Experimental report

27/10/2022

Proposal: **5-25-273** **Council:** 4/2019

Title: In Situ Study of BaTi(O/H)3 nitridation and 1H/2D isotope exchange

Research area: Chemistry

This proposal is a new proposal

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Samples:
$BaTiO_{2.5}H_{0.5}$
$BaTiO_{2.5}D_{0.5}$

Instrument	Requested days	Allocated days	From	To
D20	3	4	31/05/2021	04/06/2021

Abstract:

In the proposed experiment, we are interested in investigating the formation mechanism of $BaTiO_{2.4}N_{0.4}$ structure from the $BaTi(O/H)_3$ precursor at moderate temperatures (ca. 500°C), in situ during ammonolysis. The reaction will be carried out in a specially designed reaction chamber which will be operated at different temperatures and under different NH_3 flow rates. The aim of the study is not only to follow the formation of $BaTiO_{2.4}N_{0.4}$ but also to determine the oxygen-nitrogen exchange kinetics as a function of T and NH_3 gas flow rate. We are further interested if any ordered distribution of the oxygen/nitrogen atoms during the substitution reaction can be evidenced. Furthermore, we will study the 1H/2D isotope exchange on a deuterated sample $BaTiO_{2.5}D_{0.5}$ as a function of the temperature and time, in a solid-gas reaction, using NH_3 gas flow.

In Situ Study of BaTi(O/H)3 nitridation and 1H/2D isotope exchange

Experimental report: ILL D20 (EXP: 5-25-273)

Ionic conductivity in solid oxides is gaining more traction for the past few years due to the raising demand for improving fuel cells, batteries, and catalysts. In transition metal oxides, the oxygen mobility by incorporation of oxygen non-stoichiometry was extensively studied with the aim of achieving low temperature ionic conductivity[1]. Which established, that understanding the ion mobility mechanisms in these non-stoichiometric oxides is the key for engineering novel materials in the fields of Ionic conductors. This field took an interesting turn when Y. Kobayashi et al[2] reported their studies on $BaTiO_{3-x}H_x$ oxyhydride. Reducing an oxide with metal hydrides such as CaH_2 known to result in new oxygen deficient compounds that are otherwise hard to obtain with conventional reduction methods. This is possible because, reduction with CaH_2 believed to happen by removing the Oxygen atoms from the oxide lattice in a topotactic way at low temperatures [3]. However, when the same CaH_2 was used to reduce certain materials like $BaTiO_3$ it was observed that this is not only Oxygen removal process that is happening but also simultaneously involve Hydride (H^-) incorporation. It is common for hydrogen to bond with oxygen atoms to form hydroxide (OH^-), but it is a rarity to see the presence of negatively charged hydride (H^-) in a lattice containing electronegative oxygen atoms. With Hydride (H^-) [1.34Å] ionic size being roughly close to Oxide (O^{2-}) [1.38Å], the lattice of $BaTiO_{3-x}H_x$ seems stable. Quite interestingly, H^- becomes highly mobile around 400˚C and exchanges with other anions such as D^-, N^{3-}, F^-, and even OH^- [4], which makes the chemistry of $BaTiO_{3-x}H_x$ much richer with the scope of novel applications such as formation of mixed anionic materials and as catalyst for ammonia synthesis [5]. This is a complex system for any structural study as Hydrogen in the lattice goes undetectable by the X-rays. In addition to this, for understanding the role of H^- in any applications of $BaTiO_{3-x}H_x$ it becomes crucial to understand the dynamics of this mobile hydrogen in $BaTiO_{3-x}$ lattice.

We applied for an in-situ experimental slot at ILL D20 to explore deeper the structure of $BaTiO_{3-x}H_x$ oxyhydride as well as to study the role of H^- and its mobility during H^-/D^- ion exchange in the lattice of $BaTiO_{3-x}$. While X-rays are not sensitive to lighter elements like hydrogen owing to its electromagnetic nature, neutrons as mass waves are very sensitive to the presence of hydrogen nuclei. The neutron interaction with the hydrogen present in the material should lead to two contributions; a coherently scattered part should contribute to the diffraction pattern profile owing to material crystallinity and an in-coherently scattered part leading to the background of the same pattern. The neutron incoherent cross section of Hydrogen is so high (80.27 barn) leading to a huge unwanted background in most of the cases. But this is an ideal case for us, not only we were able to understand the presence of Hydrogen in the lattice of our material, in addition just by the looking at the level of the background, it becomes evident to say when Hydrogen enters or leaves our system.

With this scientific idea, we successfully performed three in-situ experiments in D20 ILL during our experimental period:

Initial measurements were done on all the $BaTiO_{3-x}H_x$ samples using neutron beam of wavelength $\lambda = 1.12$ Å, to determine the hydrogen content and the values of each sample were given below during the discussion of each in situ experiment. Normally, the hydrogen content depend upon the reduction conditions, with longer reduction resulting in high H^- in sample, but we ended up with different H^- containing samples even when followed the exact same conditions. For the in-situ experiments, neutron beam of wavelength 1.54 Å was used for getting higher neutron flux.

