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Permalink
https://escholarship.org/uc/item/3hx2q287

Journal
Journal of Physical Chemistry C, 120(41)

ISSN
1932-7447

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Publication Date
2016-10-20

DOI
10.1021/acs.jpcc.6b06391

Peer reviewed
Theoretical and Experimental Study on the Optoelectronic Properties of Nb$_3$O$_7$(OH) and Nb$_2$O$_5$ Photoelectrodes

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Supporting Information

ABSTRACT: Nb$_3$O$_7$(OH) and Nb$_2$O$_5$ nanostructures are promising alternative materials to conventionally used oxides, e.g. TiO$_2$, in the field of photoelectrodes in dye-sensitized solar cells and photoelectrochemical cells. Despite this important future application, some of their central electronic properties such as the density of states, band gap, and dielectric function are not well understood. In this work, we present combined theoretical and experimental studies on Nb$_3$O$_7$(OH) and H–Nb$_2$O$_5$ to elucidate their spectroscopic, electronic, and transport properties. The theoretical results were obtained within the framework of density functional theory based on the full potential linearized augmented plane wave method. In particular, we show that the position of the H atom in Nb$_3$O$_7$(OH) has an important effect on its electronic properties. To verify theoretical predictions, we measured electron energy-loss spectra (EELS) in the low loss region, as well as, the O–K and Nb–M$_3$ element-specific edges. These results are compared with corresponding theoretical EELS calculations and are discussed in detail. In addition, our calculations of thermoelectric conductivity show that Nb$_3$O$_7$(OH) has more suitable optoelectronic and transport properties for photochemical application than the calcined H–Nb$_2$O$_5$ phase.

I. INTRODUCTION

The consumption of fossil fuel stocks presents our society with a new challenge and forces the research for alternatives. Efficient harvesting of the power of the sun with solar cells would suffice to cover the worldwide energy consumption. To balance out fluctuations in the energy production novel storage technologies need to be developed simultaneously and in this regard hydrogen is intensively discussed as a very promising material for energy storage. Dye-sensitized solar cells (DSSC) and photocatalysis both apply semiconductors to generate charges which are either separated to produce current or used up for chemical reactions (e.g., the splitting of water to produce hydrogen gas). The solar energy is absorbed by the semiconductor whereby an electron is excited from the valence to the conduction band leading to electron–hole pairs. The band gap size and energy position of the conduction and valence band edges of the semiconductor are crucial for the performance of a semiconductor in photochemistry as they determine the portion of the solar spectrum absorbable by the semiconductor, the potential of the electron–hole pair and the band alignment of the device. Theoretical studies calculated the band edge energies of a high variety of oxides, predicting their applicability as photocatalyst or electrode material. Subsequent to their separation, the generated charges need to diffuse to the surface of the semiconductor. This process is endangered by charge recombination: a major loss mechanism leading to reduced quantum yields. Consequently, both the charge transport properties and the energy position of the band gap of a material have to be taken into account at evaluating its applicability as photocatalyst. Still, the ideal material system was not yet discovered and research needs to go beyond established material systems. This study focuses on the prediction of material properties of a material class which was very recently discovered as new material with attractive properties for photochemistry: Several experimental studies show the applicability of Nb$_3$O$_7$(OH) and Nb$_2$O$_5$. 

Received: June 24, 2016
Revised: September 16, 2016
Published: September 16, 2016

DOI: 10.1021/acs.jpcc.6b06391
II. COMPUTATIONAL AND EXPERIMENTAL METHODOLOGY

II.A. Calculation Details. All density functional theory based calculations were performed using the linearized augmented plane wave + local orbitals (LAPW+lo) method as implemented in the WIEN2k code. The muffin tin radii $R_{MT}$ for Nb$_2$O$_5$(OH) were set to 1.8, 1.3, and 0.55 bohr for the niobium, oxygen and hydrogen atoms, respectively. The muffin tin radii for monoclinic H–Nb$_2$O$_5$ were set to 1.74 bohr for niobium atoms and 1.58 bohr for oxygen atoms. The wave functions in the atomic spheres were expanded up to an angular momentum of $l = 10$. The plane wave cutoff in the interstitial region was set so that $R_{MT} \times K_{max} = 7$ for Nb$_2$O$_5$ and 3 for Nb$_3$O$_7$(OH), respectively. and was validated by convergence of the forces on the atoms. To obtain the electronic structure as well as optical properties we used a k-point mesh of $16 \times 16 \times 15$ for Nb$_2$O$_5$(OH) and $3 \times 18 \times 4$ for Nb$_3$O$_7$(OH).

