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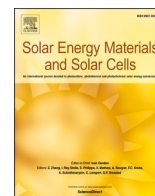
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Perspective on the photochromic and photoconductive properties of Rare-Earth Oxyhydride thin films

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ABSTRACT

Rare-Earth oxyhydrides (REH_{3-2x}O_x) are characterized by photodarkening when illuminated by photons having an energy exceeding that of the band gap. We propose that the film is segregated in hydrogen rich and hydrogen poor areas. Upon illumination, the excited electrons reduce the three-valent cations inducing an insulator to metal transition in the hydrogen rich entities. These small metallic oxyhydride clusters are responsible for the enhanced optical absorption. In the surrounding semiconductor matrix the photoexcitation induces a transition from p to n-type conductivity. This persistent photoconductivity is due to trapping of the holes by hydride ions. As a result, the Fermi level rises above the conduction band inducing a Burstein-Moss effect and a large increase in the conductivity.

1. Introduction

Cationic substitution has been the classical approach to tailor the properties of ceramic materials. In the past decade it has been recognized that also anionic substitution may serve a similar purpose [1]. Within this class of mixed anion materials, oxyhydrides have recently gained attention for a range of properties such as: hydride conductivity [2,3], catalyst for the production of ammonia [4], and their photochromic and photoconductive properties [5].

The phenomenon of photochromism – the reversible change of colour on exposure to light – has been known for a long time. However, the applications were limited mainly to sunglasses. Photochromic windows for building applications were hardly considered, since glass effectively shields the UV radiation generally needed for photodarkening. Moreover, as pointed out by Granqvist et al. customer control is very important for the appreciation of smart window applications [6]. Still, photochromic and thermochromic glass planes may find important areas of application [7].

Photochromism and the associated persistent photoconductivity in polycrystalline rare-earth oxyhydride thin films were first reported in

2011 in Y-based compounds [5]. The material shows a colour neutral darkening in the presence of this incident light, absorbing light over a wide range of wavelengths (visible to near-IR). When the light is turned off, the original transparency is recovered. Since then, several other Rare Earth oxyhydrides (RE = Sc, Y, Nd, Sm, Gd, Dy, Er) were found to form photochromic thin films, suggesting that these properties are general to the whole material class [8–12]. While cycling and aging of the samples results in an unpractically slow bleaching speeds [13,14] the interest in this material stems from the fact that it does not require UV light to darken. Any photon energy exceeding the band gap will do. This implies the feasibility of a transparent photochromic material, active when positioned within a double glazed panel. As schematically indicated in Fig. 1, a substantial fraction of the solar irradiance is obtained between the transmission edge of glass and the visible edge of the solar spectrum. The inorganic nature of the oxyhydride material would potentially allow for a decade's long lifetime. A more in-depth review of the applicational aspects of this material is given elsewhere in this issue [15].

RE-oxyhydrides are closely related to RE-hydrides which have been candidate materials for smart window device applications since the discovery of their switchable mirror behaviour in 1996 [17]. The

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¹ This paper is dedicated to Prof. Claes-Göran Granqvist, whose influential papers and didactical presentations stimulated me to enter the field of chemochromics.

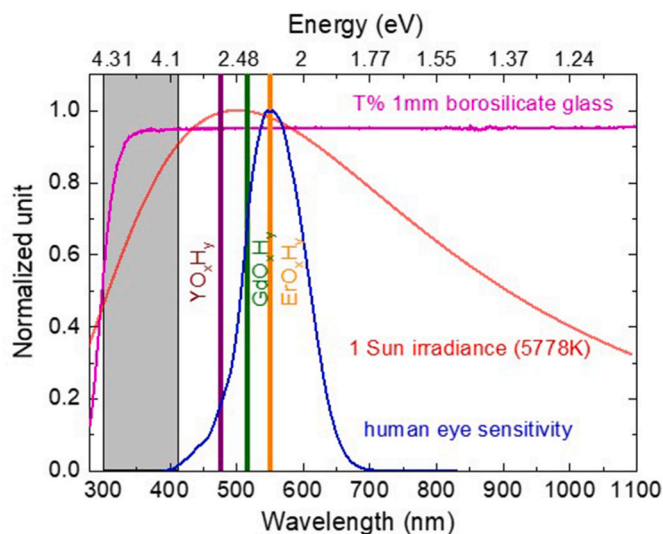


Fig. 1. Transmittance of 1 mm borosilicate window glass (purple) compared with the spectral sensitivity of the human eye (blue) according to Sharpe et al. [16] and the irradiance of 1 sun (orange) according to the AM1.5 NIST global reference solar spectrum. The vertical lines indicate the minimal indirect bandgaps observed for three RE-oxyhydrides. The region available for sunlight to darken an optically transparent photochromic window is indicated by the grey square (picture based on thesis F. Nafezarefi [14]).

switching between a metallic, reflecting fcc-YH₂, and a semiconducting transparent hcp-YH₃ state can be induced by hydrogenation in a gasochromic or electrochromic device structure. In a simple ionic picture, hydride ions oxidise the yttrium ion, such that in the trihydride state no free conduction electrons are left. As observed by Hoekstra et al. a persistent increase in the charge carrier density can also be induced by irradiation with light [18]. Thus, a critical charge carrier density for the transition from the insulating to the metallic state was established. However, these photoexcited carriers persist only below $T < 200$ K. At room temperature photochromism is observed in the mixed dihydride-trihydride phase at around 5.9 GPa by Ohmura et al. [19]. At present, the relation between this behaviour and the photochromism in RE-oxyhydrides is not clear.

In this paper we suggest a new picture of the opto-electronic properties of RE-oxyhydrides. In the first paragraphs we build on a short presentation of a number of key properties of these films, where we assume the same basic mechanism to be present in all photochromic RE-oxyhydrides. In paragraph 7 we present our current understanding of the mechanism of photochromism in these materials.

2. Preparation

RE-oxyhydride films are prepared by a 2-step procedure. The first step involves the reactive magnetron sputtering of REH₂, at room temperature on quartz substrates in an (U)HV system [5,20]. The polycrystalline dihydride thin film is characterized by a metallic appearance including a transparency window of a few % around 700–800 nm. Depending on the deposition conditions the dihydride remains stable in air, with only a thin oxide surface layer formed.

However, by increasing the pressure during reactive sputtering the porosity of the film increases, allowing for further oxidation. When a RE-dependent critical pressure is exceeded, the films become transparent on exposure to air [21]. While a full oxidation to Y₂O₃ or Y(OH)₃ is to be expected, an intermediate oxyhydride state is observed for films deposited close to the critical pressure. In fact, it was observed that the strongest photochromic effect was observed just beyond this threshold [21–24]. Not every RE-hydride could be transformed into an oxyhydride in this way. In particular CeH₂ tends to fully oxidise into Ce₂O₃ upon

exposure to air.

Epitaxial photochromic films were obtained by depositing REH₂ at 200 °C on lattice matched yttria-stabilized zirconia (111) or CaF₂ (111) substrates. After exposure to pure O₂ at room temperature, an epitaxial relation is found between (111) oriented oxyhydride film and the (111) CaF₂ or yttria-stabilized zirconia substrate [25]. These epitaxial films quickly darken on photo-excitation, but show an extremely slow bleaching speed.

3. Typical structural properties

Common to all photochromic RE-oxyhydride films investigated so far, the crystal structure is based on a cubic CaF₂-type lattice typical for REH₂. Upon oxidation, the lattice expands to accommodate the oxygen. By EXAFS it was shown that the oxide O²⁻ ion replaces part of the hydride H⁻ anions in the tetrahedral sites, pushing these hydride ions to the octahedral sites [26]. Note, however, that DFT calculations suggest that the hydrides are considerably displaced from their respective tetrahedral and octahedral positions after structural relaxation [27].

