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DOI
10.1021/acs.jpclett.9b00088

Publication date
2019

Document Version
Final published version

Published in
Journal of Physical Chemistry Letters

Citation (APA)
Cornelius, S., Colombi, G., Nafezarefi, F., Schreuders, H., Heller, R., Munnik, F., & Dam, B. (2019). Oxyhydride Nature of Rare-Earth-Based Photochromic Thin Films. Journal of Physical Chemistry Letters, 10(6), 1342-1348. https://doi.org/10.1021/acs.jpclett.9b00088

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Oxyhydride Nature of Rare-Earth-Based Photochromic Thin Films

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Supporting Information

ABSTRACT: Thin films of rare-earth (RE)—oxygen—hydrogen compounds prepared by reactive magnetron sputtering show a unique color-neutral photochromic effect at ambient conditions. While their optical properties have been studied extensively, the understanding of the relationship between photochromism, chemical composition, and structure is limited. Here we establish a ternary RE—O—H composition-phase diagram based on chemical composition analysis by a combination of Rutherford backscattering and elastic recoil detection. The photochromic films are identified as oxyhydrides with a wide composition range described by the formula REO1−xHy, where 0.5 ≤ x ≤ 1.5. We propose an anion-disordered structure model based on the face-centered cubic unit cell where the O2− and H+ anions occupy tetrahedral and octahedral interstices. The optical band gap varies continuously with the anion ratio, demonstrating the potential of band gap tuning for reversible optical switching applications.

While the structure—property relationships of single-anion materials, such as metal oxides, are to a large extent determined by variations in the cation chemistry, multianion compounds offer another dimension of control of material properties. This is due to the wide range of different characteristics, including electronegativity, polarizability, and ionic radius.1 Perhaps the least studied group of multianion compounds are oxyhydrides where both oxide (O2−) and hydride (H+) ions are present. Since the successful synthesis of the transition metal (TM) oxyhydride LaSrCoO4H0.7 by Hayward et al.,2 this material class has been extended to TM = Sc, Ti, V, Cr, Mn, Co based on the perovskite and the layered Ruddlesden–Popper crystal structure types.3 A recent report on hydride ion (H+) conductivity in La2−xSrxLi1−yHO3−y makes oxyhydrides promising materials for energy storage and conversion applications.4 Two synthesis routes for TM oxyhydrdes have been established to date. Topochemical synthesis exploits the O2−/H+ anion exchange between the parent oxide and a hydride (mostly CaH2) at moderate temperatures of 300–600 °C.3 Alternatively, some TM oxyhydrides have been prepared by high-pressure (few GPa) direct synthesis from parent oxide and hydride powder mixtures at 1000–1300 °C.5 These methods have also been employed to synthesize powders of lanthanide (Ln) oxyhydrides LnOH with Ln = La,5 Nd,6 Sm,7,8 Gd–Er,9 the second established class of oxyhydride materials. The stoichiometric LnOH are reported to crystallize either in the anion-disordered face-centered cubic (fcc) fluorite type structure (Fm3m)7–9 or in an anion-ordered superstructure with tetragonal (P4/nmm) symmetry.5,6 To date, the electronic properties of the lanthanide oxyhydrides remain largely unexplored. A recent study by Ueda et al. suggests that Tb53+-doped GdOH is a promising candidate for phosphor applications.9

