



**Walter Schottky Institute**  
**Technical University of**  
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Advanced Lab Course  
Experiment No 29

## **Optical Characterization of Hybrid Perovskites**

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# 1. Introduction

The prevention of climate change and thus, the research for sustainable energy sources is one of the main challenges worldwide in this century. Currently, a lot of research into solar cells is being done in order to generate electrical energy without CO<sub>2</sub> emission. The topic “Renewable Energies” in general is part of many classes at schools and universities and in this context, many students may be familiar with this figure:

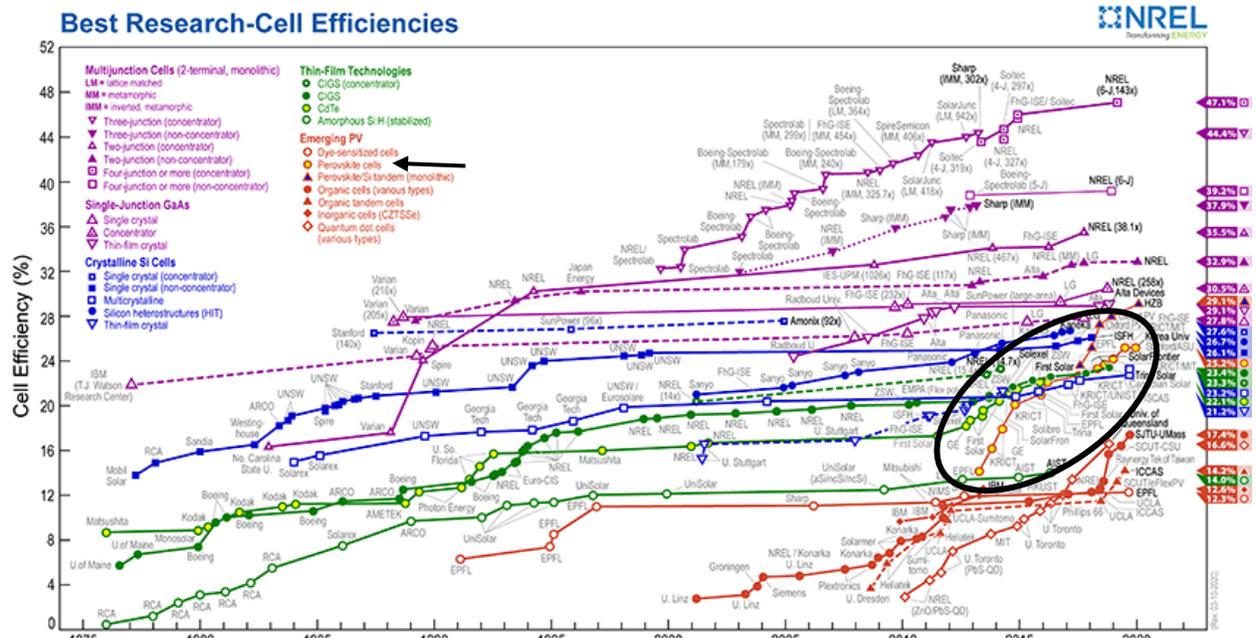


Figure 1: Comparison of the development of cell efficiencies depending on the type of cell. The marked regime shows the development for lead halide perovskite cells. Source: <https://www.nrel.gov/pv/cell-efficiency.html>

The low efficiency of the first silicon solar cells has improved a lot during the last four decades. But now, the progress for these types of solar cells is incremental as they approach the Shockley Queisser Limit. Nevertheless, research on new types of solar cells allows them to reach higher efficiencies: the largest improvements have been recorded for lead halide perovskite solar cells during the last few years (as shown in the yellow and orange trajectory).

As the previous example shows, investigation of new materials can improve the efficiency of existing technologies. In the case of lead halide perovskites, there is also research into perovskite photodetectors, LEDs and lasers. [1]

This broad range of potential applications is possible due to the optoelectronic properties of perovskites, such as their strong optical absorption and long charge carrier diffusion lengths [2]. In this lab course, first some perovskite films are fabricated. Then some optical properties of a few different perovskites are investigated.

## 2. Perovskites

### a. Overview

Often, lead halide perovskites are used in solar cells. As illustrated in Figure 1, within the last years, almost annually, new record efficiencies of perovskite based solar cells have been measured. These achievements were possible due to numerous research groups worldwide investigating perovskite semiconductors. However, only a share of the ongoing research about perovskites is on solar cell applications, with the other part being into other optoelectronic devices, such as LEDs or detectors, as well as the fundamental properties of this material. [3]

The broad range of possible applications based on lead halide perovskites stems from the electronic properties and structure of this multifaceted material.

In the year 1839, a mineral with the chemical formula  $\text{CaTiO}_3$  was discovered in the Ural Mountains and was named Perovskite. This orthorhombic mineral gave its name to the crystal structure of a family of compounds with the general formula,  $\text{ABX}_3$  [4], [5].

Concerning the composition of perovskites, the A site contains a large cation, B corresponds to a smaller cation and, to obtain an electrically neutral compound, an anion is located at X [5].