During the first in-situ experiment, the sample of $BaTiO_{2.61}H_{0.39}$ was heated in the flow of 5% D_2/He gas up to 400˚C where the H^- from the sample starts to exchange with D^- from the gas as reported by the literature [2]. If H^- is leaving from the sample (associated by D^- entering), it should be seen as decreased background. Once we confirmed the sample is devoid of all H^-, the gas flow was switched to 5% H_2/He and stayed at 400˚C for the H^-

(from the gas) to re-exchange with D^- in the sample. Likewise associated with increase in background of neutron diffraction pattern. This experiment confirmed the exchanging mechanism of H^- & D^- in the lattice of $BaTiO_{3-x}H_x$ but some anomalies were observed in the expected exchange mechanism due to the presence of surface hydrogen in the sample.

Thus, for the second in-situ experiment, we tried to eliminate the surface hydrogen from the sample. As we are always using the nanoparticles (<100nm) of $BaTiO_{3-x}H_x$ oxyhydride samples, the presence of surface hydrogen could influence the ion exchanging dynamics. To remove any traces of surface hydrogen on the surface, firstly the gas of ND_3 (with 5% D_2/He as carrier gas) was flowed through the $BaTiO_{2.66}H_{0.33}$ sample. By using the high reactivity of ND_3 we can easily remove all the surface hydrogen and by using deuterated ND_3 we won't be inserting any addition H into the sample and this was clearly observed from the lowered background in fig 1. Then the surface hydrogen cleared sample was heating up to 800˚C in 5% H_2/He atmosphere and then cooled down to room temperature. This experiment showed us that at higher temperatures, $BaTiO_{2.66}H_{0.33}$ irreversibly releases hydrogen (decomposition) and becomes $BaTiO_3$.

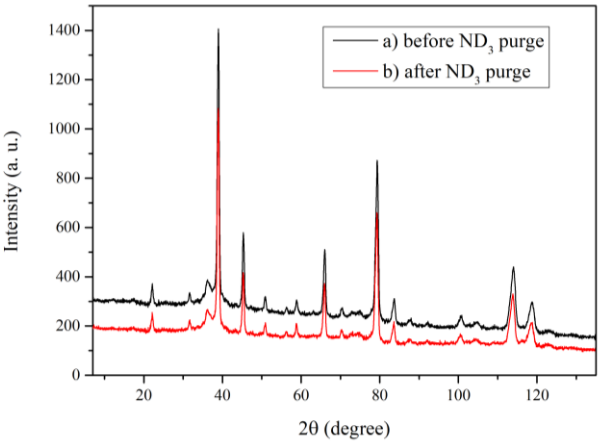

Figure 1. Neutron diffraction patterns obtained at different stages of the third in-situ experiment (λ =1.54Å). a) Neutron diffraction pattern of the $BaTiO_{2.66}H_{0.33}$ measured at room temperature in the beginning of the experiment showing background with respect to its H amount in the sample, b) Neutron diffraction pattern of the same sample after ND_3 gas was flowed through it, showing a dip in the background due to the removal of surface H by ND_3.

Third in-situ experiment similar to first experiment (with the addition of ND_3 flow) is to study H-/D- exchange dynamics. Through the $BaTiO_{2.66}H_{0.33}$ sample ND_3 gas was flowed together with 5%D_2/He and the system was heated up to the exchange temperature of 380˚C, ND_3 used together with 5% D_2/He to avoid the presence of surface hydrogen though out the process. After staying at 380˚C for some time, the gas flow changed to 5% H_2/He and the measurement continued at 380˚C until we confirm there is no change in the background level then the sample cooled to room temperature. This experiment was carried out with the hopes of seeing bulk H_x contribution to the ion exchange dynamics of $BaTiO_{2.66}H_{0.33}$ oxyhydride, but the results showed us a possibility of N^{3-} entering the sample to make it $BaTiO_{2.66}H_xN_y$ there by blocking the ion exchange mechanism of $BaTiO_{2.66}H_{0.33}$.

Further analysis is underway, the results will soon be published in the form of articles, and this work will become a part of Chavana Hareesh PhD thesis.

References:

[1] A. Maity et al., *J. Phys. D: Appl. Phys.* 48 (**2015**).
[2] Y. Kobayashi et al., *Nature Mater.* 11, 507 (**2012**).
[3] Y. Kobayashi et al., *Journal of Solid State Chemistry*. 207 (**2013**) 190–193.
[4] N. Masuda et al., *J. Am. Chem. Soc*. **2015**, 137, 15315−15321.
[5] Y. Tang et al., *Adv. Energy Mater*. **2018**, 8, 1800800.