Local structure and dehydration properties of the proton conducting oxide BaInO$_3$H

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We investigate the local structure and dehydration properties of the proton conducting brownmillerite type oxide BaInO$_3$H, using variable temperature Raman spectroscopy and inelastic neutron scattering. Analysis of the room temperature spectra suggest that Ba$_2$In$_2$O$_5$ can adopt three distinctly different, local, structures, depending on the level of hydration, whereas upon temperature increase, the material dehydrates gradually with increasing temperature. At a temperature of around 370 °C, corresponding to a hydration degree of about 35%, the material undergoes a phase transition towards an intermediate phase before reaching the fully dehydrated structure.

I. INTRODUCTION

Proton conducting, acceptor doped, oxides based on the perovskite structure, $ABO_3$, are currently receiving considerable attention due to their potential to contribute to a more sustainable future through their use as electrolytes in next-generation energy technologies, such as intermediate temperature fuel cells, hydrogen separation membranes, hydrogen sensors, and in catalytic processes.$^{12}$ The acceptor doping, such as In$^{3+}$ substituted for Zr$^{4+}$ in BaZrO$_3$, creates an oxygen deficient structure, in which protons can be incorporated by hydration. The hydration of these materials is generally performed by annealing the sample(s) in a humid atmosphere at elevated temperatures. During this process, the water molecules in the gas phase dissociate into hydroxyl groups (-OH$^-$) and protons (H$^+$) on the surface of the sample. The -OH$^-$ groups then stick to the oxygen vacancies, whilst the (other) protons bind to lattice oxygens of the oxide host lattice. The protons are not stuck to any particular oxygens, but are rather free to move from one oxygen to another and with time they will therefore diffuse into the bulk of the material. At the same time as protons diffuse into the bulk, the counter diffusion of oxygen vacancies from the bulk to the surface allows the dissociation of other water molecules on the surface of the sample. This leads to an increase of the proton concentration in the material, and so it is believed that the process continues until the (bulk) oxygen vacancies are filled. Typically one obtains a maximum protonation degree in the range 70–100%, depending on the hydration conditions, such as temperature, level of humidity, and time, as well as on the chemical composition of the material.$^4$

The proton conduction mechanism in perovskite type oxides started to emerge in the mid-nineties and is mainly based on results obtained from molecular dynamics simulations$^{15}$ and quasielastic neutron scattering data$^{5,10}$ and has later found support from several independent studies using such techniques$^{15}$ which all suggest a conductivity mechanism divided into proton transfers between adjacent oxygens and rotational diffusion of the -OH group between such transfers. However, the presence and effect of dopant atoms, local chemistry and structure, symmetry reduction and proton defect interactions complicates the description of the proton conductivity and still it is not fully understood for even the simplest systems. Therefore, it remains a great scope of detailed structural and dynamical studies to fully understand the interplay between local structure and proton conduction in this class of technologically important materials.

In a previous work, some of us investigated the local structure and coordination of protons in the average cubic structured proton conducting perovskite system BaZr$_{1-x}$In$_x$O$_{3-z/2}$ ($x = 0–0.75$), using infrared (IR) spectroscopy combined with first-principles calculations$^{19}$ Raman spectroscopy$^{15}$ and inelastic neutron scattering (INS)$^{11}$. A key result was that the In doping leads to significant local structural distortions, which become gradually more and more pronounced with increasing dopant concentration.$^{15}$ These distortions were found to be largely uncorrelated with the presence of oxygen vacancies, but instead mainly driven by the size difference between the substituting cations.$^{19}$

In the present work, we expand the In modification and focus on the end member in the series of In-doped BaZrO$_3$, i.e. Ba$_2$In$_2$O$_5$. This is an oxygen vacancy ordered variant of the orthorhombic perovskite structure that contains alternating layers of InO$_4$ tetrahedra and InO$_5$ octahedra running along the c-direction of the unit cell, see Fig. 1. Depending on the orientation, or so called “handedness”, of successive tetrahedral layers, the brownmillerite structure may be characterized by a number of different space groups, with the most common being Ima2 with the same, Pnaa with alternating, and Immm with random handedness. Neutron diffraction results by Berastegui et al.$^{12}$ and Speakman et al.$^{15}$ suggest that the average structure of Ba$_2$In$_2$O$_5$ belongs to space
II. EXPERIMENTAL

A. Sample preparation

A sample of Ba$_2$In$_2$O$_5$ was synthesized by solid state sintering by mixing stoichiometric amounts of BaCO$_3$ and In$_2$O$_3$. Since it is known that as-prepared oxygen deficient oxides may contain a significant level of protons, due to a slight hydration in air during the sintering process, a dehydrated sample was prepared by heat treatment in vacuum ($\sim$2×10$^{-6}$ mbar) at 950 °C overnight in order to remove as many protons as possible. The hydrated sample, BaInO$_3$H, was prepared by annealing a portion of the dehydrated sample at 275–300 °C under a flow of 12 ml/min of Ar saturated with water vapor at 76 °C for a period of 10 days.