A remarkable photochromic effect at ambient conditions was discovered in reactive magnetron sputtered (MS) YOxHy thin films.10 Initially, these semiconducting materials (band gap Eg ≈ 2.6 eV) were referred to as oxygen-containing yttrium hydride.10,11 It was speculated that their properties can be explained in analogy to the transparent γ-YH3 phase stabilized in the fcc structure by incorporation of oxygen into the lattice.11 A later study on sputtered YOxHy composition gradient thin films, which covers the transition from opaque to transparent state, reports atomic ratios of up to H/Y ≈ 3 as measured by heavy-ion elastic recoil detection (ERD) and nuclear reaction analysis (NRA).12 However, this result seems rather questionable considering the low H2 partial pressures during reactive MS deposition. Follow-up studies by Montero et al.13 and Nafezarefi et al.14 clarified that the transparent YOxHy materials are in fact formed by air oxidation of adsorbed metallic β-YH2 films. Further, we reported that LnOxHy thin films with Ln = Gd, Dy, Er exhibit the same photochromic effect and fcc crystal structure as YOxHy.14 On the basis of these findings and our preliminary chemical composition analysis experiments, we then adopted the term rare-earth (RE) oxyhydrides for this group of photochromic
materials. However, systematic experimental evidence for the presence of H\(^+\) ions in these REO\(_{H_2}\) is scarce. Although a recent study by Moldarev et al. supports the concept of H\(^+\) in their photochromic YO\(_{H_2}\), films, they also had to assume multiple cation charge states and/or the presence of OH\(^-\) complex ions in order to obtain charge balance.\(^{15}\) Moreover, the relationship of the photochromic REO\(_{H_2}\) thin films to the established group of stoichiometric LnOH bulk materials in terms of chemical composition and crystal structure remained unclear.

Here, we address these open questions by a combination of chemical composition analysis via ion beam methods, charge neutrality arguments, and optical characterization. We find that the photochromic REO\(_{H_2}\) films are indeed oxyhydrides—clearly distinct from hydroxides—having a wide composition range along the MH\(_3\)−M\(_2\)O\(_3\) axis. This allows us to explain their properties in the framework of O\(^2^-\)/H\(^+\) anion-disorder, linking the known (anion-ordered) structures of REH\(_3\) trihydrides, LnOH, and the RE\(_2\)O\(_3\) sesquioxides.

Recently, we reported that metallic β-MH\(_{1.9}\) thin films with M = Y, Er, Dy, Gd can be prepared by direct current (DC) reactive MS of metal targets in an Ar/H\(_2\) atmosphere.\(^{14}\) Above a certain material-dependent critical deposition pressure (p\(^*\)), the films air-oxidize at room temperature (RT) to form stable semiconducting transparent photochromic MO\(_{H_2}\). In order to obtain samples with a wide range of chemical compositions, we have extended our standard synthesis procedure as follows: (i) Sc is sputtered as the RE element with the smallest ionic radius. (ii) A variable amount of O\(_2\) is added to the Ar/H\(_2\)/O\(_2\) process gas (SN purity) resulting in a mixture containing (12.5−11.9) % of H\(_2\) and (0−4.7) % of O\(_2\). (iii) Pulsed DC plasma excitation (50 kHz, 90% duty cycle) is used to avoid arcing. (iv) Al capping layers (20 nm) were sputtered onto selected samples directly or after timed air exposure to prevent further oxidation. All samples were grown on unheated UV-grade fused silica (f-SiO\(_2\)) and polished glassy carbon substrates (HTW Germany). Structural and optical properties were investigated by a combination of X-ray diffraction (XRD, Bruker D8 Discover) and photoluminescence spectra.