Although a certain sub-stoichiometry cannot be excluded, our NRA/RBS studies suggest a common structure formula (REH_{3-2x}O_x), see Fig. 2 [9]. An alternative interpretation has been reported [12]. However, as in REH₃, the semiconducting nature of the oxyhydride suggests that RE is present in the 3+ state, with H⁻ and O²⁻ as the formal valence of the anions [9], as verified by solid-state NMR for Y and Sc systems [28,29]. This implies that these materials belong to the same REH_{3-2x}O_x class of materials as the RE-oxyhydrides studied for the purpose of exploring their ionic (H⁻) conductivity [2].

As in those bulk materials, the cubic nature of the lattice is not always preserved [30,31]. In particular, NdH_{3-2x}O_x films show a tetragonal distortion over a wide range of O/H ratios. *The fact that photochromism is nevertheless observed in these thin films, indicates that the photochromic effect is not dependent on the particularities of the lattice symmetry* [11].

Assuming that the oxidation involves the gradual addition of oxygen to the REH₂ lattice, we obtain $x = 0.5$ for the minimum amount of oxygen in the semiconducting REH_{3-2x}O_x films, if the RE is to be fully oxidized to the 3+ state. Now, 50 % of the octahedral positions have become occupied by hydrogen, assuming that the oxide ions replace tetrahedral hydride ions (Fig. 3). On further oxidation hydrogen has to be removed from the lattice and stoichiometric REOH is obtained, with an equal fraction of tetrahedral hydrogen and oxygen.

We found that replacing some of the trivalent RE-ions with divalent ions such as Ca²⁺ induces a concomitant reduction of the fraction of hydride ions, while the oxygen fraction remains constant [32]. Since the octahedral hydride has the smallest bonding energy, this suggests that it is the octahedral hydrogen that is removed by Ca²⁺-doping. We find that the photodarkening decreases with increasing Ca-doping. Extrapolating this result, we find that a doping level of 50 % Ca, which corresponds to a full removal of octahedral H, would reduce the photochromism to zero. From this we concluded, that the presence of octahedral hydrogen is key to the mechanism of the photochromic effect. However, since both DFT and NMR [27,28] suggest a structural deformation which cannot discriminate between the two hydrogen sites, it is probably better to rephrase this as the necessity of a REH_{3-2x}O_x hydrogen fraction such that $x < 1$.

So far we have assumed the films to have a uniform composition. This may not always be the case. In fact, large compositional variations have been reported in Gd-oxyhydride films consisting of GdH₂ and Gd₂O₃ [33]. Indeed, the topmost surface layer of REH_{3-2x}O_x is probably always fully oxidized. However, in contrast to [33], according to Banerjee et al. [28] solid state NMR experiments rule out the presence of YH₂. Apparently, the type and scale of inhomogeneity which was reported in Ref [33], is not an essential ingredient of the photochromic mechanism. The NMR experiments do, however, indicate regions where the hydrogen/oxygen ratio is enriched by hydrogen [28]. This ties in

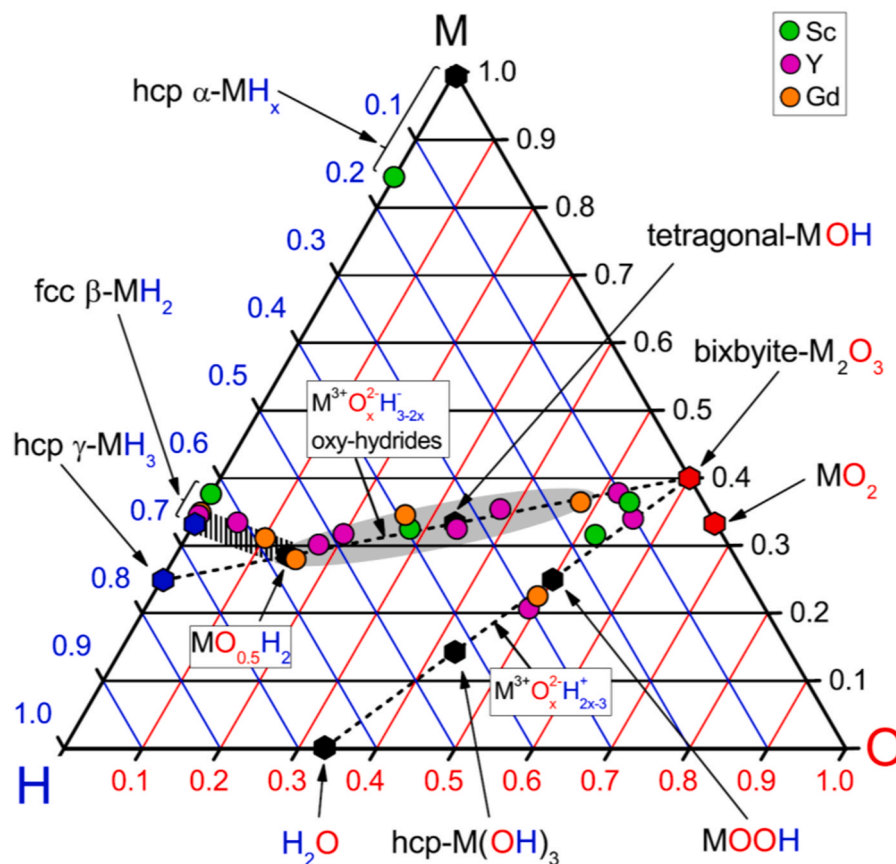


Fig. 2. Ternary M–O–H chemical composition and phase diagram where M = Sc, Y, La, Sm – Lu. Thick dashed lines indicate chemical compositions with the same charge state of cations (M^{2+} , M^{3+} , H^+) and anions (O^{2-} , H^-). Hexagons mark the (ideal) stoichiometric compounds that have been reported earlier: (i) binary compounds: MH_2 dihydride and MH_3 trihydride in blue as well as M_2O_3 sesquioxides and MO_2 in red; (ii) ternary compounds: MOH oxyhydrides, $MOOH$ oxyhydroxide, $M(OH)_3$ hydroxide, and the hypothetical $MO_{0.5}H_2$ in black. Coloured circles show the chemical compositions of MO_xH_y thin films obtained from ion beam analysis. The diameter of the data points corresponds to a composition uncertainty of approximately ± 1 atom %. The region of photochromic materials is highlighted in grey. (Figure reprinted from Ref. [9]. Note that the line connecting M_2O_3 with $M(OH)_3$ should have been described as $M_{2-x}O_3H_{3x}$).

with electronic structure calculations which indicate that intermediate $REH_{3-2x}O_x$ compositions gain energy when they segregate in $x = 1$ and $x = 0.25$ fractions [27,28]. Such a segregation would then need to take place during the oxidation process. Note, that while the computed bandgap increases with x , the observed gap depends hardly on the oxygen fraction for $x < 1$ [27], which would be consistent with a low- x fraction dominating the optical band gap of the material.

Upon photo-excitation a reversible contraction of the lattice is observed [34]. These changes were attributed to the loss of oxygen. The idea of a reversible exchange of oxygen was substantiated by extremely slow bleaching of samples kept in nitrogen [34]. However, bleaching was also demonstrated to occur at 100 K, where oxygen diffusion should be too slow to facilitate such as process [[35,36]]. The large difference between oxygen and hydrogen mobility is corroborated by 1H and ^{17}O solid-state NMR [29]. In addition, capped films were shown to bleach as well as uncapped films [11].

Since uncapped films appear to lose some hydrogen on illumination, hydrogen mobility rather than oxygen mobility seems to be a more likely key element for the photochromic mechanism [37]. Such a loss could be a side effect of a photo-induced hydrogen mobility, wherein most of the hydrogen is maintained in the (grain boundaries of the) sample. The hydrogen may thus either stay in the sample or be lost to the ambient. Hydrogen lost to the *ambient* leads to the loss in reversibility, which is often observed on cycling.

The reported reduction of the lattice constant on photo-excitation implies a reduction in the hydrogen *lattice* content. Note, that a

reduction in the overall lattice constant does not necessarily imply a uniform loss of hydrogen. As long as the lattice coherency is maintained, a local reduction of the lattice constant (e.g. in the metallic entities formed on photo-excitation) would still lead to a reduction of the average lattice constant.