B. Raman spectroscopy

The Raman spectroscopy experiments were performed in backscattering geometry using a DILOR XY800 spectrometer, equipped with a tunable Ar$^+$ laser, a long working distance 40x objective, and a liquid nitrogen cooled CCD detector. The laser was tuned to the green 514 nm line and the laser power at the sample position...
was kept at 4 mW for all measurements. A comparison of the Stokes and anti-Stokes spectra showed negligible laser heating on the sample. All spectra were collected with linear polarized light impinging on the sample and unpolarized light collected at the CCD.

The Raman spectra were measured using two different types of experimental setups. The 35–700 cm$^{-1}$ range, covering the vibrational modes of the brownmillerite host lattice, was measured in a high resolution double subtractive mode with a 800 mm focal distance. The higher-frequency region, 2500–4000 cm$^{-1}$, covering the O-H stretch vibrational modes, was measured with a single grating of 300 mm focal distance. Variable temperature measurements were performed by measuring in-situ at sequentially higher and higher temperatures. The temperature was controlled by a Linkam heating stage over the range from room temperature (RT, 20°C) to 600°C, with a small opening to prevent overpressure as the sample was dehydrated with increasing temperature. To ensure that the spectra were measured in thermodynamic equilibrium, the sample was held for 1 h at each temperature before measuring the Raman spectra and, in addition, successive measurements at the same temperature were performed in order to rule out further dehydration after this time.

All Raman spectra have been corrected for the Bose-Einstein occupation factor and normalized to a common baseline level.

C. Inelastic neutron scattering

The INS experiment was performed on the hydrated sample on the MAPS beamline at the ISIS neutron facility at the Rutherford Appleton Laboratory, Didcot, UK. The sample was loaded into an aluminium sachet, which was kept in a sample can made of aluminium and sealed with indium. The measurements were performed at ~10 K with an incident energy, $E_i$, of 650 meV, with the Fermi chopper at 600 and 300 Hz. The measuring time was one about one day.

III. RESULTS

A. Room temperature spectra

Figure 2(a) shows the RT Raman spectrum of the dehydrated material in the range 50–650 cm$^{-1}$, related to the host lattice vibrations of the brownmillerite structure. In accordance with the literature the three regions of bands can be observed. These are assigned according to the following: (i) bands below 200 cm$^{-1}$ relate to vibrational modes of the Ba ions, (ii) bands between 200 and 350 cm$^{-1}$ relate to different tilt and bend modes of the InO$_4$ and InO$_6$ moieties, and (iii) bands between 350 and 650 cm$^{-1}$ relate to symmetric In-O stretch modes of the same moieties. The only discrepancy from this classification regards In related bands, observable at 60 cm$^{-1}$ and 130 cm$^{-1}$, respectively, as will be described later.

In Fig. 2(c) is shown the Raman spectrum of the hydrated material, BaInO$_3$.H. As can be seen, the Raman spectrum of the hydrated material contains significantly less bands than the spectrum of the dehydrated counterpart. In particular, we observe that all Ba related bands, apart from the 130 cm$^{-1}$ band, as well as the strong 600 cm$^{-1}$ band, related symmetric to In-O stretch vibrations of the InO$_4$ tetrahedra, disappear upon hydration. Simultaneously, we observe the appearance of a strong band at around 530 cm$^{-1}$, related to In-O stretch vibrations of InO$_6$ octahedra, and of a band at 150 cm$^{-1}$. Furthermore, our measurements at RT after heat treatment to 370°C or above, reveal the presence of an intermediate phase in addition to the fully hydrated and dehydrated structures. This can be revealed from Fig. 2(b), which shows the RT Raman spectrum of a sample that has been heated to 370°C. As can be seen, this spectrum contains features characteristic of both the dehydrated and hydrated spectra, reflecting a partially hydrated material. However, note here that the intermediate phase is a distinct phase as opposed to a phase separation between dehydrated and hydrated regions, which can be revealed from the large difference in relative intensity amongst
the bands in the 200–250 cm\(^{-1}\) range, when compared to that of the spectrum of the dehydrated materials.

