



Delft University of Technology

Photochromic samarium oxyhydride thin films

Chaykina, D.; Colombi, G.; Schreuders, H.; Dam, B.

DOI

[10.1063/5.0147423](https://doi.org/10.1063/5.0147423)

Publication date

2023

Document Version

Final published version

Published in

AIP Advances

Citation (APA)

Chaykina, D., Colombi, G., Schreuders, H., & Dam, B. (2023). Photochromic samarium oxyhydride thin films. *AIP Advances*, 13(5), Article 055211. <https://doi.org/10.1063/5.0147423>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

RESEARCH ARTICLE | MAY 05 2023

Photochromic samarium oxyhydride thin films Diana Chaykina ; Giorgio Colombi; Herman Schreuders; ... et. al

AIP Advances 13, 055211 (2023)

<https://doi.org/10.1063/5.0147423>View
OnlineExport
Citation

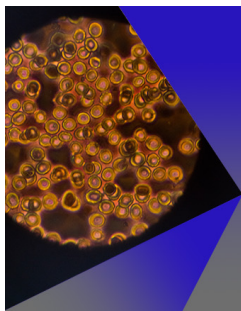
CrossMark

Articles You May Be Interested In

Effect of temperature and illumination conditions on the photochromic performance of yttrium oxyhydride thin films

Journal of Applied Physics (July 2020)

Topotactic synthesis of strontium cobalt oxyhydride thin film with perovskite structure

AIP Advances (October 2015)Universal two-dimensional characteristics in perovskite-type oxyhydrides ATiO_2H (A = Li, Na, K, Rb, Cs)*J. Chem. Phys.* (July 2017)**AIP Advances**Special Topic: Medical Applications
of Nanoscience and Nanotechnology**Submit Today!**

Photochromic samarium oxyhydride thin films

Cite as: AIP Advances 13, 055211 (2023); doi: 10.1063/5.0147423

Submitted: 1 March 2023 • Accepted: 18 April 2023 •

Published Online: 5 May 2023



Diana Chaykina,^{a)}  Giorgio Colombi,  Herman Schreuders,  and Bernard Dam 

AFFILIATIONS

Materials for Energy Conversion and Storage, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, NL-2629HZ Delft, The Netherlands

^{a)} Author to whom correspondence should be addressed: d.chaykina@tudelft.nl

ABSTRACT

Photochromism has been reported for several rare-earth (RE) metal oxyhydride thin films and is characterized by a reversible darkening of the sample when exposed to light with energy greater than its optical bandgap. Here, we extend the range of known photochromic RE-oxyhydrides to include samarium oxyhydrides. These $\text{SmH}_{3-2x}\text{O}_x$ thin films are made by reactive magnetron sputtering of as-deposited $\text{SmH}_{1.9+\delta}$ and post-oxidation in the air to the oxyhydride phase. The deposition pressure during sputtering is used to control the resultant properties of the Sm-oxyhydride film, such as the optical bandgap, cubic lattice constant, photochromic contrast, and photochromic bleaching speed. Using Sm as the RE-cation results in slower bleaching speeds compared to other lanthanides. We posit that this is due to the stability of the Sm^{2+} state and the difficulty to oxidizing it back to the original RE^{3+} state. This points to the key role of the RE-cation charge state for the optical properties of the material.

© 2023 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/5.0147423>

Photochromism and photo-conductivity in polycrystalline rare-earth (RE) oxyhydrides thin films were first reported in 2011 on Y-based compounds.¹ Since then, photochromism has been found in oxyhydride thin films based on other RE-cations ($\text{RE} = \text{Sc}, \text{Y}, \text{Nd}, \text{Gd}, \text{Dy}, \text{and Er}$)^{2–5} (Fig. 1), suggesting that these properties are general to the whole material class. These RE-oxyhydrides are generally characterized by a $\text{REH}_{3-2x}\text{O}_x$ composition and a crystal structure based on the CaF_2 -type lattice, where the anions sit in the interstitial sites of the fcc cation lattice.^{3,6} The oxide O^{2-} and hydride H^- anions preferentially occupy the more stable tetrahedral sites, and any remaining H^- anions occupy the octahedral sites.^{7,8}

