

SINGLE CRYSTAL DEGRADATION OF LEAD-FREE PEROVSKITES FOR TANDEM SOLAR CELLS

Dennis M. Jöckel¹, Songhak Yoon^{*1}, Alexander Frebel¹, Samuel Meles Neguse¹, Marc Widenmeyer², Benjamin Balke¹ and Anke Weidenkaff^{1,2}

¹Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS, Aschaffenerstrasse 121, 63457 Hanau, Germany. Tel: +49 6023 32039-892

²Department of Materials and Earth Science, Materials and Resources, Technische Universität Darmstadt, Alarich-Weiss-Strasse 2, 64287 Darmstadt, Germany

*Corresponding author. e-mail: song.hak.yoon@iwks.fraunhofer.de

Emerging Photovoltaics:

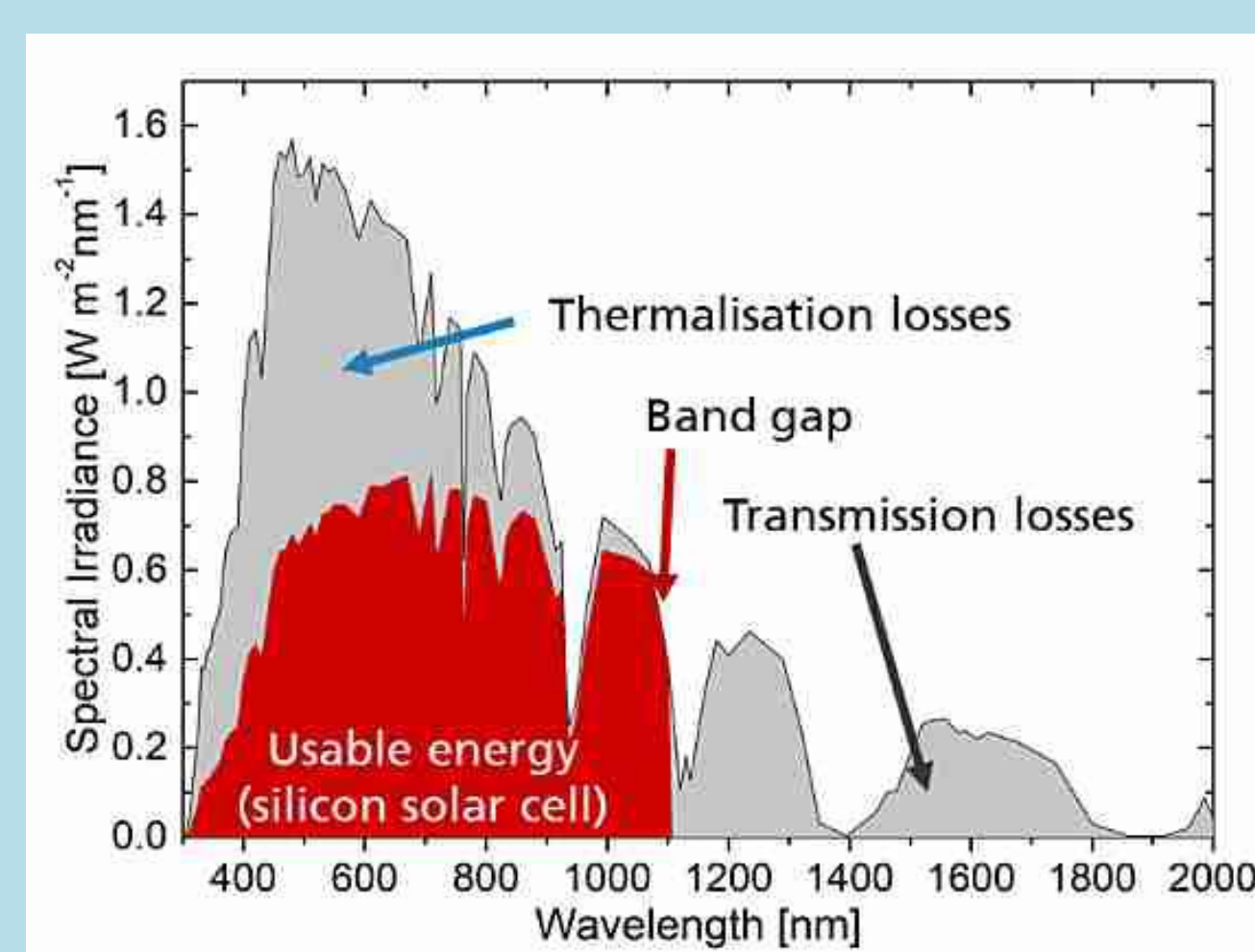


Figure 1: Absorption spectrum of a silicon solar cell [2]