Next we consider the high-frequency region, 2500–4000 cm\(^{-1}\) [Fig. 4(c)], related to the O-H stretch vibrations, which serve as a spectroscopic fingerprint of the local coordination of protons in the materials under investigation. In particular, one should note that the frequency of an O-H stretch mode is very sensitive to the degree of hydrogen bonding the proton may experience towards a neighboring oxygen and that the O-H stretch frequency decreases with the strength of the hydrogen bond. In our case, we note that the shapes of the O-H stretch regions are significantly different for the two materials, suggesting a large difference in the nature of proton sites.

To analyze the coordination of protons in more detail, we performed a peak fit analysis of the O-H stretch band for both the intermediate and dehydrated phases. The peak fit analysis of the spectrum for the hydrated material suggests that the O-H stretch band can be decomposed into six components, centered at approximately 3050, 3310, 3410, 3470, 3540, and 3570 cm\(^{-1}\), respectively, labelled I–VI in the figure. This suggests that there are six relatively distinct proton sites in the hydrated phase. For the intermediate phase, however, only three of these components are observed, namely II, III, and VI, which suggests a distribution over only three main proton sites in this phase. Further information about the nature of proton sites come from the bandwidths of the different components. Generally, the bandwidth reflects the vibrational lifetime and positional disorder, known as homogenous (Gaussian-like) and inhomogeneous (Lorentzian-like) broadening, respectively. In our case, the best fit is obtained when components I, II, IV, and V are described by Gaussians (i.e. lifetime broadening), and components III and V by Lorentzians (i.e. positional disorder). It follows that components III and VI relate to crystallographically relatively well defined positions, whereas I, III, IV, and V relate to less well defined such. The significance of this will be discussed later.

B. Phase Separation

By investigating the variations in both the lattice and O-H stretch spectra between different sample batches (not shown), two distinct proton configurations could be identified. Depending on the conditions during hydration, different ratios between the two phases was found. Note that both phases produces the same dehydrated phase spectrum after heating, excluding the possibility of sample degradation during hydration as a cause of the observed differences.

Figure 3(a) shows the low frequency lattice vibrations of the sample discussed in this paper ("type 1", upper thick line) and the second distinct phase ("type 2", lower thick line). In the same way, Fig. 3(b) shows O-H stretch spectra of the two phases. Looking at the O-H stretch spectra, it is immediately seen that the "type 2" spectrum consists of OH components I and V as defined in Fig. 3. Thus, the sample investigated in this paper is mainly of "type 1", dominated by O-H stretch components II, III, and IV. Rescaling the "type 2" spectrum, we see in the thin solid line that the proportions between component I and V in the mainly "type 1" sample is perfectly consistent with trace amounts of "type 2" domains throughout the sample. In the same way, the low frequency lattice spectrum in Fig. 3(a) show signs of "type 2" peaks (indicated by stars).

Comparing "type 1" and "type 2" vibrational spectra, several properties of their proton arrangements can be deduced. First, the "type 1" phase has a much narrower O-H stretch band, implying more well localized proton positions compared to what is seen in the "type 2" phase. Consequently, it is only in "type 1" that we observe a long-range InO\(_6\) distortion resulting in the activation of the 150 and 530 cm\(^{-1}\) phonons. This implies that "type 1" is more probable to correspond to the energetically favored structure predicted by Martinez et al. The O-H stretch component III, centered at 3400 cm\(^{-1}\) is attributed to the H(1) proton site. The H(2) site is predicted to have a lower vibrational frequency and is consequently assigned to component II at 3300 cm\(^{-1}\). Component IV could be either the antisymmetric H(1) vibration or a slightly less hydrogen bonded H(1) configuration.

The broader "type 2" OH-band consists of component V at 3550 cm\(^{-1}\) that arises from weakly hydrogen
ally observe a gradual broadening of all bands, which
up to 600◦C of the Raman spectra of the hydrated sample from RT (the same dehydration dynamics as the "type 2" bands Fig. 4), but on the other hand this component follows the dehydration phase, together with only the "type 1" bands (cf. Fig. 5(a)). Here, this component is present deep within the intermediate phase, together with only the "type 1" bands (cf. Fig. 5(a)). Notice that the very broad component I at 3000 cm−1 represnts strongly hydrogen bonded and highly disordered H(2) protons within the In(2)-O(3) layer. Notice that the hydration dynamics in Fig. 7(b) are divided in two groups in accord with the phase classification presented here.

Component VI is more difficult to assign. The very small linewidth and high frequency implies its origin in -OH groups essentially free from hydrogen bonds. On one hand this component is present deep within the intermediate phase, together with only the "type 1" bands (cf. Fig. 5(a)), but on the other hand this component follows the same dehydration dynamics as the "type 2" bands (cf. Fig. 5(b)).