Recently, it was shown that the deposition pressure used during sputtering affects the composition (O:H ratio) of RE-oxyhydride films because this deposition pressure influences the porosity of the as-deposited film, which then oxidizes to different extents upon exposure to air.⁶ Several other properties scale with the deposition pressure (or composition), namely the lattice constant, optical bandgap, electronic conductivity, photochromic contrast, and photochromic bleaching speed.^{6,9,10} This suggests that the anions play an important role in determining the properties of the oxyhydride film, something further confirmed by the effect of the aliovalent substitution of Y by Ca in Y-oxyhydride thin films.¹¹

Yet, it is not only the anions that impact the resultant properties of RE-oxyhydrides—the choice of RE-cation is also significant. When comparing Sc, Y, and Gd, for example, the lattice constant of the RE-oxyhydride increases with cation size, and the largest photochromic contrast, along with the fastest bleaching speeds, are found for Gd-oxyhydrides.⁶ There are also differences among RE-cations from the same period (lanthanides), such as Gd and Nd. While Gd-oxyhydrides form cubic crystal structures, Nd-oxyhydrides exhibit a tetragonal distortion.⁵ However, their photochromic properties are similar, suggesting that cubic symmetry is not an essential ingredient in photochromism.

Here, we use samarium as the cation in our RE-oxyhydride thin films (Fig. 1) because, compared to other RE-cations, Sm is more difficult to oxidize and is often found in a RE^{2+} state rather than the RE^{3+} that is present in oxyhydrides.¹² Since we suspect that photochromism involves the reduction of some RE-cations ($\text{RE}^{3+} \rightarrow \text{RE}^{2+}$) during darkening and oxidation during bleaching, we decided to investigate the use of Sm-oxyhydrides. These Sm-based films are deposited by reactive magnetron sputtering of an Sm target (99.9%, Mateck) at 75 W in an Ar/H_2 gas mixture of 7:1 onto unheated fused silica substrates ($10 \times 10 \text{ mm}^2$, Mateck). The combined $\text{Ar} + \text{H}_2$ pressure, called the deposition pressure (p_{dep}), was varied between 0.3 and 1.0 Pa, resulting in as-deposited $\text{SmH}_{1.9+\delta}$ films

H																	He								
Li	Be											B	C	N	O	F	Ne								
Na	Mg											Al	Si	P	S	Cl	Ar								
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr								
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe								
Cs	Ba																	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra																	Cn	Nh	Fl	Mc	Lv	Ts	Og	
		This work Photochromic RE-oxhydride thin films RE-oxhydride bulk powders No known RE-oxhydride																							
		La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu																							
		Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr																							

FIG. 1. Periodic Table highlighting the RE-cations that have been reported as photochromic oxyhydride thin films (red)²⁻⁶ with this present work highlighted as yellow, bulk RE-oxyhydrides that have not been investigated for photochromism (green),¹⁶⁻²¹ and RE-cations for which oxyhydrides have not yet been reported (gray).

with different porosities, which then oxidize to the Sm-oxyhydride phase upon air-exposure with a varying O:H ratio as a function of p_{dep} .^{5,6,13}

This is seen in Fig. 2, where the material properties of Sm-based films follow all the trends characteristic of the other RE-oxyhydride thin films (RE = Sc, Y, Nd, Gd, Dy, and Er).^{2,3,5} Specifically, the film deposited at a low pressure (0.3 Pa) shows a small transmission window, similar to other RE-dihydrides [Fig. 2(a)].^{14,15} As well, this material has a cubic crystal structure that is expected for SmH_{1.9+δ}, although with a slightly larger lattice constant that may be due to thin film stress.

