

Temperature-Dependent Photochromic Performance of Yttrium Oxyhydride Thin Films

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Yttrium oxyhydride (YHO) is a rare-earth-metal oxyhydride that has attracted considerable attention due to its outstanding photochromic properties. The transparency of YHO thin films across the infrared and visible spectral regions is reduced considerably under UV illumination (photodarkening) and recovers when the illumination is removed (bleaching). Although oxygen diffusion has been shown to be necessary for these processes, the exact mechanism for the photochromic behavior is not yet understood. In this work, infrared spectroscopy is utilized to investigate the effect of temperature on the photochromic properties of YHO thin films. The measurements show that YHO can photodarken at temperatures as low as 5 K, where anion diffusion is expected to be severely limited. The bleaching of the films is small, but not zero, for temperatures between 5 and 50 K. A stepwise recovery of the transmittance is observed as the temperature of the films is increased above 100 K up to 250 K. The temperature-dependent data show that anion diffusion is not required to explain the photochromic behavior of YHO, and that an additional mechanism (or mechanisms), e.g., electronic charge transfer, contributes to the photochromic behavior of YHO, as well as other rare-earth-metal oxyhydrides.


earth metal oxyhydrides exhibit similar photochromic behaviors at ambient conditions.^[2,3] The remarkable advantage of the latter class of materials is the ability to deposit thin films at room temperature using, e.g., magnetron sputtering^[3–5] or electron-beam evaporation,^[6] with little to no additional processing, which offers excellent scaling potential for industrial applications. It was recently shown that rare-earth oxyhydrides can also be synthesized as bulk samples.^[7] Furthermore, the ability to incorporate different anions offers tantalizing possibilities for creating new materials with unique properties that are not possible with single-anion compounds.^[8] However, many of the fundamental properties of rare-earth-metal oxyhydrides have yet to be understood, which has hindered their widespread use in applications.

Photochromism is the phenomenon in which the optical properties of a material are altered due to the absorption of electromagnetic radiation. This effect can be utilized for a broad range of applications, with a specific focus on smart windows, displays, and energy-saving applications. While it is well known that yttrium hydride (YH_x)^[1] exhibits photochromic properties at high pressures (GPa), it was recently demonstrated that rare

Of the rare-earth-metal oxyhydrides, yttrium oxyhydride (YHO) has been a strong subject of recent experimental^[2,9–12] and theoretical^[13,14] investigations. Thin films of YHO exhibit photochromic behavior, in which a decrease in the transmittance, and consequently an enhancement of light absorption, of the films (referred to as photodarkening) is observed upon illumination with photons with energies between 1.8 and 3.1 eV.^[10,15] The photodarkening rate has been shown to depend on both the intensity and the energy of the illuminating light.

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Removal of the illumination is followed by recovery of the film's transmittance to the initial, transparent state (referred to as bleaching). Yttrium atoms in photochromic YHO have been shown to possess mixed oxidation states, either +2 or +3.^[16] Initially, the darkening process was postulated to arise from the formation of dilute metallic domains that arise from photoinduced changes in the charge state of Y.^[17,18] Recently, oxygen was shown to play a key role in the photochromic process of YHO.^[19] Indeed, photodarkened YHO thin films bleach back to their transparent pre-illuminated state much more rapidly in air than in an inert ambient. It was proposed that the photochromic process could be explained in terms of light-induced breathing, whereby the exchange of oxygen atoms between the films and the ambient atmosphere during the darkening and bleaching processes results in contraction and expansion of the YHO lattice, respectively. Despite these observations, the fundamental mechanism for anion diffusion and its connection to the photochromic behavior of YHO is not well understood.

In this work, we use transmittance infrared (IR) spectroscopy to study the dependence of photodarkening and bleaching of

photochromic YHO thin films on temperatures in the range of 5 and 295 K. The photodarkening process of photochromic YHO demonstrates no dependence on temperature, as YHO can photodarken after exposure to UV light at temperatures as low as 5 K, where anion diffusion is expected to be highly limited. Bleaching of the films, however, is strongly influenced by temperature: a small recovery of the transmittance is observed between 5 and 50 K, whereas a slow, stepwise recovery occurs between 100 and 250 K. Based on our results, we suggest that anion diffusion does not contribute to the darkening or bleaching processes at low temperatures, and that other mechanisms, e.g., charge transfer, are needed to fully explain the photochromic process.

