Experimental report

16/05/2016

Proposal:	**5-21-1086**	**Council:**	10/2014
Title:	Characterisation of the cation ordering, oxygen vacancy distribution and proton sites in hexagonal and cubic BaTi1-xScxO3-d		
Research area:	Materials		

This proposal is a new proposal

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Samples: BaTi1-xScxO3-d (x=0.10)
BaTi1-xScxO3-d (x = 0.70)

Instrument	Requested days	Allocated days	From	To
D2B	4	4	11/05/2015	15/05/2015

Abstract:

Sc-doped BaTiO3 shows promising proton conducting characteristics. This system undergoes a structural phase transition from a cubic perovskite to a 6H perovskite structure as the Sc doping decreases. The hydration behaviour within the series is indicative of filling oxide ion vacancies and we find that the proton conductivity is significantly lower in the hexagonal structure. Neutron powder diffraction will be used to study the cation ordering and oxygen ion vacancy distributions in the host materials as a function of Sc doping to investigate the structural driving force for the phase transition. Additionally, the proton positions in hydrated materials will be determined in order to understand the difference in the observed conductivity properties.

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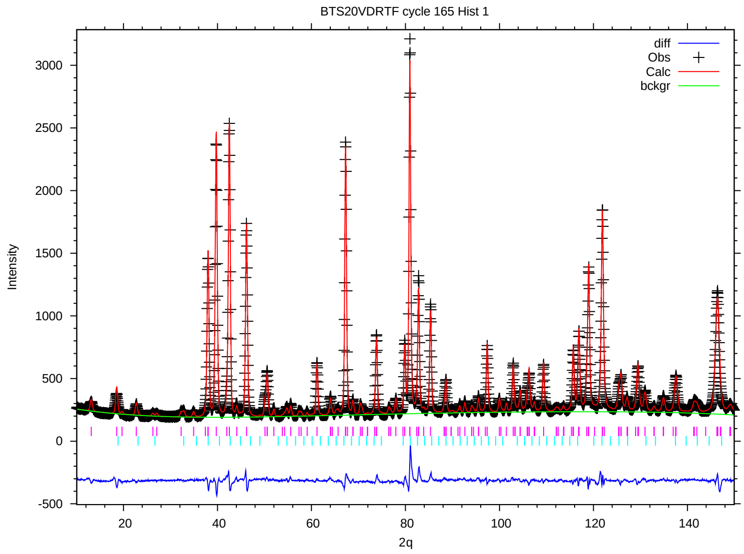
The neutron diffraction experiment was designed in order to complement previous X-ray studies, in order to provide structural information about cation ordering, vacancy ordering and hydrogen positions in the series $BaTi_{1-x}Sc_xO_{3-\delta}$. For low values of x (< 0.33) the structure is hexagonal 6H, whereas above this value of x a cubic structure is observed in the as-prepared material. Two samples from the series, $BaTi_{0.8}Sc_{0.2}O_{3-\delta}$ (BTS20) and $BaTi_{0.3}Sc_{0.7}O_{3-\delta}$ (BTS70), exhibiting the two structures of interest, were prepared and subsequently treated to produce vacuum dried, hydrated (H_2O) and deuterated (D_2O) samples, in each case from the same batch of starting material. The diffractometer D2B was used to collect room temperature and 5 K data at a wavelength of 1.594 Å. The resolution offered by the instrument D2B was needed in order to investigate whether any small monoclinic or triclinic distortion was present in the 6H structure, previously reported within this structure type[1].

All data sets were successfully collected at both temperatures, giving 12 high quality diffraction patterns for analysis. Both room temperature and 5K data were collected to ensure no structural phase transitions occurred as location of the hydrogen/deuteron position was performed with the low T data, where thermal displacement could be minimised. Initial Rietveld fits of the vacuum dried samples at RT and 5K for BTS20 are illustrated in Figure 1 below, each showing the absence of any structural phase transition. In the case of BTS20 a small impurity was observed, Sc_2O_3, that could also be modelled.



