

Experimental report

24/08/2023

Proposal: 7-05-552

Council: 10/2022

Title: Vibrational properties of Barium Indate-Zirconate Perovskite Oxyhydride

Research area: Materials

This proposal is a new proposal

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Samples: BaZr_{0.5}In_{0.5}O_{2.25}H_{0.5}

4 samples of Brium titanate oxyhydrides if formula BaTiO_{3-x}H_x with $x < 0.6$

Instrument	Requested days	Allocated days	From	To
IN1 LAG	1	1	13/05/2023	14/05/2023

Abstract:

Perovskite type oxyhydrides, ABO_{3-x}H_x are a novel class of hydride-ion (H⁻) conducting materials that may find diverse applications in the fields of catalysis, topochemical synthesis, and electrochemistry, but fundamental questions surrounding the mechanism of hydride-ion conductivity remain to be answered. In previous QENS experiments on BaTiO_{3-x}H_x we observed either long-range diffusion or localized motions of hydride-ions depending on the concentration of oxygen vacancies, highlighting that a key element for a robust understanding of hydride-ion dynamics in perovskite materials is a solid knowledge of the local coordination environment around the hydride-ions. With this proposal we want to investigate the local coordination environment around the hydride-ions in the very novel perovskite oxyhydride BaZr_{0.5}In_{0.5}O_{2.25}H_{0.5}. Because the vibrational frequencies and intensities of hydride-ion modes are very sensitive to the surrounding species of hydride-ions, they are a very powerful probe of the local structure of BaZr_{0.5}In_{0.5}O_{2.25}H_{0.5}. We propose therefore to perform a one-day inelastic neutron scattering experiment at base temperature with the spectrometer IN1-LAGRANGE.

Vibrational properties of Barium Indate-Zirconate Perovskite Oxyhydride

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1 Introduction

Hydrogen dynamics play a key role in the fields of catalysis, topochemical synthesis, and electrochemistry and have, therefore, been studied from many different points of view. The typical materials of interest are perovskite oxides incorporating hydrogen. In most cases, hydrogen is present as interstitial protonic (H^+) species, which are bonded covalently to lattice oxygens of the oxide host. At elevated temperatures, the O-H bond may break to allow jump diffusion of protons from one oxygen to a neighboring one, leading to long-range proton conductivity, such as observed in the acceptor-doped $BaZrO_3$ perovskites (e.g., $BaZr_{1-x}In_xO_{3+2x}$, $x > 0$) [1]. In rare cases, hydrogens can be also present as substitutional hydride-ions (H^-) on the lattice oxygens, thus forming, so called, oxide-hydrides. In the presence of oxygen vacancies, hydride-ions can exhibit long-range diffusion via jumps between neighboring vacancies, such as observed in $BaTiO_{3-x}H_x$ [2]. Accordingly, a key element for a robust understanding of hydride-ion dynamics in perovskite materials is a solid knowledge of the local coordination environment around the hydride-ions. With this experiment, we aim to investigate hydrogen dynamics in the oxide-hydrides $BaZr_{0.8}In_{0.2}O_{2.7}H_{0.2}$ (BZIOH20) and $BaZr_{0.9}In_{0.1}O_{2.85}H_{0.1}$ (BZIOH10).

The sample preparation was done via a H_2 gas annealing at 800 °C of the parent phases $BaZr_{0.8}In_{0.2}O_{2.9}$ and $BaZr_{0.9}In_{0.1}O_{2.95}$ (same procedure as in ref. [3]). Approximately 3.5 g of BZIOH20 and 4 g of BZIOH10 powder samples were evenly distributed into aluminum foils, subsequently rolled and inserted in cylindrical aluminum cells. The experiments were performed at 10 K on IN1 (LAGRANGE). The Si(111), Si(311) and Cu(220) monochromators yielded the energy window 0–500 meV, and a resolution of ~ 0.8 meV with the Si crystals and $\sim 2-3$ % Ei with the Cu crystal. The data reduction was done within Mantid [4] and included a normalization to monitor counts and an empty cell subtraction.