The MO\(_{H_2}\) chemical composition is determined by a combination of Rutherford backscattering spectrometry (RBS) and ERD analysis at the 2 MV Van-de-Graaff accelerator at Helmholtz-Zentrum Dresden-Rossendorf (Dresden, Germany). RBS (ERD) measurements were performed with a 1.7 MeV \(^{4}\)He\(^+\) beam at 0° (70°) incidence and 160° (30°) scattering angle using semiconductor detectors with a solid angle of 3.3 msr (5.6 msr) and an energy resolution of ~15 keV. The ERD detector was covered by a 6.6 μm Al stopper foil to discriminate recoiled He from forward scattered He. A special set of Sc, Y, and Gd dihydride reference samples was prepared by hydrogenating Pd-capped (20 nm) metal layers (150 nm) in a pressure cell at 1 bar of H\(_2\) at RT. Employing the hydrogenography method,\(^{16}\) the change in optical transmittance is used to verify that all films were initially loaded to H/M ratios above the dihydride to trihydride phase transition, followed by unloading to dihydride in air after opening the pressure cell. Because of the tensile strain induced by hydrogen desorption,\(^{17}\) we expect that these dehydrogenated layers have a H/M ratio corresponding to the lower end of the β-MH\(_3\) existence range, i.e., ScH\(_{1.69}\)\(^{18}\) YH\(_{1.90}\)\(^{17}\) and GdH\(_{1.80}\) (see Figures S1−S3 for XRD characterization). These dihydride samples turned out to be crucial to accurately calibrate the solid angle of the ERD detector. For each sample, the RBS and ERD spectra were fitted self-consistently using the SIMNRA\(^{19}\) program and the SRIM2013 stopping power database.\(^{20}\)

The result of this analysis is illustrated in Figure 1, showing the experimental ion beam spectra and corresponding simulations of a set of YO\(_{H_2}\) films with different O/H ratios. The areal densities (atoms/cm\(^2\)) of Y and O are obtained from RBS data, taking into account the Al or Pd capping layers. The overall fit accuracy benefits from the nearly background-free oxygen signal with good counting statistics, which is achieved by the use of carbon instead of f-SiO\(_2\) substrates. The H areal density is obtained from the ERD signal taking into account the energy loss and straggling of H recoils in the Al stopper foil as well as geometric straggling\(^{21}\) due to the variation of the scattering angle across the detector area. The combined RBS and ERD analysis allows for a quantification of the element concentrations (in atom %) with an uncertainty below 2 atom %. The RBS spectrum of Pd-capped hydrogenated Y shows that the film contains no oxygen (O detection limit 1 atom %) except for a thin surface layer within the C substrate.
- probably a result of surface polishing. It is important to note here, that no other light elements, in particular F, could be detected in the MO\textsubscript{H}\textsubscript{x} films discussed in this work. Together with the previously observed characteristic transmittance window (Figure 5) and lattice constants,\textsuperscript{14} this increases the confidence that our RE hydride samples are nearly ideal β-MH\textsubscript{x} reference materials. Besides oxygen, fluorine is a common impurity in rare-earth metals - especially in Y.\textsuperscript{22} In the past, we observed high concentrations of O (up to 7 at.%) and F (up to 13 at.%) in many commercial Y metal sputter targets of nominal 99.9% purity. Such high F concentrations complicate the chemical analysis and obscure subsequent interpretation of charge balance and electronic properties. Hence, we use high-purity Y targets supplied by Stanford Advanced Materials (United States) to avoid these problems.

The RBS and ERD simulations shown in Figure 1 confirm that the MO\textsubscript{H}\textsubscript{y} film composition is homogeneous throughout the depth of the films. We have observed chemical gradients in a few samples prepared at deposition pressures far above the critical values of p* = 0.3 Pa (Sc), 0.5 Pa (Y), and 0.7 Pa (Gd).\textsuperscript{14} However, the interpretation of the composition–property relationships of such graded (and likely porous) films is rather ambiguous. Therefore, we have excluded these samples from further analysis.

Figure 2 shows the results of the ion beam chemical composition analysis of our (Sc,Y,Gd)O\textsubscript{H}\textsubscript{x} thin films in a generalized ternary M–O–H composition-phase diagram. This construction is based on the similar properties of the binary RE metal oxides and hydrides. At ambient conditions, the RE metals form stable M\textsubscript{2}O\textsubscript{3} sesquioxides (except CeO\textsubscript{2}) with a cubic bixbyte (I\textsubscript{a}3) structure (except La, Pr, and Nd).\textsuperscript{23} All RE metals readily dissolve hydrogen, forming a random interstitial α-MH\textsubscript{x} alloy where H occupies a fraction of the tetrahedral sites in the hexagonal close-packed (hcp) RE lattice. Upon hydrogenation, a phase transition to the metallic fcc (Fm\textsubscript{3m}) β-MH\textsubscript{x} occurs for all REs. Further hydrogenation leads to a metal to insulator transition near H/M = 3. For most REs, this is accompanied by a structural phase transition to hcp γ-MH\textsubscript{x} (except Sc, La, Pr, Nd). Moreover, the REs form hcp M(OH)\textsubscript{x} hydrides\textsuperscript{25} and various MOOH oxy-hydroxide phases.