The structural relaxations were done using the GGA functional. Since it is well-known that local exchange correlation functionals underestimate band gaps, the electronic structure calculations were performed using the TB-mBJ approach. This functional usually predicts band gaps with higher accuracy than GGA. However, we also performed all calculations with GGA and with LDA functionals so that a detailed comparison of the results obtained using different exchange-correlation functionals with the experiment is possible. This comparison demonstrated that the TB-mBJ approach is suitable for the Nb oxides studied here (see section III.D, below).

The linear optical properties of Nb$_2$O$_5$(OH) and Nb$_3$O$_7$(OH) were derived from the OPTIC program included in the WIEN2k simulation package. The imaginary part of the dielectric tensor ($\varepsilon_2$) was calculated according to ref 35. The real part of the dielectric function ($\varepsilon_1$) is derived from the Kramers-Kronig relation. Both the optical conductivity $\sigma(\omega) = \frac{w}{2\pi} \varepsilon_2(\omega)$ and the energy loss function $L(\omega) = (\varepsilon_1(\omega))^2 + (\varepsilon_2(\omega))^2$ can be calculated directly from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.

Core loss electron energy-loss spectra of Nb–M$_4$ and O–K edges were calculated with the X-ray absorption module of the WIEN2k code. The application of Fermi’s golden rule is possible for the used experimental scattering geometry as the dipole approximation is fairly valid. We had to account for the core hole to achieve a satisfying agreement between theoretical and experimental core loss data at the O–K and Nb–M$_4$ edges. This was done using the static core hole approach. One of the relevant core electrons was removed, the number of valence electrons was increased by one and a self-consistent calculation was done so that the electrons adjust to the presence of the core hole. This calculation was done for every nonequivalent oxygen and niobium atom in the unit cell using a $2 \times 2 \times 1$ supercell.

The BoltzTraP code was used to calculate the electrical conductivity under constant relaxation time $\tau$. These calculations are based on the Boltzmann transport theory and necessary information about the band dispersion is obtained by corresponding DFT calculation.

II.B. Experimental Details. In addition to the theoretical calculations, we performed electron energy-loss spectroscopy (EELS) measurements in a transmission electron microscope (TEM). The Nb$_2$O$_5$(OH) sample was synthesized according to the procedure described by Betzler et al. Monoclinic H–Nb$_2$O$_5$ was obtained by calcination of Nb$_2$O$_5$(OH) at 850 °C. Low loss data were acquired to get experimental information about the optical response of the samples. In addition core loss data were recorded to investigate the coordination and bonding characteristic of the crystal lattices. The low loss spectra were detected using a double corrected FEI-TEAM 0.5 microscope operated at 300 kV. An energy resolution of 0.15 to 0.18 eV (determined by the full width at half-maximum of the zero-loss peak) was achieved using a monochromator and a spectrometer entrance aperture of 1 mm under parallel illumination of the sample (convergence angle below 0.2 mrad). The linear fit method enables the determination of the band gap of materials from the low-loss region (energy losses between 0 and 50 eV). In addition optical extinction data were detected for a spectral region of 250 to 1200 nm. The Tauc method was applied to determine the band gap based on optical data and it was used compared to the band gaps measured by EELS. The element specific edges were measured using a Zeiss Libra microscope operated at 200 kV with parallel illumination (convergence angle about 0.2 mrad). An energy resolution of 0.3–0.4 eV was achieved for the determination of the O–K and Nb–M$_4$ edges using a monochromator and a collection angle of 17 mrad. The spectra were detected with a dispersion of 0.07 eV/channel.

III. RESULTS AND DISCUSSION

III.A. Structural Optimization. We considered three systems in our study: monoclinic H–Nb$_2$O$_5$, orthorhombic...
Figure 1. Schematic representation of the crystal structures of the artificial reference compound Nb3O8 (left, a) and Nb3O7(OH) (right, a) and monoclinic H–Nb2O5 (b). Black, red, and green spheres represent Nb, O, and H atoms, respectively.

Nb3O7(OH) and an auxiliary Nb3O8 system. Please note that all relaxed structures used in this manuscript can be found as crystallographic cif files in the Supporting Information.

**Nb3O7(OH) and Nb3O8.** Nb3O7(OH) has an orthorhombic structure isomorphous with Nb3O7F, which crystallizes in Cmmm (number 65) space group. The experimental unit cell parameters are $a = 20.74$, $b = 3.823$, $c = 3.936$ Å. It is well-known that it is very difficult to find the exact position of H atoms by means of X-ray diffraction. Therefore, theoretical studies are important here. Zhang et al. based their DFT calculations on a suggested position for the H atom: Here the H atom is attached to an oxygen atom O(8) between two Nb(3) sites (Nb(2) and (3) are situated in edge-sharing octahedra, while Nb(1) sits in a corner-sharing one). We used their structural model as starting point for our structure relaxation. The structure of Nb3O7(OH) which we obtained is quite similar to the structure of Zhang et al., a perspective diagram is shown Figure 1a. The largest difference between our results and the structure found by Zhang et al. concern the region close to the OH group: the O–H distance increased by 0.359 Å (1.07 Å in relaxed, −1.429 Å in unrelaxed structure model) and the Nb–O distance by 0.053 Å (2.030 Å in relaxed, −1.977 Å in unrelaxed state).