An example of the tunability of the properties of metal halide perovskites is shown in the following figure:

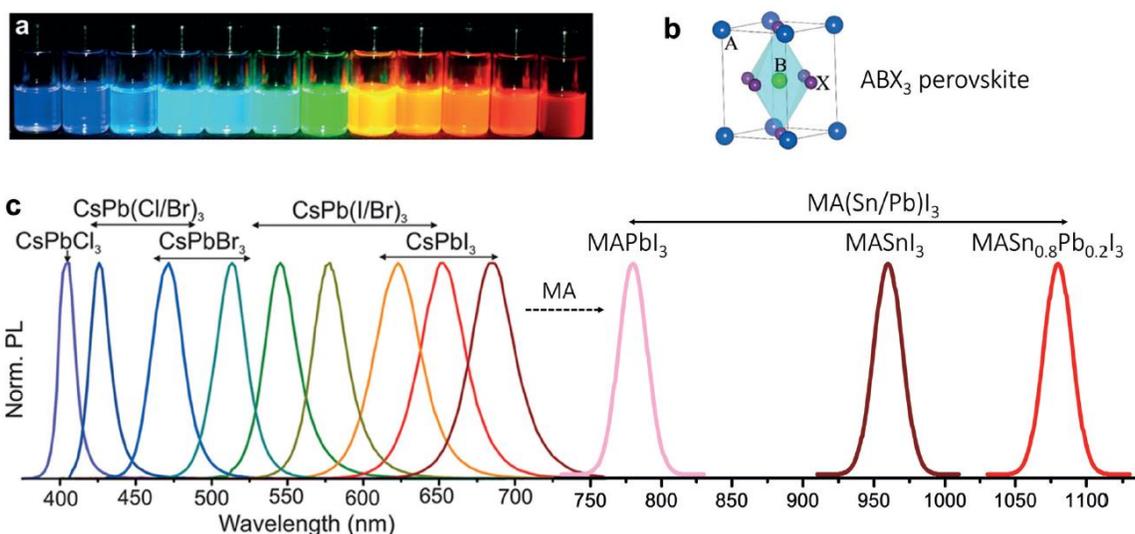


Figure 2 Example for PL peaks of different  $\text{ABX}_3$  perovskites. The different bandgaps can also be expected from the different colors of the perovskite solutions by the illumination under UV light, taken from [6].

By exchanging the molecules or atoms at the A, B and X sites of the material, one can change the bandgap and thus also shift the position of the photoluminescence peak over the entire visible spectrum as shown in Figure 2 [6]. For perovskite devices, this flexibility regarding the choice of ions at each site can not only be used to engineer the bandgap suitable for the specific application but also increase the stability and the performance [3].

Despite the range of potential optoelectronic applications, commercial devices based on lead halide perovskites are still rare. Currently, the low stability to light, moisture and air of these materials is one of the main issues. In perovskite solar cells, nonradiative recombination prevents these cells from higher efficiencies. This recombination can occur in the perovskite layer or at the interface to the transport layer [3], [7].

Nevertheless, under laboratory conditions, it was possible to measure a photoluminescence quantum efficiency of around  $\eta = 90\%$  for  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , which belongs to the group of hybrid organic-inorganic perovskites [2].

## b. Hybrid Organic-Inorganic Perovskites

In hybrid organic-inorganic perovskites (HOIPs) or ‘hybrid perovskites’, there is an organic molecule located on the A site of the perovskite [5]. Thus, by combining organic and inorganic compounds in this class of perovskites, one can benefit from features of both materials [8].

In this lab course, the focus is on two lead iodide based HOIPs, which are described in the following text:

### i. MAPI

In  $\text{MAPbI}_3$  or MAPI, a methyl ammonium (MA) molecule with the formula  $(\text{CH}_3\text{NH}_3)^+$  is located at the A site as also shown in the following figure. In this case, a lead atom is at the B site and iodide at the X site. One example for the photoluminescence peak of this perovskite can be seen in Figure 2.

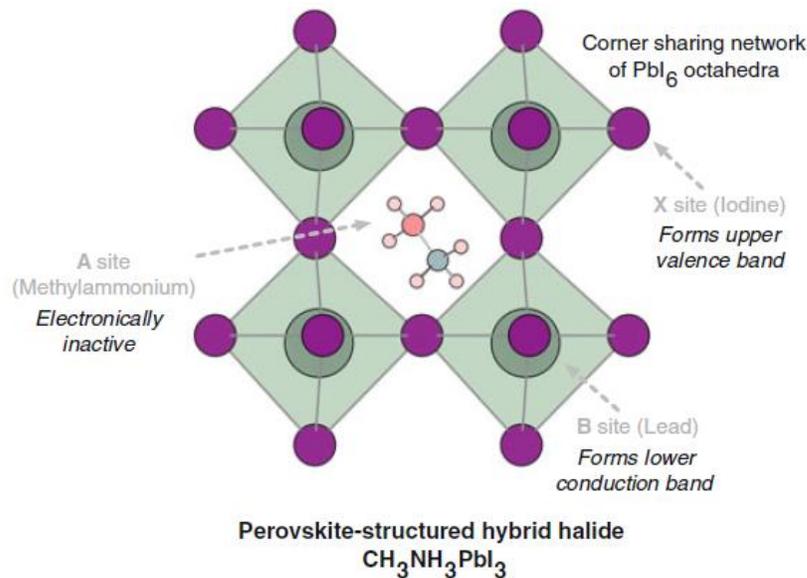


Figure 3 Methylammonium lead iodide perovskite (MAPI) as well as the A, B, and X sites of the perovskite, figure taken from [4]

Changing the X site shifts the bandgap over the visible region towards green emission for  $\text{MAPbBr}$ .

## ii. BAPI

The composition of BAPI is slightly altered from the standard formula  $ABX_3$ : This perovskite is a so-called 2D layered organic inorganic perovskite [9]. In general, these have the structure  $A_2MX_4$  and consist of alternating layers: Between the metal halide ( $MX_4^{2-}$ ) layers, there are ammonium bilayers ( $A^+$ ) [8].

## iii. Comparison of MAPI and BAPI

Even though MAPI and BAPI both are lead-halide organic-inorganic hybrid perovskites, there are some significant differences in the crystal structure and electronic states between these two materials. Understanding these is required in order to interpret the data recorded in this lab course.

The most basic difference between MAPI and BAPI is the crystal dimensionality. As shown in the following figure, MAPI has a 3D structure of the inorganic components, whereas BAPI has a 2D structure [9].

