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ADVANCED PHYSICS - PROJECT COURSE 5.0 c

PROJECT REPORT

Photoconductivity in rare earth metal-oxy-hydrides

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Abstract

In this project the evolution of resistivity under light exposition in materials like rare earth metal-oxy-hydrides is studied. These materials observe a decrease of the resistance when exposed under the light of a 19,5 W power lamp, and slowly tend to return to their initial resistance. After having developed a resistance measurement setup, the photoconductivity of different samples (Gd, YHO) was measured in function of the oxygen concentration and in different conditions such as the face of illumination.

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0.1 Introduction

In the past few years technologies using photochromic properties have developed in various fields. Hydrogen sensors, displays and smart windows are among one of the most promising industrial applications, especially because they enable the development of completely independent passive devices [1]. Indeed, photochromism allows a self reversible transformation of optical properties in some materials when they absorb an electromagnetic radiation. But they appear to be also interesting in a field that is only growing due to the ecological context of our planet: renewable energies. Photochromic materials, by a reversibly changing colour under illumination, are relevant in solar energy with principally high-density optical memories [2]. This reversible change is accompanied by a decrease of resistivity, founding applications in hydrogen-storage devices [3].

Materials like rare earth metal-oxy-hydrides (REMOH) allow photoinduced switching of optical properties, such as the optical transmission accompanied by the change in resistance. As a result, the transparency of a thin film upon illumination can be reduced from approximately 90% to 40% in the visible region. The darkening of the sample can be clearly observed after few minutes of illumination, and returns to its initial yellow clear state after several hours. Nonetheless, the mechanisms behind these reversible changes are still poorly understood: since 2011, Yttrium composition have been investigated in order to understand better the origin of this effect. [4]

The nature of conductivity is coming from the band theory. Materials possessing conductive behaviors have the Fermi level inside of at least one band, valence or conduction. This allow their electrons from the valence band to pass through the gap and reach the conduction band. Illuminating a photochromic material will lead to an increase of the conductivity: this is therefore the result we are expecting to obtain as already measured in 2011 by T. Mongstad [2].

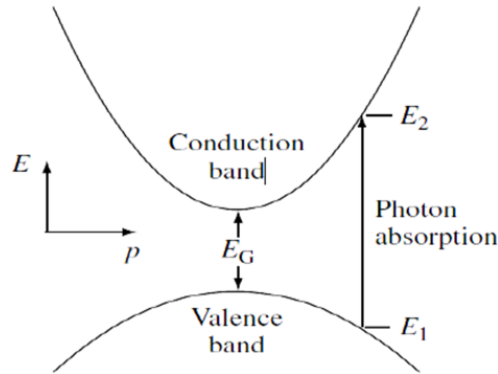


Figure 1: Illustration of the band theory.

Raising oxygen concentration in photochromic materials has also an impact on resistivity, as it induces the creation of a band gap. Above the threshold $\delta = \frac{[O]}{[Y]} = 0.5$, we can observe a metallic-to-insulator transition [1].

In this project, resistivity changes under illumination for REMOH will be studied for different oxygen concentration and different conditions: through direct illumination and with an illumination through the substrate. The samples used are Yttrium materials (Sets of YHO with different oxygen compositions), and Gadolinium (GdHO), a material appearing to have resistance reversible effects that can be measured.

0.2 Experimental setup

These samples are composed of a transparent glass substrate with a thin film material deposited on it by reactive magnetron sputtering. The thickness of the film is in order of few hundreds of nanometers (typically 800 nm for YHO), while the substrate is 1 mm. [1]

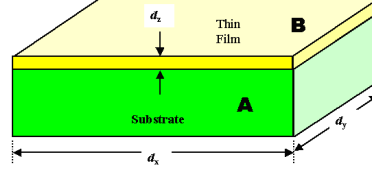


Figure 2: Schematic illustration of a sample used in experiments

To measure the resistance, the two-point measurement was used: 2 probes connected directly to the sample, fixed on a plastic support. This method is equivalent of measuring the resistance with a multimeter by connecting the 2 leads to a resistor. The current is measured with a fixed voltage and the resistance can be calculated with the Ohm's law:

$$R = \frac{U}{I} \quad (1)$$

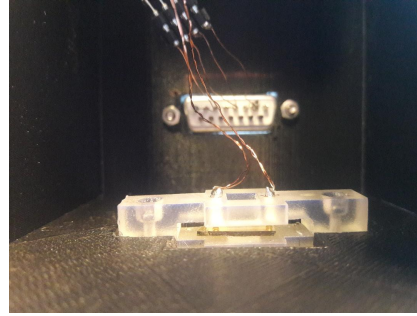
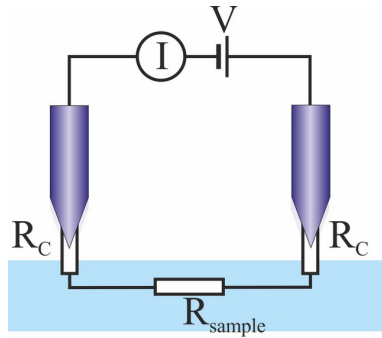


Figure 3: (a) Schematic illustration of the 2 points measurement (b) device used for the experiment: the 2 probes are in contact with the sample, and the plastic support is made to let the sample in direct contact with illumination.

The sample is then put in a black box printed in 3D that can be closed to avoid any illumination. Once closed, only a circular hole remain on the top to install a lamp. The probes were welded to wires connected to a fixed output on the side of the box. Connectors are part of the device, allowing to change the plastic support in the case samples of different sizes would be used. All the wires were first stripped and welded in the right place to allow the operation of the current measurement.

During the experiments, the illumination source is a lamp which can be switched on and off, having a power of 19,5 W and a wavelength of 455 nm. The intensity is therefore largely enough to allow resistance changes in the sample, as well as the darkening after some minutes. Due to heating power, a cooler is install on the lamp in form of a small fan which can be switched on/off at any moment.

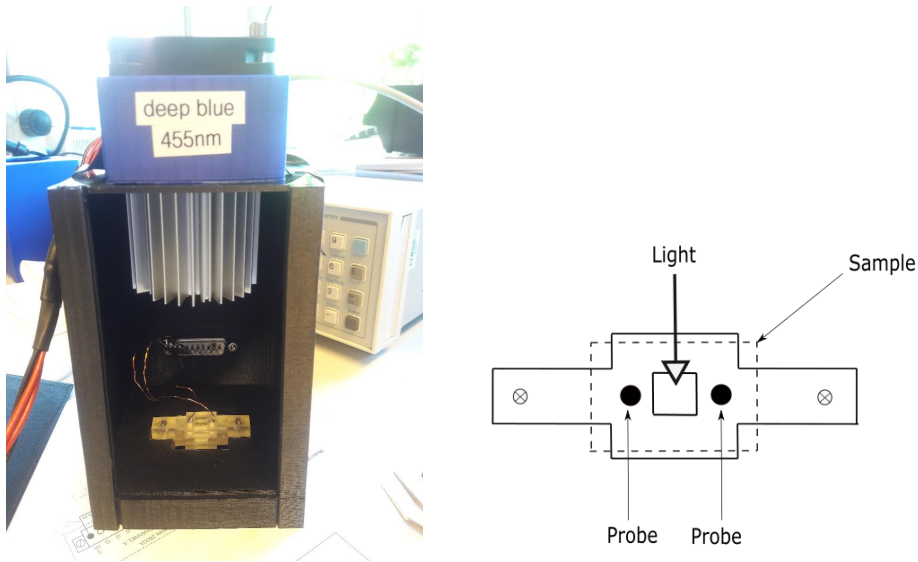


Figure 4: (a) View of the interior of the device composed by the box with the lamp on it. (b) Schematic illustration of the plastic support containing the sample.

The exterior of the box can be connected to an instrument. The one used in the experiments is a Keithley 2602A, which acquires the current measured by the device. This instrument is driven on the computer through a LabView Virtual Instrument which automates the measurements. Each current measurement is made every 10 ms, the resistance is calculated with the Ohm's law and the data is saved in a file on the computer. For all the samples measured, the voltage was fixed at 5 V, but it is possible to change this value directly in the VI.

High resistance samples (typically YHO films with a high Oxygen concentration) can reach without illumination $R \approx 10 \text{ G}\Omega$, which is close to the corresponding current limit the Keithley can measure. For that reason, some samples couldn't be measured (for example transparent samples with a high Oxygen concentration).

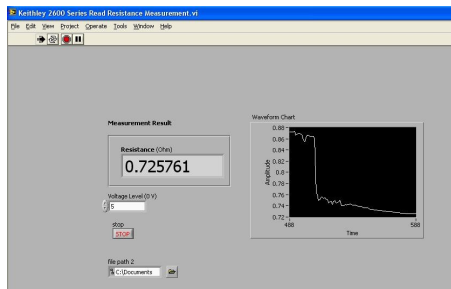


Figure 5: Front panel of the Virtual instrument used.