To study the bare effects of the hydrogen atom on the electronic structure, optoelectronic and transport properties, we also performed calculations for an artificial Nb3O8 reference compound. Nb3O8 is not known experimentally and was defined by removing the H atom from the crystal lattice of Nb3O7(OH) while leaving all structural parameters as in the original Nb3O7(OH) compound.

H–Nb2O5. Nb2O5 exhibits more than 15 different polymorphs. Monoclinic H–Nb2O5 is the thermodynamic stable polymorph which forms after calcination of Nb2O5(OH) at 500 °C. Its crystal structure was determined experimentally by Gatehouse et al. and Kato. It crystallizes in the space group P21/m (number 10), with lattice parameters $a = 21.153$, $b = 3.823$ and $c = 19.356$ Å and $\gamma = 119.5^\circ$. There are 15 inequivalent Nb sites in this structure, one of them corresponds to a disordered position: the corresponding Nb atom occupies the 2i Wyckoff positions, each of the statistical displacements of $y = \pm 0.2285$ is occupied with concentration of 0.5. We ignored this partial fractional occupancy by occupying instead Wyckoff position 1a [at (0.0, 0.0, 0.0)] with occupation 1.0. This geometry was then optimized by minimizing the forces exerted on the atoms, keeping the overall unit cell parameters constant. The relaxed structure of H–Nb2O5 we thereby obtained is shown in Figure 1b. The changes with respect to the original experimental structure are generally small: the bond lengths typically changed by 0.001–0.050 Å, only in one case the Nb–O bond length increased by 0.20 Å and in one case the O–O bond length increase by 0.11 Å. The largest change of course concerns the Nb atom that was transferred from the 2i site to the 1a site. In the relaxed structure all Nb atoms are coordinated octahedrally by oxygen.

**III.B. Electronic Band Structures.** The response range of a semiconductor in the visible light regime is determined by the size of its band gap and its band structure, while its ability to successfully participate at the chemical reaction depends on the energetic position of the gap. The electronic band dispersions of orthorhombic Nb3O7 and Nb3O7(OH) as well as monoclinic H–Nb2O5 are plotted in Figure 2a–c along the high symmetry lines inside the irreducible Brillouin zone (IBZ). The band structure calculation of all three compounds was performed using the TB-mBJ approach. It is very difficult to predict the accurate position of the H atom in the crystal lattice of Nb3O7(OH) from both experiment as well as theory. As described above we model the H positions following Zhang et al. The energetically lowest position for H atom can be found in the octahedra of Nb(3) atom as it is shown in Figure 1a. The use of the suggested relaxed crystal structure shows semiconducting properties with an indirect band gap for Nb3O7(OH) and a fundamental band gap of 1.70 eV. The comparison with the reference compound Nb3O8 exhibits that the presence of hydrogen in the crystal lattice shifts the Fermi
energy to the top of the valence bands resulting in a change from metallic (Nb$_3$O$_8$) to semiconducting (Nb$_3$O$_7$(OH)) properties. In addition the uppermost valence band shows a much larger dispersion for Nb$_3$O$_7$(OH) than Nb$_3$O$_8$ and the conduction bands are shifted to lower energies by 0.5 eV in Nb$_3$O$_7$(OH). Other than these changes of the band structure due to the H atom are small (Figure 2a,b).

Like Nb$_3$O$_7$(OH) monoclinic H–Nb$_2$O$_5$ is also an indirect band gap semiconductor with a larger fundamental band gap of 2.56 eV (Figure 2). The valence band maximum (VBM) and conduction band minimum (CBM) occur at R and Y symmetry points in Nb$_3$O$_7$(OH) while they appear at D, E, Z, C, and B symmetry points of the IBZ in H–Nb$_2$O$_5$. Indirect transitions need a momentum transfer supplied by phonons to realize $k$-conservation. The calculated findings for the band gaps are summarized in Table 1. In addition experimentally determined values are given which were obtained using both absorption spectroscopy and electron energy-loss spectroscopy. Optical spectroscopy yields a band gap of 3.1 eV for both compounds, while a slightly larger band gap of 3.2 eV is determined for H–Nb$_2$O$_5$ from EEL spectra. This compares well with the calculated optical band gaps of the two compounds which were found to be 3.1 eV for Nb$_3$O$_7$(OH) and 3.0 eV for H–Nb$_2$O$_5$. The band gaps of the two niobium oxide phases are similar to TiO$_2$ and allow the absorption of light from the UV region ($\lambda < 390$ nm) of the solar spectrum.