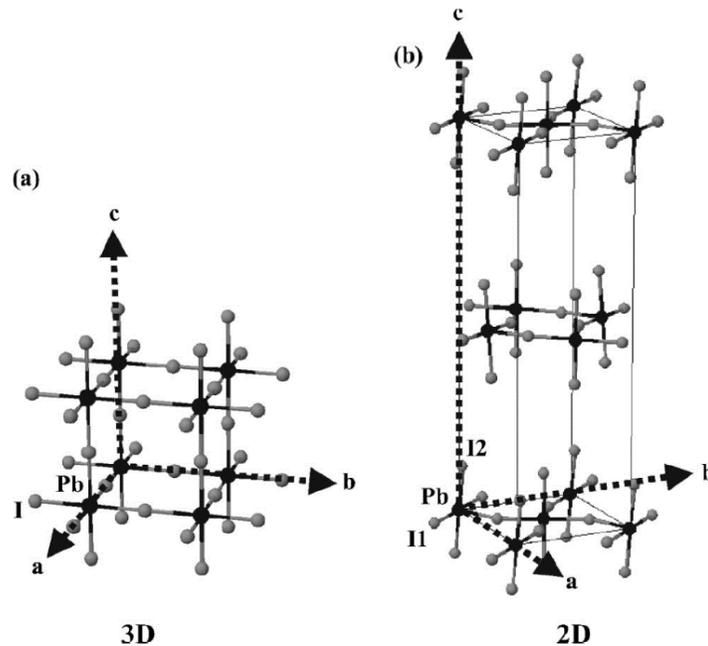


Figure 4 Sketch of the structure of the inorganic components of MAPI (a) and BAPI (b). Figure taken from [9].

The dimensionality has not only an influence on the crystal structure, it also influences the charge carrier interactions, which then is visible in the absorption and photoluminescence spectra of these perovskites [9].

Furthermore, MAPI and BAPI have different electronic band structures as shown in Figure 5. Here, they were determined based on LCAO band calculations. Both perovskites have a direct bandgap [9]. The layered nature of BAPI increases

Coulombic interactions between electrons and holes, which creates stable excitonic states at room temperature with binding energies exceeding 200meV.

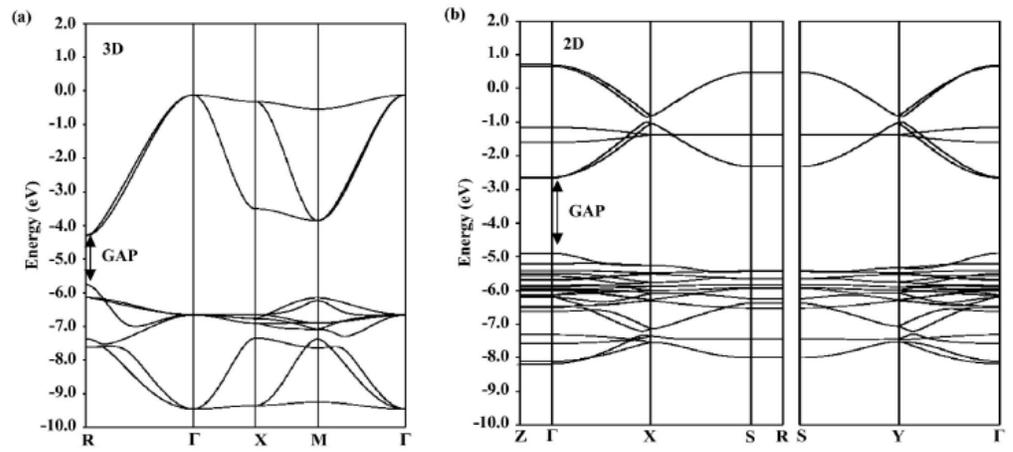


Figure 5 Energy band diagram of MAPI and BAPI. From [9]

### 3. Techniques

#### a. Spin-Coating:

Semiconductors can be fabricated via many different deposition methods. For high purity single crystals, molecular beam epitaxy is used, which requires large ultrahigh vacuum set-ups with e.g. vacuum pumps, cooling and heating cells to evaporate the material.

For solution-processable semiconductors, spin coating can be an option: Here, a thin layer of a material is formed on a substrate by the solution spreading out due to rotation, based on a balance of viscosity and the centrifugal force. Therefore, this technique is faster and cheaper than other semiconductor fabrication techniques. Many large molecules or structures, such as some organic molecules used in perovskites, are too heavy or unstable for evaporation techniques. In this case, spin coating is the preferred fabrication method. The three main steps of spin coating are shown in the following schematic:

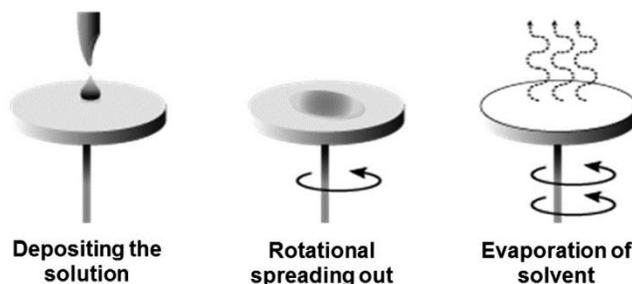


Figure 6 Steps of spin coating a solution on a sample: The rotation spreads the solution over the sample. After an annealing step, the sample is ready to measure. Source: <https://doi.org/10.1016/j.irbm.2018.07.002>

Before starting, a substrate is mounted on a stage of a spin coater. Usually it is held by a vacuum chuck. Then, in the first step, a few droplets of a solution are deposited at the center of the sample. Afterwards, the droplet spreads over the entire sample surface due to rotation of the spin coater. Usually, rotation speeds between 2000 rpm and 6000 rpm are chosen. While the spin coater is rotating, the solvents evaporate and the solute crystallizes to form a layer with a thickness in the range of 0,1  $\mu\text{m}$  to a few microns. The entire process usually takes a few minutes. Thus, compared to vapor deposition, spin coating is one or two orders of magnitude faster.

Furthermore, one can adapt the rotation parameters to the sample: depending on the viscosity and the percentage of solvents, it can be useful to adapt the rotation speed during the deposition of the solution. This is, since the solution can be deposited on a sample already rotating at full speed, on a sample with increasing speed or on a not rotating sample.