Before any measurement, tests were done with Aluminium foil and a $1 \text{ k}\Omega$ resistor. For this resistor, the value obtained was 1012Ω , therefore the difference can be neglected for REMOH materials having a resistance in the order of several $\text{G}\Omega$.

Finally, it can be precised that this setup is easily adaptable. We can reverse the plastic support in order to illuminate from the substrate side, it is compatible with different lamps and instruments and we can measure different samples of different sizes. All the setup was made from scratch in this project.

0.3 Results and discussion

During the measurements, the lamp is switched on at $t = 0$ s and then switched off and on every 5 min.

Y262 has a thickness of 800 nm. The oxygen concentration for each sample is presented in the following tab:

	δ	Transaprency
Y262 - 1	0.953	transparent
Y262 - 2	0.889	transparent
Y262 - 3	0.685	transparent
Y262 - 4	0.459	opaque
Y262 - 5	0.415	opaque

The resistivity under illumination is then showed for each of these samples:

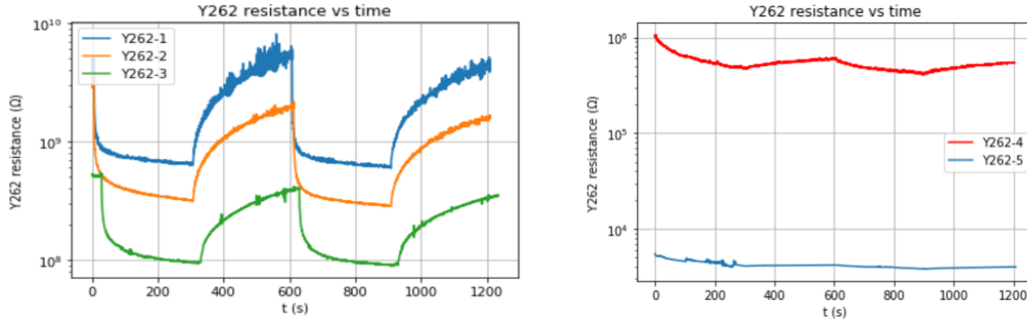


Figure 6: resistance of Y262 samples under illumination during 30 min.

A logarithmic scale is used. As expected, the resistance decreases under illumination and tend to return slowly to its initial resistance. Samples 4 and 5 were plotted in different graph due to their very low resistance. If we can still observe in sample 4 a change in resistivity, the sample 5 remains approximately constant. It is indeed opaque and should not be photochromic. To characterize the evolution of resistivity depending on the oxygen concentration, the initial value R_0 in function of δ was plotted:

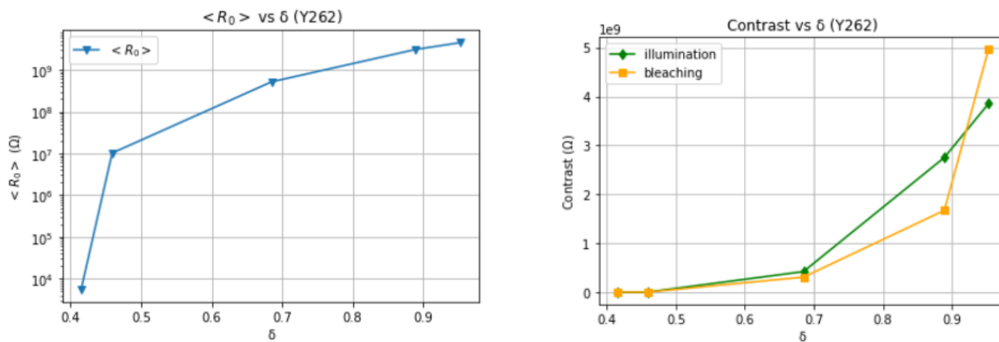


Figure 7: Evolution of R_0 and contrast in function of δ .

The second graph represents the evolution of the contrast with δ . the illumination curve is the difference in resistivity between R_0 and R_{5min} , and the bleaching the difference between R_{10min} and

R_{5min} . The more a sample has a high oxygen concentration, the more it has a high initial resistance and a bigger contrast.

The same experiments were reproduced for other Yttrium samples: Y263-1 and Y263-2.