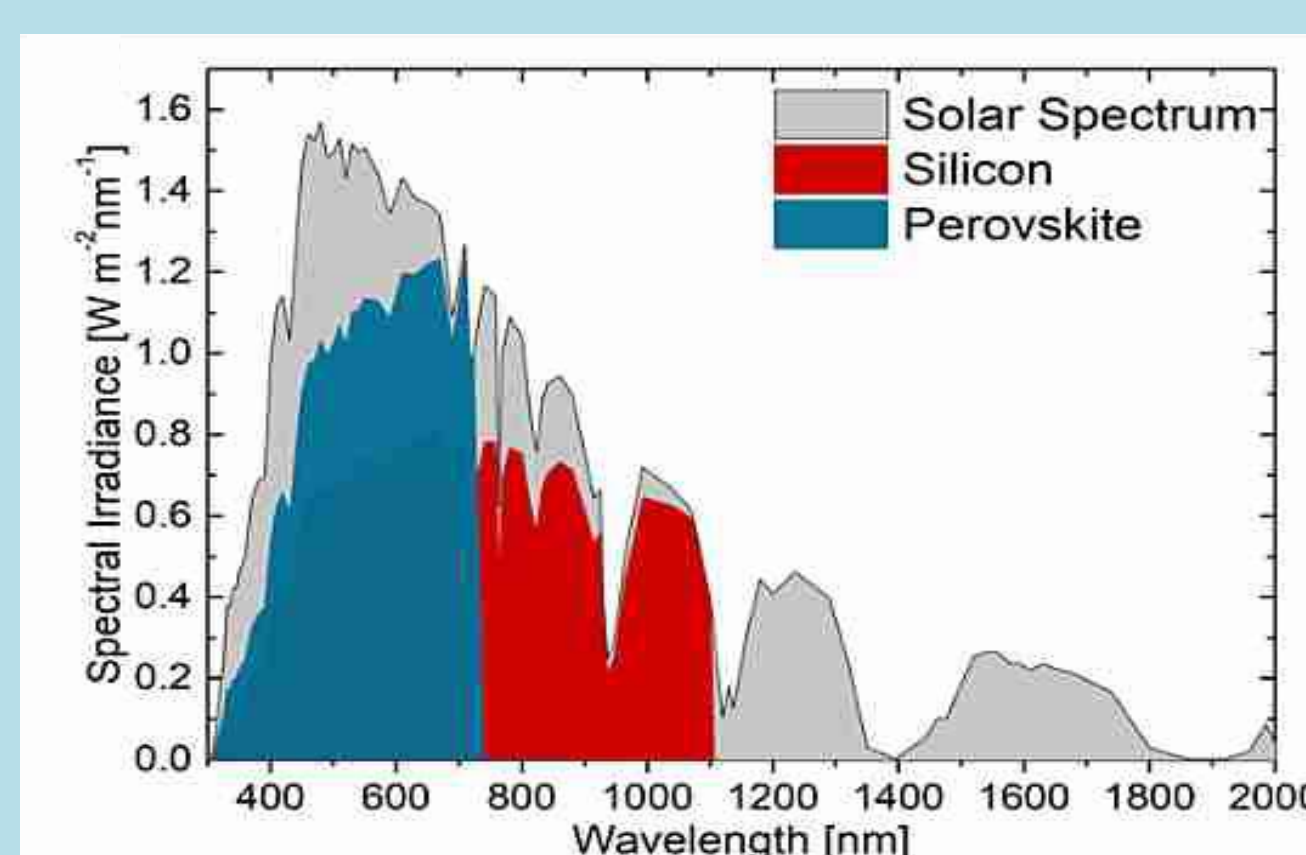


Figure 2: Absorption spectrum of a perovskite solar cell [2]