C. Variable temperature spectra

In Fig. 5(a) we present the 50–720 cm−1 range of the Raman spectra of the hydrated sample from RT up to 600 ◦C. Upon increasing temperature, we generally observe a gradual broadening of all bands, which appears to be a generic feature and reflects the decreased phonon lifetime due to an increase in the anharmonic phonon-phonon scattering processes with increasing temperature.2 When the temperature is increased to 370–380 ◦C, we observe a more sudden change of the spectrum, which suggests a structural phase transition away from the hydrated phase. Most noticeable is the appearance of a band at 620 cm−1, related to symmetric InO6 stretch vibrations, which is consistent with the fact that once the material dehydrates, oxygen vacancies are being formed and concomitantly the transformation of InO6 octahedra to InO4 tetrahedra occurs. We also observe the appearance of four Ba related bands at 82, 92, 102, and 180 cm−1, respectively, of oxygen bands in the range 215–243 cm−1, and of an InO4 tilt band at 60 cm−1. Upon further temperature increase, these new bands increase in intensity. In addition, we point out a significant peak shift of the 620 cm−1 band, which downshifts gradually with increasing temperature to reach a position of 595 cm−1 at 600 ◦C. No additional qualitative changes of the spectra occur upon increasing temperature, but instead a smooth change of the spectral features towards the shape of the spectra for the dehydrated material occurs.

Figure 5(b) shows the temperature dependence of the O-H stretch region of the Raman spectra, and as can be seen there is a gradual decrease in intensity over the whole O-H stretch band with increasing temperature, which is consistent with a gradual dehydration of the material. In this context, one should note that a quantitative assessment of the intensity of the O-H stretch band is, generally, not straightforward, since the Raman scattering cross section with O-H stretch vibrations, which is consistent with the hydration dynamics in Fig. 7(b) is shown in Fig. 6. As can be seen in the figure, the shape of the O-H stretch region of the vibrational spectra, using INS, since in INS the intensity of a particular vibration is directly proportional to the number of vibrating species. A comparison of the INS and Raman spectra of the hydrated material is shown in Fig. 6. As can be seen in the figure, the shape of the O-H stretch band is similar in the Raman and INS spectra, which suggests that there is indeed no strong dependence of the Raman scattering cross section with O-H stretch frequency. In effect, this justifies a direct relation between the temperature dependent changes in intensity of the O-H stretch band to changes in hydration level.

The temperature dependence of the hydration level relative to that at RT is shown in Fig. 7(a). It can be seen that the material dehydrates gradually with increasing temperature. Up to a temperature of 370 ◦C, the rate of dehydration is relatively weak, reaching a hydration level of ca. 70% at 370 ◦C. At this point, the hydration level

![Figure 4](image-url)
FIG. 5. (Color online) Variable temperature Raman spectra measured in (a) the lattice and (b) the O-H stretch frequency regions, respectively. Spectra in thick lines indicate the fully hydrated sample and the appearance of the intermediate phase.

FIG. 6. Comparison between the O-H stretch region of the Raman, IR, and INS spectra of BaInO$_3$H.

drops abruptly down to a level of ca. 40% at 380 °C, concurrent with the transition from the hydrated to intermediate phase. Upon further temperature increase, the dehydration curve flattens out, to eventually reach a level of only a few percent at 600 °C.

More quantitative information about the dehydration process can be obtained by analyzing the temperature dependence of the different parts of the O-H stretch band. Fig. 7(b) shows the temperature dependence of the integrated intensities of the peak fitted six components relative to their intensity at RT. Overall, we observe an intensity decrease of each of the six components up to a temperature of 370 °C, at which a more abrupt change in hydration level can be observed. On a closer analysis, we can also make a distinction between the different components. More specifically, we observe that components I, V, and VI exhibit a weak temperature dependence before the transition, after which the dehydration drops more drastically, quite comparable to the temperature dependence of the total hydration level [cf. Fig. 7(a)]. However, for components II and IV, the temperature dependence of dehydration is stronger before the phase transition temperature. Component III differs from the others in that it largely does not change until the hydrated to intermediate phase transition temperature is reached.

IV. DISCUSSION

By combining the results obtained from variable temperature Raman spectroscopy and INS, we can now understand several properties of the local structure, proton sites, and dehydration mechanism of the proton conducting oxide BaInO$_3$H. One of the key results in this study is that the dehydration process is characterized by
The intermediate phase is similar to the spectrum of the dehydrated structure in that, even though the crystal structure. As the structure of the dehydrated material, $\text{Ba}_2\text{In}_2\text{O}_5$, has previously been found to be centrosymmetric with respect to the InO$_6$ octahedra, one can expect that this non-centrosymmetric distortion activates otherwise Raman-inactive vibrations, even though that the total number of Raman active vibrations will decrease upon hydration due to the overall increase in symmetry.