As the deposition pressure increases to 0.6 Pa and above, an optical bandgap opens [Figs. 2(a)–2(c)] and the lattice expands gradually [Figs. 2(e) and 2(f)], all signs of the formation of the oxyhydride composition. Between 0.3 and 0.6 Pa, there is a so-called critical deposition pressure (p^*), which marks the turning point where the porosity of the as-deposited film is sufficient to begin incorporating O^{2-} upon air-exposure.^{2,5,6} In general, the optical band gaps of these Sm-oxyhydrides are less sensitive to the p_{dep} than those of

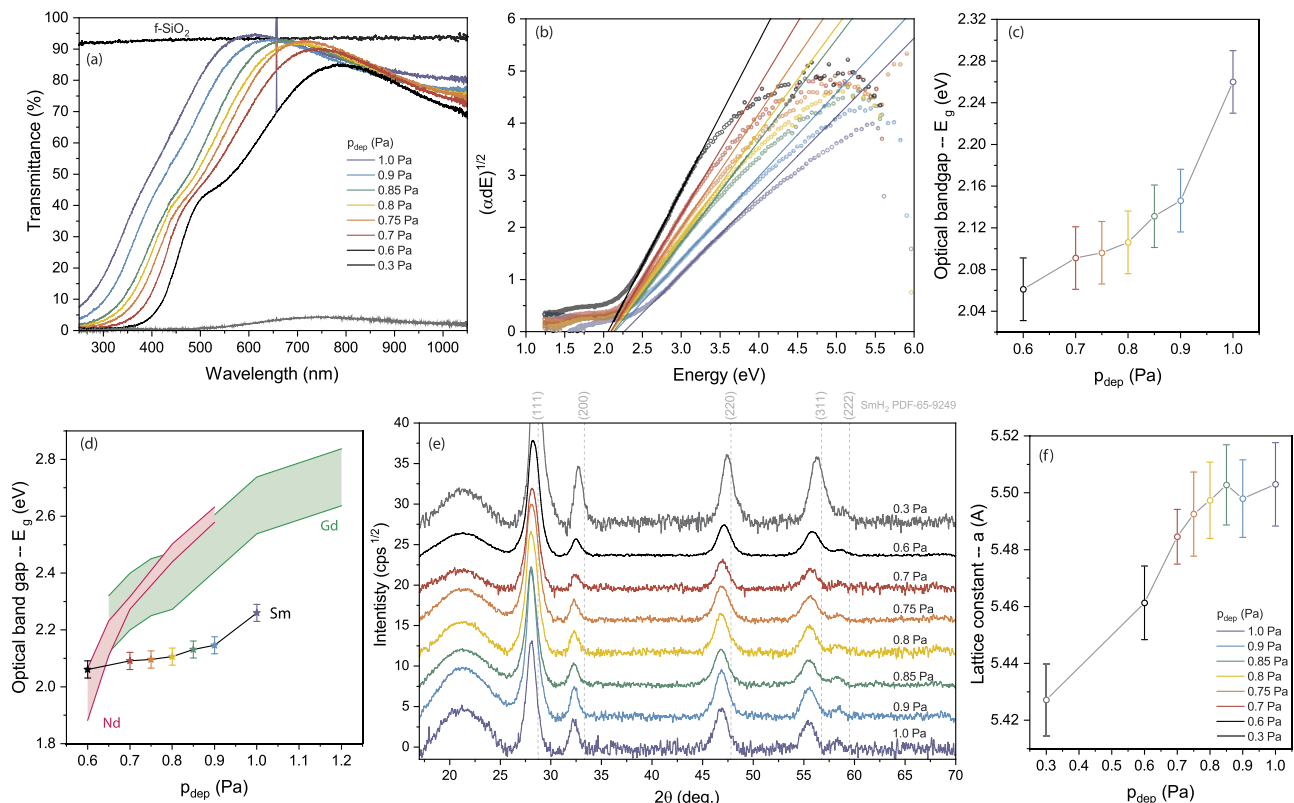


FIG. 2. (a) Optical transmission spectra for Sc-based film films deposited at various deposition pressures (p_{dep}). (b) Tauc plots for Sm-oxyhydrides used to determine the optical band gaps of the materials via the x-intercept. (c) The optical band gaps of the Sm-oxyhydrides as a function of p_{dep} . (d) A comparison of the optical bandgap dependence on p_{dep} for Nd⁵, Gd⁶, and Sm-oxyhydrides (this work). (e) XRD patterns acquired in Bragg-Brentano geometry for the Sm-based materials studied here with a reference for SmH₂ (PDF-65-9249) and the (f) cubic lattice constants derived from these patterns as a function of p_{dep} .

