Neutron Diffraction Probing Hydrogen in Monoclinic H_2VOPO_4

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Abstract

Light hydrogen atoms are resolvable with neutrons; however, the massive incoherent background inhibits the diffraction quality. To improve the signal, isotope treatment by deuteration becomes a prerequisite for a successful crystallographic understanding of hydrogen-containing materials by neutron diffraction. Thanks to the low-background and high-resolution time-of-flight neutron diffractometer, this work demonstrates a direct and successful measurement of high-quality neutron diffraction patterns of H_2VOPO_4 powders, a precursor of a high-capacity alkali-ion battery cathode. The Rietveld refinement identifies the hydrogen coordinates, occupancy, and thermal parameters in the H_2VOPO_4 lattice. The result highlights the unique capability of neutron diffraction for the structure characterization of hydrogen-containing materials, potentially without requiring costly and possibly artifact-inducing deuteration for neutron diffraction.

Keywords: Neutron diffraction; Hydrogen-containing material; Crystalline powders; Energy storage; Energy conversion; High resolution

1 Introduction

Probing hydrogen (H), the lightest element, in crystalline materials is rather challenging because of the lack of sensitivity in many structure characterizations such as x-rays, electrons etc. Non-destructive neutron diffraction, on the other hand, possesses a unique capability of detecting H. The distinguished negative coherent scattering length (-3.74 fm) [1] not only contributes to the remarkable sensitivity of H, but also gives strong contrasts to differentiate from other elements that commonly have a positive value of scattering length. However, H simultaneously boosts the scattering background in neutron diffraction, due to the large values of both the incoherent scattering length (25.3 fm) and the cross section (80.27 barn) [1]. The high background negatively impacts the diffraction pattern quality and thus the crystallography analysis. The deuteration, substituting natural hydrogen with the costly isotope deuterium (D), is usually recommended in studying H-containing material via neutron diffraction. This isotope can help reduce the incoherent background (from 25.3 to 4.04 fm and from 80.27 to 2.05 barn) [1]. However, both the high cost and the limited availability raise considerations of this approach. The positive coherent scattering length of D also mitigates the contrast with many other elements

that also have close scattering length values. Last but not least, deuteration may change material structure in some instances [2].

This work demonstrates a direct measurement of a high-quality neutron diffraction pattern of a H-containing powder sample. The success is attributed to the high neutron flux, high d-space resolution, low instrument background, and high detector efficiency of the time-of-flight neutron diffractometer at the Spallation Neutron Source (SNS). Monoclinic H_2VOPO_4, which possesses about 22% hydrogen in atomic fraction, is selected as the model material in this study. It is an important precursor for the ε-$VOPO_4$ synthesis, an attractive intercalation compound used as cathode material of alkali-ion batteries [3]. Its structure was reported to follow *C*2/*c* space group via Xray diffraction (XRD), but the information of H in the lattice is missing [4,5] because of the little sensitivity of lightweight elements in XRD. The neutron powder diffraction in this work fills that gap by uncovering the H arrangement and vacancy in H_2VOPO_4.

2 Experiment

The monoclinic H_2VOPO_4 powders were synthesized by combining VCl_3 (Sigma-Aldrich, 97%) and P_2O_5 (Sigma-Aldrich, ≥98%) in 30 mL 190-proof ethanol. The solution was placed in a 4748 Type 125 mL PTFE-lined reactor (Parr Instrument Co.), and the reaction was set to 180 °C for 72 hours. The hydrothermal product was filtered and then dried at 65 °C overnight to yield the H_2VOPO_4 powders. To form the ε-$VOPO_4$ powders, the hydrogen of H_2VOPO_4 was removed by annealing at 550 °C in flowing oxygen for 3 hours.