Pb-based hybrid perovskite PV materials are well recognized to be one of the most promising candidates to be used in combination with silicon, because of their superior absorption of high-energetic photons (shown in Figure 2). However, because of toxicity and stability issues, lately lead-free double perovskites like $\text{Cs}_2\text{AgBiBr}_6$ gained more interest. By using simulated solar irradiation in combination with variously controlled humidity, in this study crystal structure, surface irregularities, and optical bandgap changes of $\text{Cs}_2\text{AgBiBr}_6$ were studied.

Although $\text{Cs}_2\text{AgBiBr}_6$ is considered to be relatively stable under ambient conditions[3], we were able to strongly alter the crystals surface, while the bandgap narrowed, and the Raman peaks broadened. Here we showed that irregularities as well as minor secondary phases like $\text{Cs}_3\text{Bi}_2\text{Br}_9$ can be formed on the surface of $\text{Cs}_2\text{AgBiBr}_6$ upon light exposure with controlled humidity. Our research includes peak broadening analysis from Raman spectra and bandgap value estimation by Tauc plots from UV-Vis spectra.

Solar simulation and degradation:

The focus of our study is to investigate the change of optical properties of $\text{Cs}_2\text{AgBiBr}_6$. For that we performed different solar exposure experiments with the VeraSol LED Simulator from Oriel Instruments. The spectrum of the solar simulator in comparison to the AM1.5 Global spectrum is illustrated in Figure 3. All solar simulations were carried out under standard AM1.5G conditions while varying the humidity of the samples.

