Experimental report

27/09/2024

Proposal: **5-24-696** **Council:** 10/2022

Title: High temperature structural study of the novel oxide ion conductor Ba3Ti0.9Mo1.1O8.1

Research area: Chemistry

This proposal is a new proposal

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Samples: Ba7Nb4MoO20
Ba3Ti0.9Mo1.1O8.1

Instrument	Requested days	Allocated days	From	To
D2B	3	3	31/03/2023	03/04/2023

Abstract:

New materials, which exhibit high ionic conductivity (¿ 10 mS cm-1) at intermediate temperature (< 600 °C), are needed for the next generation of ceramic hydrogen fuel cells. Such fuel cells will be more cost-effective, with greater longevity offering a key alternative to fossil fuels. We have reported significant oxide ion conductivity in a family of cation deficient disordered hexagonal perovskite derivatives, Ba3NbMO8.5 (M = Mo, W) and Ba7Nb4MoO20. We have now discovered a new oxide ion conductor Ba3Ti0.9Mo1.1O8.1 which has the highest oxide ion conductivity to date. Previous results have shown that hexagonal perovskite derivatives undergo structural rearrangements upon heating which results in an enhancement of the oxide ion conductivity.

In order to determine the exact position of the extra oxygen atoms in of Ba3Ti0.9Mo1.1O8.1, and to reveal the presence (or absence) of any thermal rearrangement of the oxygen sites, we propose to perform a variable temperature neutron diffraction study on the D2B diffractometer.

Experiment 5-24-696

High temperature structural study of the novel oxide ion conductor $Ba_3Ti_{0.9}Mo_{1.1}O_{8.1}$

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 conductor, in the hexagonal perovskite derivative $Ba_3Ti_{0.9}Mo_{1.1}O_{8.1}$, which has a higher conductivity to YSZ. Impedance spectroscopy results show that $Ba_3Ti_{0.9}Mo_{1.1}O_{8.1}$ is also an oxide ion conductor, with a very high bulk oxide ion conductivity of 0.008 S cm^{-1} at 550 °C. This is significantly higher than the oxide ion conductivity of both $Ba_3NbMoO_{8.5}$ [3] and $Ba_7Nb_4MoO_{20}$ [4]. This is exceptional and in order to realise structure property relationships in hexagonal perovskite derivatives we have performed a full structural elucidation of $Ba_3Ti_{0.9}Mo_{1.1}O_{8.1}$ using neutron diffraction.

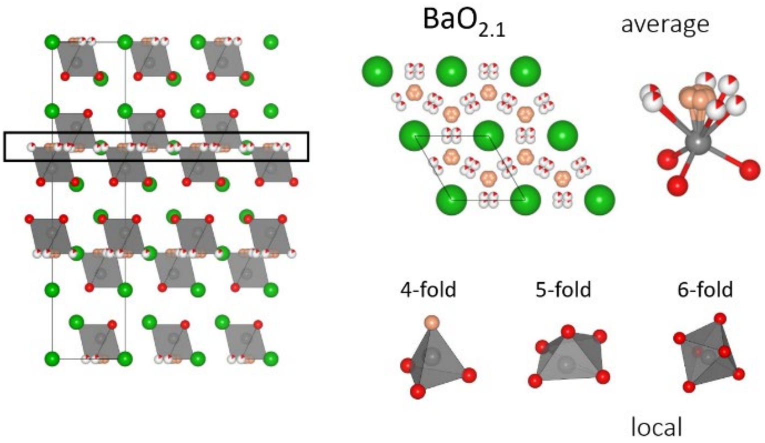

Figure 1 Average crystal structure of $Ba_3Ti_{0.9}Mo_{1.1}O_{8.1}$. Colours: green spheres, Ba; grey, V tetrahedra; red spheres, O; white shaded spheres interstitial O.

A variable temperature neutron diffraction study of the novel oxide ion conductor $Ba_3Ti_{0.9}Mo_{1.1}O_{8.1}$ has been performed on D2B between 25 °C and 700 °C. An good fit was obtained at room temperature with the structural model of Ba_3TiMoO_8 suggested by Mössner and Kemmler-Sack [5] (Figure 2). A Fourier difference map was calculated to determine the position of the additional oxygen. The Fourier difference map displayed two distinct areas of missing scattering density. The first area surrounds the Ba1 position suggesting that this site is highly disordered along the *ab* plane and the atomic displacement parameters for Ba1 should be modelled anisotropically. The second area of leftover scattering density corresponds to the additional oxygen and is located at interstitial sites close to the apical O1 position. The missing scattering density around O1 site could be assigned the atomic position of (0.544, 0.623, 0.007), split Wyckoff site 36*i*. Thus, it was chosen as the starting position for O3 site and added to the model and an excellent Rietveld fit was obtained (Figure 2).