The synthesized powders were filled and sealed in vanadium cans with a 6 mm diameter for neutron powder diffraction. It was carried out at VULCAN diffractometer [6] at SNS at Oak Ridge National Laboratory. The 20Hz chopper and the high-resolution guide were configured. The incident neutron beam size was determined by the $6\times12mm^2$ slits. Each powder sample was measured for one hour under the nominal 1.4MW power of SNS operation. The neutron events that were received from the ^{3}He linear position sensitive detector bank at $2\theta=90°$ were reduced to a histogram. Under the same configuration, the standard Si powder sample and vanadium rod sample were measured for instrument calibration and incident spectrum normalization, respectively. Rietveld refinement including Fourier map calculation of the neutron diffraction pattern, was carried out using GSAS [7].

3 Results and discussion

A high-quality neutron diffraction pattern of H_2VOPO_4 powders was successfully measured despite the challenge of the high H content. In Figure 1(a), the raw diffraction histograms are compared between H_2VOPO_4 and $VOPO_4$. The strong incoherent scattering from the H atoms raises the background of H_2VOPO_4 150% more than $VOPO_4$. Nevertheless, the coherent scattering that gives rise to the Bragg peaks of H_2VOPO_4 is still pronounced, which does not seem to be weaker than those of $VOPO_4$ in general. After the normalization to the incident beam spectrum, the high-resolution diffraction pattern, though with an elevated background, exhibits sharp and clear Bragg peaks to allow the crystallographic analysis (Figure 1(b)).

The Rietveld refinement over the neutron diffraction probes the lightweight H atoms at an 8f site of the initial structure model without H [4,5]. Figure 1(b) shows the full pattern fitting with least residuals. If the H was removed in the fitting, the significant mismatch would be observed (Figure 1(b) inset), which indicates the pronounced contribution of H to the Bragg peaks. It thus illustrates the high fidelity of probing this lightweight element via neutron diffraction. This refinement determined the lattice parameters, atoms' positions in the lattice, site fractional occupancies, and anisotropic displacement parameters in H_2VOPO_4 (Table 1). It is worth noting that no fitting constraints were applied to those variables, except for the V atom because its coherent scattering length is so weak [1] to make it not sensitive to neutron diffraction.

The crystal structure resulting from the refinement is illustrated in Figure 2. The framework of H_2VOPO_4 composes of connecting PO_4 tetrahedra and VO_6 octahedra. A PO_4 shares the four corners (two O(1) and two O(2)) with the four neighboring VO_6, respectively. A VO_6 also shares the two O(3) corners with another two VO_6 octahedra, respectively. The two hydrogen atoms bond with the O(3). In addition, each H atom could have a weaker hydrogen bond with the O(1) of a neighboring VO_6. This structure of H_2VOPO_4 is found to be consistent with $MnPO_4 \cdot D_2O$ [8], which was determined using deuteration.

The properties of the bonds are revealed from the structure refinement. In the PO_4 tetrahedron, the bond lengths of P–O(1) and P–O(2) are consistent. It indicates the strong covalent bonds with sp^3 hybridization at the P(V) ion. Differently, the VO_6 octahedron is stretched along V–O(3) in comparison to V–O(1) and V–O(2). It results from the Jahn-Teller effects of the V(III) ion that has 2 electrons at the 3*d* orbitals. This distortion of the octahedron is also correlated to the bond to H. Due to the existence of the O(3)–H bond, the V–O(3) bond is weakened and thus elongated. Similarly, the H···O(1) hydrogen bond also influences the bonds of O(1) while the O(2) is nearly screened from H atoms. Therefore, it is observed that both the V–O(1) and P–O(1) bonds have slightly larger lengths than V–O(2) and P–O(2), respectively.

In the H_2VOPO_4, the O(3)–H bond length is 1.013Å, and the H–O(3)–H angle is 108.7°. The geometry of H–O–H group is slightly changed from that in the H_2O molecule, compared to the 0.9572Å bond length and the 104.52° bond angle in H_2O [9]. Both values are larger in the H_2VOPO_4. This may be attributed to the V–O(3) bond, which attracts the electron cloud around O(3) to weaken the O–H interaction and enhance the repulsion between the two H atoms.