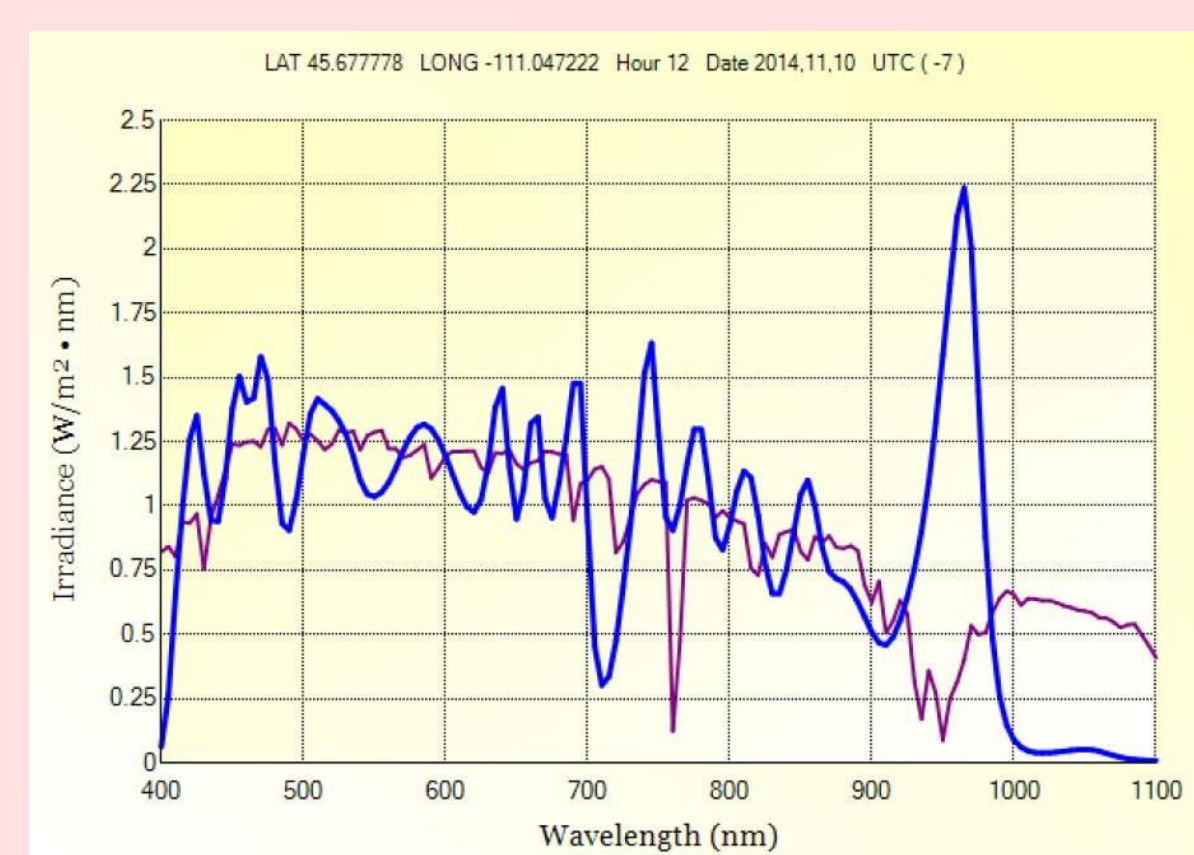


Figure 3: Solar Spectra of VeraSol Simulator in blue and AM1.5G in purple (ORIEL Instruments)

- **Humidity:** While performing the simulations we used different approaches on sealing the samples, as well as open, dry, and wet samples.



Figure 4: Visible sample change due to moisture

- **Solar simulation:** For the simulated sun exposure, the crystals were put under the simulator for varying time spans (50 h – 160 h) and later measured and compared to dark references that experienced the same atmospheric conditions except for solar radiation.



Figure 5: Dry (left) and wet (right) samples under solar radiation

- **Humidity and solar simulation:** In order to simulate the most challenging environments that the absorber material could be exposed to in future solar cell applications, we exposed wet samples to simulated sun light for up to one week.

Results:

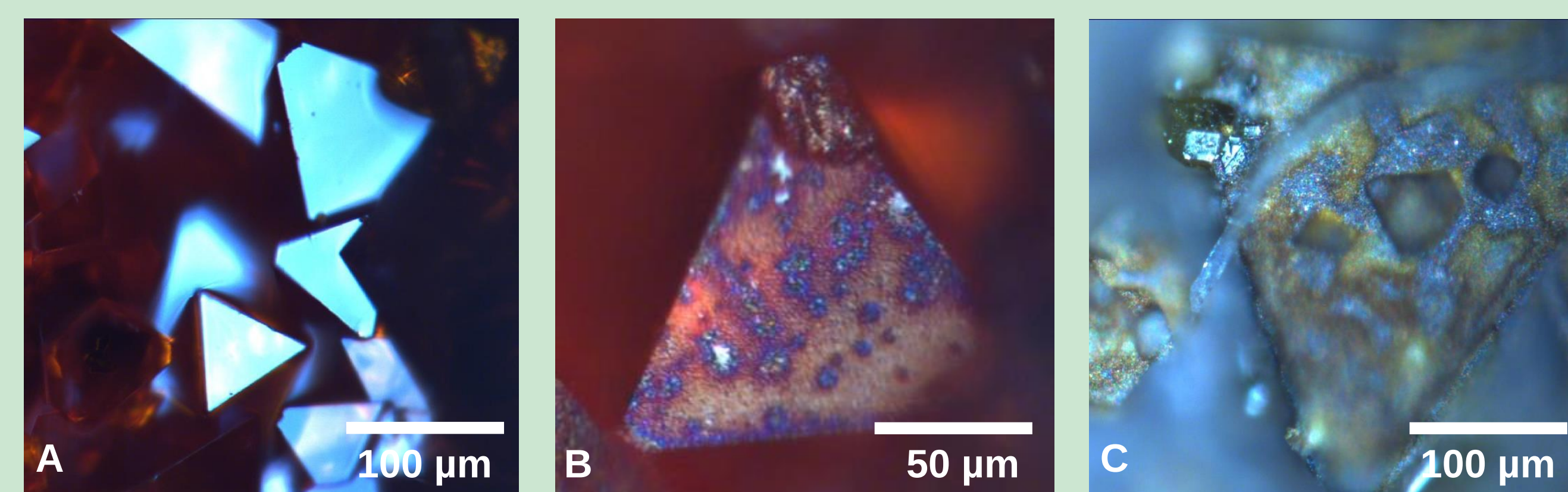


Figure 7: Sample change observed under optical microscope; A: Dark Reference; B: Sample under atmospheric conditions and solar light; C: Sample under wet conditions and solar light