Figure 1 shows the evolution of the IR transmittance spectra at 295 K of YHO thin films deposited with $P_d = 1.0$ and 1.5 Pa during photodarkening under UV light (Figure 1a and 1c, respectively), and during bleaching when the UV light is removed (Figure 1b and 1d, respectively). For both films, ΔT increases with increasing energy of the incident light, which is in accordance with previous reports in the literature.^[2,3,5,17] After 40 min of UV illumination, the photodarkened films show an

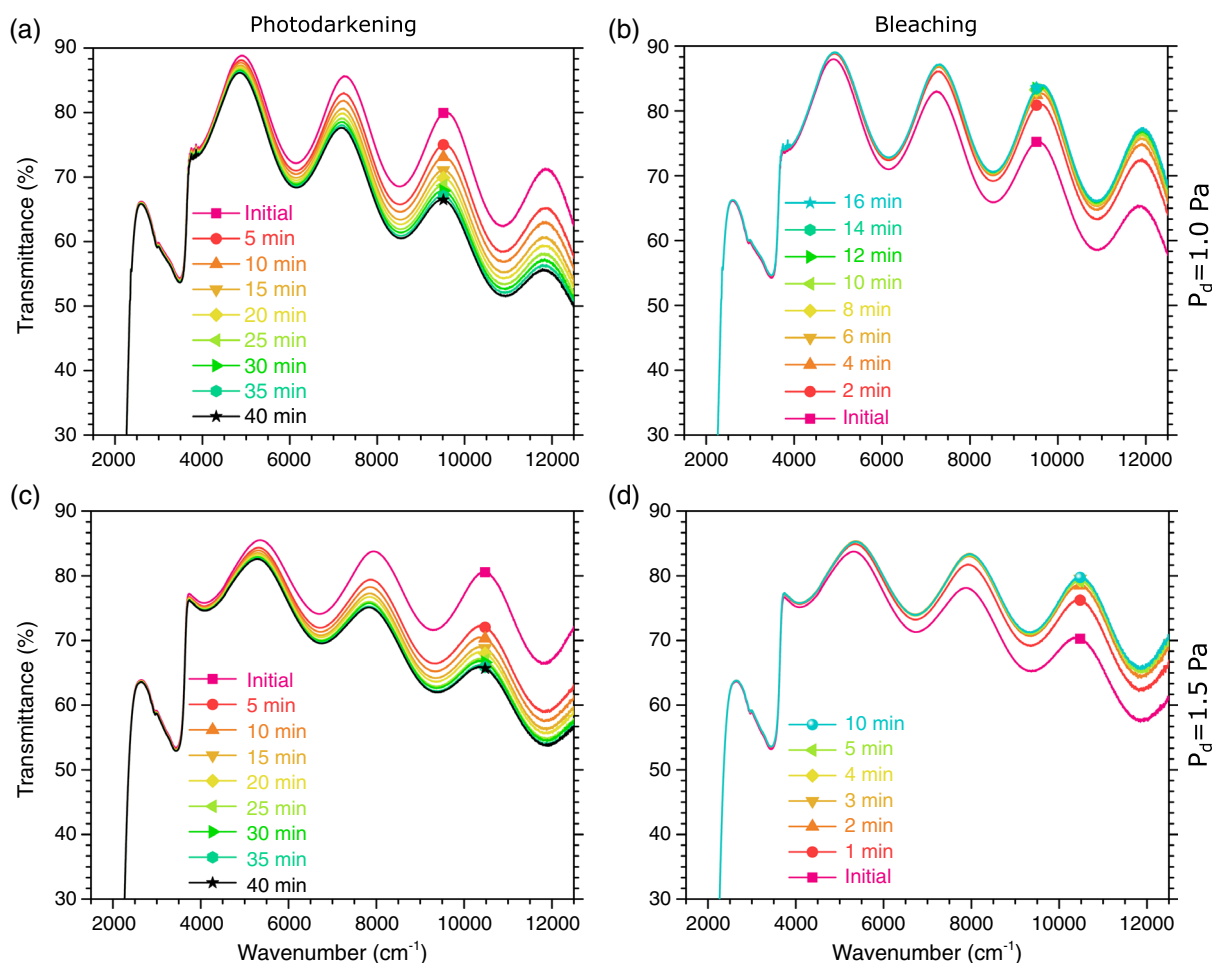


Figure 1. a–d) Infrared transmittance spectra (solid curves) of photochromic YHO thin films at 295 K during photodarkening for between 0 and 40 min (a,c) and during subsequent bleaching for between 0 and 16 min (b,d). (a,b) and (c,d) are for the films deposited at 1.0 and 1.5 Pa, respectively.

average ΔT over the range from 4000 and 12000 cm^{-1} of about 8%. Upon removal of the UV illumination, the YHO thin films begin to bleach, and the initial transparencies of the films are recovered within 16 min ($P_d = 1.0$ Pa) and 10 min ($P_d = 1.5$ Pa).

Following this recovery, the films were cooled (without UV illumination) to 5 K and subsequently UV illuminated to produce the photodarkened state. **Figure 2a** and **2b** show the evolution of the IR transmittance spectra measured at 5 K during the photodarkening process for the two YHO films shown in Figure 1. (The increase in temperature of the films due to UV illumination is not more than 1–2 K.) The corresponding ΔT for the films are shown in Figure 2c and 2d, respectively. Compared to the process at 295 