The partial density of states (PDOS) reveal deeper insights into the band structure of Nb$_3$O$_7$(OH) and H–Nb$_2$O$_5$ (Figure 3a,b). The partial DOS confirms that the top of the valence

![Figure 2. Calculated band structures of Nb$_3$O$_8$ (left side, a), Nb$_3$O$_7$(OH) (b), and monoclinic H–Nb$_2$O$_5$ (c). In addition the density of states is given for Nb$_3$O$_8$ on the right side of part a.](image)

<table>
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<th>Band Gaps of Nb$_3$O$_7$(OH) and Nb$_2$O$_5$ determined experimentally and from calculation (in [eV])</th>
<th>Nb$_3$O$_7$(OH)</th>
<th>monoclinic H–Nb$_2$O$_5$</th>
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<td>3.07 (±0.05)</td>
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<td>EELS</td>
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<td>3.2 (±0.1)</td>
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bands of both compounds primarily originate from the O-2p orbitals, and the bottom of the conduction band mainly from Nb-4d orbitals with a negligible contribution of H-1s orbitals. The valence band of both Nb$_3$O$_7$(OH) and H$^{-}\text{Nb}_2$O$_5$ is divided into two distinct regions: The energy region at $-6.0$ eV to $\sim -4.0$ eV is dominated equally by the 4d/2p orbitals of Nb and O atoms, while small contributions of Nb-5s/5p orbitals and H-1s orbital are also observed. A strong overlap is observed for the O-2p and Nb-4d orbitals with the 5s orbitals of Nb atoms and the oxygen 2s orbitals with the 5s orbitals of Nb atoms also show strong interplay at 5.5 eV. The second energy region at $-4.0$ to $0.0$ eV is mainly assigned to O-2p but the Nb-4d orbitals contribute significantly less along with minor participation of 2s/5s/5p orbitals of O/Nb/H atoms. The 2s/5s orbitals of O/Nb atoms (from $-3.7$ to $-0.0$ eV) and the 1s/2s orbitals of H/O atoms of Nb$_3$O$_7$(OH) present strong interactions with each other at $-2.2$ eV, while the 2s/5s of O/Nb atoms (from $-1.30$ to $0.0$ eV) in Nb$_2$O$_5$ only partially interact. The H-1s orbitals are more than $-3.0$ eV deeper in energy than the VBM since the H atom is coordinated solely by one O atom leading to negligible hybridization over all other atoms. The bands above the Fermi level at energy 2.34 eV (Nb$_3$O$_7$(OH)) and 2.56 eV (Nb$_2$O$_5$) $\sim 4.0$ eV are robustly assigned to Nb-4d orbitals combined with O-2p orbitals and minor participation of the remaining orbitals of Nb/O/H atoms.

From the above discussion it becomes clear that the O-2p (VBM) and Nb-4d (CBM) orbitals are predominately responsible for optical excitations in Nb$_3$O$_7$(OH) and H$^{-}\text{Nb}_2$O$_5$. Furthermore, the investigations show that doping with H-1s causes a shifting of all peaks at the VBM toward lower regions as well as a broadening of these peaks (Figure 3a,b/2).

III.C. Optical Properties. It is known that semiconductors play an important role in the field of optoelectronic devices where the band gap defines the threshold energy of electromagnetic radiation and differentiates between transparency and absorbing region. The optical properties of Nb$_3$O$_7$(OH) and H$^{-}\text{Nb}_2$O$_5$ were calculated by linear response formalism and the complex dielectric function (namely $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$) of Nb$_3$O$_7$(OH) and H$^{-}\text{Nb}_2$O$_5$ are calculated.

In Figure 4a, the calculated frequency dependent perpendicular and parallel parts (defined along the crystallographic c-direction) of the imaginary $\varepsilon_2(\omega)$ dielectric function are shown for Nb$_3$O$_7$(OH) and H$^{-}\text{Nb}_2$O$_5$. In Nb$_3$O$_7$(OH), the threshold energy for the perpendicular polarization is 3.19 eV and thus a bit smaller than the energy (3.33 eV) for parallel polarization while the threshold energy for both polarization axes is nearly the same for H$^{-}\text{Nb}_2$O$_5$ (3.40 eV).