Both with the naked eye and under an optical microscope, the change on the surface of various samples due to atmospheric and wet environments and simulated solar exposure was clearly observable. Figure 7 shows the dark reference (A), a crystal with a slightly degraded surface (B) and a sample whose colour and surface were completely altered (C). The same results were found in different simulation runs. The most significant changes were in samples that had been exposed to both wet environments and radiation, while samples that had been exposed only to radiation or only to wetness underwent lighter but very different changes. Dark references and sealed samples mostly did not show any visual sign of degradation.

Analysis:

Raman spectroscopy was used to determine structural changes in the crystal lattice of $\text{Cs}_2\text{AgBiBr}_6$ single crystals. While some peaks are on the same positions, shoulders and new peaks are formed in the heavily altered samples which supports the finding of secondary phases under the microscope.

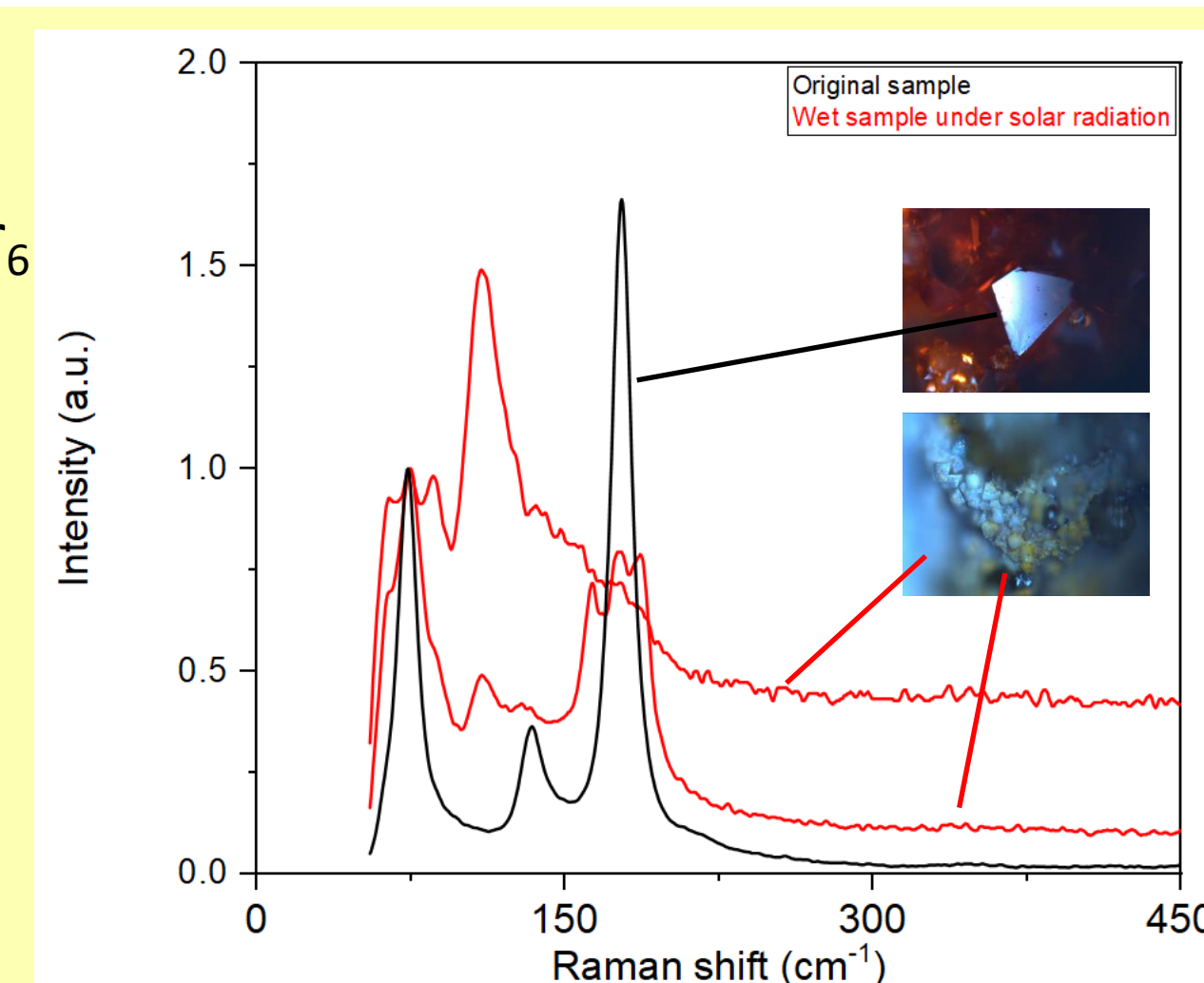


Figure 8: Raman spectroscopy (original and altered sample)