The vacancies of the lightweight element H and O are probed via the refinement. Without constraints, it is calculated to have a small amount of vacancies at the H and the O(3) sites while the O(1) and O(2) sites are fully occupied within the fitting errors. The loss of H and O follows the atom ratio of a water molecule, showing an equivalued formula $VPO_4 \cdot 0.945H_2O$. The variation of H_2O content is commonly observed via thermogravimetry, depending on the synthesis process [4]. Therefore, the stoichiometry changes do not lead to an oxidation of V, and the O(1) and O(2) bonding to V and P are well maintained.

The anisotropic displacement parameters (U_{ij}) are calculated for each atom except V. The light H exhibit relatively large U_{ij} values with strong anisotropy. It may be contributed by the dynamic vibration of H that has a single bond to O(3) and also be attributed to some possible static local displacement in disorder [10]. The refined coordinates and the U_{ij} give the average state of the H atom.

4 Conclusion

The high-quality time-of-flight neutron diffraction pattern was directly measured for the H_2VOPO_4 powder sample. The site position, occupancy, and the anisotropic thermal vibration of the hydrogen atoms were probed. The presence of H was correlated to the distortions of VO_6 octahedron and the PO_4 tetrahedron. This work successfully demonstrated the practice of probing H in the lattice at the advanced time-of-flight neutron diffractometer, without the need to impose additional material treatments like deuteration. The characterization exhibits potential extensions on studying a general catalogue of H-containing (small to medium amount) crystalline compounds in the form of powders or polycrystals, such as hydrides, hydroxides, hydrate, and so on, for engineering and energy applications.

5 Acknowledgements

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6 References

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7 Figure Captions

Figure 1 (a) As-collected neutron diffraction histograms for H_2VOPO_4 and $VOPO_4$. (b) Normalized neutron diffraction pattern and Rietveld refinement of H_2VOPO_4. (The inset shows a refinement without hydrogen contribution while the parameters of the other atoms are unchanged.)

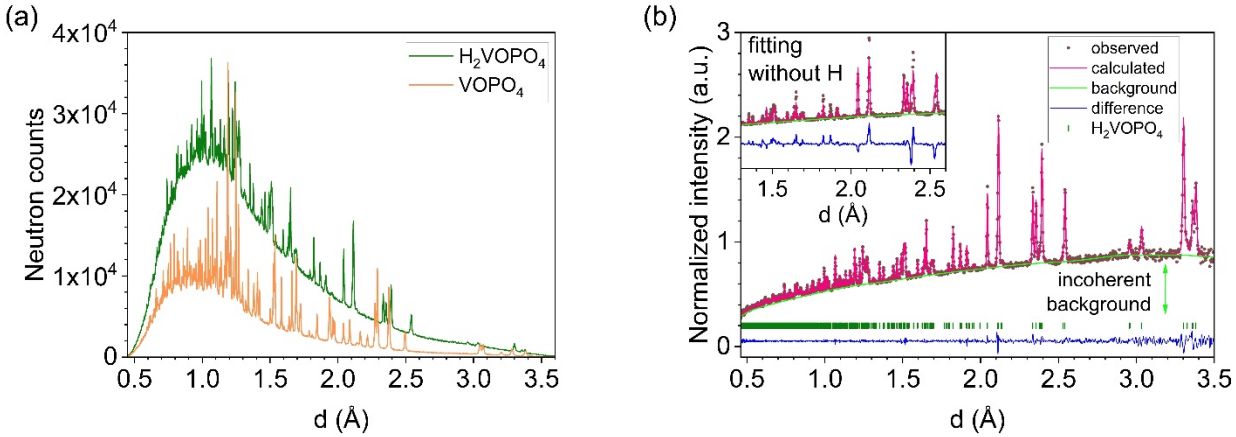
Figure 2 The crystal structure and bond lengths of H_2VOPO_4 based on neutron diffraction.

