m$. Recent research has also shown that on cooling $Sr_3V_2O_8$ to 10 K, it undergoes a change in crystal symmetry from $R\bar{3}m$ to $C2/c$ at 104 K.

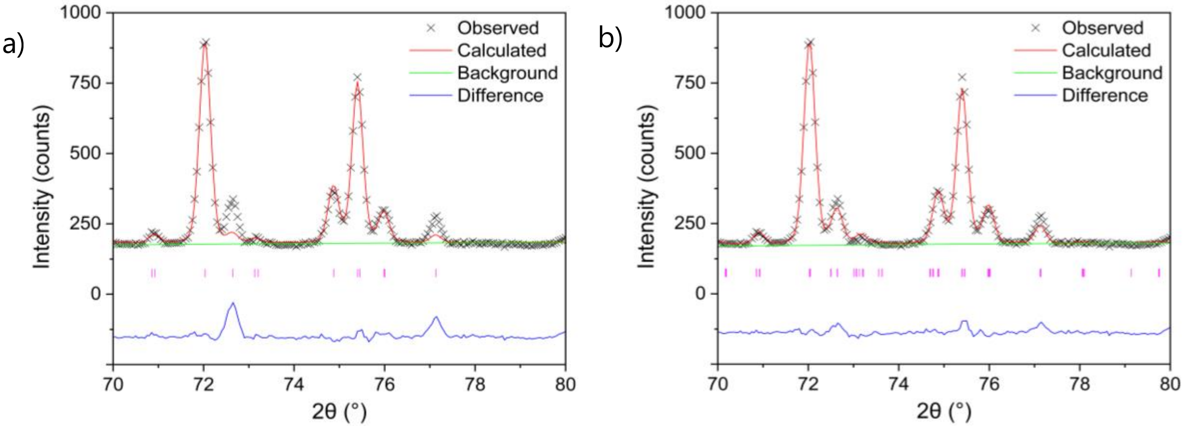

Figure 2. Rietveld fits to a) the $R\bar{3}m$ crystallographic model, and b) the $C2/c$ crystallographic model, to the neutron diffraction data of $Sr_{2.95}Ca_{0.05}V_2O_8$ at 20 °C between 70-80 2θ. The black crosses illustrate the observed data, the red line illustrates the Rietveld fit and the green line illustrates the background function. The difference between the observed data and the Rietveld fit is shown by the blue line and the reflection positions are indicated by the pink vertical lines.

When fitting the data to the $C2/c$ crystallographic model, the 'goodness of fit' parameters for $Sr_{2.95}Ca_{0.05}V_2O_8$ decrease from a χ^2, R_p and R_{wp} of 7.09, 3.54 % and 5.47 % for the $R\bar{3}m$ crystallographic model to 4.11, 2.79 % and 3.85 % respectively, and an excellent fit to the $C2/c$ model was observed.

At 600 °C, an excellent fit to the $R\bar{3}m$ palmierite structure is observed for all x (Figure 7) so that upon heating, the $Sr_{3-x}Ca_xV_2O_8$ phases undergo a crystallographic phase transition from space group $C2/c$ to $R\bar{3}m$. Further analysis of the data show that there are shorter O2-O2 distances with increased Ca^{2+} doping, allowing for easier hopping of the oxide ions along this pathway and enhancement of the 3D oxide ion pathways. This could potentially give rise to the observed increase in the overall ionic conductivity.

References

1) O. H. Kwon and G. M. Choi, Solid State Ionics **177**, 3057 (2006).

2) E. D. Wachsman and K. T. Lee, *Science* **334**, 935 (2011).

3) S. Fop, J. A. Dawson, D. N. Tawse, M. G. Skellern, J. M. S. Skakle, and A. C. Mclaughlin, *Chem. Mater.* **34**, 8190 (2022).