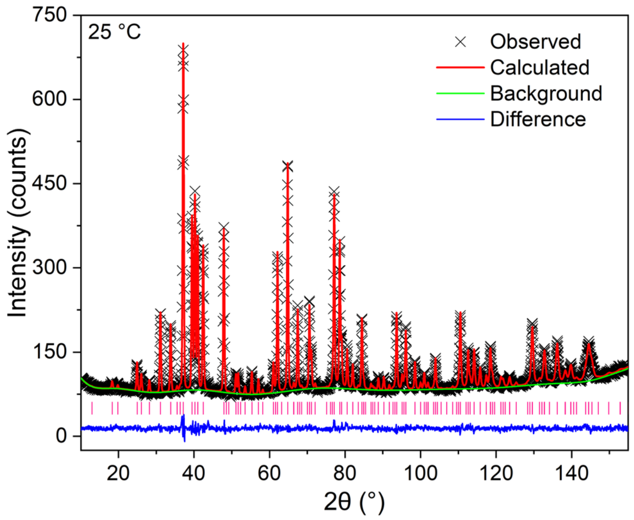

Figure 2. Rietveld refinement fit to the *R*-3*m* model from variable temperature neutron diffraction data of $Ba_3Ti_{0.9}Mo_{1.1}O_{8.1}$. Black dots indicate the observed data, the red line the Rietveld fit, the blue line the difference between the observed and the calculated patterns, the green line the background function and the pink bars are the reflection positions.

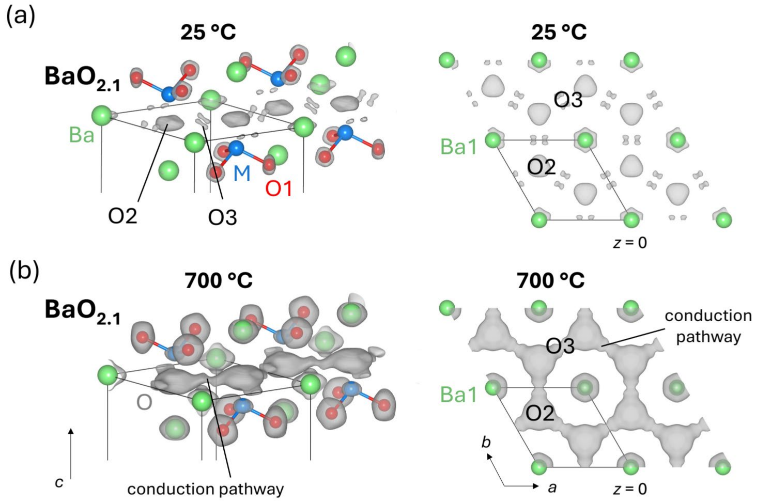

Figure 3 Oxide ion disorder and conduction pathways in $Ba_3Ti_{0.9}Mo_{1.1}O_{8.1}$. Nuclear scattering density distribution at 25 °C (a) and 700 °C (b) reconstructed via maximum entropy (MEM) analysis. Connectivity between the oxygen O2 and O3 isosurfaces at 700 C identifies long-range oxide ion conduction pathways along the ab plane. Grey isosurfaces are drawn at 1 fm $Å^{-3}$. The structural model is superimposed to the nuclear scattering density; O2 and O3 atoms are omitted for clarity.

There was no change in the crystal structure upon heating and a smooth variation of the cell parameters and bond lengths/angles was observed. MEM analysis of the neutron diffraction data collected at 700 °C shows connected distributions of oxide ions, a direct evidence of oxide ion diffusion on O2-O3 pathways along the $BaO_{2.1}$ layer. The static oxygen disorder becomes dynamic at high temperatures, thus creating low energy conduction pathways with an interstitialcy mechanism (Figure 3).

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 et al, *J. Am. Chem. Soc.*, 2016, **138**, 16764; K. S. McCombie et al, *J. Mater. Chem. A*, 2018, **6**, 5290.
4) S. Fop *et. al. Nature Materials* **19**, 752 (2020).
5) B. Moessner and S. Kemmler-Sack, *J. Less. Common. Metals* **114**, 333 (1985).