Furthermore, there are absorption peaks at 3.82/5.16 eV and around 5.81 eV ($\varepsilon_1^2(\omega)$) and 4.53/5.70 eV ($\varepsilon_2^2(\omega)$) in
produce at the energy points 11.96 eV/(6.57, 12.45)eV beyond these energies. In addition plasma frequencies are feature at 8.08 eV, while shows three maxima at 3.74 eV, 4.72 and 5.54 eV and a smaller peaks at 7.98 eV for $\varepsilon_1$ for Nb$_3$O$_7$(OH) and a smaller peaks at 7.98 eV. The transitions of electrons from the VBM (O-$2p$ orbitals) to CBM (Nb-4$d$ orbitals).

Additional absorption peaks are situated at 9.10 eV ($\varepsilon_2^1(\omega)$) and 10.01 eV ($\varepsilon_2^2(\omega)$) in Nb$_2$O$_5$(OH) and at 8.4 eV for both polarizations in Nb$_2$O$_5$. These peaks result from transitions of electrons from the orbitals below 4.0 eV. The difference of the absorption peaks observed for Nb$_2$O$_5$(OH) and Nb$_2$O$_5$ is attributed to their different crystal structures.

The calculated real part of the dielectric function, which describes the electronic polarizability of the material, were extracted from the imaginary part of the dielectric function using the Kramers–Kronig expression for the perpendicular $\varepsilon_2^1(\omega)$ and parallel $\varepsilon_2^2(\omega)$ polarization (Figure 4b). $\varepsilon_2^1(\omega)$ shows three maxima at 3.74 eV, 4.72 and 5.54 eV and a smaller feature at 8.08 eV, while $\varepsilon_2^2(\omega)$ exhibits two maxima at 4.01 and 5.10 eV for Nb$_2$O$_5$(OH) and a smaller peaks at 7.98 eV. The spectra of H–Nb$_2$O$_5$ shows one dominant peak at 4.04 eV and one smaller peak at 8.08 eV for $\varepsilon_2^1(\omega)$ respectively 4.18 and 7.98 eV for $\varepsilon_2^2(\omega)$. Both optical components of $\varepsilon_1(\omega)$ in Nb$_2$O$_5$(OH)/Nb$_2$O$_5$ are positive until 9.51/9.24 eV ($\varepsilon_2^1(\omega)$) and (6.21, 10.05)/(5.89, 8.77)eV ($\varepsilon_2^2(\omega)$) and become negative beyond these energies. In addition plasma frequencies are produce at the energy points 11.96 eV/(6.57, 12.45)eV ($\varepsilon_2^1(\omega)/\varepsilon_2^2(\omega)$) in Nb$_2$O$_5$(OH) and 13.21 eV/(6.63, 13.59 eV) in H–Nb$_2$O$_5$ ($\varepsilon_2^1(\omega)/\varepsilon_2^2(\omega)$) in the positive direction with $\varepsilon_2^1(\omega)/\varepsilon_2^2(\omega) = 0$. The static values of Nb$_2$O$_5$(OH) are 4.12 eV ($\varepsilon_2^1(\omega)$) and 3.98 eV ($\varepsilon_2^2(\omega)$) while H–Nb$_2$O$_5$ is characterized by static values of 4.30 eV ($\varepsilon_2^1(\omega)$) and 4.58 eV ($\varepsilon_2^2(\omega)$). This means that Nb$_2$O$_5$(OH) and H–Nb$_2$O$_5$ obey the Penn model, which states that larger optical band gaps results in smaller static values.

On the basis of the dielectric function the perpendicular $\sigma^\perp(\omega)$ and parallel $\sigma^\parallel(\omega)$ components of the optical conductivity were calculated for both compounds (Figure 5). There is considerable more optical anisotropy in Nb$_3$O$_7$(OH) compared to H–Nb$_2$O$_5$ (almost isotropic) for both polarizations. For Nb$_3$O$_7$(OH), the maximum values of $\sigma^\parallel(\omega)$ are situated around 5.83 eV (4.33 × 10$^{15}$s$^{-1}$) and 9.13 eV (4.25 × 10$^{15}$s$^{-1}$) and of $\sigma^\perp(\omega)$ at 5.73 eV (4.75 × 10$^{15}$s$^{-1}$) and 10.01 eV (3.95 × 10$^{15}$s$^{-1}$). H–Nb$_2$O$_5$ expresses two peaks for both components; for $\sigma^\parallel(\omega)$, these peaks are situated at 5.83 eV (4.44 × 10$^{15}$s$^{-1}$) and 8.96 eV (4.08 × 10$^{15}$s$^{-1}$) and for $\sigma^\perp(\omega)$ at 5.70 eV (5.96 × 10$^{15}$s$^{-1}$) and 8.47 eV (4.82 × 10$^{15}$s$^{-1}$). The difference between the optical conductivity of the two compounds is attributed to their electronic structure as these peaks are mainly composed by the states close to the Fermi level.