Our results show that the chemical composition of the Sc, Y, and Gd-based thin films follow the same general trends in the M–O–H diagram. Two material groups can be clearly distinguished by considering the formal valencies and demanding charge neutrality (indicated by dashed lines). The RE oxyhydrides with a composition range of M\textsuperscript{2+}O\textsubscript{x}H\textsubscript{2−x} (0.5 ≤ x ≤ 1.5) are found on the line connecting MH\textsubscript{2} and M\textsubscript{2}O\textsubscript{3}. In particular, at x = 1 this includes the stoichiometric LnOH bulk compounds mentioned earlier. At x = 0.5, the data points deviate from the M\textsuperscript{2+}O\textsubscript{2−}H\textsubscript{3−x} line toward MH\textsubscript{2} (hatched area). This is consistent with our previous work showing that as-deposited films sputtered in Ar/H\textsubscript{2} are metallic dihydrides that oxidize in air to form transparent photochromic films.\textsuperscript{14} We obtain gray opaque films with compositions between MH\textsubscript{2} and MO\textsubscript{1.5}H\textsubscript{0.5} by sputtering at pressures near p*. Their composition range in the ternary M–O–H diagram suggests that initially the air-oxidation proceeds via insertion of oxide ions into the MH\textsubscript{2} lattice accompanied by oxidation of M\textsuperscript{2+} cations to M\textsuperscript{3+}. The opaque character of these films is characteristic for intermixed metallic and dielectric phases indicating nucleation of semiconducting MO\textsubscript{1.5}H\textsubscript{0.5} in β-MH\textsubscript{x}. Note that MO\textsubscript{1.5}H\textsubscript{0.5} (x = 0.5) marks the (ideal) composition where the conduction band is fully depleted of electrons (all cations are in the M\textsuperscript{3+} state) resulting in a metal–insulator transition that is observed in terms of the appearance of an optical band gap. Increasing the pressure above p* or adding small amounts of O\textsubscript{2} during deposition leads to the formation of transparent semiconducting oxyhydrides with compositions between MO\textsubscript{1.5}H\textsubscript{0.5} and M\textsubscript{2}O\textsubscript{3}. In contrast, the RE hydroxides with the composition range M\textsuperscript{2+}O\textsubscript{2−}H\textsubscript{3−x} (1.5 ≤ x ≤ 3) are located on the line connecting M\textsubscript{2}O\textsubscript{3} and M(OH)\textsubscript{3}. These transparent films were obtained by further increasing the O\textsubscript{2} fraction in the Ar/H\textsubscript{2}/O\textsubscript{2} mixture during reactive sputtering.

XRD analysis confirms that all RE oxyhydride films in Figure 2 have fcc unit cell symmetry, where the lattice constant is expanded by (1.0–2.8)% relative to the dihydride because of oxygen incorporation (see XRD analysis in the Supporting Information). Moreover, the lattice constants of sputtered dihydrides, oxyhydrides, and oxides show a systematic variation with the RE ion radius according to the lanthanide contraction effect.\textsuperscript{14} By combining the structural similarities of the known stoichiometric compounds and the chemical composition results, we propose a generalized simplified structure model for the RE oxyhydrides as shown in Figure 3. It is based on the fcc (Fm\textsubscript{3m}) structure where the 4 lattice sites are occupied by the RE cations and the compounds differ only in the average anion occupation of the 8 tetrahedral and 4 octahedral interstices per unit cell. In this framework, the M\textsubscript{2}O\textsubscript{3} oxides can be described by a random 6/8 occupation of