K, photodarkening of the films at 5 K results in higher photochromic contrast ($\Delta T = \approx 26\%$ and 14% for $P_d = 1.0$ and 1.5 Pa, respectively) and faster initial darkening rate. We caution, however, that the photochromic response in YHO thin films is known to be affected by other factors, e.g., deposition pressure^[15] and previous darkening–bleaching cycles (so-called memory effect).^[2] The deposition pressure is inversely related to the

photochromic contrast and, has been demonstrated for both YHO^[15,20] and a related material, gadolinium oxyhydride.^[21] The memory effect caused by consecutive darkening–bleaching cycles leads to higher photochromic contrast and faster photodarkening rates, which is consistent with the photodarkening behavior observed at 5 K. Additional experiments are needed to fully elucidate the individual effects of photodarkening temperature and deposition pressure from those due to memory on the photochromic performance. It should also be noted that the photochromic contrast in the IR spectral region where O–H vibrations typically occur (3000–3500 cm^{-1}) exhibits a significant ΔT at 5 K compared to the essentially null change at 295 K. Such a change might be indicative of the presence of and changes to OH-related species, but our data do not allow us to draw a definitive conclusion at this time.

The mechanism(s) responsible for the photochromic effect observed in YHO, as well as other rare-earth-metal oxyhydride, thin films is still under debate. In YHO thin films, it was recently suggested that oxygen out-diffusion from the lattice followed by

