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Thermochromic effect in $YH_{3-\delta}$ and $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$

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Pure $YH_{3-\delta}$ and $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ exhibit large differences in their thermochromic properties. Whereas the transmittance of $YH_{3-\delta}$ decreases by 9% to 36%, in $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ it decreases by 64% to 83% between 30 °C and 160 °C. This thermochromic effect is caused by hydrogen desorption upon temperature increase. The main difference between the two systems is that the face-centered-cubic to hexagonal-close-packed phase transition between $YH_{2+\delta}$ and $YH_{3-\delta}$ is absent in $Mg_{0.1}Y_{0.9}H_x$, i.e., the YH_x stays cubic for all $2 \leq x \leq 3$. Because of this, there are no plateaus in the pressure–composition isotherms of $Mg_{0.1}Y_{0.9}H_x$ and the steepness of the optical transition upon hydrogen desorption increases drastically compared to pure YH_x. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1446993]

Since the discovery of switchable mirrors based on rare-earth hydride films,[1] a lot of research has been done on this type of materials. Alloying with magnesium has for example resulted in color neutral switchable mirrors.[2] The mirrors can be switched between a metallic, reflecting state and an insulating, transparent state by either gasochromic,[1] electrochromic[3,4] or chemochromic[5] means. Furthermore, they display photochromic[6] and piezochromic[7] changes in their optical properties. In this letter, we show that they can also exhibit strong thermochromic effects.

One speaks of a thermochromic effect if the optical properties of a sample change with temperature. Since it is relatively simple to tune the temperature of a material, thermochromism is of considerable technological interest. Possible applications of thermochromic materials are smart windows or temperature sensors.[8] A well known thermochromic material is, e.g., pure VO_2 (Ref. 9) or VO_2 doped with W (Ref. 10), Li (Ref. 11), or F (Ref. 12), which displays a sudden transmittance drop in the near infrared (850 to 2500 nm). This is related to a first-order structural phase transition. Continuously changing materials include alcohol/water solutions of $CoCl_2$ (Ref. 13) and an aqueous solution of 3,5-dinitro salicylic acid.[8,13] However, thermochromism appears only in a rather limited frequency and temperature range.

Here, we consider thermochromic materials which change *continuously* in optical appearance with temperature over a large frequency range. We investigated two systems in H_2 gas: YH_x and $Mg_{0.1}Y_{0.9}H_x$. As discussed by Van der Molen *et al.*,[14] the major difference between these two systems is that YH_x exhibits a face-centered-cubic (fcc) to hexagonal-close-packed (hcp) transition when $YH_{2+\delta}$ transforms to $YH_{3-\delta}$, whereas the segregated YH_x in $Mg_{0.1}Y_{0.9}H_x$ stays fcc for all $x > 2$. A Mg content of 10 at. % is chosen, because this is the lowest concentration that stabilizes fcc $YH_{3-\delta}$.

Polycrystalline Y and $Mg_{0.1}Y_{0.9}$ films of typically 260 and 280 nm thickness are coevaporated under ultrahigh vacuum conditions (10^{-9} mbar) on Al_2O_3 substrates. Y is evaporated with an electron gun and Mg with a Knudsen cell. To protect the films against oxidation and to promote hydrogen dissociation a 9 nm thin Pd layer is deposited on top of the films. The film composition is checked with Rutherford backscattering spectrometry. Optical transmittance spectra are recorded in a Bruker IFS 66/S spectrometer. The films are hydrogenated in 1 bar of H_2 at temperatures between 30 °C and 160 °C.

To investigate thermochromism, a sample is loaded a few times to the transparent state in 1 bar H_2 in a closed gas cell at room temperature. Subsequently, the temperature of the sample is increased stepwise, while transmittance spectra are recorded. A large difference is observed between both samples (see Fig. 1).[15] Whereas the transmittance of $YH_{3-\delta}$ is only slightly temperature dependent, the transmittance of the film containing Mg decreases rapidly. Oxidation effects can be neglected as the process is reversible.

To compare the performance of the two systems quantitatively, the transmittance is normalized to 1 at 30 °C (see Fig. 2). Whereas the transmittance of $YH_{3-\delta}$ decreases only by 9% to 36%, in $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ it decreases by 64% to 83% between 30 °C and 160 °C. Both materials show a *continuous* decrease in transmittance with temperature. However, the wavelength dependence is rather different. $YH_{3-\delta}$ displays a *minimal* change of the transmittance with temperature at ≈ 800 nm. On the other hand, $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ exhibits a *maximal* change with temperature at ≈ 550 nm (see also Fig. 1). The large and almost linear variation of the transmittance of $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ makes it attractive for temperature sensors.[8]