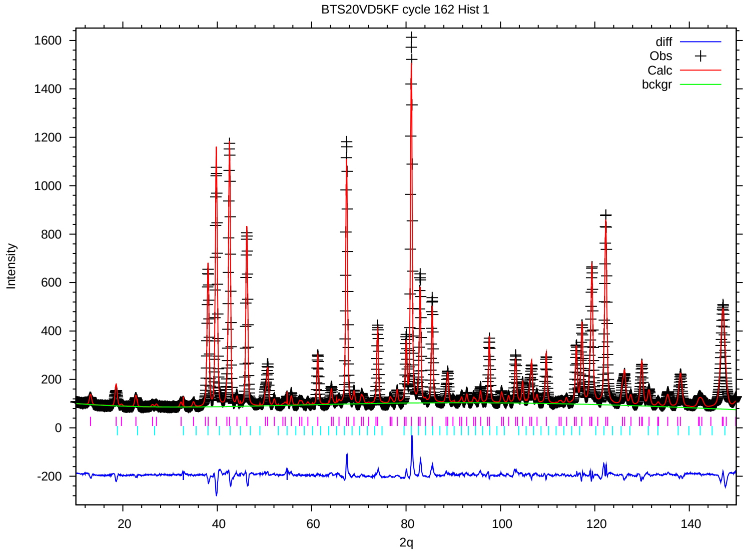


Figure 1 Rietveld fit for BTS20 vacuum dried samples, at room temperature (top) and 5K (bottom), showing no structural phase transitions occurred on cooling

Data Analysis Motivation and Results

Neutron powder diffraction data were used to characterise the phases and probe the following structural features:

- Cation ordering of Sc and Ti, due their high scattering length contrast (b_{Sc} = 12.29 fm, and b_{Ti} = -3.438 fm)
- Oxygen vacancy distribution as a function of the Sc content/ structure type
- Preferred proton site, by exploiting the scattering contrast of H and D (b_H = -3.742 fm, and b_D = 6.674 fm).

Neutrons were chosen due to their sensitivity to adjacent elements in the periodic table, their sensitivity to light elements in the presence of heavy elements and the great sensitivity to hydrogen/deuterium. Our previous X-ray diffraction data was unable to answer these questions satisfactorily[2,3].

BTS20: Hexagonal 6H type

Rietveld refinement of the 5 K and RT data for the vacuum dried samples (as illustrated in Figure 1) showed clear preference of the Sc for non face-sharing position within the 6H structure. The oxygen vacancy was found to sit in the equatorial plane of the face-sharing TiO_6 polyhedra, as found in the 6H structures for oxygen deficient $BaTiO_3$[4]. We can also postulate that the structural driving force for the hexagonal:cubic phase transition as x increases is due to the strong preference of Sc for the non face-sharing site. Above x=0.33 the Sc must start to populate the face-sharing site and our synthetic results start to show growth of the cubic phase from this point in the phase diagram.

To locate the hydrogen (deuteron) position required a careful approach, as the H/D content is very low (only *ca.* 3.5% of the atomic species per formula unit are protons/deuterons). Figure 2 shows the effect of the presence of H/D in the structure on the low angle peaks of the 6H structure type. The strong positive/negative scattering length contrast significantly changes the intensities of these peaks. We used a combination of Fourier mapping and chemical sense, coupled with some prediction from DFT calculations, to locate the H/D position. We found a chemically sensible position that improved the fits but were unable to perform a free refinement of the position and occupancy, due to the low H/D content. However, the results clearly show that the H/D position is associated with the equatorial oxygen position in the face-sharing TiO_6 polyhedra.