other RE-oxyhydrides based on Gd and Nd [Fig. 2(d)],^{5,6} although the expected increase in bandgap with p_{dep} (thus, the O:H ratio) is still present. This may be due to differences in the electronic band structure of Sm-based compounds, but we cannot exclude that a weaker propensity for oxidation resulted in an inhomogeneous or more H-rich film compared to previous work with other cations. In terms of crystal structure, the Sm-oxyhydrides follow a cubic crystal structure, which is consistent with bulk stoichiometric SmHO powders.^{17–19}

The photochromic properties of Sm-oxyhydride thin films are shown in Fig. 3(a), where the relative contrast ($\Delta T = |T_0 - T|/T_0$) increases during 0.5 h of illumination by a narrow wavelength LED ($\lambda = 385 \text{ nm}$, $I = 75 \text{ mW/cm}^2$). When the light is turned off, the contrast decreases to its original value. The maximum contrast achieved after 0.5 h is shown in Fig. 3(b), while the time required to “bleach” back to the original transparency, quantified as a time constant based on first-order kinetics,^{2,22} is shown in Fig. 3(c). As expected from previous work,⁶ the contrast is highest and the bleaching speed is slowest for the samples deposited at the lowest pressure (0.6 Pa), and the opposite is true for the highest pressure (1.0 Pa). In addition, we find again that the contrast and bleaching speeds do not show the same trend with p_{dep} , implying that bleaching is not the determining factor for the darkening rate.⁵

In general, the photochromic contrast is similar to that of Nd- and Gd-oxyhydrides,^{5,6} although direct comparison is not possible due to differences in film thickness, measurement temperature, and illumination time, all of which influence the maximum contrast. The same is true for the bleaching speed, which we compare only by order of magnitude. The bleaching speeds of Sm-oxyhydride thin films appear slower ($\tau_B \sim 35\text{--}80 \text{ min}$) than what was found for Gd-oxyhydrides ($\tau_B < 10 \text{ min}$ for $\text{GdH}_{3-2x}\text{O}_x$ deposited at $p_{\text{dep}} \geq 0.8 \text{ Pa}$).⁶ Fast bleaching speeds ($< 10 \text{ min}$) are found only for Sm-oxyhydrides deposited at higher p_{dep} (1.0 Pa) and measured at 30°C , compared to 21°C for $\text{GdH}_{3-2x}\text{O}_x$. Since bleaching is a thermally activated process,^{11,23} we can conclude that Sm-oxyhydrides exhibit slower bleaching kinetics than their Gd-based counterparts. This could be due to the characteristic difficulty of Sm to oxidize from the $2+$ state back to the $3+$ state compared to other lanthanides.¹² This points to the importance of the persistent RE^{2+} state for the reversible optical changes we observe during photochromism.

With this work, we add Sm to the series of known photochromic RE-oxyhydride thin films (Fig. 1). We have shown that $\text{SmH}_{3-2x}\text{O}_x$ thin films can be prepared by post-oxidation of an as-deposited $\text{SmH}_{1.9+\delta}$ thin film, controlling the extent of oxidation by the deposition pressure (p_{dep}). These Sm-based films have similar properties to previous studies on other RE-oxyhydride thin films ($\text{RE} = \text{Sc}, \text{Y}, \text{Nd}, \text{and Gd}$) and follow the same p_{dep} dependence for the optical bandgap, crystal lattice size, and photochromic properties. However, the unexpectedly slow bleaching kinetics of the Sm-oxyhydrides suggests that the redox behavior of the RE-cation plays an important role in the photochromic mechanism of these compounds.