Avoiding variations of the concentration or the viscosity and using always the same processing parameters results in very similar layers. The surrounding gas during the fabrication can also influence the properties of the layer.

One of the main disadvantages of spin coating are the poisonous components, which is one of the reasons, why perovskite samples usually are processed in a glove box under nitrogen atmosphere. Another benefit from the fabrication in the glove box is the low concentration of oxygen and water, which avoids the degradation of the perovskite.

## b. Linear Absorption

In this lab course a Lambda 900 UV-Visible Spectrometer system from Perkin Elmer is used to measure the transmission of light through thin film perovskite samples. In this spectrometer, a deuterium lamp and a tungsten-halogen lamp are mounted to generate a broad spectrum with wavelengths between 185 nm and 3000 nm. As you can see in the sketch below, two monochromators generate a focused beam with a narrow range of wavelengths from the emitted light. By sweeping the wavelength in small steps, the transmission is recorded and the resulting values indicate the available optical transitions in the investigated sample. This data allows the band gap energy and excitonic binding energies to be calculated.

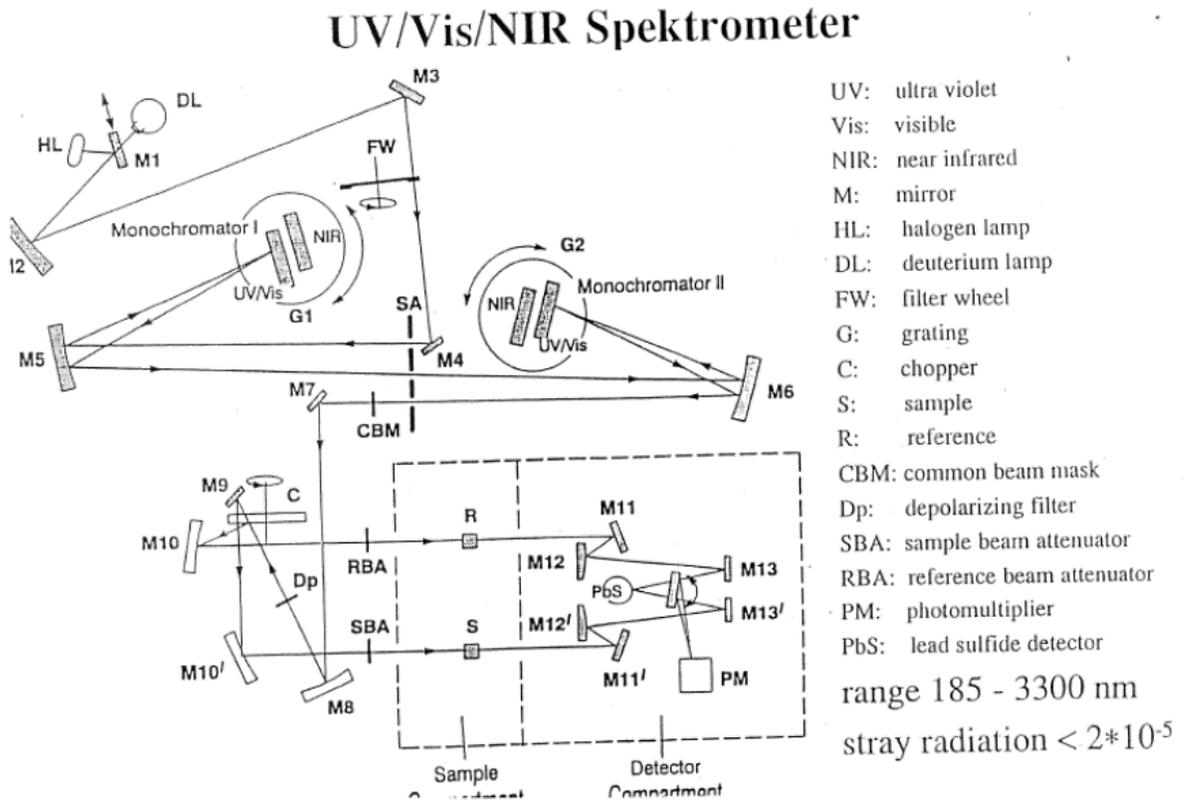


Figure 7 Schematic sketch of beam path in this spectrometer. Source: Fortgeschrittenenpraktikum Nr.50: Photovoltaik, Bayerl, Janssen, Dietmüller; TU München

As shown in the figure above, not only a sample but also a reference sample is mounted in the spectrometer. To determine the signal from the investigated sample, a reference sample with the same substrate as in the sample of interest is mounted in the reference beam. By reducing the signal from the investigated sample by the reference signal, one obtains the signal of the investigated layer without the signal of the substrate.

### c. Photoluminescence (PL)

The following text is about photoluminescence measurements, which includes steady-state PL and time-resolved PL measurements, as well as PL quantum efficiency measurements. These three experiments are possible at two different set-ups in this case. By combining these experiments, the material specific photoexcitation can be investigated.

Photoluminescence describes the phenomena whereby excited stated of the material decay by emitting a photon, mainly fluorescence and phosphorescence, as illustrated in the following figure for an arbitrary material [10]:

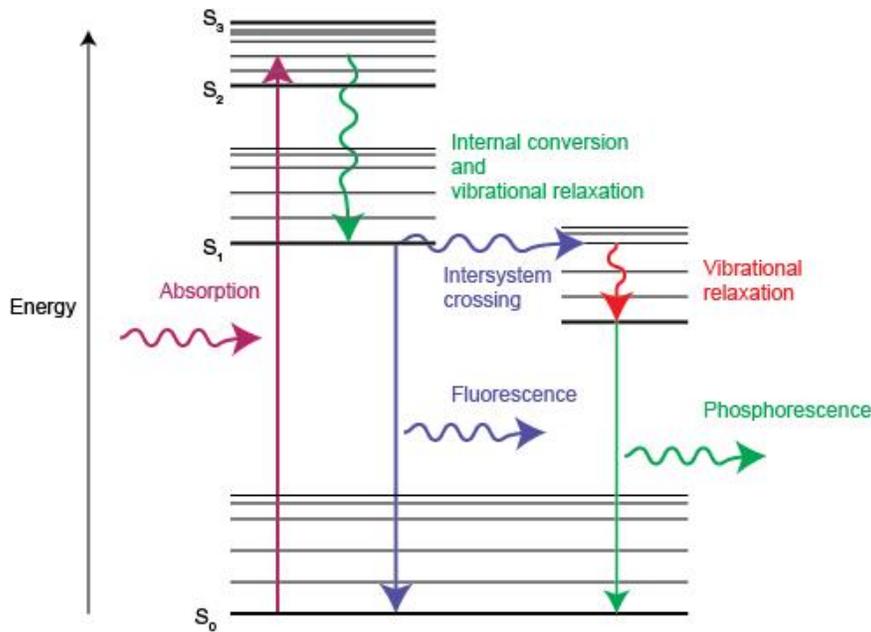


Figure 8 Light absorption leads to photoluminescence including fluorescence and phosphorescence.  
Source: <https://www.renishaw.com/en/photoluminescence-explained--25809>

From analysis of Figure 8, it becomes also clear, why these processes can be observed for multiple excitation wavelengths: If the absorbed light has an energy larger than the energy difference between  $S_1$  and  $S_0$ , relaxation processes happen until the system is lowest level of this state. Since these processes are orders of magnitude faster than the emission of photons via fluorescence and phosphorescence, the excitation with high energy photons leads to the same recorded photoluminescence [10].

In order to improve the efficiency of optoelectronic perovskite materials and applications, the photoluminescence needs to be understood and maximized. This can be realized by reducing non-radiative recombination since it limits the number of extracted charges and the voltage that can be built up across the device. Furthermore, one wants to prolong the lifetime of excited carriers in a solar cell to give them enough time to reach the electrodes and be extracted [11]. In the following section one way how the PLQE as well as the lifetimes can be calculated will be explained:

If a material is in an excited state, it can return in the ground state via radiative recombination by emitting a photon. Otherwise, the transition from the excited state to the ground state happens via nonradiative decay, which can be due to defects in the material. These processes then have the rate constants  $k_{rad}$  and  $k_{nonrad}$  [12].

The quantum efficiency of a process is defined as the fraction of absorbed photons which lead to emission of a photon, which is then described as rate of radiative recombination divided by the total rate of recombination. For the quantum efficiency, this gives the formula [12],

$$PLQE = \eta = \frac{dn/dt_{rad}}{dn/dt} \quad [13].$$

In general, the decay rate of excitations is given by

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_3 n^3$$

with  $n$  being the charge carrier density. Here, the rate constant for monomolecular carrier recombination  $k_1$  can be mediated by excitons or traps.  $k_2$  describes bimolecular recombination. Recombination with three particles with the rate constant  $k_3$  is due to Auger recombination and is neglected in the following calculations [11].

$n$  depends on the photoexcitation density. Thus, in experiments, the value of  $n$  can be changed by adapting the output power of the laser or the absorption coefficient at the wavelength used. In general, for low excitation densities,  $k_1$  dominates the recombination processes. For higher values of  $n$ , the other rate constants dominate [11].

However, not only the excitation density but also the analyzed material influences the factors relevant for the decay rate as well as the resulting formulas for the PLQE and PL spectra due to different dominating recombination mechanisms:

- **Excitonic material:**

Here, the decay rate depends linearly on  $n$ , which then gives the formula

$$\frac{dn}{dt} = -k_{rad} \cdot n - k_{nonrad} \cdot n = -(k_{rad} + k_{nonrad}) \cdot n$$

Integrating this decay rate gives the formula

$$n(t) = n_0 \cdot \exp[-(k_{rad} + k_{nonrad})t] = n_0 \cdot \exp[-at]$$

showing an exponential decay with the initial carrier density  $n_0$ . The lifetime of the charge carriers then is calculated with  $\tau = \frac{1}{a}$  and can be determined from time-resolved photoluminescence measurements as described later.

Using the equations, the PLQE formula can be converted to

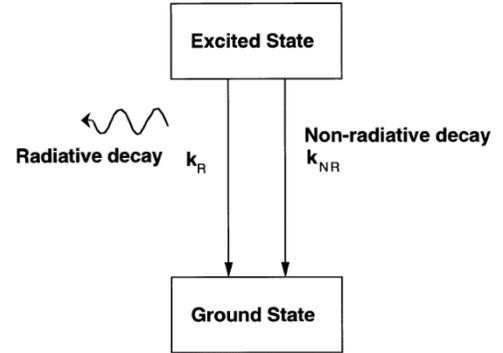


Figure 9 Transitions from the excited state to the ground state can happen either via radiative decay or via non-radiative decay. From [12]

$$PLQE = \eta = \frac{dn/dt_{rad}}{dn/dt} = \frac{k_{rad} \cdot n}{k_{total} \cdot n} = \frac{k_{rad}}{k_{rad} + k_{nonrad}}$$

which is independent from  $n$  and constant for different excitation densities [12], [13]

- **Free carrier dominated material:**

In a perovskite with a recombination mediated by free carriers, monomolecular and bimolecular processes are relevant. The decay rate then is

$$\frac{dn}{dt} = -k_1 \cdot n - k_2 \cdot n^2$$

The number of charge carriers and the fluence-dependent PLQE then are described by the equations

$$n(t) = - \frac{k_1}{k_2 - \left(k_2 + \frac{k_1}{n_0}\right) \exp(-k_1 t)}$$

and

$$PLQE = \eta = \frac{dn/dt_{rad}}{dn/dt} = \frac{k_2 n^2}{k_1 n + k_2 n^2}$$

To solve these equations, different types of photoluminescence measurements are required:

### i. PLQE

The photoluminescence quantum efficiency is defined as the fraction of photons emitted by the sample compared to the number of photons that are absorbed by the sample, which then gives the following equation [14]:

$$\eta = \frac{\text{number of photons emitted}}{\text{number of excitations decayed}}$$

In a simple photoluminescence set-up, this fraction cannot be analyzed due to the broad distribution angle of the emitted PL and scattered laser light. This problem can be solved using an integrating sphere, which is a hollow sphere with a highly reflecting coating on the inner side. In our PLQE set-up, this sphere has an inner diameter of 10 cm and a so-called Spectralon coating. Due to this coating, independent from the incoming angle, light in the sphere is isotropically distributed within the sphere [14].