Figure 2. Ternary M–O–H chemical composition and phase diagram where M = Sc, Y, La, Sm–Lu. Thick dashed lines indicate chemical compositions with the same charge state of cations (M\textsuperscript{2+}, M\textsuperscript{3+}, H\textsuperscript{+}) and anions (O\textsuperscript{2−}, H\textsuperscript{−}). Hexagons mark the (ideal) stoichiometric compounds that have been reported earlier: (i) binary compounds: MH\textsubscript{2} dihydride and MH\textsubscript{3} trihydride in blue as well as M\textsubscript{2}O\textsubscript{3} sesquioxides\textsuperscript{22,24} and MO\textsubscript{2} in red; (ii) ternary compounds: MOH oxyhydrides,\textsuperscript{20} MOOH oxy-hydroxide, M(OH)\textsubscript{x} hydroxide,\textsuperscript{20} and the hypothetical MO\textsubscript{1.5}H\textsubscript{0.5} in black. Colored circles show the chemical compositions of MO\textsubscript{H}\textsubscript{x} thin films obtained from ion beam analysis. Note that the diameter of the data points corresponds to a composition uncertainty of approximately ±1 at.%. The region of photochromic materials is highlighted in gray.
tetrahedral sites by O\(^{2-}\), where anion-ordering would lead to a distortion of the fcc symmetry resulting in the bixbyite-M\(_2\)O\(_3\) structure. The idealized structure of stoichiometric MH\(_2\) is an fcc (Fm\(_{3m}\)) lattice where all 8 tetrahedral sites are occupied by H\(^+\) ions. Additional filling of the 4 octahedral sites by H\(^+\) leads to the idealized MH\(_3\) structure. While the trihydrides of La, Ce, Pr, and Nd remain in the fcc structure up to H/M \(\approx 3\), the most common hcp structure of the RE γ-MH\(_4\) can be interpreted as a distorted fcc lattice where the cubic (111) axis is parallel to the hcp c-axis. The structure of the stoichiometric LnOH powder materials was previously described as a fcc (Fm\(_{3m}\)) where the tetrahedral sites are randomly occupied by O\(^{2-}\) and H\(^+\) with a 1:1 ratio. The corresponding anion-ordered structure is tetragonal (P4/nnm).\(^5\)

The resulting generalized picture of anion-disordered fcc symmetry as shown in Figure 3 illustrates that in the M\(^{13}\)O\(_{14}\)H\(_{5−2x}\) oxyhydrides the cation-to-anion ratio changes from 1:1.5 in M\(_2\)O\(_3\) to 1:3 in MH\(_4\). This implies that the MOH composition (\(x = 1\)) marks a transition point regarding the occupation of tetrahedral and octahedral interstices. For \(x > 1\), the octahedral sites are empty and additional structural tetrahedral vacancies are forming with increasing oxygen content up to a maximum amount of 25% in the M\(_2\)O\(_3\) structure. In the case of \(x < 1\), all tetrahedral sites are occupied and the octahedral sites are successively filled with hydride ions with increasing hydrogen content.

We observe photochromism of the oxyhydrides over a wide composition range for both \(x < 1\) and \(x > 1\), as shown by the highlighted gray area in Figure 2. However, the exact composition boundaries for photochromic MOH\(_{5−2x}\) remain unclear. Regarding the lower boundary, we did not obtain any oxyhydrides with \(x < 0.5\) by either postoxidation of metallic β-MH\(_3\) films or direct growth using oxygen-poor Ar/H\(_2\)/O\(_2\) gas mixtures. This suggests that, in contrast to what was reported by You et al.,\(^12\) H/M ratios above 2 in RE oxyhydride films cannot be achieved by reactive MS. This is because the typical H\(_2\) partial pressures of a few 10 mPa during sputtering are far below the equilibrium pressure of the MH\(_2\) → MH\(_3\) phase transition (\(p_{H2} \approx 0.1\) Pa)\(^{26,27}\) and the addition of O\(_2\) to the process gas favors further dehydrogenation. Therefore, we prepared a γ-YH\(_{2.7+δ}\) (\(x = 0\)) thin film by hydrogenation of a Pd-capped sputtered Y metal film at \(p_{H2} = 3.2\) kPa in a vacuum cell mounted into our in situ spectrometer. This trihydride did not show photochromism at RT, whereas air-oxidized RE dihydride films with \(x \approx 0.5\) are photochromic. Hence, this value is marked as the O-poor boundary for photochromic RE oxyhydrides in Figure 2.

