Experimental report

03/10/2022

Proposal:	**7-01-550**	**Council:**	10/2020
Title:	Local structure and vibrational properties of strontium vanadium oxyhydrides		
Research area:	Materials		

This proposal is a new proposal

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Samples: AtiO3-xHx (A=Ba; Sr, Ca)

Instrument	Requested days	Allocated days	From	To
IN1 LAG	3	2	01/10/2021	03/10/2021

Abstract:

This proposal concerns the investigation of the local structure and vibrational dynamics of hydride-ions in a series of strontium vanadium oxide-hydrides by inelastic neutron scattering. The series of samples are featured by different dimensionalities in the hydride-ion sublattice, ranging from ordered rows, to planes, and finally to a disordered 3D anion lattice. The aim of this study is thus to investigate how the local coordination and vibrational dynamics of the hydride-ions change as a function of dimensionality, and possibly how it is influenced by the magnetism. Besides, being of considerable fundamental interest, understanding the nature of local structure and dynamics of the hydride ions in these materials is of great importance for developing efficient synthesis routes that allow the development of new oxyhydrides with tailored properties.

Experimental report for experiment 7-01-550[1]

1 Scientific background and experimental details

Perovskite type oxyhydrides, $ATiO_{3-x}H_x$, A = Ca, Sr, and Ba, with $x < 0.6$ [1], are a novel class of hydride ion (H^-) conducting materials that may find diverse applications in, *e.g.,* the fields of catalysis, topochemical synthesis, and electrochemistry, but fundamental questions surrounding the local structure and dynamics in these materials remain to be answered. With this experiment, we wanted to investigate the nature of the vibrational dynamics of $ATiO_{3-x}H_x$ type oxyhydrides, how it depends on A and x, by inelastic neutron scattering (INS) experiments.

The INS experiment was performed on IN1 (Lagrange), setup with the Si(111), Si(311) and Cu(220) monochromators, respectively. The pyrolytic graphite crystals analyzers, set to reflect neutrons with the fixed average energy of 4.5 meV, allowed us to scan energy transfers in the range $0 - 500$ meV. This setting yielded an instrumental resolution of ≈ 0.8 meV with the Si crystals and of $\approx 2 - 3$ % E_i with the Cu crystal. The samples, approximately 5 g powder specimens of $BaTiO_{2.88}H_{0.12}\square_0$ (BTOH), $SrTiO_{2.81}H_{0.13}\square_{0.06}$ (STOH), and $CaTiO_{3-x}H_x$ (CTOH), respectively (where $\square$ denotes oxygen vacancies), were filled into standard aluminum cells (hollow cylinders of 15 mm in outer-diameter and 12 mm in inner-diameter, with 30 mm in height exposed to the beam), unsealed to keep the material in contact with a low pressure helium exchange gas (~ 100 mbar). The temperature was maintained at 5 K, and each sample as well as an empty cell was measured during approximately 8 hours. The data was reduced within the LAMP software available at the ILL and analyzed with Python routines. In addition, to identify the vibrational modes observed we conducted, for each sample, density functional theory (DFT) calculations on two supercell including one hydrogen atom in presence or absence of a nearest neighboring oxygen vacancy: $Ba_8Ti_8O_{22}H_1\square_1$ ($[\square] = 1$) and $Ba_8Ti_8O_{23}H_1$ ($[\square] = 0$), respectively, for the comparison with BTOH, and $Sr_8Ti_8O_{22}H_1\square_1$ and $Sr_8Ti_8O_{23}H_1$ for the comparison with STOH. The frequencies of the hydrogen vibrational modes were computed with Phonopy and VASP using the PBEsol exchange-correlation functional. The geometry of the cubic unit-cells of composition given above were first optimized until the forces relaxed bellow 10^{-4} eV/Å. For this purpose, $5 \times 5 \times 5$ Monkhorst pack meshes were used to converge the electronic structures within a 10^{-7} eV energy change criteria. The force constants were then computed within a finite-displacement approach with Gamma-point calculations in $2 \times 2 \times 2$ supercells.

2 Preliminary results

Figure 1 shows the INS spectra of the three samples BTOH, STOH and CTOH, as measured at T = 5 K. The spectra for BTOH and STOH are overall quite similar to each other and manifested by a particularly strong band at around 110 meV, and a series of bands at higher energies, whereas the spectrum of CTOH is virtually featureless, possibly due to the lack of H species in this sample. A lack of H species in CTOH was later confirmed by ^1H magic-angle spinning nuclear magnetic resonance analysis, and hence this sample was not subjected to any more analysis. For a detailed analysis, the INS spectra of BTOH and STOH were subjected to a peak-fitting analysis using Gaussian components. Since the low-energy part (i.e. < 100 meV) relates solely to host lattice vibrations of the perovskite, this analysis was focused on the higher-energy range of 100–400 meV, which should related to vibrational modes involving the H species. We found that the spectra could be adequately fit to 9 Gaussian components. The peak positions for all Gaussian components are compiled in Figure 1. Included in Figure 1 are data obtained from a similar analysis of a sample of composition $BaTiO_{2.82}H_{0.12}\square_{0.06}$, as investigated on the INS spectrometer TOSCA at ISIS [2], as well as the result from our DFT calculations.