As shown in Figure 10, at one of the ports of the sphere, a CCD spectrometer is connected in order to record the spectra. Direct reflection of the laser beam into the spectrometer needs to be avoided, which is realized by a baffle.

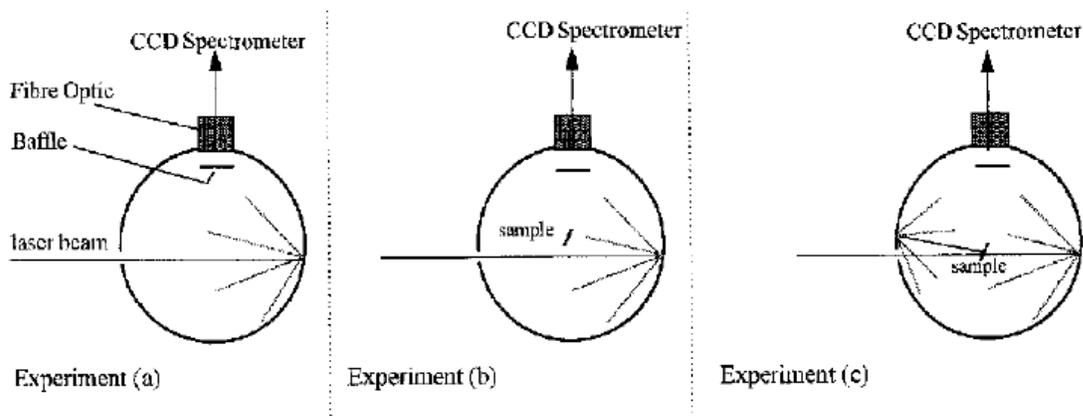


Figure 10 For a PLQE measurement, three different measurements are performed: a) with an empty sphere; b) the sample is in the sphere, but not in the direct laser beam path; c) the sample is in the sphere and in the laser beam path; Figure taken from [14]

As shown in this figure, a PLQE measurement consists of three measurements: for the first measurement, the light from the laser source is directed into the sphere in order to analyze the excitation intensity, i.e. the number of incident photons. Then, in the second measurement, the sample is positioned in the sphere but not in the direct light beam path. With this step, the photoluminescence from excitation light scattered in the sphere is analyzed: only the fraction  $\mu$  of the scattered light is absorbed by the sample. Finally, in the third measurement, the sample is placed in the beam path. From this step, a fraction  $A$  can be calculated, which describes the total light absorbed by the sample [14], [15].

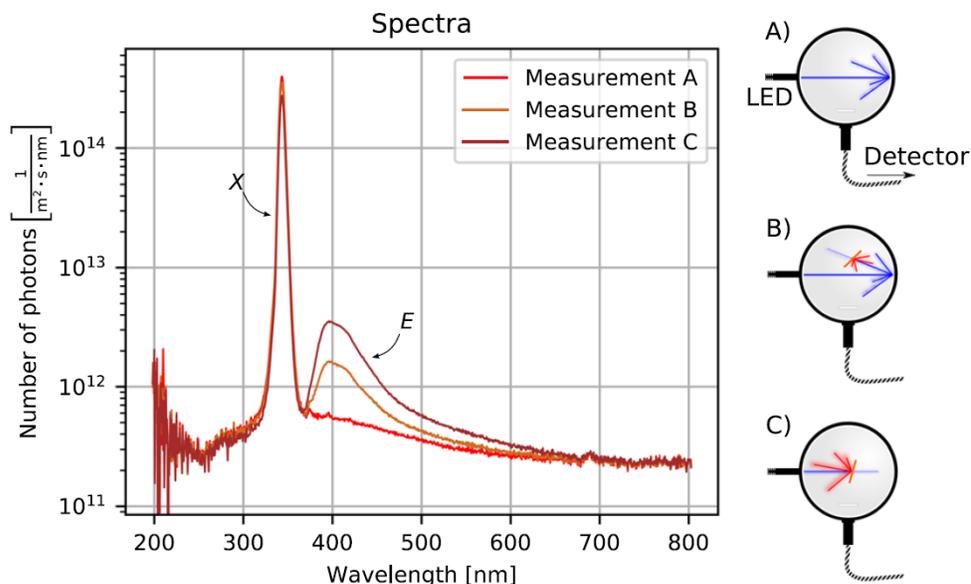


Figure 11 Example of recorded signals from the three measurements shown on the right; peak X stems from the light source; E represents the emission from a sample. Taken from [15]

In Figure 11, these three spectra for another material are plotted as an example. By combining the integrated signal from the light source for the different steps, the absorption  $A$  and the quantum efficiency  $\eta$  can be calculated. This calculation is the main part of the preparation, since it is required for the data analysis of the report.

The calculation is based on the assumption that the light source always emits the same number of photons per measurement time for each of the three experiments. Thus, for this light source, a laser with a highly stable intensity needs to be chosen.

## ii. Steady-State PL

The steady-state photoluminescence is a time-averaged record of the photoluminescence spectrum, which provides information about the PL signal: with this experiment, none of the values for the PLQE or the rate constants discussed above is determined but this type of experiment shows the line shape of the PL peak, which provides together with the absorption spectrum the position of energy levels and energy loss mechanisms in the material [11].