4. Defects

In a bleaching mechanism driven by H-mobility, small point defects may facilitate the diffusion process. Reactively sputtered films investigated by positron annihilation, indicate the presence of nanovoids/ultrasmall voids and yttrium vacancies. In-situ experiments indicate the formation of anion vacancies upon photodarkening. This was inferred from the detection of a small ($\sim 10^{-5}$) irreversibly formed fraction of Y–H divacancies, likely related to hydrogen liberated from octahedral sites [13].

H-mobility can also be facilitated by large volume defects such as grain boundaries. Films deposited at room temperature on quartz substrates are generally characterized by a columnar structure. Depending on the film thickness and the deposition conditions, the distance between the grain boundaries separating the columns is between 20 and 100 nm [8,24,38]. The grain size of the epitaxial films of Ref. [25] is not explicitly mentioned but, given the lattice mismatch with the substrate, these films are certainly not single-crystalline. However, due to the temperature treatment, a large grain size is to be expected which might be correlated with the poor bleaching speed. A similar line of thinking

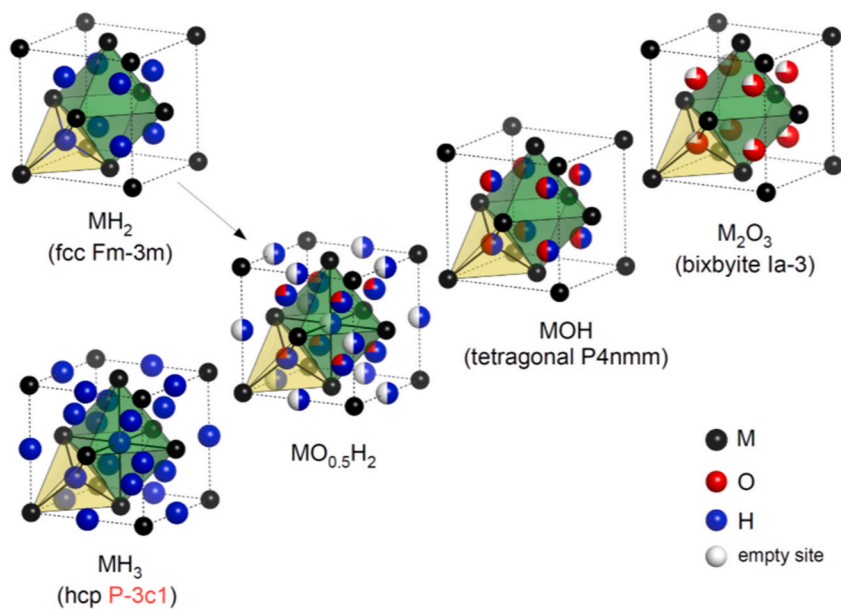


Fig. 3. Generalized crystal structure evolution of rare-earth oxyhydrides with different H^-/M and O^{2-}/M ratios based on the fcc-fluorite ($Fm\bar{3}m$) structure motif. The arrow indicates the metal-insulator transition taking place in the as-deposited film on exposure to air. This involves the incorporation of oxygen and a partial rearrangement of the hydride ions. Further oxidation takes place due to a replacement of hydrogen by oxygen. The anion sublattice disorder is visualized by multi-coloured spheres in terms of partial occupancy of tetrahedral (yellow polygon) and octahedral (green polygon) sites. The space groups of the anion-ordered crystal structures of fcc- MH_2 , hcp- MH_3 , tetragonal MOH, and bixbyite- M_2O_3 are given in parentheses. Figure reprinted from Ref. [26].

was recently presented by Moldarev et al. [39] who observed an increase in grain size after ion irradiation. Note, however, that ion irradiation may also induce lattice damage and introduce impurities. In practice, it will be hard to separate the effect of point defects and larger volume defects on the photochromic properties. Moreover, if on photo-excitation the hydrogen is stored in larger defects such as grain boundaries, the activation barrier to re-enter the lattice may be equally important in our understanding of the bleaching speed.

5. Typical optical properties

When exposed to light the photochromic film undergoes a visually colour-neutral darkening, caused by a large decrease in transmittance. Early on it was recognized that the photodarkening in $REH_{3-2x}O_x$ can be understood as resulting from the formation of small metallic particles. On the basis of a Bruggeman analysis of the optical spectrum in the darkened and bleached states it was concluded that a volume percentage 5–10 % of metallic particles in a dielectric matrix would explain the photo-darkened state observed [40].

To investigate whether an inter band transition ($h\nu > E_g$) is needed, we prepared samples with distinct bandgaps. The bandgap of the photochromic RE-oxyhydride films depends mainly on the nature of the RE-ion and the O/H ratio [9,21]. Since the darkening contrast rapidly decreases with O/H ratio, we compared a Dy- with an Y-oxyhydride film both prepared close to the critical deposition pressure, which have a clearly distinguishable band gap (see Fig. 4). We find a close correlation between band gap and the critical wavelength for photodarkening. Photons having energies large enough to excite charge carriers over the indirect band gap result in a darkened state. The measurements suggest a very weak photochromism for sub-band gap excitation at best. So far, we were unable to distinguish whether this is due to excitation from gap states, or an artifact due to stray light. Note, that in the case that a strong sub-bandgap excitation is reported in [33], this happened in a compositionally much more inhomogeneous film.

The kinetics of the optical darkening is quite distinct from the bleaching process. Typically $\sim 2/3$ of the total reduction in

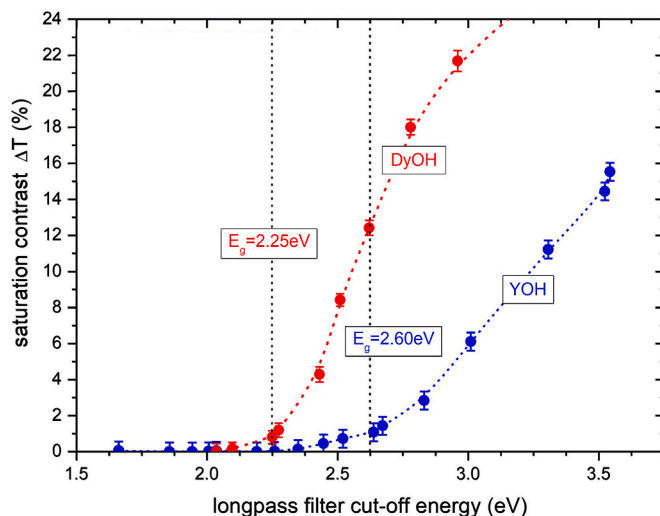


Fig. 4. Saturation contrast as a function of the stop band limit of a long pass filter for two RE-oxyhydride thin films, with distinct indirect band gaps (Method described in chapter 4 of the thesis of F. Nafezarefi [14]).

transmittance occurs in the first 30 s, which is followed by a slow saturation that can take 0.5–2 h. In contrast, the bleaching process is much slower and may take several hours. In general, bleaching appears to be thermally activated [25, 35, 11], resulting in decreased bleaching times at elevated temperatures. So far, we could not positively identify any optical bleaching effect when applying ‘sub-band-gap’ light to the sample during bleaching.

The bleaching time depends on factors such as the size of the RE-ion and the oxygen fraction [21]. When increasing the oxygen fraction, the bleaching time decreases at the expense of a reduced photochromic contrast. An optimal combination of contrast and bleaching time was obtained in $GdH_{3-2x}O_x$ with an optical transmission reduction of 20 %

and a bleaching time τ_B of 9 min [21]. Unfortunately, the bleaching behaviour appears to depend also on the freshness of the sample, the humidity of the air it has been exposed to, and the number of switching cycles (the so-called memory effect [14]). This makes sample-to-sample comparisons rather tricky, and it is of course disadvantageous for any application.

Interestingly, we find that the indirect optical gap widens on illumination, see Fig. 5. We suggested this to be indicative of a Burstein-Moss type of behaviour [41]. This implies the presence of a large number of charge carriers photo-induced in the semiconducting matrix, in line with the Kelvin probe measurements by Mongstad et al. showing a 0.2 eV reduction on illumination [42]. As shown in Fig. 5, the optical gap slowly reverts back to its initial value when the light is turned off, on a (very) similar time scale as the optical bleaching.