2 Results and discussion

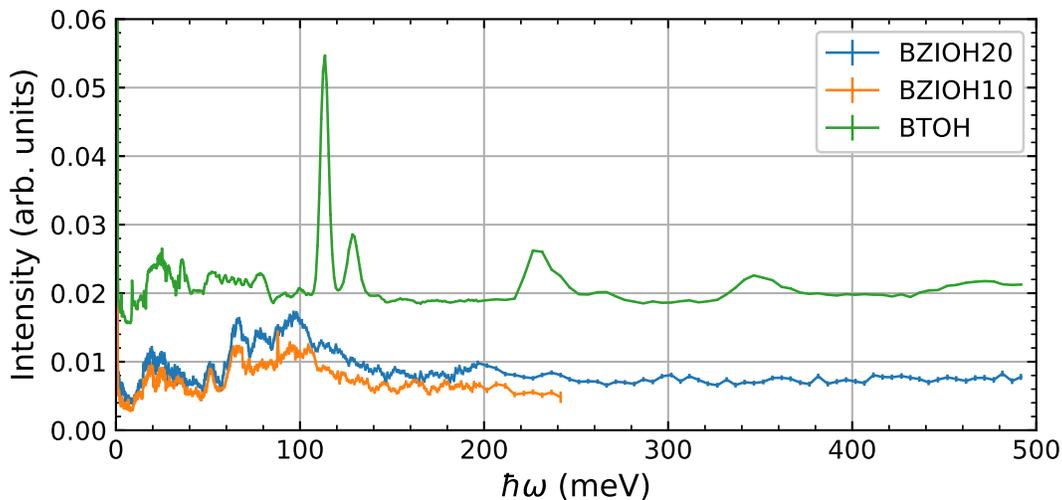


Figure 1: INS spectra at $T = 10$ K of BZIOH20 (blue line) and BZIOH10 (orange line). The green line shows the data for $BaTiO_{2.88}H_{0.12}$ (BTOH) measured on IN1 (proposal 7-01-550), scaled and shifted for the comparison.

Figure 1 shows the INS data of each sample, as recorded on IN1. The spectra have similar features, characterized by a series of peaks at low energies, below 100 meV, and a flat background at higher energies.

Below 100 meV are expected the vibrational states of the perovskite structure, while above 100 meV are expected the vibrational states of the hydrogen atoms. The absence of peaks above 100 meV indicates the absence of substitutional hydrogen on the lattice oxygen sites. Figure 1 also shows for the comparison the INS spectra of BaTiO_{2.88}H_{0.12} (BTOH) recorded on IN1, which has a perovskite structure similar to BZIOH20 and BZIOH10, and which incorporates hydrogen in oxygen sites. The INS spectra of BTOH, BZIOH20, and BZIOH10 were therefore expected to be very similar. Moreover, the features below 100 meV are weak in intensity, indicating the absence of any form of hydrogen in the sample considering its very large cross section (82 barns) compared to the cross section of the perovskite structure elements (<6.5 barns).

Despite our preliminary characterization (X-ray diffraction and thermogravimetric measurements) which indicated an oxidation of the sample, this experiment showed that the preparation method, originally used to synthesize BaZr_{0.5}In_{0.5}O_{2.25}H_{0.5} in ref. [3], is not successful to obtain BaZr_{0.8}In_{0.2}O_{2.75}H_{0.2} and BaZr_{0.9}In_{0.1}O_{2.85}H_{0.1}. In a further attempt to measure hydrogen vibrational properties of the barium indate-zirconate perovskite oxide-hydride, we will use a BaZr_{0.5}In_{0.5}O_{2.25}H_{0.5} sample, and verify its hydrogen content via other methods, such as solid-state nuclear magnetic resonance, in advance of the neutron experiment.

References

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