In our set-up, the excitation source is a pulsed laser and the steady-state PL signal is recorded over a time which is long compared to the expected decay times. This spectrum then typically looks similar to the signal in the top part of Figure 12 and can be described by CCD counts or intensity against wavelength.

## iii. Time-resolved PL and lifetime analysis

From the previous chapter, some equations are known, but it is not yet possible to determine concrete values for the rate constants due to too many unknown values. This last experiment of time-resolved photoluminescence provides the missing information.

In order to do a time-resolved PL measurement, one uses a set-up as shown in Figure 12: The sample is excited by a pulsed light source. The photoluminescence is then again recorded with a spectrograph and a camera. In order to get the time

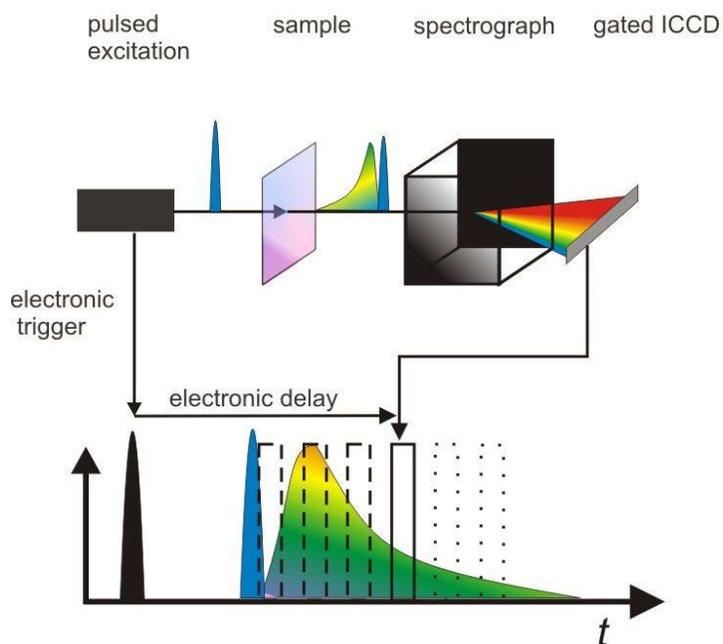


Figure 12 Sketch of a set-up for time-resolved PL experiments. Source: [https://ufd.kaust.edu.sa/detail/facilities/time-resolved-photoluminescence-spectroscopy-\(trpl\)](https://ufd.kaust.edu.sa/detail/facilities/time-resolved-photoluminescence-spectroscopy-(trpl))

resolved PL, the time at which the camera records the PL signal is triggered from the light source. Then, many spectra are recorded and each time, the delay between the trigger and the recording time is increased a bit. This then results in a time-resolved spectrum as shown at the bottom of Figure 12.

Finally, the intensity of a specific wavelength or the overall PL intensity is plotted on a logarithmic scale against the time delay. This gives a decaying signal which has different shapes depending on the material of the sample and in some cases also influenced by the fluence used during the measurement:

For **excitonic samples**, the time-dependent photoluminescence signal is

$$PL(t) = k_{rad} \cdot n(t) = k_{rad} \cdot n_0 \cdot \exp[-(k_{rad} + k_{nonrad})t] = k_{rad} \cdot n_0 \cdot \exp[-at].$$

Starting from a plot of the PL (as described above) with a shape described by  $\exp(-at)$ , a suitable fit of the decay and some calculations enable to determine the rate constants as well as the lifetime  $\tau = \frac{1}{a}$  [11], [12].

For **free carrier dominated samples**, at low fluences the photoluminescence

$$PL(t) = k_2 \cdot n^2(t) = k_2 \cdot (n_0 \cdot \exp(-k_1 t))^2 = k_2 \cdot n_0^2 \cdot \exp(-2k_1 t)$$

also enables to calculate the rate constants from a similar fit [13].

In our lab, the steady-state and the time resolved PL are both measured with the same set-up, but with different acquisition time settings of the camera.

## 4. Preparation

To prepare for this lab course, think about the answers of the following questions. In the colloquium at the beginning, we will talk about them.

### a. Spin Coating:

- What is the purpose of the annealing step?
- What are two main reasons for spin coating in a glove box?

### b. UV-Vis:

- In this lab course, we shine light on samples and measure the transmission  $T$ . In this context, one usually uses the formula  $1 = A + R + S + T$ . What can we learn by measuring  $T$ ? Why can we neglect the reflection  $R$  and the scattering  $S$  here?
- Measurements in the UV-Vis always start at the wavelength with the higher value and then sweep to the lower wavelength. Why do we measure that way round?

### c. PLQE and Photoluminescence

- How do you need to combine the three experiments at the integrating sphere to calculate the PLQE? To determine  $\eta$ , use the values  $\mu$  and  $A$ .
- How can you calculate  $k_{\text{rad}}$  and  $k_{\text{nonrad}}$  in excitonic systems by combining a PLQE and a transient PL measurement? Hint: Which formulas do you get for carrier kinetics and PLQE?
- How can you calculate  $k_1$  and  $k_2$  in a free carrier system by combining a PLQE and a transient PL measurement? Hint: Which formulas do you get for carrier kinetics and PLQE?

While this might look like a time-intensive preparation, it will simplify the final data analysis.

## 5. Experiments

### a. Sample Fabrication

**!!! Since working at the glovebox is quite challenging and time-consuming at the first attempts, the samples for the spectroscopic analysis are already prepared for you. The glovebox and spin-coating as fabrication technique are only presented by the supervisor.**

In this Lab Course a few different samples will be investigated and most of them are fabricated with spin coating. The sample fabrication takes place in a glove box under nitrogen atmosphere.



*Figure 13 Glovebox under nitrogen atmosphere with all necessary materials and tools*

For the fabrication of perovskite thin films, a suitable amount of precursors needs to be weighed and dissolved in a solvent. Just mixing these two components by hand results in a non-uniform solution. In the next step, the solution is put on a hot plate at 80°C with integrated magnetic mixer for roughly one hour. Afterwards, the solution is ready to be used for the final sample fabrication.