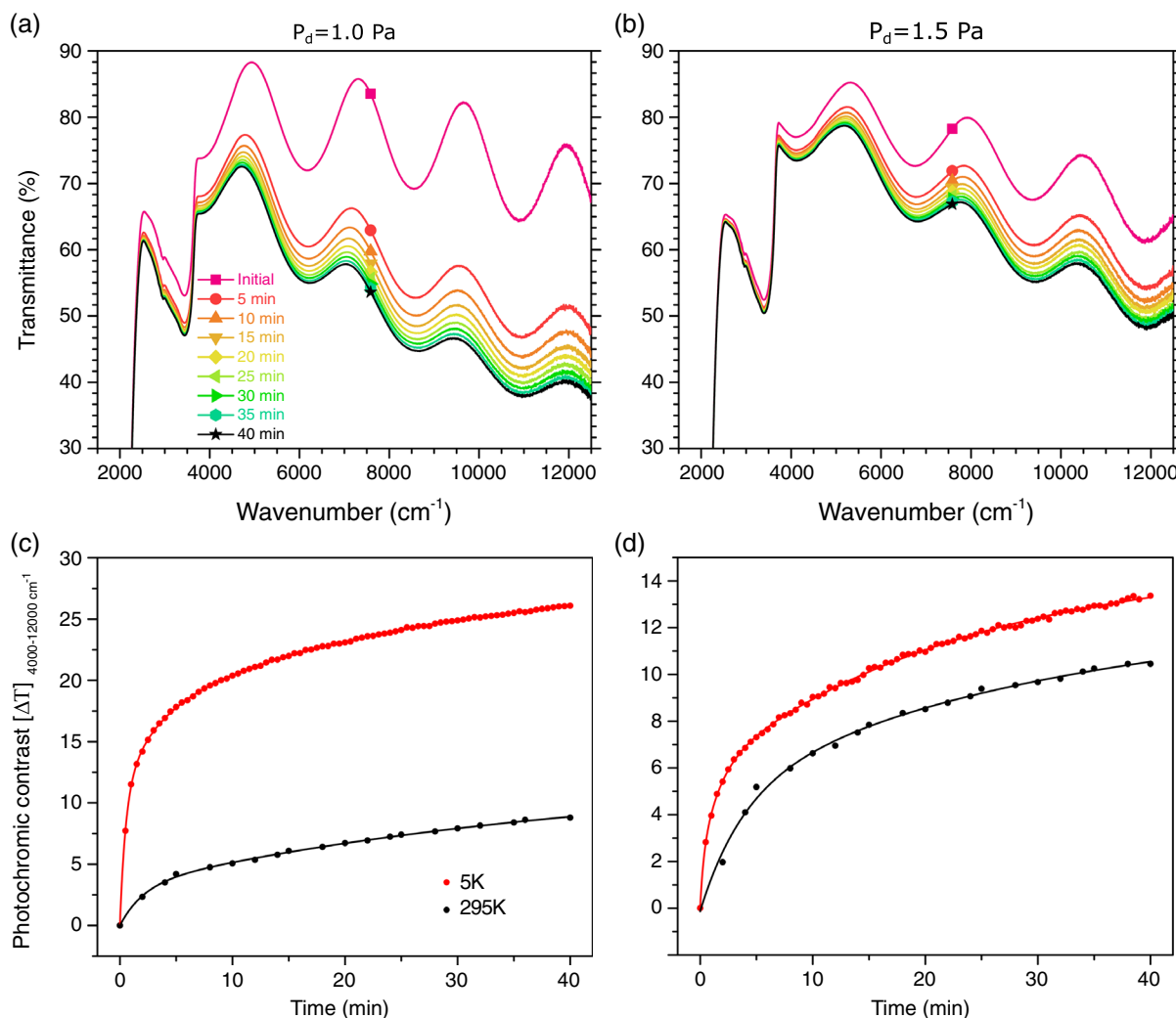


Figure 2. a,b) Infrared transmittance spectra (solid curves) of photochromic YHO thin films in their initial transparent state and after photodarkening at 5 K between 5 and 40 min for samples deposited at 1 Pa (a) and 1.5 Pa (b). c,d) The average photochromic contrast (filled circles) as a function of the UV illumination time for the films deposited at 1.0 and 1.5 Pa, respectively. Here, the solid lines serve as guides to the eye.

formation of metallic YHO domains is necessary for the photodarkening process.^[18,19] In contrast, it was proposed that photon-induced hydrogen transfer between phases^[22,23] could also explain the photochromic mechanism. In either case, the ability of the films to achieve the darkened state at 5 K suggests that anion transfer is not responsible for this process at low temperatures. Furthermore, if the photodarkening process relied solely on anion transport, then a lower illumination temperature should decrease the darkening rate, even accounting for memory effects. Instead, we observe that the darkening rate increases strongly at 5 K compared to 295 K. We propose, therefore, that the darkening process does not require in- or out-diffusion of anions from the film. Instead, we favor a model where charge transfer, by UV-illumination-induced bond breakage, is responsible for photodarkening.