III.D. Comparison of the Calculation with Experimental EELS Data. The quality of the calculation was investigated using experimental low loss EEL spectra which were compared to theoretical spectral components of the energy loss function.
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Figure 5. Calculated optical conductivity \( \sigma(\omega) \) of \( \text{Nb}_3\text{O}_7(\text{OH}) \) and monoclinic \( \text{H}--\text{Nb}_2\text{O}_5 \).

Figure 6. Comparison of the calculated energy loss functions \( L(\omega) \) with experimental low loss EEL spectra for \( \text{Nb}_3\text{O}_7(\text{OH}) \) and \( \text{H}--\text{Nb}_2\text{O}_5 \).

\( L(\omega) \) for both compounds. Figure 6 shows the spectra \( L(\omega) \) which were calculated theoretically using the TB-mBJ functional. The peaks in \( L(\omega) \) have a direct proportionality to the energy loss of fast electrons which transmit through materials. A plasma frequency is produced for the energy points in \( \varepsilon_1(\omega) \) for which \( \varepsilon_1(\omega)/\varepsilon_1(\omega) = 0 \) applies. These are then responsible for the plasmon resonance in \( L(\omega) \). Because of the lack of interband transitions the valence shell electrons are regarded as free which results in plasma peaks in both optical spectra of \( L^\perp(\omega)/L^\parallel(\omega) \). The low-loss spectra were measured along [100] \( L^\perp(\omega) \) and [001] \( L^\parallel(\omega) \) direction for \( \text{Nb}_3\text{O}_7(\text{OH}) \) and off-zone axis for \( \text{Nb}_2\text{O}_5 \). The experimental spectra for the two crystal directions of \( \text{Nb}_3\text{O}_7(\text{OH}) \) show broad features at 7 eV and a double peak structure between 12 and 15 eV. The first peak is similar for both crystal directions and can nicely be reproduced by theory which yields a value of 7.1 eV for \( L^\perp(\omega) \) and \( L^\parallel(\omega) \). The peak intensity of the experimentally observed double peak varies for the two crystal directions: The experimental \( L^\perp(\omega) \) exhibits an enhanced intensity for the first peak at 12 eV, while the second peak at 15 eV is more intense for the experimental \( L^\perp(\omega) \). This is also nicely reproduced by theory which exhibits a maximum at 12.47 eV for \( L^\perp(\omega) \) and 15.0 eV for \( L^\parallel(\omega) \). The theoretical spectrum \( L^\perp(\omega) \) and \( L^\parallel(\omega) \) of \( \text{H}--\text{Nb}_2\text{O}_5 \) shows similar features which are positioned at 6.7 and 14.2 eV. Therefore, the experimental spectrum was not acquired along a certain crystal direction. The first peak is similar for both crystal directions and can nicely be reproduced by theory which yields a value of 7.1 eV for \( L^\perp(\omega) \) and \( L^\parallel(\omega) \). The peak intensity of the experimentally observed double peak varies for the two crystal directions: The experimental \( L^\perp(\omega) \) exhibits an enhanced intensity for the first peak at 12 eV, while the second peak at 15 eV is more intense for the experimental \( L^\perp(\omega) \). This is also nicely reproduced by theory which exhibits a maximum at 12.47 eV for \( L^\perp(\omega) \) and 15.0 eV for \( L^\parallel(\omega) \). The theoretical spectrum \( L^\perp(\omega) \) and \( L^\parallel(\omega) \) of \( \text{H}--\text{Nb}_2\text{O}_5 \) shows similar features which are positioned at 6.7 and 14.2 eV. Therefore, the experimental spectrum was not acquired along a certain crystal direction. The feature observed experimentally resembles the two dominant peaks in the theoretical spectra of \( L^\perp(\omega) \) and \( L^\parallel(\omega) \).

There is a good agreement between experiment and calculated low-loss features for both compounds, which proves the validity of our structure models. Some finer details of the calculated spectrum could not be resolved experimentally. This might be due to the experimental point spread function which limits the energy resolution.