6. Electronic transport properties

Already in the seminal paper by Mongstad et al. [5] it was pointed out that the optical darkening of $\text{REH}_{3-2x}\text{O}_x$ correlates with an increase of the conductivity. Quantitatively, it was found that the conductivity may actually increase over 4–6 orders of magnitude upon illumination [25, 41 [43]]. In addition, resistive switching in a random-access memory device was obtained by insertion of hydrogen in an oxygen rich $\text{YH}_{3-2x}\text{O}_x$ or $\text{LaH}_{3-2x}\text{O}_x$ sample sandwiched between a Pd and a Mo thin film [44].

The photo-induced conductivity persists after the illumination has ceased, and decays together with the photodarkening (Fig. 6a). Interestingly, in the fully bleached state, Hall effect measurements show a p-type behaviour [41]. The large mobility of these carriers lead to the assumption of a large polaron type of conduction. On illumination, a transition to n-type behaviour was reported [41], in accordance with the Seebeck data from Komatsu et al. on epitaxial films [25].

So far, it proved to be impossible to quantitatively model the change in electro-optical properties on illumination. Assuming the formation of metallic particles to explain the optical absorption, we were unable to adequately model the relationship between the optical absorption and the photoconductivity, even when we assumed extremely anisotropic metallic particles (see Figure S11 in [41]).

Plotting the logarithm of the change in the absorption versus the double logarithm of the relative conductivity, a linear relationship was found (Fig. 6b). This empirical relationship can be written as:

$$\sigma(\Delta\alpha) = \sigma_0 e^{B(\Delta\alpha)^f} \quad (1)$$

The fact that the conductivity in the photo-darkened state ($\sigma(\Delta\alpha)$) scales proportionally with the conductivity in the bleached state (σ_0), is again not consistent with a model where the conductivity increases as a result of the percolation of metallic particles [25].

Alternatively, Komatsu et al. considered a model involving a global change in defect structure, e.g. by the formation of hydroxide groups [25]. However, while solid-state NMR does show the presence of hydroxide groups in RE-oxyhydride films, the concentration of these groups does not increase but rather decreases on photo-darkening [28, 29]. In addition, since no adequate models were found to describe the change in opto-electronic properties for such a case [41], we concluded that the photodarkening involves the formation of metallic particles **as well as a change** in the properties of the surrounding matrix.

The latter is in line with the observation of a Burstein-Moss effect inferred from the change in the optical bandgap during photodarkening and bleaching. Given the observed n-type conductivity, the Burstein-Moss effect would be caused by an excess of electrons in the conduction band, forcing optically excited electrons into higher energy orbitals. Thereby, the change in electronic properties of the surrounding semiconductor matrix rather than the percolating metallic entities appears responsible for the increase in electronic conductivity on photo-excitation. The envisaged changes in the Fermi level of the semiconducting matrix on illumination are depicted in Fig. 7.

The excess of charge carriers in the semiconducting matrix would be due to an inability of excited electrons to recombine, leading to a persistent conductivity. The linear behaviour observed in Fig. 6b suggests that, during bleaching, the oxidation of the metallic entities (involving $\text{RE}^{2+} \rightarrow \text{RE}^{3+}$) correlates with a reduction in the Fermi level of the semiconducting matrix.

7. Elements of the photochromic mechanism in $\text{REH}_{3-2x}\text{O}_x$

Based on the experimental evidence provided so far, we now embark on a synthesis to sketch a possible mechanism for the photochromic behaviour in these materials. The formation of metallic nano-particles suggests an analogy with the classical silver chloride based photochromics [45,46].

a. The AgCl analogy

The photochromic AgCl/glass system is characterized by a glass matrix embedded with small AgCl crystals, containing a small fraction of interstitial Ag^+ -ions. Upon a bandgap excitation, the electrons are trapped by these ions ($\text{Ag}^+ + e^- \rightarrow \text{Ag}^0$), which become mobile due to charge neutrality, and cluster at the boundaries between the silver chloride particles and the glass matrix. To accommodate the excited holes Cu^+ -ions are added as hole traps ($\text{Cu}^+ + h^+ \rightarrow \text{Cu}^{2+}$), which prevents the formation of chlorine gas [47]. The photoexcitation takes place when the photon energy exceeds the bandgap. The diversity in shape and size of the metallic particles results in an increase in absorption between 400 and 800 nm [47]. Interestingly, it was shown that one can selectively bleach these particles by exposing the sample to the appropriate plasma frequency, albeit with a certain threshold [47]. The idea behind this is that electrons are excited from the metallic particles by the plasmon resonance, thus allowing for the release of Ag^+ ions and the dissolution of the silver particles.

In our case, we are dealing with a chemically more or less uniform semiconducting material instead of having semiconducting nano-particles in a glass matrix. On illumination of the $\text{REH}_{3-2x}\text{O}_x$ film, part of the semiconductor becomes metallic, which is apparently related to a change in the RE-valency. As in the AgCl case, we find that the threshold value for optical darkening is closely related to the bandgap of the $\text{REH}_{3-2x}\text{O}_x$ semiconductor (Fig. 4). As described in paragraph 5, so far we were

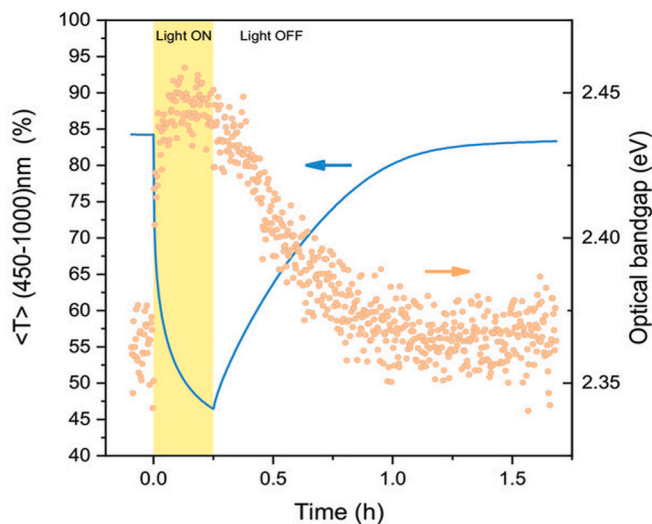


Fig. 5. Correlation between the change in the optical transmission and the optical bandgap in a $\text{GdH}_{3-2x}\text{O}_x$ thin film during a photochromic cycle. Figure reprinted Ref. [41].