To identify the cause of the thermochromic effect, we discuss the quantities determining the optical transmittance, T_{opt}, in more detail. Generally, T_{opt} is a function of both the temperature, T, and the equilibrium hydrogen concentration,
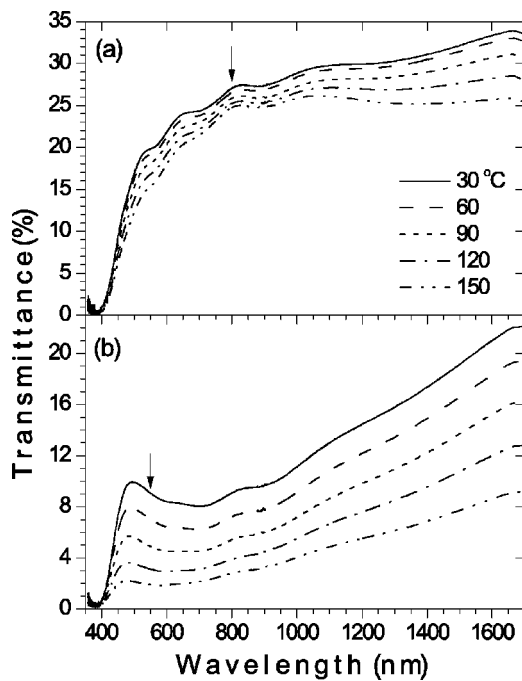
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FIG. 1. Transmittance spectra of (a) 260 nm $YH_{3-\delta}$ and (b) 280 nm $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ (on sapphire and covered with ≈ 9 nm of Pd) in 1 bar of H_2 at temperatures between 30 °C and 150 °C. Spectra in (a) are recorded in the fourth-loading cycle, those in (b) in the third-loading cycle. Arrows indicate the wavelengths at which there is a minimal respectively maximal change of the transmittance with temperature (see Fig. 2).

FIG. 3. Pressure–composition isotherm (squares) at 30 °C of (a) $YH_{3-\delta+\Delta x}$ and (b) $Mg_{0.1}Y_{0.9}H_{2.9-\delta+\Delta x}$ as a function of Δx, the amount of hydrogen per metal atom that is desorbed. The measurements are performed in the third desorption cycle using GITT. Also shown is the normalized transmittance at 670 nm (circles). At $\Delta x = 0.0$ the sample is fully loaded with hydrogen, around $\Delta x = -0.8$ the sample is unloaded.

x, in the sample which is itself a function of temperature and H_2 pressure. At constant pressure, we have $T_{opt}[T, x(T)]$. However, the explicit temperature dependence is negligible. This is demonstrated using lateral diffusion samples[14,16] with only a small Pd strip covering part of the surface. The un-
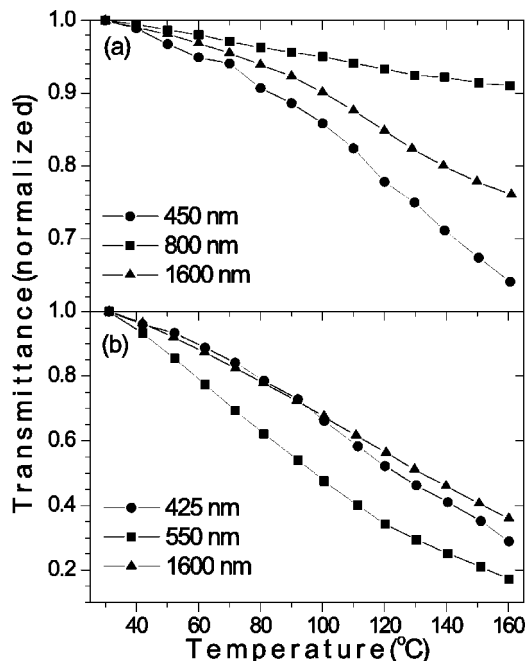

FIG. 2. Dependence of the normalized transmittance of (a) $YH_{3-\delta}$ at 450 (circles), 800 (squares), and 1600 nm (triangles) and (b) $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ at 425 (circles), 550 (squares), and 1600 nm (triangles) on temperature. $YH_{3-\delta}$ shows a minimal change of the transmittance with temperature at about 800 nm, whereas $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ shows a maximal change with temperature at about 550 nm (see arrows in Fig. 1).

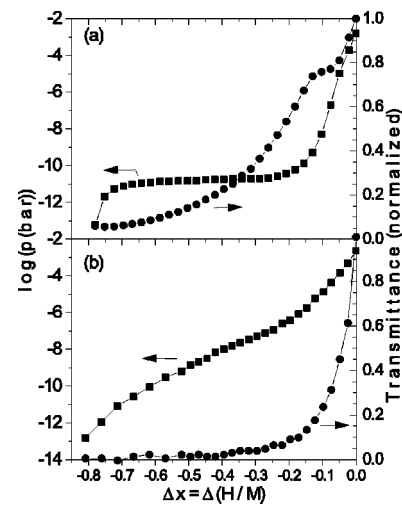covered part is capped by a thin Y_2O_3 oxide layer which is impermeable for hydrogen. Having prepared an area of insulating, transparent material of $YH_{3-\delta}$ or $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ beneath the oxide via lateral diffusion of hydrogen from the Pd strip, we monitor the transmittance as a function of temperature. In this case, hydrogen can only leak out of the oxide covered area if the time scale of lateral diffusion $\tau_{diff} = l^2/D$ (l distance to Pd strip and D the diffusion constant) is smaller than the time scale of the experiment (≈ 1 h). For most of the transparent area, this is not at all the case, and, consequently, we measure $T_{opt}(T)$ at constant H concentration. Interestingly, we find a negligible change in the transmittance of the diffusion region below the oxide with increasing temperature for both systems. Thus, T_{opt} depends only implicitly on temperature via the equilibrium hydrogen concentration x: $T_{opt}[x(T)]$. This conclusion is confirmed by Leeuwerink[17] who investigated the transmittance of $YH_{3-\delta}$ at temperatures between 20 and 350 K. During cooling down from 350 K the transmittance first increases until a temperature of 250 K is reached. For lower temperatures, the transmittance stays constant since hydrogen is trapped in the sample. At this temperature the hysteresis in resistivity-versus-temperature loops also closes.[18] Therefore, the thermochromic effect results from changes in the equilibrium hydrogen concentration.