Element specific electron energy-loss edges give further insights into the local surrounding of the elements in the crystal structure. Both crystal structures \( \text{Nb}_3\text{O}_7(\text{OH}) \) and monoclinic \( \text{H}--\text{Nb}_2\text{O}_5 \) are composed of edge- and corner-sharing \( \text{NbO}_6 \) octahedra. This is why no significant differences were observed for the electron energy-loss near edge structure (ELNES) of the experimental \( \text{Nb}--\text{M}_3 \) and \( \text{O}--\text{K} \) edges of the two compounds. In this regard the \( \text{Nb}--\text{M}_3 \) and \( \text{O}--\text{K} \) edge spectra were only calculated for \( \text{Nb}_3\text{O}_7(\text{OH}) \) to elucidate the contribution of the different lattice sites to the ELNES of the edges. The theoretical spectra were calculated using the WIEN2k code as X-ray absorption spectra (XAS) assuming that EEL spectra are practically the same as XAS spectra for the investigated energy losses. This approximation is valid since the EELS data were acquired within the dipole regime, i.e. small scattering angles. The spectra were obtained as weighted superpositions of spectra generated at each of the inequivalent atomic positions.
Figure 7 summarizes the experimental spectrum, the weighted superposition and the individual contributions of atoms in inequivalent lattice sites. 

Pentavalent Nb$_5$O$_3$ is characterized by a Nb−M$_{3,4}$ edge which exhibits two white lines with high-energy shoulders and is consistent with previously reported ELNES data.\(^{50}\) The experimental data of the Nb−M$_5$ edge of Nb$_5$O$_3$(OH) likewise shows one broad line with a maximum at about 3 eV above the onset and a shoulder around 4.2 eV. Our calculations which are based on the dipole selection rule $(\Delta l = \pm 1)^{51}$ nicely reproduce the ELNES of this edge, which is explained by excitations from the Nb-3p$_{3/2}$ level to unoccupied Nb-4d states while dipole allowed transitions from 3p$_{3/2}$ to Nb-5s play a minor role. From the calculations it is obvious that the substructuring of the white line is related to the inequivalent Nb sites in either edge or corner-sharing NbO$_6$ octahedra. Niobium which sits in the center of edge-sharing NbO$_6$ octahedra (depicted as Nb(2) and Nb(3) in Figure 7) mainly contributes to the main peak, while the share of the Nb(1) atoms which sit in corner-sharing octahedra dominates the shoulder of the Nb−M$_5$ spectrum.

The experimental O−K edge, which results from transitions of the 1s core electrons to unoccupied states with $p$ character shows five dominant peaks at 2.0, 6.0, 14.0, 22.0, and 33.0 eV above the onset. The entire spectrum could be reproduced nicely by calculations as shown in Figure 7. This was achieved by including the core hole effect into the calculations using the final state rule. Doing so we performed eight supercell calculations for each inequivalent O-site. The calculations exhibit a huge difference between contributions stemming from different inequivalent oxygen atoms; The first three peaks at 2.0 eV, 6.0 and 13.0 eV at the theoretical scale mainly originates from the following O atoms contributions as follows: (1) the first peak originates from O(1), O(3), and O(4) with minor contribution of O(2, 5−8); (2) the second peak appears mainly due to contributions from O(6) and O(3); (3) the third peak is almost equally contributed by O(6), O(1), and O(3) with minor participation of other O atoms. The remaining two peaks are produced by equal contribution of all O atoms only O(2) participates more at the last peak. Figure 7 shows a nice agreement between the theory and experiment for the O−K edge and Nb−M$_5$ edge, likewise proving our structure model for Nb$_5$O$_3$(OH).

III.E. Transport Properties. The electronic transport properties are crucial for the performance of a material in functional devices as electrons and holes need to diffuse through the material subsequent to their generation. These properties are dominated by the effective masses of holes/electrons and their mobilities. The effective masses of electrons and holes were calculated for Nb$_5$O$_3$(OH) and H−Nb$_5$O$_3$ by fitting the electronic dispersion curves (E−K curve) around the CBM and VBM niveau:

$$m^* = h^2 \frac{\partial^2 E}{\partial k^2}^{-1}$$

where $m^*$ and $h$ are the effective mass and reduced Planck constant. The calculated effective masses of electrons ($m_e^*$) are 0.147 $m_e$ for Nb$_5$O$_3$(OH) and 0.112 $m_e$ for H−Nb$_5$O$_3$. Values of 0.351 $m_e$ and 0.959 $m_e$ were found for the masses of holes ($m_h^*$) for Nb$_5$O$_3$(OH) and H−Nb$_5$O$_3$, respectively. The inverse relation of the effective mass with the mobility of carriers $\mu_e/\mu_h$ is given by

$$\mu_e = \frac{e \tau}{m_e^*} \text{ and } \mu_h = \frac{e \tau}{m_h^*}$$

with $\tau$ being the relaxation time and $e$ the charge of an electron. Accordingly greater effective mass of holes or electrons yield smaller mobilities and vice versa. Both compounds express a higher mobility of electrons resulting in n-type conductivity with Nb$_5$O$_3$(OH) exceeding H−Nb$_5$O$_3$.