Further information about the non-centrosymmetric InO$_6$ distortion, which is present both in the dehydrated and intermediate phase, can be found in the linewidths of the 150 and 530 cm$^{-1}$ bands as a function of temperature. The thermal line-width broadening is given by the Klemens model, which takes into account the anharmonic decay of one optical phonon into two acoustic phonons. By this process the linewidth $\Gamma$ increases with temperature $T$ according to $\Gamma(T) \sim \Gamma(0) \left[ 1 + 2/\left( \exp(\hbar\omega/2k_B T) - 1 \right) \right]$, where $\omega$ is the frequency of the optical phonon. Deviations from this rule is a sign of additional processes that decrease the phonon lifetime $\tau$ ($\tau \sim 1/T$) and implies a strong enhancement in the scattering channels. Such enhancement commonly arises from increased disorder, and consequently anharmonicity, of the atomic species involved in the vibration at hand.

In Fig. 8(a) we show the temperature evolution of the 150 and 530 cm$^{-1}$ linewidths. Fit to the Klemens-like behavior is given by the solid lines. The measured linewidth agrees well with the Klemens model until the hydrated-intermediate phase transition temperature is reached, indicating no loss of coherence in the InO$_6$ distortion below 370 °C. Above 370 °C however, both modes shows an anomalous increase of $\Gamma$ with increasing temperature. This is a clear indication of decoherence in the InO$_6$ distortion, which we interpret as due to the gradual release of H(1) hydrogens above 370 °C, see Fig. 9. The only O-H stretch component with relatively constant area below 370 °C is component III, see Fig. 7(b), which suggests that this component relates to H(1) protons in the structure. As for the H(2) protons, these can be expected to be more loosely bound to the oxygens, suggesting that the corresponding O-H(2) stretch band is positioned at lower wavenumbers that the O-H(1) stretches, thus H(2) protons may be related to component I and/or II.

Thus, the intermediate structure is distinct from the dehydrated structure in that, even though the crystal
FIG. 9. Spectral linewidth (FWHM) of the (a) In mode at 150 cm$^{-1}$ and (b) O mode at 530 cm$^{-1}$. In the hydrated phase, the linewidth of both modes follows a simple anharmonic behavior according to Klemens[17] with the linewidth increasing almost linearly with temperature (solid lines). The anomalous increase in linewidth above the hydrated-to-intermediate phase transition is attributed to a gradual decoherence of the non-centrosymmetric distortion of the In(1)-O octahedra as H(1) protons are released, as schematically depicted in (c).

structure approaches the dehydrated structure upon dehydration, the non-centrosymmetric InO$_6$ distortion is still present. Second, based on the arguments presented in Martinez et al. we expect two distinct proton positions in the hydrated structures. Thus, the number of OH components are expected to be two (three if the possibility of one symmetric and one antisymmetric vibration, each involving two adjacent H(1) protons are taken into account). Instead, six O-H stretch components were observed in the experiment. The large number of observed O-H stretch components can be explained by locally different proton arrangements throughout the sample. This would amount to a mixture involving the most energetically favorable proton configurations considered by Martinez et al.[14]

V. SUMMARY AND CONCLUSIONS

To conclude, our results suggest that Ba$_2$In$_2$O$_5$ can adopt three distinctly different structures, depending on the hydration level. In particular, we find that the appearance of an intermediate structure appearing between the hydrated and dehydrated structures at 370 °C. The Raman spectrum of the intermediate phase is very similar to the spectrum of the completely dehydrated phase and it is the hydrated-intermediate transition, occurring at ~65% hydration level, that presents the major change in crystal symmetry. The anomalous linewidth broadening of the In(1) related Raman peak with increasing temperature past the hydrated-intermediate transition indicates a decoherence of the proton induced non-centrosymmetric In(1) position, together with the final release of protons, as the main structural effect in the intermediate-dehydrated transition. The dehydration occurs through the release of H(2) protons at temperatures below the intermediate transition, after which also the H(1) protons are released. The O-H stretch spectrum is not consistent with a single phase sample. Two distinct hydrated phases were identified. The local proton configuration in the "type 1" phase gives rise to long-range InO$_6$ distortions and is assigned to correspond to the energy minima predicted by Martinez et al.[14]. The relatively narrow frequency distribution imply a rather weak local disorder compared to similar oxides. "Type 2" is of higher energy and contain significantly more disordered proton arrangements.

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