In order to discuss the O-rich boundary for photochromism, the effect of the anion ratio on optical properties has to be considered. Transmittance spectra of YO\(_x\)H\(_y\) films are presented in Figure 4. The dense YH\(_4\) film prepared at \(p = 0.3\) Pa (i.e., far below the critical deposition pressure for Y) shows a transmittance window centered around 700 nm characteristic of metallic β-YH\(_4\) dihydride, which is caused by a combination of weak interband and free-electron absorption.\(^28\) The RE oxyhydride and hydroxide films are transparent semiconductors. The optical band gap of Y oxyhydride increases continuously with increasing O\(^{2-}\) content from (2.5 ± 0.1) eV at \(x \approx 0.7\) up to (4.9 ± 0.2) eV at \(x \approx 1.4\) (Figure 5). An extrapolation of this nonlinear trend (dashed line) leads to good agreement with the band gaps of Y\(_2\)O\(_3\) (5.6 eV) and YH\(_3\) (2.6 eV), which are determined by the O 2p → Y 3d and H 1s → Y 3d interband transition, respectively.\(^29\) Therefore, the upper valence band of the RE oxyhydrides is likely formed by a mixture of occupied H 1s and O 2p states where the valence band maximum (VBM) shifts to lower energies with increasing O\(^{2-}\) concentration because of the higher electronegativity of oxygen (\(\chi_O = 3.44\)) compared to hydrogen (\(\chi_H = 2.20\)). The resulting band gap widening of the Y oxyhydrides does not depend linearly on the anion composition. This “band gap bowing” effect also occurs in many other semiconducting multitianion compounds such as oxysulfides,\(^30,31\) oxynitrides,\(^32\) and III–V materials.\(^33\) Its origin can be traced back to the mismatch in atomic orbital energy

**Figure 3.** Generalized crystal structure evolution of rare-earth oxyhydrides with different H\(^+/\)M and O\(^{2-}/\)M ratios based on the fcc-fluorite (Fm\(_{3m}\)) structure motif. Anion sublattice disorder is visualized by multicolored spheres in terms of partial occupancy of tetrahedral (yellow polygon) and octahedral (green polygon) sites. The corresponding anion-ordered crystal structures of fcc-MH\(_2\), hcp-MH\(_3\), tetragonal MOH,\(^5,6\) and bixbyite-M\(_2\)O\(_3\)\(^24\) are given in parentheses. The arrows indicate metal–insulator transitions.
It seems plausible that these established principles also apply to the electronic structure of the oxyhydrides. However, comprehensive studies on this topic are still lacking.

Figure 5 shows that the band gaps of the Sc- and Gd-based oxyhydrides follow the same trend as YO$_x$H$_{3-x}$ which is reasonable considering the similarity in band gaps of the oxides: Sc$_2$O$_3$ ($\sim 5.8$ eV) and Gd$_2$O$_3$ (5.4 eV) as well as the trihydride GdH$_3$ (2.5 eV). Slightly lower $E_g$ values (0.3 eV) for $M =$ Sc, Gd are observed in oxyhydrides with low oxygen content ($x \approx 0.5$). This is in agreement with our work on MO$_x$H$_{3-x}$ with $M =$ Y, Gd, Dy, Er and indicates that the effect of different RE cations on $E_g$ is relatively weak compared to anion-alloying. Moreover, all RE hydroxide thin films have large optical band gaps ($E_g \approx 5.5$ eV) which are independent of the anion composition and similar in value to the sesquioxides, suggesting that the unoccupied H 1s orbitals do not interfere with the states at the VBM and CBM. Given the chemical similarity of the RE elements, we suppose that the anion-composition dependence of the optical band gap of most lanthanide oxyhydrides closely resembles the trend shown in Figure 5. Notable exceptions are expected for $M =$ Ce, Pr, Eu, Tb where the M 4f orbitals are located within the O 2p band gaps, respectively.