The mechanism for photochromism is far from settled. At its heart is the electron-hole pair generated by the bandgap excitation.^{5,24} We believe that the excited electron reduces the Y^{3+} while the hole oxidizes the H^- ion to H^0 , particularly the octahedral

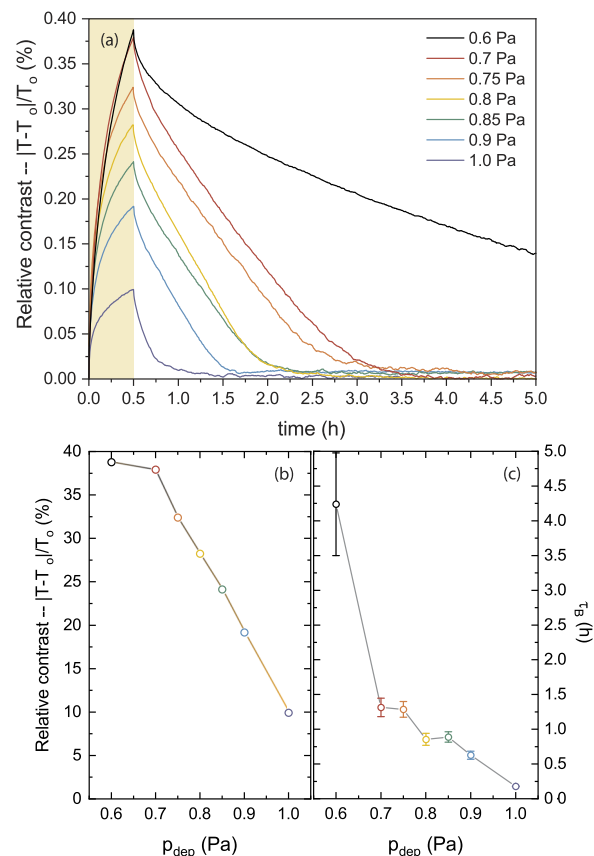


FIG. 3. (a) Photochromic properties of Sm-oxyhydride thin films illuminated for 30 min at 30°C . Two parameters are calculated from these measurements: (b) the relative photochromic contrast and (c) the bleaching speed, which changes with the p_{dep} .

H^- .¹¹ Probably some (filamentary) clustering of the reduced yttrium takes place, which causes the optical absorption.^{25–27} The nature and the role of the oxidized H^- are still unclear. In the absence of an optical excitation, the bleaching process is dominant, meaning that energy is gained by bleaching. Y^{2+} is supposed to revert back to the Y^{3+} state by donating its electron to the oxidized hydrogen species. Clearly, according to the energy scheme proposed by, e.g., Dorenbos,¹² the implied oxidation of the RE-ion is less favorable for Sm than it is for Gd ions. The slow bleaching process is, therefore, in accordance with the proposed oxidation/reduction mechanism we propose. It would be interesting to test other RE-cations that are often found in the RE^{2+} oxidation state,²⁸ such as Eu and Yb. However, these could not yet be made to form RE-oxyhydrides due to the propensity of both the metallic sputtering targets and the dihydride films to fully oxidize.