The large difference in magnitude of the thermochromic effect between the two systems is due to differences in thermodynamical and optical behavior. To investigate this, pressure–composition isotherms are measured during hydrogen desorption together with the transmittance using a laser-diode with $\lambda = 670$ nm as a function of Δx, the amount of hydrogen per metal atom that is desorbed (see Fig. 3). This is done electrochemically with an EG&G Princeton Applied Research 273A potentiostat/galvanostat to be able to determine the hydrogen concentration. To avoid effects related to the kinetics of hydrogenation, we employ the galvanostatic intermittent titration technique (GITT).[19] The isotherms of the two systems are markedly different. The plateau in Fig.

3(a) is due to the coexistence of hcp $YH_{3-\delta}$ and fcc $YH_{2+\delta}$. On the other hand, there is no plateau in Fig. 3(b) since YH_x remains cubic there.[14] The amount of hydrogen desorbed from $YH_{3-\delta}$ and $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ upon temperature increase can be estimated from the isotherms at $30\,°C$ in the single phase region where $-0.15 < \Delta x < 0.0$ using:[20]

$$\frac{d \ln p}{d(1/T)} = \frac{2\Delta\bar{H}}{R}, \tag{1}$$

where p is the hydrogen gas pressure, $\Delta\bar{H}$ the partial molar heat of solution of H in a metal, and R the gas constant. Then,

$$\left.\frac{dx}{dT}\right|_p = \frac{dx}{d \ln p} \cdot \frac{d \ln p}{dT}, \tag{2}$$

$$\Delta x = \Delta T \cdot \left(-\frac{2\Delta\bar{H}}{RT^2} \right) \cdot \frac{1}{\dfrac{d \ln p}{dx}}. \tag{3}$$

If it is assumed that both systems have the same heat of solution for hydrogen, the change in x with temperature is inversely proportional to $d \ln p/dx$. The presence of a plateau induces a larger slope between $-0.15 < \Delta x < 0.0$ (see Fig. 3). Thus, more hydrogen is desorbed from $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ than from $YH_{3-\delta}$. From Fig. 3, we find $\Delta x_{YH_{3-\delta}}/\Delta x_{Mg_{0.1}Y_{0.9}H_{2.9-\delta}} = 0.38 \pm 0.09$.

Figure 3(b) also shows the other consequence of the absence of the fcc–hcp phase transition. Namely, a steepening of the optical transition upon hydrogen desorption compared to pure YH_x. This is in agreement with observations by Van Gogh *et al.*[21] in fcc $La_{1-z}Y_zH_x$ alloys. Thus, for a given change in hydrogen concentration the decrease in transmittance is larger in $Mg_{0.1}Y_{0.9}H_x$ than in YH_x. Since the difference in the isotherms even leads to a *larger* hydrogen desorption for $Mg_{0.1}Y_{0.9}H_x$ with temperature, both effects enhance the difference in optical appearance. Combining the change in transmittance with hydrogen desorption of Fig. 3 with the measurements in Fig. 1 one can determine the amount of hydrogen desorbed in both systems between $30\,°C$ and $160\,°C$ using the change in transmittance at 670 nm. In $YH_{3-\delta}$ and $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ an amount of 0.035 ± 0.002 H/M, respectively, 0.10 ± 0.02 H/M is desorbed. Thus, $\Delta x_{YH_{3-\delta}}/\Delta x_{Mg_{0.1}Y_{0.9}H_{2.9-\delta}} = 0.35 \pm 0.02$ in strikingly good agreement with the estimate from the isotherms.

In conclusion, the thermochromic effect is caused by hydrogen desorption upon heating. The large difference in magnitude of the thermochromic effect between YH_x and $Mg_{0.1}Y_{0.9}H_x$ can be fully accounted for by the suppression of hcp $YH_{3-\delta}$ in $Mg_{0.1}Y_{0.9}H_x$. Therefore, there is no phase coexistence of fcc and hcp $YH_{3-\delta}$ in $Mg_{0.1}Y_{0.9}H_x$ and the shape of the isotherms and the optical transitions are differ-

ent in both materials. The combination of both phenomena is responsible for a much larger thermochromic effect in $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$ than in $YH_{3-\delta}$.

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