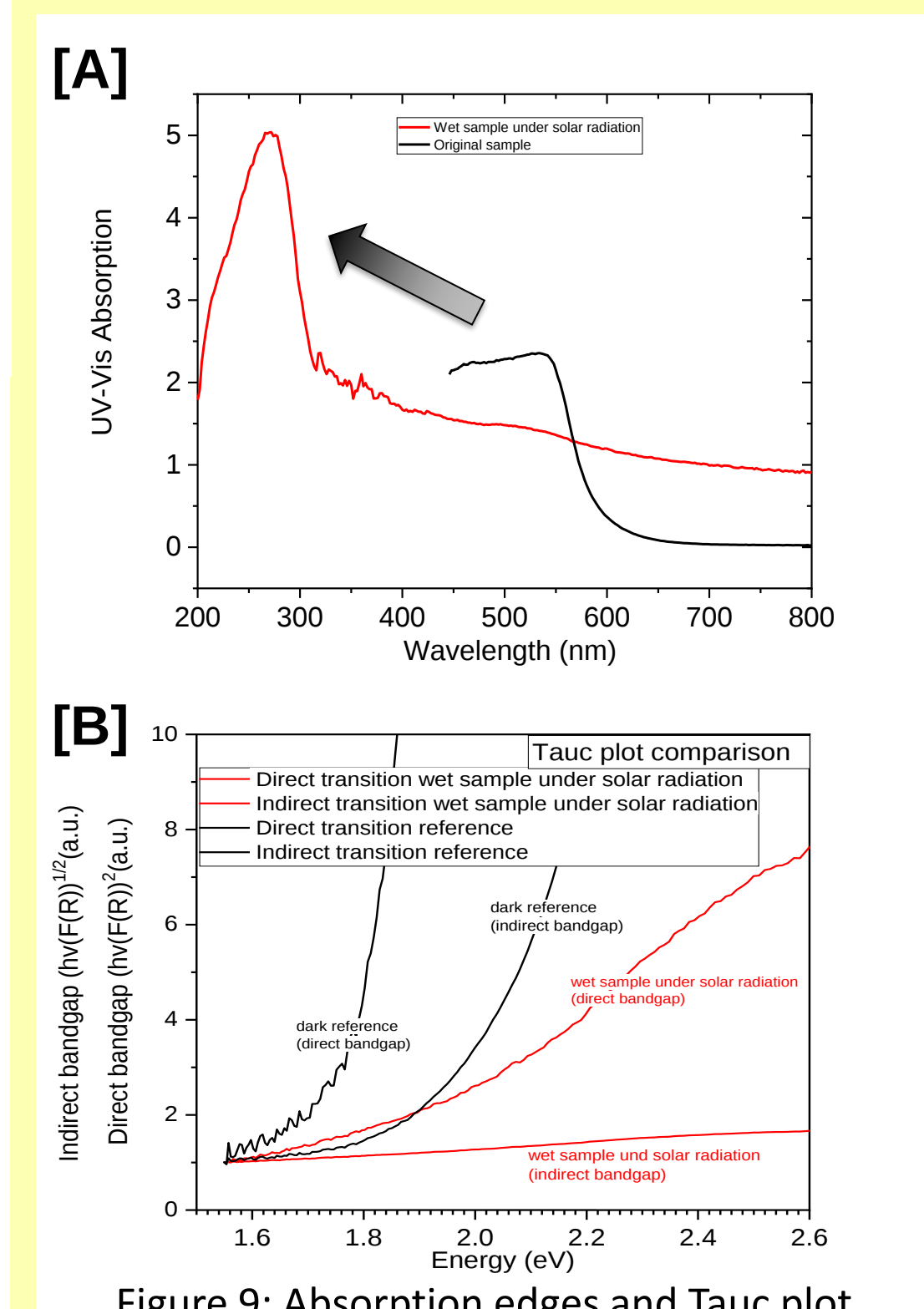


Figure 9: Absorption edges and Tauc plot

By UV-Vis spectroscopy a drastic change of the absorption edge of a wet sample under simulated solar irradiation in comparison to the original sample could be determined (Figure 9 [A]). The same data was analyzed with the Kubelka-Munk function to calculate the absorption coefficient. In Figure 9 [B] the Tauc plot of both samples can be seen. Normalization of the absorption and the Tauc plots led to the results that the absorption properties of the material significantly deteriorated. Furthermore, a minor indirect bandgap narrowing could be observed (indirect: 2.03 eV to 1.92 eV; direct: 2.16 eV to 1.99 eV).

Conclusion and outlook:

We found valid evidence that $\text{Cs}_2\text{AgBiBr}_6$ single crystals undergo severe changes under different atmospheric conditions (Figure 10). We conclude