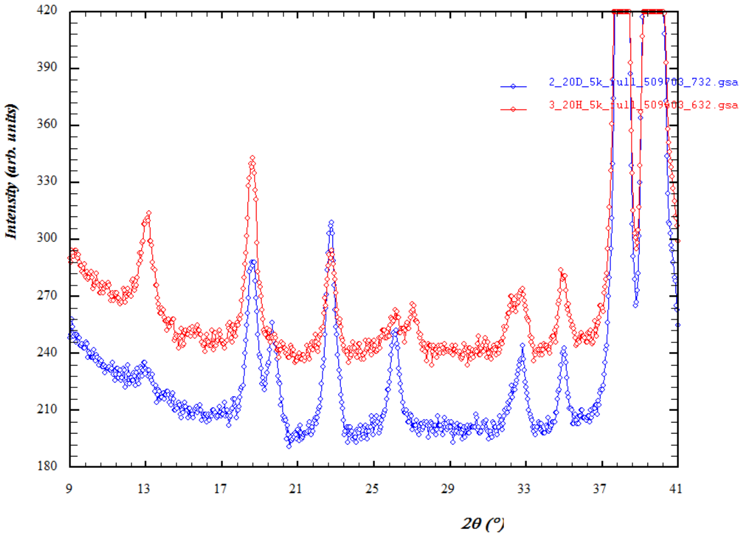


Figure 2 Expansion of the low angle raw data for the hydrated and deuterated BTS20, showing the impact of the scattering length contrast between H and D on the observed diffraction data.

BTS70: Cubic type

Rietveld refinement of the 5 K and RT data for the vacuum dried samples showed no sign of a superstructure that would be indicative of Sc/Ti ordering. The refinement gave the simple cubic perovskite structure, with *a* = 4.15 Å, in the *Pm-3m* space group, also leading to a single oxygen position that was found to exhibit the expected level of vacancies. However, the background was found to be structured, indicative of some local order/disorder, as illustrated in Figure 3. Further experiments using the PDF data collection and analysis procedure will be required to investigate this. On hydration / deuteration these vacancies were found to be filled and a similar approach to the BTS20 sample located a chemically sensible H/D position.

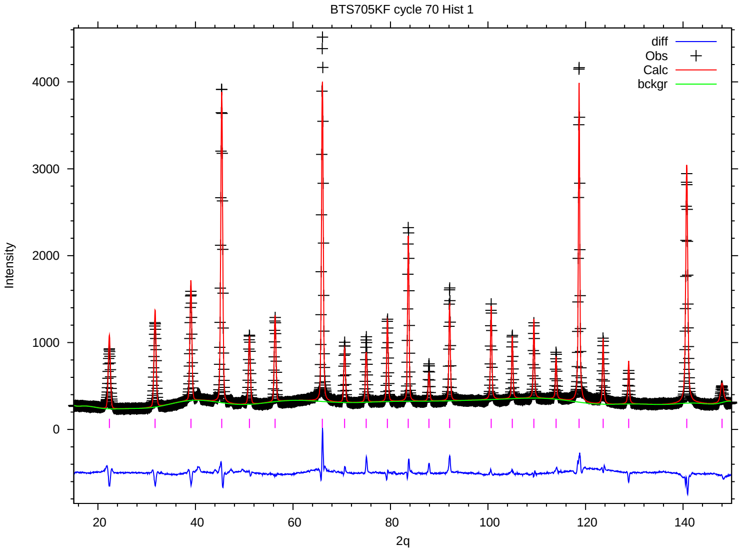


Figure3 Rietveld fit for BTS70 vacuum dried sample, at 5K, showing no peaks indicative of superstructure that would be expected for Sc/Ti ordering or vacancy ordering.

Summary/Conclusions

We consider this experiment a complete success. Cation ordering was observed in the 6H structure type along with distinct oxygen vacancy ordering. On hydration (deuteration) the oxygen vacancy becomes filled and a hydrogen (deuteron) location could be identified within the structure. For the cubic structure, no cation ordering was observed, with only the simple small cubic unit cell with statistical occupancy by the Sc/Ti atoms. This gives a single oxygen position that was seen to show vacancies in the as-prepared material that were filled upon hydration (deuteration). Once again a hydrogen (deuteron) location could be identified within the structure. Some further work to look at local order will be required for the cubic structure type.

The implication of this work is that a structural origin for the differences in the proton conductivity of the two structures has been identified; BTS20 is a poorer proton conductor due to the ordering of the proton onto the site in the equatorial plane of the face-sharing TiO_6. This leads to no obvious mechanism for the proton to hop from one oxygen type to another within the structure without significant input of energy (heat). In BTS70, the structure is inherently disordered, allowing the proton to migrate through the structure much more easily, which is observed in conductivity measurements. Our results are also supported by DFT calculations by our Norwegian collaborators.

This results of this work are about to be submitted for publication and have also been accepted for an Oral contribution at EPDIC-15 in Bari, a poster presentation at ECM-30 in Basel and are under review for an oral contribution at SSPC-18 in Oslo.

References

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