This work was supported by the Mat4Sus research program with Project No. 680.M4SF.034, funded by the Dutch Research Council (NWO).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Diana Chaykina: Conceptualization (equal); Formal analysis (equal); Methodology (equal); Visualization (lead); Writing – original draft (equal). **Giorgio Colombi:** Conceptualization (equal); Formal analysis (equal); Investigation (lead); Methodology (lead); Visualization (supporting). **Herman Schreuders:** Investigation (supporting); Methodology (supporting). **Bernard Dam:** Conceptualization (equal); Funding acquisition (lead); Supervision (lead); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- ¹T. Mongstad, C. Platzer-Björkman, J. P. Maehlen, L. P. A. Mooij, Y. Pivak, B. Dam, E. S. Marstein, B. C. Hauback, and S. Z. Karazhanov, “A new thin film photochromic material: Oxygen-containing yttrium hydride,” *Sol. Energy Mater. Sol. Cells* **95**(12), 3596–3599 (2011).
- ²F. Nafezarefi, H. Schreuders, B. Dam, and S. Cornelius, “Photochromism of rare-earth metal-oxy-hydrides,” *Appl. Phys. Lett.* **111**(10), 103903 (2017).
- ³S. Cornelius, G. Colombi, F. Nafezarefi, H. Schreuders, R. Heller, F. Munnik, and B. Dam, “Oxyhydride nature of rare-earth-based photochromic thin films,” *J. Phys. Chem. Lett.* **10**, 1342–1348 (2019).
- ⁴S. M. Aðalsteinsson, M. V. Moro, D. Moldarev, S. Droulias, M. Wolff, and D. Primetzhof, “Correlating chemical composition and optical properties of photochromic rare-earth oxyhydrides using ion beam analysis,” *Nucl. Instrum. Methods Phys. Res., Sect. B* **485**, 36–40 (2020).
- ⁵D. Chaykina, F. Nafezarefi, G. Colombi, S. Cornelius, L. J. Bannenberg, H. Schreuders, and B. Dam, “Influence of crystal structure, encapsulation, and annealing on photochromism in Nd oxyhydride thin films,” *J. Phys. Chem. C* **126**(4), 2276–2284 (2022).
- ⁶G. Colombi, T. De Krom, D. Chaykina, S. Cornelius, S. W. H. Eijt, and B. Dam, “Influence of cation (RE = Sc, Y, Gd) and O/H anion ratio on the photochromic properties of REO_xH_{3–2x} thin films,” *ACS Photonics* **8**(3), 709–715 (2021).
- ⁷G. Colombi, S. Cornelius, A. Longo, and B. Dam, “Structure model for anion-disordered photochromic gadolinium oxyhydride thin films,” *J. Phys. Chem. C* **124**, 13541–13549 (2020).
- ⁸G. Colombi, R. Stigter, D. Chaykina, S. Banerjee, A. P. M. Kentgens, S. W. H. Eijt, B. Dam, and G. A. de Wijs, “Energy, metastability, and optical properties of anion-disordered REO_xH_{3–2x} (RE = Y, La) oxyhydrides: A computational study,” *Phys. Rev. B* **105**, 054208 (2022).
- ⁹C. C. You, T. Mongstad, J. P. Maehlen, and S. Karazhanov, “Engineering of the band gap and optical properties of thin films of yttrium hydride,” *Appl. Phys. Lett.* **105**(3), 031910 (2014).
- ¹⁰C. C. You, T. Mongstad, E. S. Marstein, and S. Z. Karazhanov, “The dependence of structural, electrical and optical properties on the composition of photochromic yttrium oxyhydride thin films,” *Materialia* **6**, 100307 (2019).
- ¹¹D. Chaykina, I. Usman, G. Colombi, H. Schreuders, B. Tyburska-Pueschel, Z. Wu, S. W. H. Eijt, L. J. Bannenberg, G. A. de Wijs, and B. Dam, “Allovalent calcium doping of yttrium oxyhydride thin films and implications for photochromism,” *J. Phys. Chem. C* **126**(34), 14742–14749 (2022).
- ¹²P. Dorenbos, “Modeling the chemical shift of lanthanide 4f electron binding energies,” *Phys. Rev. B* **85**(16), 165107 (2012).