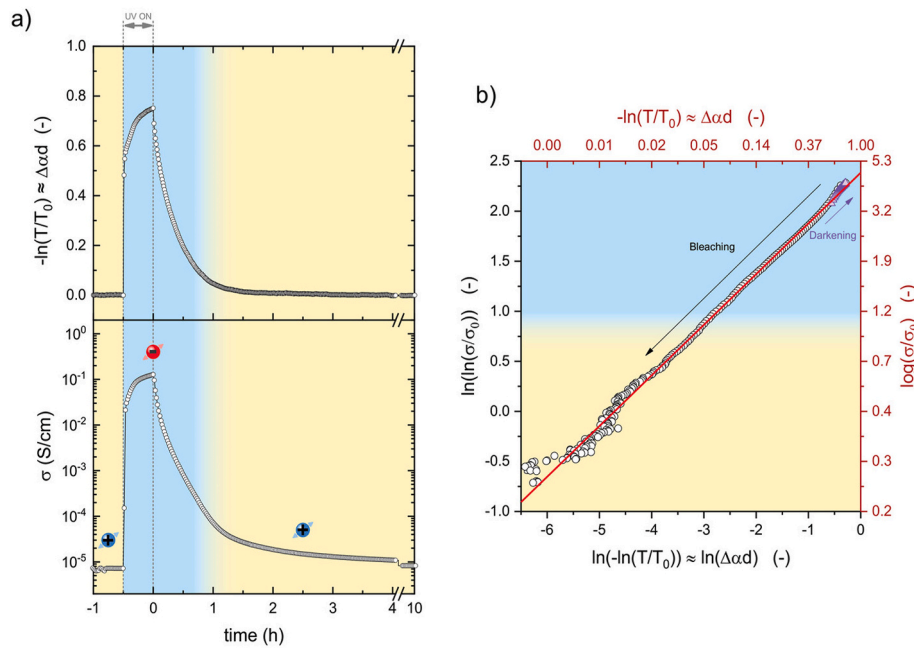


Fig. 6. a) Photo-induced effects on relative optical transmittance (top) and material conductivity (bottom) of Gd oxyhydride measured at 303 K. Blue and red overlaid icons indicate the polarity of the dominant charge carriers at different stages of the cycle: holes when the material is in its transparent state, and electrons upon darkening. b) Relation (linearized) between the increase of optical absorption ($-\ln(T/T_0) \approx \Delta\alpha d$) and relative conductivity (σ/σ_0). The black points refer to the bleaching, while the purple ones to the darkening process. In both panels, the background colours highlight the regime where optical absorption and conductivity are dominated by the photo-induced effects ($\sigma \gtrsim 10 \sigma_0$ - blue), and the rest of the experimental range (yellow). Figure reprinted from Ref. [41].

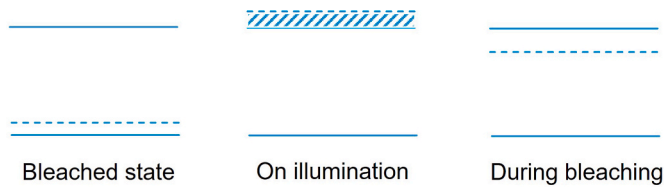


Fig. 7. Sketch on the behaviour of the Fermi level (dotted line) in the semi-conducting matrix on illumination. In the fully bleached state the film shows p-type behaviour. On illumination the material becomes n-type with a Fermi level increase to above the bottom of the conduction band. During bleaching the Fermi level slowly decreases to below the conduction band edge and on further bleaching the material will become p-type again.

not able to unequivocally demonstrate optical bleaching effects by sub-bandgap excitation. This suggests the presence of an activation barrier that precludes the excitation of electrons in the metallic nano-particles from entering the surrounding semiconductor matrix [46]. Possibly, this high activation energy corresponds to the presence of a Schottky barrier at the interface, too high to be overcome by photo-excitation (see Fig. 8). Given that the optical bleaching experiments are taking place in the dark state, we have assumed a Fermi level just below the conduction band edge, which leads to a downward band bending in the n-type semiconductor.

b. The local insulator-to-metal transition

The transformation of the semiconductor into a metallic entity appears to be an analogue of the insulator-metal transition observed in RE-hydride, which takes place when the amount of hydride ions (and/or the formal valency of RE) is reduced to less than $x = 2.7$. As suggested by Ng et al. [49] a Mott-type transition to the metallic state takes place due to the overlapping defect states of electrons trapped in Y(4d) orbitals surrounding the octahedral holes of the fcc structure. At present it is not clear what the maximum oxygen content is allowing for a

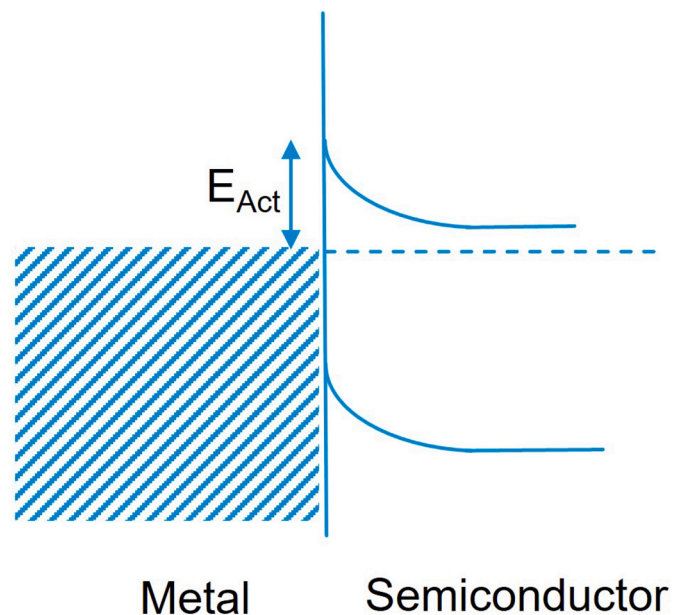


Fig. 8. Sketch of the activation barrier between the metallic entity formed after illumination (left) and the surrounding n-type semiconducting $REH_{3-2x}O_x$ (right) matrix, when illumination has ceased. Optical bleaching is hindered by the barrier that metallic charge carriers experience if they are to be excited into the conduction band of the semiconducting matrix. Given that the experiments are taking place in the dark state, we have drawn a Fermi level close to the conduction band edge, which probably leads to a downward band bending. Note, that also the finite size of the metal particle influences the nature of the band bending [48].

metal-insulator transition similar to that in REH_x , if at all. So far, no computational evidence has been provided for such a transition in any RE-oxy (hydri)de phase.

The formation of metallic entities during photoexcitation is confirmed by a number of experiments, without providing as yet the exact size, shape and nature of these particles. Most recently Montero et al. [50] observed changes in the magnetic susceptibility of ‘GdOH’ which lead to an increase in the Curie-Weiss temperature when compared to the transparent state. This reversible change points to the formation of metallic domains. Similarly, Doppler broadening positron annihilation spectroscopy indicates the reversible formation of metallic particles on photo-excitation [51]. Furthermore, comparing films during optical cycling it was shown by NMR that the photo-darkening involves the reduction of RE^{3+} to RE^{2+} creating domains with RE and 2H nuclei being subject to Knight shifts [29].

c. Anion mobility

A local reduction in the RE-valency can only be maintained if the amount of surrounding counter ions is simultaneously reduced. In analogy with the AgCl case, we posit that the photo-excited holes are trapped by the hydride ions, ($H^- + h^+ \rightarrow H^0$), thereby allowing for the transition to the metallic state. The hydrogen may stay in the lattice, precipitate in the film voids, or evolve as molecular hydrogen. The hydrogen evolution observed in vacuum [37] and the increase in the mobile H-signal observed by solid state NMR on photo-darkening [28, 29], support this idea. Unfortunately, these NMR measurements do not distinguish between atomic and molecular hydrogen.

d. Why only such a small fraction of metallic particles?

In most estimates the fraction of metallic particles does not exceed 10 %. One may wonder, whether the formation of these particles is limited to specific sites. This is not easily answerable. The only parameter which relates specifically to the amount of photo-darkening is the hydrogen concentration. Therefore we propose that metallic entities are only formed at sites having a high hydrogen concentration, i.e. $x < 0.5$, where the distinction between tetrahedral and octahedral hydrogen disappears due to strong structural relaxation [27]; possibly the presence of $REH_{3-2x}O_x$ fractions with $x = 0.25$ are required for the formation of a metallic entity on illumination.

e. The photodarkening/bleaching mechanism

Summarizing now our view on the photochromic effect in $REH_{3-2x}O_x$ thin films we arrive at the following picture. On illumination, the bandgap excitation produces holes and electrons. In entities having a high concentration of hydrogen, e.g. $x = 0.25$, the electrons are able to reduce the RE to the 2+ state, while simultaneously holes recombine with (‘octahedral’) hydride ions. In the remaining semiconducting matrix a similar recombination between holes and hydride ions takes place. This prevents the excited electrons from recombining, which in this case induces a persistent n-type conductivity. The high concentration of electrons in the conduction band results in a Burstein-Moss effect. We assume that the mobile hydrogen diffuses to the grain boundaries, while some of it may escape to the ambient. On bleaching, i.e. in the absence of illumination, there is a driving force for the hydrogen to oxidise the metallic entities. Several activation barriers may be involved for this process. First, the (molecular) hydrogen needs to re-enter the lattice. Subsequently diffusion barriers are encountered. Part of the hydrogen will be reduced by the excited electrons in the semiconductor matrix. In parallel, the remaining hydrogen enters the metallic entities where it will be reduced by the RE^{2+} -ions. In line with this finding, we concluded that the anomalously slow bleaching of Sm-oxyhydride films [10] is related to the well-known less favourable oxidation of Sm^{2+} as compared to e.g. Gd^{2+} [52].

f. Correlation of the electronic conduction with the optical darkening

At this point we cannot easily explain the correlation between the optical darkening (which is mainly related to the density of metallic particles in a dielectric matrix) and the electronic transport properties. The latter, we posit, is mainly determined by the electronic nature of the semiconducting matrix. However, as we pointed out above, the formation of metallic particles necessarily affects the nature of the surrounding semiconducting matrix through the formation of Schottky junctions. In fact, a 5 % density of nanometre sized particles implies a small average distance of ~ 15 nm (for spherical metallic particles with a size of ~ 5 nm), as compared to the depletion which is at least of the same order of magnitude. This implies that the *electronic* nature of the semiconductor is affected by the presence of the metallic particles. In addition, the photoexcitation induces a large density of charge carriers in the conduction band. Both effects will influence the Fermi level.