To elucidate the prospects of Nb$_5$O$_3$(OH) and H−Nb$_5$O$_3$ in functional devices the thermoelectric conductivity was calculated under constant relaxation time approximation using the BoltzTraP code.\(^{52}\) In Figure 8, the thermoelectric conductivity $\sigma_{\text{te}}$ is plotted as a function of the chemical potential $\mu_e$(eV) at 300 K for both Nb$_5$O$_3$(OH) and H−Nb$_5$O$_3$. The $\sigma_{\text{te}}(\mu_e, T = 300 \text{ K})$ plots are separated into a region below the Fermi level $E_F$, which is assigned to hole carriers (p-type), and a region above $E_F$ assigned to electrons (n-type). For Nb$_5$O$_3$(OH), the $\sigma_{\text{te}}(\mu_e, T = 300 \text{ K})$ plot shows a sharp increase in the n-type region with reaching a value of 1.26 $\times$ $10^{20}$($\Omega \text{ ms}$)$^{-1}$ compared to the p-type region (0.57 $\times$ $10^{20}$($\Omega \text{ ms}$)$^{-1}$). The thermo-electric conductivity of H−Nb$_5$O$_3$ is likewise characterized by a greater value of 3.92 $\times$ $10^{19}$($\Omega \text{ ms}$)$^{-1}$ in the n-type region compared to the p-type region were $\sigma_{\text{te}}(\mu_e, T = 300 \text{ K})$ equals 2.97 $\times$ $10^{19}$($\Omega \text{ ms}$)$^{-1}$.

It is worth to note that even though both compounds behaves like n-type semiconductors, the thermoelectric conductivity of electrons is by a factor of 3 higher in...
Nb2O5(OH) than in H−Nb2O5. This is in line with the high photochemical efficiency of Nb2O5(OH) observed experimentally.1024

IV. CONCLUSION

In summary, we investigated the electronic structure, optical and electronic transport properties of Nb2O5(OH) and H−Nb2O5 using the TB-mBJ31 functional and developed a model to simulate the presence of hydrogen in the crystal lattice of Nb2O5(OH). The calculated band structures showed that both compounds are wide and indirect band gap semiconductors, with the calculated optical band gaps being similar to the ones determined experimentally. For both compounds mainly Nb-4d orbitals construct the CBM while O-2p orbitals form the VBM so that transitions between these orbitals are mainly responsible for optical transitions featuring sharp peaks in the dielectric function. Compared to H−Nb2O5, Nb2O5(OH) shows a greater optical anisotropy and a higher thermoelectric conductivity \( \sigma^{\text{th}} (\mu, T = 300 \, \text{K}) \). Both compounds express n-type conductivity, and the thermoelectric conductivity of electrons is by a factor three higher in Nb2O5(OH) compared to H−Nb2O5. Similarly, the thermoelectric conductivity of holes is twice as high in Nb2O5(OH) than in H−Nb2O5.

Experimental low-loss EEL spectra (energy losses between 0 and 50 eV) were recorded in the TEM for Nb2O5(OH) and H−Nb2O5. A good agreement between theory and experiment was discovered. These findings validate the results of the calculations and the model for hydrogen positioning. In addition, the WIEN2k code35 was applied to simulate the ELNES of the Nb−M3 and O−K edge of Nb2O5(OH) revealing the contribution of inequivalent lattice sites of the Nb and O atoms.

The results of this study allow an interpretation of the applicability of the two niobium oxide phases orthorhombic Nb2O5(OH) and monoclinic H−Nb2O5 as photocatalysts or electrode materials. Both compounds exhibit suitable properties but Nb2O5(OH) exceeds H−Nb2O5 due to higher charge carrier mobility.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b06391.

Crystallographic cif files for monoclinic H−Nb2O5 (CIF)

Crystallographic cif files for orthorhombic Nb2O5(OH) (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The theoretical results were developed within the CENTEM project, Reg. No. CZ.1.05/2.1.00/03.0088 and CENTEM PLUS (LO1402). We would like to acknowledge support of supercomputer MetaCenter (LM2010008) and CERT-SC (CZ.1.05/3.2.00/08.0144). J.M., C.S., and S.B.B gratefully acknowledges financial support of the "Nanosystems Initiative Munich (NIM)" and for the support of work at the Molecular Foundry by the Office of Science, Office of Basic Energy Sciences, the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. J.M., P.B., and O.S. are supported by COST Action MP1306 EUspec and W.K. also by the CZ LD15147 of The Ministry of Education, Youth, and Sports.

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