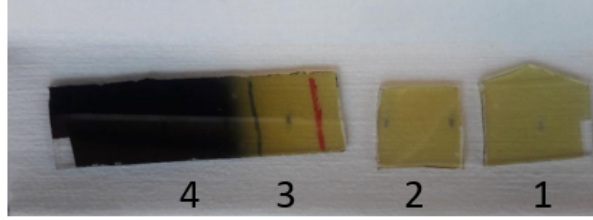


Figure 8: picture of samples Y263-1. Each number correspond to the sample measured with a different oxygen concentration, from 1 (higher δ) to 4 (lower δ).

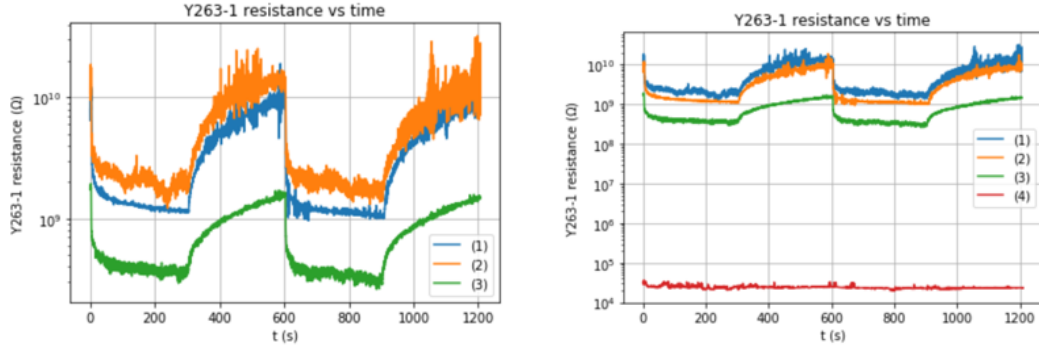


Figure 9: resistance of Y263-1 samples under illumination during 30 min.

We can graphically assume the same results seen for Y262. The second graph of Y263-1 shows that once again, when the oxygen concentration is high, the resistance can be approximately constant.

Because the exact composition of these samples is unknown, the evolution of R_0 and δ is plotted in function of the increasing oxygen composition, and each sample corresponds to the points 1, 2 and 3.

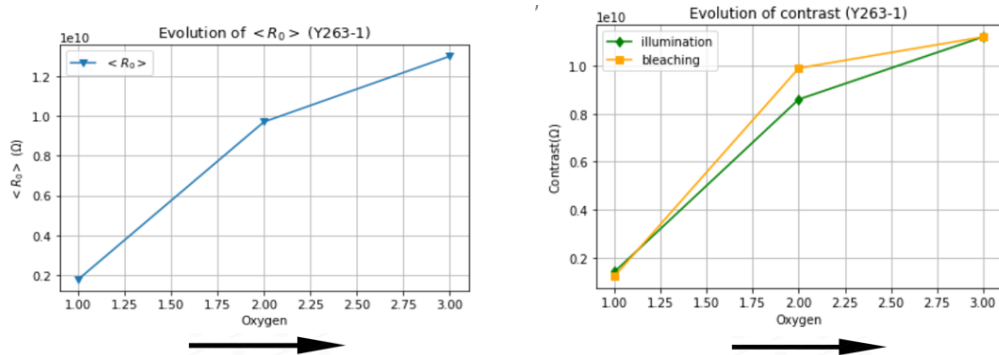


Figure 10: Evolution of R_0 and contrast in function of δ for Y263-1 samples.

And for Y263-2:

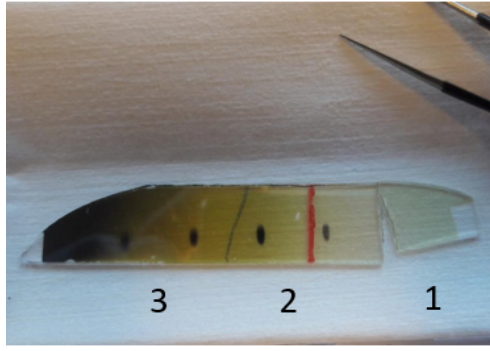


Figure 11: picture of samples Y263-2. Each number correspond to the sample measured with a different oxygen concentration, from 1 (higher δ) to 3 (lower δ).