- ¹³M. Zubkins, I. Aulika, E. Strods, V. Vibornis, L. Bikse, A. Sarakovskis, G. Chikvaidze, J. Gabrusenoks, H. Arslan, and J. Purans, “Optical properties of oxygen-containing yttrium hydride thin films during and after the deposition,” *Vacuum* **203**, 111218 (2022).
- ¹⁴P. Ngene, T. Radeva, M. Slaman, R. J. Westerwaal, H. Schreuders, and B. Dam, “Seeing hydrogen in colors: Low-cost and highly sensitive eye readable hydrogen detectors,” *Adv. Funct. Mater.* **24**(16), 2374–2382 (2014).
- ¹⁵P. Ngene, T. Radeva, R. Westerwaal, H. Schreuders, and B. Dam, “Eye readable metal hydride based hydrogen tape sensor for health applications,” *Proc. SPIE* **9202**, 920203 (2014).
- ¹⁶B. Malaman and J. F. Brice, “Etude structurale de l’hydrure-oxyde LaHO par diffraction des rayons X et par diffraction des neutrons,” *J. Solid State Chem.* **53**, 44–54 (1984).
- ¹⁷H. Ubukata, T. Broux, F. Takeiri, K. Shitara, H. Yamashita, A. Kuwabara, G. Kobayashi, and H. Kageyama, “Hydride conductivity in an anion-ordered fluorite structure LnHO with an enlarged bottleneck,” *Chem. Mater.* **31**(18), 7360–7366 (2019).
- ¹⁸H. Yamashita, T. Broux, Y. Kobayashi, F. Takeiri, H. Ubukata, T. Zhu, M. A. Hayward, K. Fujii, M. Yashima, K. Shitara *et al.*, “Chemical pressure-induced anion order-disorder transition in LnHO enabled by hydride size flexibility,” *J. Am. Chem. Soc.* **140**(36), 11170–11173 (2018).
- ¹⁹N. Zapp and H. Kohlmann, “The lanthanide hydride oxides SmHO and HoHO,” *Z. Naturforsch. B* **73**(8), 535–538 (2018).
- ²⁰K. Ooya, J. Li, K. Fukui, S. Iimura, T. Nakao, K. Ogasawara, M. Sasase, H. Abe, Y. Niwa, M. Kitano, and H. Hosono, “Ruthenium catalysts promoted by lanthanide oxyhydrides with high hydride-ion mobility for low-temperature ammonia synthesis,” *Adv. Energy Mater.* **11**(4), 2003723 (2020).
- ²¹N. Zapp, D. Sheptyakov, and H. Kohlmann, “Computational chemistry-guided syntheses and crystal structures of the heavier lanthanide hydride oxides DyHO, ErHO, and LuHO,” *Crystals* **11**(7), 750 (2021).
- ²²F. Nafezarefi, S. Cornelius, J. Nijskens, H. Schreuders, and B. Dam, “Effect of the addition of zirconium on the photochromic properties of yttrium oxy-hydride,” *Sol. Energy Mater. Sol. Cells* **200**, 109923 (2019).
- ²³D. Chaykina, T. de Krom, G. Colombi, H. Schreuders, A. Suter, T. Prokscha, B. Dam, and S. W. H. Eijt, “Structural properties and anion dynamics of yttrium dihydride and photochromic oxyhydride thin-films examined by *in situ* μ SR,” *Phys. Rev. B* **103**(22), 224106 (2021).
- ²⁴C. C. You and S. Z. Karazhanov, “Effect of temperature and illumination conditions on the photochromic performance of yttrium oxyhydride thin films,” *J. Appl. Phys.* **128**(1), 013106 (2020).
- ²⁵G. Colombi, B. Boshuizen, D. Chaykina, L. Hsu, H. Schreuders, T. J. Savenije, and B. Dam, “Relation between photochromism and photoconductivity in REO_xH_{3–2x} thin films,” *Advanced Optical Materials* (to be published).
- ²⁶J. Montero, F. A. Martinsen, M. García-Tecedor, S. Zh Karazhanov, D. Maestre, B. Hauback, and E. S. Marstein, “Photochromic mechanism in oxygen-containing yttrium hydride thin films: An optical perspective,” *Phys. Rev. B* **95**, 201301(R) (2017).
- ²⁷J. Montero and S. Z. Karazhanov, “Spectroscopic ellipsometry and microstructure characterization of photochromic oxygen-containing yttrium hydride thin films,” *Phys. Status Solidi A* **215**(19), 1701039 (2018).
- ²⁸G. G. Libowitz and A. J. Maeland, *Hydrides, Book Section 26* (North-Holland Publishing Company, 1979), pp. 299–336.