Our ongoing photodarkening experiments with wavelength-dependent excitation indicate that photon energies larger than $E_g$ are required to trigger photochromism in RE oxyhydrides. Using UV excitation by Hg vapor lamps with $\lambda = 254$ nm, we observe weak photochromism in YO$_x$H$_{3-x}$ oxyhydrides with band gaps up to 4.2 eV. According to Figure 5 this corresponds to $x = 1.3$ ($c_{1H} \approx 15$ atom %) which is marked as the oxygen-rich boundary for photochromism in Figure 2.

In conclusion, we have established a ternary RE–O–H composition-phase diagram demonstrating that (i) the previously reported photochromic Y-based thin films are O$^2-/H^+$ multianion compounds which are members of the REO$_x$H$_{3-x}$ oxyhydrides material class including Sc and (most of) the lanthanides and (ii) an anion-disordered fcc lattice model can be used to describe the crystal structure of the RE oxyhydrides linking the known REH, RE$_2$O$_3$, and LnOH phases. These oxyhydride films are photochromic over nearly their entire composition range of $0.5 \leq x \leq 1.5$, which implies that the presence of both oxide and hydride ions is crucial for the photochromic effect at ambient conditions. We notice a general trend toward decreased photochromic contrast and faster bleaching kinetics with increasing O$^2-/H^+$ ratio—in agreement with the report of Moldarev et al. On the basis of our results, we expect that the stoichiometric bulk LnOH compounds ($x = 1$) should be photochromic as well. Moreover, the RE oxyhydride optical band gap can be adjusted over a wide range by controlling the O$^2-/H^+$ anion ratio in order to adapt the photochromic response for applications such as energy-saving smart windows and adaptive eyewear. Further systematic investigation of the electronic structure and defect formation is required to clarify the origin and physical limitations of the photochromic effect in the REO$_x$H$_{3-x}$ materials.

### ASSOCIATED CONTENT

- Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.9b00088.

Structural characterization by XRD, SEM, and AFM and further experimental details (PDF)
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Dr. Nathan Nesbit for facilitating access to the SEM and performing SEM measurements, Bart Boshuizen for programming the in-situ spectrometer control software, and Marcel Bus for performing AFM measurements. This work is part of the Open Technology research program with project number 13282, which is (partly) financed by The Netherlands Organisation for Scientific Research (NWO).

REFERENCES

(1) Kageyama, H.; Hayashi, K.; Maeda, K.; Attfield, J. P.; Hiroi, Z.; Rondinelli, J. M.; Poeppelmeier, K. R. Expanding frontiers in materials chemistry of transition metal oxyhydrides. Sol. Energy Mater. Sol. Cells 2018, 177, 106−109.

(2) Furukawa, T.; Hirayama, M.; Yonemura, M.; Kamiyama, T.; Tanaka, I.; Kanno, R. An optical method to determine the thermodynamics of hydrogen absorption and desorption in metals. Appl. Phys. Lett. 2007, 91, 231916.

(3) Takenouchi, A.; Otomo, K. N.; Sakai, M.; Saiyo, Y.; Kigirne, T.; Kosaka, M.; Michimura, S.; Hasegawa, S.; Nakamura, O. Purification of commercial yttrium metal: Removal of fluorine. J. Cryst. Growth 2017, 468, 701−704.