that when using the material in novel solar cells, particular attention must be paid to preventing moisture from entering the structure. Solar radiation seems to significantly accelerate the degradation of the material.

However, we find that the root cause of degradation is water. Therefore, the double perovskite can only be used as novel absorber material in solar applications if the layer is sealed from moisture, humidity, and precipitation. Further studies will be carried out on $\text{Cs}_2\text{AgBiBr}_6$ thin films.

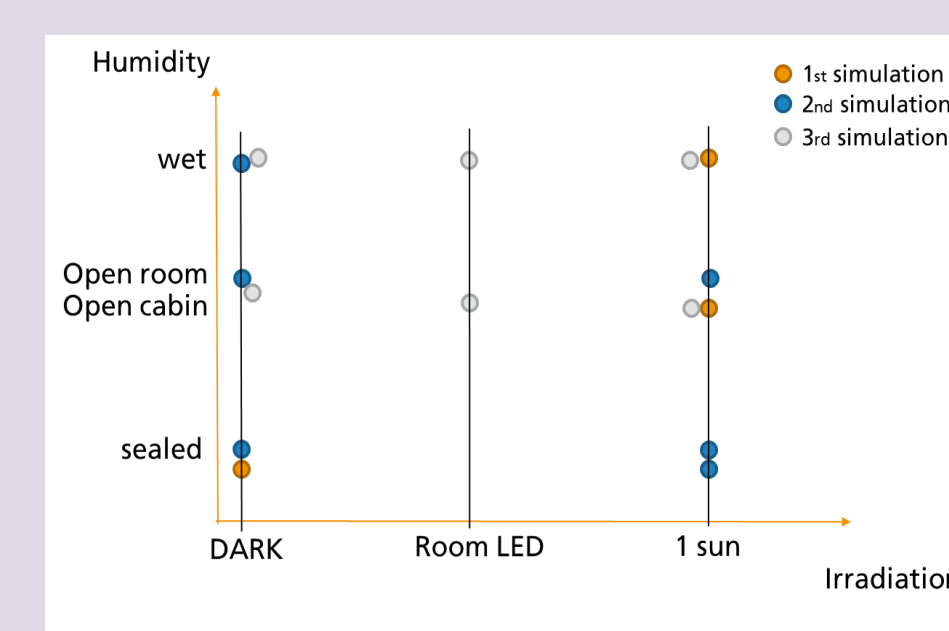


Figure 10: Performed simulations

References:

- [1] F. Haase, et al. *Sol. Energy Mater. Sol. Cells* 2018, 186, 184-193
- [2] A. J. Bett. *Perovskite silicon solar cells*. 2020, 13-14
- [3] McClure, et al. *Chem. Mater.* 2016, 28, 1348–1354

Acknowledgements:

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