Given the extraordinary ability of the YHO thin films to photodarken even at 5 K, we have also investigated its effect on the bleaching process. **Figure 3** shows the change in the average ΔT between 4000 and 12000 cm^{-1} versus the time after the UV illumination was stopped (i.e., only the probing IR beam was incident on the sample) of the YHO thin films deposited at $P_d = 1.0$ Pa (a) and 1.5 Pa (b) for temperatures ranging between 5 and 250 K. These bleaching measurements started with the samples held at 5 K for a period of about 40 min, with a new spectrum acquired every 30 s. As can be seen in Figure 3, the film remains in its darkened state at 5 K, with only a small amount of bleaching ($\Delta T \approx 1.5\text{--}2\%$) occurring even 40 min after the UV illumination was stopped. The average ΔT due to the drift of the spectrometer response over the same duration is $<0.7\%$. Furthermore, transmittance measurements (not shown) of the YHO film deposited at $P_d = 1.5$ Pa from 295 to 5 K show that the films remain transparent ($\Delta T < 0.2\%$) while illuminated with the IR beam, i.e., the probing IR beam does not photodarken the films. Therefore, the small bleaching observed at 5 K is considered a real result and not an experimental artifact. Subsequent heating of the samples between 10 K and 50 K produced no

significant change in ΔT . For temperatures between 50 and 200 K, the samples were heated in steps of 25 K, with the set temperature stabilized to within ± 0.5 K. Transmittance spectra of the films were measured until the bleaching rate slowed considerably, which was typically after 5–10 min. Above 200 K, the samples were heated in temperature steps of ≈ 50 K (with the set temperature stabilized to within ± 0.5 K) for 10–15 min until the transparent state was fully recovered. In both cases, transmittance spectra were acquired every 30 s. Bleaching of the films remained slow during heating for temperatures up to and including 100 K. Above 100 K, the bleaching process becomes stronger, with similar amounts ($\Delta T = 4\text{--}5\%$) of transparency recovered at each temperature. These results establish that the bleaching of photochromic YHO thin films is a thermally-driven process.

The ability of the YHO films to recovery transparency below 100 K is remarkable because anion diffusion is considerably slowed down in this temperature range.^[24] The prefactor and the thermal activation energy for hydride diffusion in YH_x (for x between 1.91 and 2.03) were shown to vary between $(1.0\text{--}4.8) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and 0.38–0.53 eV, respectively.^[24] Assuming that the H^- diffusion parameters in YHO are similar to the ones for H^- in YH_x , then the diffusivity of H^- at 100 K is estimated to be $\approx 10^{-30} \text{ cm}^2 \text{ s}^{-1}$. The ionic radius of O^{2-} is similar to that of H^- ,^[8,25] and, to first approximation, one could expect that the diffusion of O^{2-} will be similar or slower compared to that of H^- . Our results below 100 K indicate that anion transport should not solely be responsible for bleaching and that an additional mechanism (or mechanisms) is needed. We consider one possible mechanism that can explain the partial bleaching at low temperatures, which could potentially be the underlying mechanism for photochromism in rare-earth-metal oxyhydrides: photo-driven charge transfer. Photochromic YHO consists of semiconducting and metallic phases when exposed to UV light,^[18] and interfacial charge transfer between these inhomogeneous domains could also explain the small recovery. Such a mechanism was recently proposed to explain the photochromic effect in $\text{MoO}_3\cdot\text{TiO}_2$ crystalline-core amorphous-shell nanorods.^[26] However, further studies on multi-phase systems and charge transfer in YHO are needed to fully understand the photochromic mechanism.

In summary, we have used IR spectroscopy to show that the photochromic performance of YHO thin films is dramatically influenced by temperature, which yields new insights into the fundamental mechanisms responsible for the photodarkening and bleaching processes. Both the ability of the films to photodarken at 5 K and the small amount of bleaching ($\Delta T \approx 1.5\text{--}2\%$) that occurs between 5 and 50 K indicates that the photochromic behavior of YHO is not due solely to anion diffusion, either into or out of the film, as was previously postulated based on measurements at 295 K. The stepwise recovery of the transmittance at successively higher temperatures indicates that the mechanism(s) responsible for bleaching are complex and require further investigations to clarify their origin.