(4) Zinkevich, M. Thermodynamics of rare earth sesquioxides. Prog. Mater. Sci. 2007, 52, 597−647.

(5) Abadi, G.; Imanaka, N. The binary rare earth oxides. Chem. Rev. 1999, 98, 1479−1514.

(6) Beall, G. W.; Milligan, W.; Wolcott, H. A. Structural trends in the lanthanide trihydroxides. J. Inorg. Nucl. Chem. 1977, 39, 65−70.

(7) Kooij, E. S.; van Gogh, A. T. M.; Griessen, R. In situ resistivity measurements and optical transmission and reflection spectroscopy of electrochemically loaded switchable YH3 films. J. Electrochem. Soc. 1999, 146 (8), 2990−2994.

(8) Huber, J. N.; Rector, J. H.; Wijngaarden, R. J.; Jetten, S.; de Groot, D.; Dam, B.; Koeman, N. J.; Griessen, R.; Hjörvarsson, B.; Olafsson, S.; et al. Synthesis of yttriumtrihydride films for ex-situ measurements. J. Alloys Compd. 1996, 239, 158−171.

(9) van Gogh, A. T. M.; Nagengast, D. G.; Kooij, E. S.; Koeman, N. J.; Rector, J. H.; Griessen, R.; Flipse, C. F. J.; Smeets, R. J. J. G. Structural, electronic, and optical properties of LaY3, YH3 switchable mirrors. Phys. Rev. B: Condens. Matter Mater. Phys. 2001, 63, 195105.

(10) Miyake, T.; Arayasiwian, F.; Kino, H.; Terakura, K. GW quasiparticle band structure of YH3. Phys. Rev. B: Condens. Matter Mater. Phys. 2000, 61, 16491−16496.

(11) Meyer, B. K.; Polity, A.; Farangis, B.; He, Y.; Hasselkamp, D.; Kraemer, T.; Wang, C. Structural properties and bandgap bowing of ZnO1−xSx thin films deposited by reactive sputtering. Appl. Phys. Lett. 2004, 85, 4929.

(12) Persson, C.; Platzer-Björkman, C.; Malmström, J.; Törndahl, T.; Edoff, M. Strong valence-band offset bowing of ZnO1−xSx enhances p-type nitrogen doping of ZnO-like alloys. Phys. Rev. Lett. 2006, 97, 146403.

(13) Xie, R.; Hintzen, H. T. Optical properties of (oxy)nitrile materials: A Review. J. Am. Ceram. Soc. 2013, 96, 665−687.

(14) Vurgafman, I.; Meyer, J. R.; Ram-Mohan, L. R. Band parameters for III−V compound semiconductors and their alloys. J. Appl. Phys. 2001, 89, 8515.

(15) Wei, S.; Zunger, A. Band offsets and optical bowings of chalcopirites and Zn-based II-VI alloys. J. Appl. Phys. 1995, 78, 3846.

(16) Afnan’s, E. V.; Shamuilla, S.; Badylevich, M.; Stemsins, A.; Edge, L. F.; Tian, W.; Schom, D. G.; Lopes, J. M. J.; Roeckerath, M.; Schubert, J. Electronic structure of silicon interfaces with amorphous
and epitaxial insulating oxides: Sc₂O₃, Lu₂O₃, LaLuO₃. Microelectron. Eng. 2007, 84, 2278–2281.

(36) Prokofiev, A. V.; Shelykh, A. I.; Melekh, B. T. Periodicity in the band gap variation of LnₓX₃ (X = O,S,Se) in the lanthanide series. J. Alloys Compd. 1996, 242, 41–44.

(37) Lee, M. W. Lin, C. H. Determination of the optical constants of the y-phase GdH₃ thin films. J. Appl. Phys. 2000, 87, 7798.

(38) Gillen, R.; Clark, S. J.; Robertson, J. Nature of the electronic band gap in lanthanide oxides. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 125116.