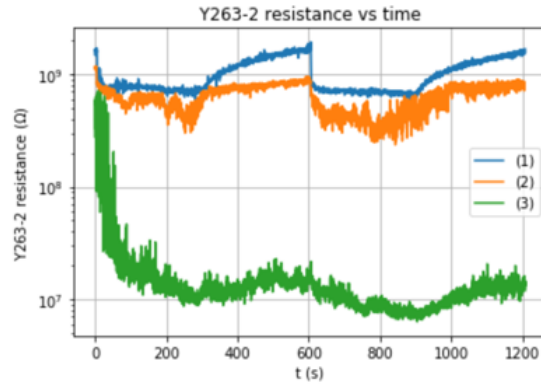


Figure 12: resistance of Y263-2 samples under illumination during 30 min.

Unfortunately, there is a lot of noise in this result. This might come from the fact that these samples are a bit older and were more exposed to air. Like Y263-1, the exact composition of Y263-2 is unknown.

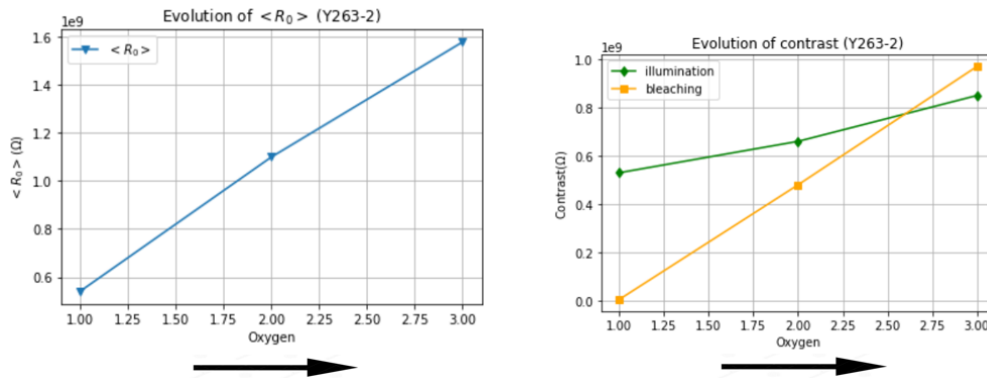


Figure 13: Evolution of R_0 and contrast in function of δ for Y263-2 samples.

To characterize the photoconductivity with different conditions, measurements with illumination through the substrate side were made. The substrate is transparent glass. the sample Yttrium TS6 has a thickness of 230 nm and has the following composition:

	Composition
Yttrium	33.8 %
Oxygen	29.8 %
Hydrogen	36.4 %

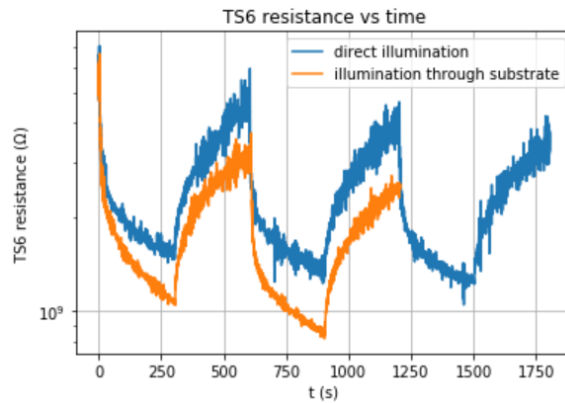
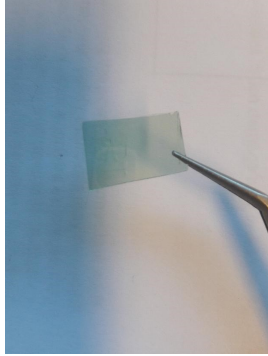


Figure 14: (a) picture of the sample TS6. (b) Evolution of the resistivity of TS6 with direct illumination and illumination through the substrate side 1 day after.

The graph seems to indicate that an illumination through the substrate allows a bigger decrease in the resistance. However, this result might be affected by external factors, for instance the fact that the sample had still the effect of the previous illumination. It was measured approximately 1 day after the first measurement on the other face (the material face).