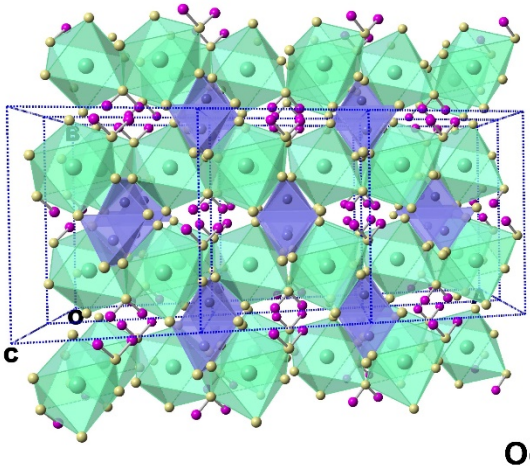
8 Tables

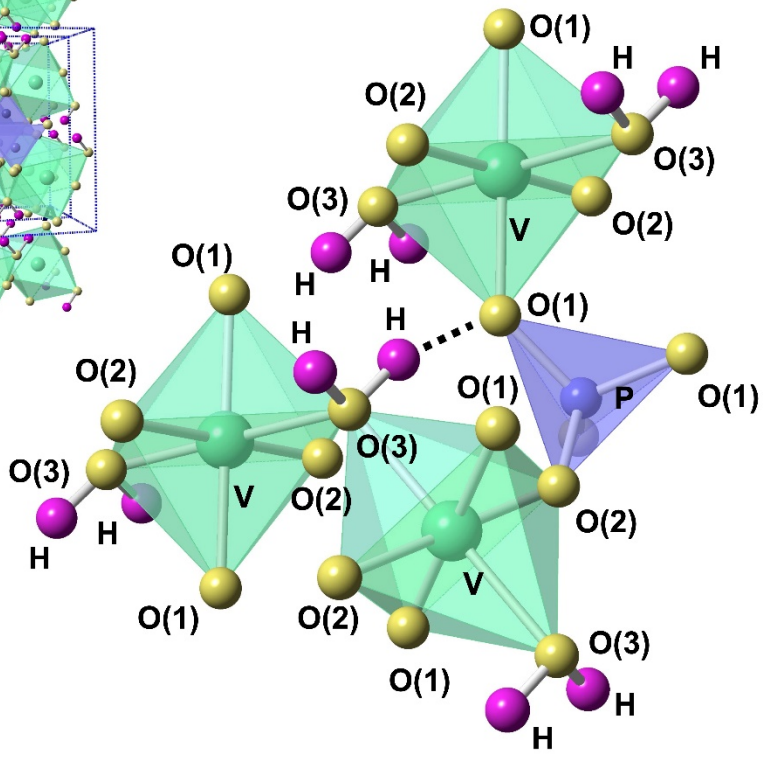
Table 1 Crystal structure of H_2VOPO_4 (Space group: *C2/c*. a = 6.7093(2)Å; b = 7.7895(2)Å; c = 7.3565(1)Å; β = 115.308(2)º).

9 Supplementary data

Crystallographic Information File (CIF) of H_2VOPO_4.


(a)
Neutron counts
4x10^4
3x10^4
2x10^4
1x10^4
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
d (Å)
H2VOPO4
VOPO4
(b)
Normalized intensity (a.u.)
3
2
1
0
fitting
without H
1.5
2.0
2.5
d (Å)
observed
calculated
background
difference
H2VOPO4
incoherent
background
0.5
1.0
1.5
2.0
2.5
3.0
3.5
d (Å)





V–O(1): 1.983(2)Å
V–O(2): 1.929(2)Å
V–O(3): 2.148(1)Å
P–O(1): 1.535(3)Å
P–O(2): 1.528(3)Å
H–O(3): 1.013(5)Å
H…O(1): 1.679(5)Å