The comparison of the energy of the peak-fitted Gaussian components for BTOH and STOH, with the one for $Ba_8Ti_8O_{22}H_1\square_1$, suggest that the two strong peaks at 113 and 129 meV in BTOH and at 107 meV

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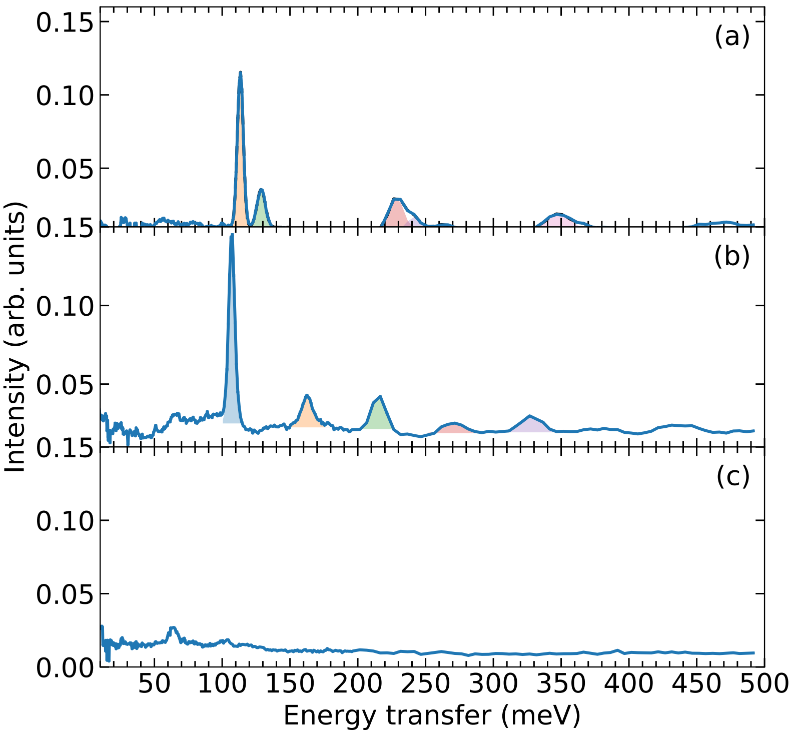
[1] One may note that this proposal initially concerned a study of $SrVO_2H$, but, after approval by the ILL, was changed to a study of $ATiO_{3-x}H_x$, A = Ca, Sr, and Ba perovskites.



	Experiment			
	BTOH	CA3	STOH	
ω_1	100.1	98.4		
$\omega_\perp$	113.4	112.9	107.0	
$\omega_\parallel$	128.8	127.7	162.8	
$2\omega_\perp$	228.4	227.5	215.2	
$\omega_\perp + \omega_\parallel$	241.0	239.8	271.1	
$2\omega_\parallel$	262.8	255.5	328.0	
$3\omega_\perp$	348.0	340.8		
$2\omega_\perp + \omega_\parallel$	366.1	350.5		
$2\omega_\parallel + \omega_\perp$	380.8	370.0		
	Calculations			
	$Ba_8Ti_8O_{22}H_1\square_x$		$Sr_8Ti_8O_{22}H_1\square_x$	
	$x = 1$	$x = 0$	$x = 1$	$x = 0$
$\omega_\perp^1$	91.6	106.1		96.59
$\omega_\perp^2$	107.4		102.0	
$\omega_\parallel$	129.0	130	154.7	163.5

Figure 1: INS spectra at T = 5 K of (a) BTOH, (b) STOH, and (c) CTOH, together with the peak fits. Table: compilation of peak positions in meV after fitting the INS data with Gaussian components (see Figure 1). The data for CA3, of composition $BaTiO_{2.82}H_{0.12}\square_{0.06}$, is taken from [2]. The DFT calculations give the frequencies of vibrational modes associated with H solely in the supercells $Ba_8Ti_8O_{22}H_1\square_x$ and $Sr_8Ti_8O_{22}H_1\square_x$ (with $x = 0, 1$).

and 163 meV in STOH can be assigned to the Ti-H vibrational modes $\omega_\perp$ and $\omega_\parallel$, respectively, corresponding to motions perpendicular or parallel to the Ti-H axis. Note, the spectra for BTOH and $Ba_8Ti_8O_{22}H_1\square_1$ are in excellent agreement, which is expected regarding their similar stoichiometries only differing in oxygen vacancies concentration. They match also the DFT results anticipating a frequency split of $\omega_\perp$ when an oxygen vacancy adjoins the hydrogen atom. The very small peak intensity at 100 meV (see Figure 1), reflect the lack of such splitting in BTOH and is supported by the negligible amount of oxygen vacancies in the sample. The intensity ratio $I(\omega_1)/I(\omega_\perp)$ is around 2.5% for BTOH and almost 10% for CA3, suggesting that CA3 incorporates four times more neighboring $H - \square$ pairs than BTOH. Similarly, the spectra for STOH and $Sr_8Ti_8O_{22}H_1\square_1$ are in good agreement. However, the stoichiometry of STOH is hard to asses from the INS peak positions because no degeneracy is observed in the hydrogen vibrational modes of $Sr_8Ti_8O_{22}H_1\square_1$ or $Sr_8Ti_8O_{22}H_1\square_0$. Hence, more calculations are ongoing to understand this difference with $Ba_8Ti_8O_{22}H_1\square_1$.

References

[1] Kobayashi, Y. et al. An oxyhydride of BaTiO3 exhibiting hydride exchange and electronic conductivity. *Nature materials* **2012**, *11*, 507–11.

[2] Eklöf-Österberg, C.; Mazzei, L.; Granhed, E. J.; Wahnström, G.; Nedumkandathil, R.; Häussermann, U.; Jaworski, A.; Pell, A. J.; Parker, S. F.; Jalarvo, N. H.; Börjesson, L.; Karlsson, M. The role of oxygen vacancies on the vibrational motions of hydride ions in the oxyhydride of barium titanate. *J. Mater. Chem. A* **2020**, *8*, 6360–6371.