The bleaching process reverses the optoelectronic nature of the material. On the one hand the number of charge carriers in the conduction band, and thereby the conductivity, slowly decreases due to recombination with hydrogen entering the lattice again. On the other hand, the size and density of the metallic entities, and thereby the photodarkening, decrease when hydrogen oxidises the RE^{2+} . It is not easy to see how these two effects could be correlated in the way they do, especially since the reduction in size and density of the metallic entities affect the band bending of the semiconductor matrix in a way that cannot be modelled without detailed understanding.

8. Outlook of photochromic rare-earth oxyhydrides

It is clear that more research is needed to come to a final understanding of the mechanism of photochromics in $REH_{3-2x}O_x$. Here, we want to indicate a few directions for further study.

a. Dopants

It would be interesting to explore whether impurities can be introduced which function as an alternative trapping centres for the photo-excited charge carriers. Similar to the case of Cu^+ substitution in AgCl, a more favourable trapping centre would prevent the formation of volatile H_2 . This would improve the durability and reversibility of the photochromism in $REH_{3-2x}O_x$. One possibility would be to substitute a small fraction of an easy to oxidise RE such as Gd by an ion more difficult to oxidise to the 3+ state such as Er [52]. If the Er remains in the 2+ state on oxidation of the as-deposited dihydride, it could function as a hole trapping centre.

b. Phase segregation

To improve the photo-darkening contrast we need to know about the nature of the metallic phases formed and the reasons for their limitation in size and density. Therefore, in the bleached phase we need to further explore the nature and the extent of the phase segregation. Are specific $REH_{3-2x}O_x$ compositions (such as $x = 0.25$) involved, or is the presence of additional secondary phases necessary for the occurrence of the photochromic effect. In addition, the size, shape and nature of the metallic particles formed on photodarkening needs to be established in order to quantify the relation between the optical and electrical behaviour.

c. Opto-electronic correlation

The correlation between the optical and electrical behaviour calls for an in-depth study in relation with structural properties such as the density of the metallic nano-particles formed on photo-excitation, the nature of the band structure and the density of defects. Especially, a careful study of the optical properties during photodarkening and bleaching in conjunction with the electrical transport properties should be fruitful to gain an understanding on the nature of the correlation

between the two parameters. Furthermore, a study of optical bleaching involving excitations covering the whole optical band gap would give interesting information on the relative position of the metallic Fermi level and the bottom of the conduction band of the semiconductor matrix.

9. Conclusion

RE-oxyhydride thin films darken over a wide optical range when illuminated by photons having an energy exceeding that of the optical gap. Apparently, the excited electrons reduce trivalent RE-ions while the holes are trapped by hydride ions. We propose that the photochromic darkening of $\text{REH}_{3-2x}\text{O}_x$ is due to the formation of metallic entities in the low-x fraction of the sample. The close correlation between the photo-darkening and the photo-conductivity suggest a model wherein the formation of metallic entities is accompanied by a change in the properties of the semiconducting matrix. We propose, that the metallic entities induce a Schottky barrier with respect to the surrounding semiconducting matrix. This results in a transition in this matrix from p-type to an n-type conductivity, an increase in the optical bandgap due to the Burstein-Moss effect, and a large increase in the conductivity. The behaviour of the $\text{REH}_{3-2x}\text{O}_x$ system is of interest not only because of its photochromism. Its study is also promising in view of its potential for electronic devices [44] and as solid state ionic conductors [2, 3, 4, 30]. In general, it points to the wide scope opportunities that multi-anion compounds may provide to us [1].