Gadolinium Oxyhydrides is an other REMOH having photochromic properties. The same experiment was done for the sample GdHo1:

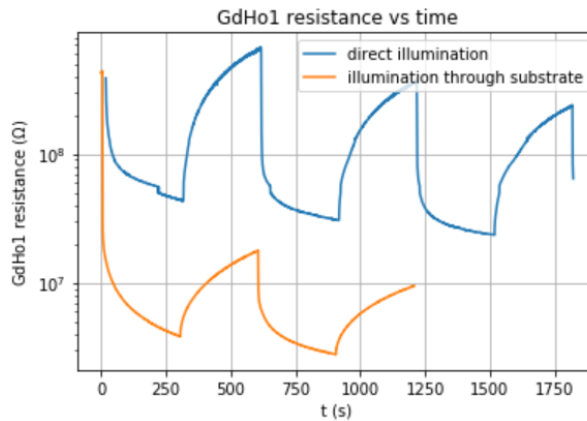


Figure 15: Evolution of the resistivity of GdHo1 with direct illumination and illumination through the substrate side 1 day after.

Here the noise is almost inexistent, mainly because the sample was not exposed to air before. The graph gives us the same result as Yttrium TS6, but with the same doubts.

The darkening of the sample was also observed, after 30 min. of illumination. We can observe the darkening of the sample especially in the center but also homogeneously in all the area.

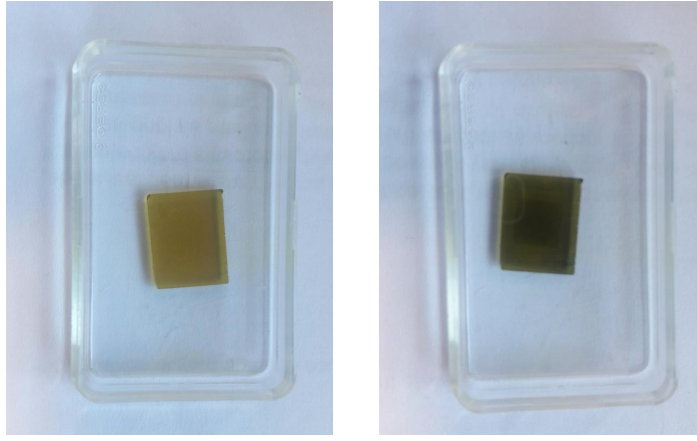


Figure 16: Darkening of the sample after the experiment: the darkest part is in the center where the sample was directly in contact with light, while the rest of the area was protected by the plastic support.

This shows that the middle of the sample receives the highest intensity. Because our probes are a little bit out of this area, we might have not measured the strongest effect in the experiments. However, we measured all the samples with exactly the same method, therefore the comparison between different oxygen concentration or the face orientation is still legit.

0.4 Conclusion

In this project, the photoconductivity of REMOH materials (YHO, GdHo) were studied after having built an experimental setup to measure the resistance.

First, how the oxygen concentration affects the resistivity: a higher oxygen concentration leads higher resistivity and a higher contrast between the phase of illumination. Secondly, how an illumination through the substrate face allows a decrease in resistivity. Photodarkening of samples were also observed.

Even if the results obtained seem consistent, they had sometimes a lot of noise and some doubts persist for Yttrium TS6 and GdHo1. Otherwise, with the use of the Keithley 2602A, we were unable to measure samples with too high (over $10\text{ G}\Omega$).

0.5 Acknowledgments

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Bibliography

- [1] Dmitrii Moldarev, Marcos V. Moro, Chang C. You, Elbruz M. Baba, Smagul Zh. Karazhanov, Max Wolff, and Daniel Primetzhofer, *Yttrium oxyhydrides for photochromic applications: Correlating composition and optical response*, Phys. Rev. Mater., 2, no. 11, 115203, Nov. 2018.
- [2] Trygve Mongstad, Charlotte Platzer-Bjorkman, Jan Petter Maehlen, Lennard P.A. Mooij, Bernard Dam, Erik S. Marstein, Smagul Zh. Karazhanov, *A new thin film photochromic material: Oxygen-containing Yttrium hydrides*, Solar Energy Materials & Solar cells, 95, 3596-3599, 2011.
- [3] Sigurbjörn Már Aðalsteinsson, BSc; Marcos V Moro, PhD; Dmitry Moldarev, MSc; Sotirios Droulias, PhD; Max Wolff, PhD; Daniel Primetzhofer, *Characterization of photochromic rare-earth oxyhydride thin films using a multi-method ion beam analysis approach*, NIMB Proceeding, D, 19, 00291, 2019
- [4] Chang Chuan You, Trygve Mongstad, Erik Stensrud Marstein, Smagul Zh. Karazhanov, *The dependence of structural, electrical and optical properties on the composition of photochromic yttrium oxyhydride thin films*, Materials, 000, 100307, 2019