The temperature dependence of the photochromic behavior presents intriguing possibilities for YHO films that require materials and devices exhibit tunable optical properties when subjected to extreme thermal changes in space, e.g., IR stealth,^[27,28] particularly between the in-sun and in-eclipse conditions. Given their

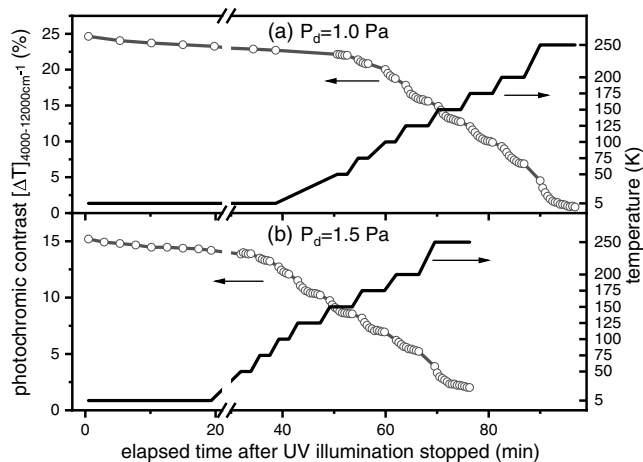


Figure 3. Change in the photochromic contrast (open circles, left axis) of the photodarkened YHO thin films versus the elapsed time after removal of the UV illumination, i.e., during the bleaching process. The temperature of the thin film during the measurement (solid curve, right axis) is indicated. (a) and (b) are for the films deposited at 1.0 and 1.5 Pa, respectively.

common photochromic behavior, the conclusions regarding the darkening and bleaching processes could extend beyond YHO and into other rare-earth-metal oxyhydride materials.

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Experimental Section

Thin films of metallic yttrium hydride (YH_{2-x}) were deposited onto glass substrates using reactive magnetron sputtering under deposition pressures (P_d) of either 1 or 1.5 Pa. Post-deposition oxidation to convert YH_{2-x} to YHO was performed by exposing the films to ambient air at room temperature in accordance with the processing conditions reported in the literature.^[5,17] The photochromic behavior of the films implies that the H:O ratio falls within the range determined from compositional analysis measurements.^[4,16] The films were subsequently stored in an inert atmosphere (N_2). The thicknesses of the synthesized YHO films, as measured using a Step-200 profilometer, were found to be 1250 ± 50 nm.

Infrared (IR) transmittance spectra were measured using a Bruker IFS 125HR Fourier transform spectrometer purged with dry N_2 gas and equipped with a quartz light source, a CaF_2 beam splitter, and a liquid-nitrogen-cooled InSb detector. All measurements utilized a spectral resolution of 4 cm^{-1} with the empty sample holder serving as the background single-channel spectrum. The samples were cooled in He exchange gas in a Janis PTSHI-950-5 low vibration pulse tube cryostat equipped with two sets of ZnSe windows. The temperatures of the samples were varied between 5 and 295 K ($\pm 1\%$) using a Lakeshore Model 335 temperature controller. The sample holder was rotated such that the unpolarized IR beam was incident at an angle of $40 \pm 3^\circ$ on the surface of the film. Photodarkening experiments were performed by illuminating the films with a collimated UV laser diode (ThorLabs CPS405, $\lambda = 405 \pm 5$ nm, 4.5 mW power) along the direction perpendicular to the IR beam path and through two sets of sapphire windows. This geometry allowed variable temperature measurements of the optical transmittance during UV illumination. The IR beam aperture was set to 0.5 mm and focused within the UV-illuminated part of the film. Bleaching experiments were performed using the same geometry as the darkening ones but with the UV laser diode blocked. The photochromic performance was evaluated using the difference in the transmittance $\Delta T(\nu, t) = T_i(\nu, 0) - T_f(\nu, t)$ between initial (i) and final (f) states. Here, T is transmittance, ν is wavenumber (cm^{-1}), and t is the time between states i and f. For our analysis, we consider the value of ΔT averaged between 4000 and $12\,000 \text{ cm}^{-1}$.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

All authors contributed equally to this work.

Keywords

mixed-anion materials, photobleaching, photochromic effect, photodarkening, yttrium oxyhydride

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