CRediT authorship contribution statement

Bernard Dam: Writing – original draft, Supervision, Funding acquisition, Conceptualization. **Fahimeh Nafezarefi:** Investigation. **Diana Chaykina:** Writing – review & editing, Investigation. **Giorgio Colombi:** Writing – review & editing, Formal analysis. **Ziyang Wu:** Writing – review & editing, Investigation. **Stephan W.H. Eijt:** Writing – review & editing, Investigation. **Shrestha Banerjee:** Writing – review & editing, Investigation. **Gilles de Wijs:** Writing – review & editing, Investigation. **Arno Kentgens:** Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] Hiroshi Kageyama, Katsuro Hayashi, Kazuhiko Maeda, J. Paul Attfield, Zenji Hiroi, James M. Rondinelli, Kenneth R. Poeppelmeier, Expanding frontiers in materials chemistry and physics with multiple anions, *Nat. Commun.* 9 (2018) 772, <https://doi.org/10.1038/s41467-018-02838-4>.
- [2] Keiga Fukui, Soshi Iimura, Albert Iskandarov, Tomofumi Tada, Hideo Hosono, Room-temperature fast H^- conduction in oxygen-substituted lanthanum hydride, *J. Am. Chem. Soc.* 144 (2022) 1523–1527, <https://doi.org/10.1021/jacs.1c11353>.
- [3] Keiga Fukui, Soshi Iimura, Junjie Wang, Tomofumi Tada, Takashi Honda, Kazutaka Ikeda, Toshiya Otomo, Hideo Hosono, Stabilization factor of anion-excess fluorite phase for fast anion conduction, *Chem. Mater.* 33 (2021) 1867–1874, <https://doi.org/10.1021/acs.chemmater.1c00064>.
- [4] Kayato Ooya, Li Jiang, Keiga Fukui, Soshi Iimura, Takuya Nakao, Kiya Ogasawara, Masato Sasase, Hitoshi Abe, Yasuhiro Niwa, Masaaki Kitano, Hideo Hosono, Ruthenium catalysts promoted by lanthanide oxyhydrides, with high hydride-ion mobility for low-temperature ammonia synthesis, *Adv. Energy Mater.* 11 (2021) 2002723, <https://doi.org/10.1002/aenm.202003723>.
- [5] T. Mongstad, C. Platzer-Bjorkman, J.P. Maehlen, L.P.A. Mooij, Y. Pivak, B. Dam, E. S. Marstein, B.C. Hauback, S.Z. Karazhanov, A new thin film photochromic material: oxygen-containing yttrium hydride, *Sol. Energy Mater. Sol. Cells* 95 (2011) 3596, <https://doi.org/10.1016/j.solmat.2011.08.018>.
- [6] C.G. Granqvist, S. Green, G.A. Niklasson, N.R. Mlyuka, S. von Kræmer, P. Georén, Advances in chromogenic materials and devices, *Thin Solid Films* 518 (2010) 3046–3053, <https://doi.org/10.1016/j.tsf.2009.08.058>.
- [7] Yujie Ke, Jingwei Chen, Gaojian Lin, Shancheng Wang, Yang Zhou, Jie Yin, Pooi See Lee, Yi Long, Smart windows: electro-, thermo-, mechano-, photochromics, and beyond, *Adv. Energy Mater.* 9 (2019) 1902066, <https://doi.org/10.1002/aenm.201902066>.
- [8] F. Nafezarefi, H. Schreuders, B. Dam, S. Cornelius, Photochromism of rare-earth metal-oxy-hydrides, *Appl. Phys. Lett.* 111 (2017) 103903, <https://doi.org/10.1063/1.4995081>.
- [9] S. Cornelius, G. Colombi, F. Nafezarefi, H. Schreuders, R. Heller, F. Munnik, B. Dam, Oxyhydride nature of rare-earth-based photochromic thin films, *J. Phys. Chem. Lett.* 10 (2019) 1342–1348, <https://doi.org/10.1021/acs.jpcclett.9b00088>.
- [10] Diana Chaykina, Giorgio Colombi, Herman Schreuders, Bernard Dam, Photochromic samarium oxyhydride thin films, *AIP Adv.* 13 (2023) 055211, <https://doi.org/10.1063/5.0147423>.
- [11] Diana Chaykina, Fahimeh Nafezarefi, Giorgio Colombi, Steffen Cornelius, Lars J. Bannenberg, Herman Schreuders, Bernard Dam, Influence of crystal structure, encapsulation, and annealing on photochromism in Nd oxyhydride thin films, *J. Phys. Chem. C* 126 (2022) 2276–2284, <https://doi.org/10.1021/acs.jpcc.1c10521>.
- [12] S.M. Adalsteinsson, M.V. Moro, D. Moldarev, S. Droulias, M. Wolff, D. Primetzhofner, Correlating chemical composition and optical properties of photochromic rare-earth oxyhydrides using ion beam analysis, *Nucl. Instrum. Methods Phys. Res. B* 485 (2020) 36–40, <https://doi.org/10.1016/j.nimb.2020.09.016>.
- [13] Ziyang Wu, Lidwin de Wit, Melanie Beek, Giorgio Colombi, Diana Chaykina, Herman Schreuders, Henk Schut, Maciej Oskar Liedke, Maik Butterling, Andreas Wagner, Marcel Dickmann, Ekkes Brüick, Bernard Dam, Stephan W.H. Eijt, The memory effect in photochromic rare-earth oxyhydride thin films studied by in-situ positron annihilation spectroscopy upon photodarkening-bleaching cycling, *Phys. Rev. Mater.* 8 (2024) 045201, <https://doi.org/10.1103/PhysRevMaterials.8.045201>.
- [14] F. Nafezarefi, Photochromic Properties of Rare-Earth Oxyhydrides, TU Delft, 2020, <https://doi.org/10.4233/uuid:eb54d12f-079a-41a4-8d75-1a0fdf2af412>. PhD Thesis.
- [15] J. Montero, Photochromism in rare earth oxyhydrides for large-area transmittance control, *Sol. Energy Mater. Sol. Cell.* (2024) this issue.
- [16] L.T. Sharpe, A. Stockman, W. Jagla, H. Jagle, A luminous efficiency function $V^*(\lambda)$ for daylight adaptation, *J. Vis.* 5 (2005) 948–968, <https://doi.org/10.1002/col.20602>.
- [17] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, Yttrium and Lanthanum hydride films with switchable optical properties, *Nature* 380 (1996) 231–234, <https://doi.org/10.1038/380231a0>.
- [18] A.F.Th Hoekstra, A.S. Roy, T.F. Rosenbaum, R. Griessen, R.J. Wijngaarden, N. J. Koeman, Light-induced metal-insulator transition in a switchable mirror, *Phys. Rev. Lett.* 86 (2001) 5349–5352, <https://doi.org/10.1103/PhysRevLett.86.5349>.
- [19] Ayako Ohmura, Akihiko Machida, Tetsu Watanuki, Katsutoshi Aoki, Satoshi Nakano, K. Takemura, Photochromism in yttrium hydride, *Appl. Phys. Lett.* 91 (2007) 151904, <https://doi.org/10.1063/1.2794755>.
- [20] José Montero, Fredrik A. Martinsen, Martynas Lelis, Smagul Zh Karazhanov, Björn C. Hauback, Erik S. Marstein, Preparation of yttrium hydride-based photochromic films by reactive magnetron sputtering, *Sol. Energy Mater. Sol. Cells* 177 (2018) 106–109, <https://doi.org/10.1016/j.solmat.2017.02.001>.
- [21] Giorgio Colombi, Tom De Krom, Diana Chaykina, Steffen Cornelius, Stephan W. H. Eijt, Bernard Dam, Influence of cation (RE = Sc, Y, Gd) and O/H anion ratio on the photochromic properties of $\text{REO}_3\text{H}_{3-2x}$ thin films, *ACS Photonics* 8 (2021) 709–715, <https://doi.org/10.1021/acsp Photonics.0c01877>.
- [22] Chang Chuan You, Trygve Mongstad, Jan Petter Maehlen, Smagul Karazhanov, Engineering of the band gap and optical properties of thin films of yttrium hydride, *Appl. Phys. Lett.* 105 (2014) 031910, <https://doi.org/10.1063/1.4891175>.
- [23] Chang Chuan You, Dmitrii Moldarev, Trygve Mongstad, Daniel Primetzhofner, Max Wolff, Erik Stensrud Marstein, Smagul Zh Karazhanov, Enhanced photochromic response in oxygen-containing yttrium hydride thin films transformed by an oxidation process, *Sol. Energy Mater. Sol. Cells* 166 (2017) 185–189, <https://doi.org/10.1016/j.solmat.2017.03.023>.
- [24] M. Zubkins, I. Aulika, E. Strods, V. Vibornijs, L. Bikse, A. Sarakovskis, G. Chikvaidze, J. Gabrusenoks, H. Arslan, J. Purans, Optical properties of oxygen-containing yttrium hydride thin films during and after the deposition, *Vacuum* 203 (2022) 111218, <https://doi.org/10.1016/j.vacuum.2022.111218>.
- [25] Yuya Komatsu, Ryota Shimizu, Ryuhei Sato, Markus Wilde, Kazunori Nishio, Takayoshi Katase, Daiju Matsumura, Hiroyuki Saitoh, Masahiro Miyauchi, Jonah R. Adelman, Ryan M.L. McFadden, Derek Fujimoto, John O. Ticknor, Monika Stachura, Iain McKenzie, Gerald D. Morris, W. Andrew MacFarlane, Jun sugiyama, katsuyuki fukutani, shinji tsuneyuki, and taro hitosugi, repeatable

- photoinduced insulator-to-metal transition in yttrium oxyhydride epitaxial thin films, *Chem. Mater.* 34 (2022) 3616–3623, <https://doi.org/10.1021/acs.chemmater.1c03450>.
- [26] Giorgio Colombi, Steffen Cornelius, Alessandro Longo, Bernard Dam, Structure model for anion-disordered photochromic gadolinium oxyhydride thin films, *J. Phys. Chem. C* 124 (2020) 13541–13549, <https://doi.org/10.1021/acs.jpcc.0c02410>.
- [27] Giorgio Colombi, Rens Stigter, Diana Chaykina, Shrestha Banerjee, Arno P. M. Kentgens, Stephan W.H. Eijt, Bernard Dam, Gilles A. de Wijs, Energy, metastability, and optical properties of anion-disordered $\text{RO}_x\text{H}_{3-2x}$ (R = Y, La) oxyhydrides: a computational study, *Phys. Rev. B* 105 (2022) 054208, <https://doi.org/10.1103/PhysRevB.105.054208>.
- [28] Shrestha Banerjee, Diana Chaykina, Rens Stigter, Giorgio Colombi, Stephan W. H. Eijt, Bernard Dam, Gilles A. de Wijs, Arno P.M. Kentgens, Exploring multi-anion chemistry in yttrium oxyhydrides: solid-state NMR studies and DFT calculations, *J. Phys. Chem. C* 127 (2023) 14303–14316, <https://doi.org/10.1021/acs.jpcc.3c02680>.
- [29] Shrestha Banerjee, Diana Chaykina, Giorgio Colombi, Bernard Dam, Gilles A. de Wijs, and Arno P.M. Kentgens, Studying Photochromism in Scandium Oxyhydrides: Solid-State NMR Studies and DFT Calculations, to be published.
- [30] Hiroki Ubukata, Thibault Broux, Fumitaka Takeiri, Kazuki Shitara, Hiroki Yamashita, Akihide Kuwabara, Genki Kobayashi, Hiroshi Kageyama, Hydride conductivity in an anion-ordered fluorite structure LnHO with an enlarged bottleneck, *Chem. Mater.* 31 (2019) 7360–7366, <https://doi.org/10.1021/acs.chemmater.9b01968>.
- [31] Marius Widerøe, Helmer Fjellvag, TrulsNorby, Finn WillyPoulsen, Rolf WillestofteBerg, NdHO , a novel oxyhydride, *J. Solid State Chem.* 184 (2011) 1890–1894, <https://doi.org/10.1016/j.jssc.2011.05.025>.
- [32] Diana Chaykina, Ismene Usman, Giorgio Colombi, Herman Schreuders, Beata Tyburska-Pueschel, Ziyang Wu, Stephan W.H. Eijt, Lars J. Bannenberg, Gilles A. de Wijs, Bernard Dam, Aliovalent calcium doping of yttrium oxyhydride thin films and implications for photochromism, *J. Phys. Chem. C* 126 (2022) 14742–14749, <https://doi.org/10.1021/acs.jpcc.2c04456>.
- [33] Marcus Hans, Tuan T. Tran, Sigurbjörn M. Aðalsteinsson, Dmitrii Moldarev, Marcos V. Moro, Max Wolff, Daniel Primetzhofner, Photochromic mechanism and dual-phase formation in oxygen-containing rare-earth hydride thin films, *Adv. Opt. Mater.* 8 (2020) 2000822, <https://doi.org/10.1002/adom.202000822>.
- [34] E.M. Baba, J. Montero, E. Strugovshchikov, E.O. Zayim, S. Karazhanov, Light-induced breathing in photochromic yttrium oxyhydrides, *Phys. Rev. Mater.* 4 (2020) 025201, <https://doi.org/10.1103/PhysRevMaterials.4.025201>.
- [35] Elbruz Murat Baba, Philip Michael Weiser, Esra özkan zayim, and smagul karazhanov, temperature-dependent photochromic performance of yttrium oxyhydride thin films, *Phys. Status Solidi RRL* 15 (2021) 2000459, <https://doi.org/10.1002/pssr.202000459>.
- [36] D. Chaykina, T. de Krom, G. Colombi, H. Schreuders, A. Suter, T. Prokscha, B. Dam, S. Eijt, Structural properties and anion dynamics of yttrium dihydride and photochromic oxyhydride thin films examined by in situ μSR , *Phys. Rev. B* 103 (2021) 224106, <https://doi.org/10.1103/PhysRevB.103.224106>.
- [37] Dmitrii Moldarev, Stolz Levin, Marcos V. Moro, Sigurbjörn M. Aðalsteinsson, Ioan-Augustin Chioar, Smagul Zh Karazhanov, Daniel Primetzhofner, Max Wolff, Environmental dependence of the photochromic effect of oxygen-containing rare-earth metal hydrides, *J. Appl. Phys.* 129 (2021) 153101, <https://doi.org/10.1063/5.0041487>.
- [38] Marcus Hans, Tuan T. Tran, Sigurbjörn M. Aðalsteinsson, Dmitrii Moldarev, Marcos V. Moro, Max Wolff, Daniel Primetzhofner, Photochromic mechanism and dual-phase formation in oxygen-containing rare-earth hydride thin films, *Adv. Opt. Mater.* 8 (2020) 200822, <https://doi.org/10.1002/adom.202000822>.
- [39] D. Moldarev, M. Wolff, D. Primetzhofner, Modification of the photochromic properties of oxygen-containing yttrium hydride by irradiation with keV and MeV ions, *J. Phys. Chem. C* 127 (2023) 24676–24682, <https://doi.org/10.1021/acs.jpcc.3c06010>.
- [40] J. Montero, F.A. Martinsen, M. García-Tecedor, S. Zh Karazhanov, D. Maestre, B. Hauback, E.S. Marstein, Photochromic mechanism in oxygen-containing yttrium hydride thin films: an optical perspective, *Phys. Rev. B* 95 (2017) 201301, <https://doi.org/10.1103/PhysRevB.95.201301> (R).
- [41] Giorgio Colombi, Bart Boshuizen, Diana Chaykina, Leyi Hsu, Herman Schreuders, Tom J. Savenije, Bernard Dam, Polaron Large, Conduction, photoconductivity, and photochromism in $\text{GdO}_x\text{H}_{3-2x}$ oxyhydride thin films, *Adv. Opt. Mater.* 11 (2023) 2202660, <https://doi.org/10.1002/adom.202202660>.
- [42] Trygve Mongstad, Annett Thøgersen, Aryasomayajula Subrahmanyam, Smagul Karazhanov, The electronic state of thin films of yttrium, yttrium hydrides and yttrium oxide, *Sol. Energy Mater. Sol. Cells* 128 (2014) 270–274, <https://doi.org/10.1016/j.solmat.2014.05.037>.
- [43] Suraya Kazi, Dmitrii Moldarev, Marcos V. Moro, Daniel Primetzhofner, Max Wolff, Correlating photoconductivity and optical properties in oxygen-containing yttrium hydride thin films, *Phys. Status Solidi RRL* 17 (2023) 2200435, <https://doi.org/10.1002/pssr.202200435>.
- [44] Tomoyuki Yamasaki, Ryosei Takaoka, Soshi Iimura, Junghwan Kim, Hidenori Hiramatsu, Hideo Hosono, Characteristic resistive switching of rare-earth oxyhydrides by hydride ion insertion and extraction, *ACS Appl. Mater. Interfaces* 14 (2022) 19766–19773, <https://doi.org/10.1021/acsami.2c03483>.
- [45] W.H. Armistead, S.D. Stookey, Photochromic silicate glasses sensitized by silver halides, *Science* 144 (1964) 150, <https://doi.org/10.1126/science.144.3615.150>.
- [46] T.P. Seward III, Thermally darkenable photochromic glasses, *J. Appl. Phys.* 46 (1975) 689, <https://doi.org/10.1063/1.321631>.
- [47] T.P. Seward III, Coloration and optical anisotropy in silver-containing glasses, *J. Non-Cryst. Solids* 40 (1980) 499–513, [https://doi.org/10.1016/0022-3093\(80\)90125-8](https://doi.org/10.1016/0022-3093(80)90125-8).
- [48] Zhen Zhang, John T. Yates Jr., Band bending in semiconductors: chemical and physical consequences at surfaces and interfaces, *Chem. Rev.* 112 (2012) 5520–5551, <https://doi.org/10.1021/cr3000626>.
- [49] K.K. Ng, F.C. Zhang, V.I. Anisimov, T.M. Rice, Electronic structure of lanthanum hydrides with switchable optical properties, *Phys. Rev. Lett.* 78 (1997) 1311–1314, <https://doi.org/10.1103/PhysRevLett.78.1311>.
- [50] Jose Montero, Peter Svedlindh, Lars Osterlund, Photo-induced reversible modification of the Curie-Weiss temperature in paramagnetic gadolinium compounds, *Solid State Commun.* 378 (2024) 115419, <https://doi.org/10.1016/j.ssc.2023.115419>.
- [51] Ziyang Wu, Tom de Krom, Giorgio Colombi, Diana Chaykina, Gijs van Hattem, Henk Schut, Marcel Dickmann, Egger Werner, Christoph Hugschmidt, Ekkes Brück, Bernard Dam, Stephan W.H. Eijt, Formation of vacancies and metallic-like domains in photochromic rare-earth oxyhydride thin films studied by in-situ illumination positron annihilation spectroscopy, *Phys. Rev. Mater.* 6 (2022) 065201, <https://doi.org/10.1103/PhysRevMaterials.6.065201>.
- [52] P. Dorenbos, Modelling the chemical shift of lanthanide 4f electron binding energies, *Phys. Rev. B* 85 (2012) 165107, <https://doi.org/10.1103/PhysRevB.85.165107>.