The samples analyzed in this FoPra consist of a thin perovskite film on a glass substrate in an encapsulating layer. Before the spin coating step can be started, the glass substrate is positioned in the spin coater and some low pressure is applied to fix the sample. Then the cap of the spin coater is closed. After this preparation, one of the prepared bottles filled with a perovskite solution is taken in one hand. With the other hand, 100µl of the solution are taken out of the bottle by using a pipette. Afterwards, the bottle is put back in the metallic bottle holder while still holding the pipette in the other hand.

Now, the spin coating can start: here, dropping the solution on the substrate and starting the rotation need to be done immediately after each other. This requires some preparation: One puts one hand next to the controller of the spin coater with one finger already lying on “Start” button. Put the pipette above the open part of the cap pointing onto the glass substrate with the tip of the pipette. Then, one pushes the button of the pipette in order to quickly drop the solution on the substrate and start the rotation of the spin coater with your other hand immediately afterwards.

The spin coater stops after a short time. Open the cap, undo the low pressure that was used to hold the sample. Put the wet sample carefully on the hotplate (120°C) to anneal the perovskite film.

With this procedure MAPI, MAPbBr<sub>3</sub>, BAPI and one surprise sample are fabricated one after another. After a few minutes on the hotplate, the samples are put in a sample box and discharged from the glove box.

At this point, you don't know, which sample contains which perovskite. Since it is part of your task in the report to solve this question, from now on you should try to keep your samples in the same order.

## b. Absorption Measurements:

Advance warning: due to the many FoPras in the UV-Vis-lab which might hinder the chair's regular measurements, the experiments performed at the UV-Vis need to be scheduled carefully. Since during Corona-times there are restrictions concerning the maximum number of people allowed per room, this experimental part can't always take place the way as it was planned. In this case, the corresponding data will be given to you without doing the measurements at the UV-Vis.

If it is possible to do the measurements at the UV-Vis, then the set-up will already be running to warm up the lamp. First, start the measurement software Lambda 900 under Windows. Next, the settings need to be chosen. Some of them can be chosen based on your prepared values. Before starting the actual measurements, a signal of a blank is recorded. Afterwards, the transmission signal is recorded for the four samples one after another.

## c. PLQE

In the following experimental part, the PLQE is analyzed in three measurements, which all are performed with the same set-up. In our lab, the light source is a precision laser diode with a wavelength of 405nm. This wavelength has been chosen since the energy of the emitted photons is large enough to excite all the different perovskites. Additionally, this light source was chosen due to its high stability, which is relevant in our case to facilitate the emission of a constant number of photons and thus a small error in the PLQE results.

The coating of the inner side of the integrating sphere is highly reflective, but nevertheless some losses occur. This requires a calibration of the sphere and the detector as well as a calibration file for the data analysis to calculate the actual number of photons from the counts measured by the CCD detector.

For the first experiment, the signal from the empty sphere is measured. In this case, no sample is mounted in the sample holder. This so-called experiment (a) is performed one time. To save the data of the experiment, open the folder "FoPra" on the desktop and create a new folder. Name this folder with the number of your FoPra group. Save all your measurements in this folder and name the files with the sample names and the type of experiment to simplify later analysis.

After recording the spectrum, the light source is blocked and one of the ports is opened. At the inner side of this port, one of the samples is now fixed such that it is not in the direct light path. Then the laser diode is unblocked again and the spectrum of this experiment (b) is recorded.

Finally, the sample within the sphere is moved into the direct beam bath and experiment (c) starts.

Experiment (b) and (c) are required for all samples and with different excitation densities. Thus, after experiment (c) with the first sample, the laser diode is blocked again, then the port of the sphere is carefully opened and the next sample is mounted. After this, the next experiments have to be performed as described before.

#### d. Photoluminescence and Lifetime Analysis

As already mentioned, steady-state photoluminescence and time resolved photoluminescence are recorded with the same set-up but with different settings of the detector. For these experiments, a pulsed ytterbium laser system is used, which is already running with a blocked output when you start the measurements. For control and the settings of this laser system, your supervisor is responsible, please don't change anything at the laser system.

**Safety warning: with the current set-up, the laser beam never leaves the optical table.**

- **Put jewelry, watches etc. in your pocket to avoid potential reflections!**
- **Always block the laser beam while exchanging the sample!**
- **Don't put your eyes at the beam height!**

In the first step, the steady-state photoluminescence is recorded for your samples: mount your first sample in the sample holder. Then, you and your supervisor will optimize the angle of the incoming laser beam in order to maximize the signal. At the computer, the settings of the spectrograph and the camera will be adapted for a steady state measurement.

Record the photoluminescence signal of your sample as shown to you by your supervisor and save the file as described in the previous experimental PLQE section. Afterwards, the laser beam is blocked, the next sample is mounted and the same measurement procedure as for the first sample is executed.

For the time-resolved measurements, your supervisor will help you changing the settings in the software of the camera to enable time-resolved measurements. Mount your first sample again in the sample holder and start the measurements. Save these data in your folder as well. Then, for this sample a so-called 'fluence series' is started: the set-up is changed in order to excite the sample with another fluence and thus with another number of photons. Depending on the type of perovskite film on the sample, the spectra of the fluence series show a different behavior. Afterwards, as for the steady state measurement, block the laser beam, exchange the sample and do the next measurement.

## 6. Report:

The written report of this lab course should contain two parts: First, a written answer of all questions from the preparation part is required. A summary of the topic or any theory about perovskites or the techniques used in this lab course is not required. In the second part, analyze your results from the lab and answer the following questions:

- Absorption (from UV-Vis):
  - Plot the transmission and absorption spectra for all samples. Assume  $R=0$  and  $S=0$ .
  - Which information can you gain from the positions of the peaks?
  - Try to explain the different shapes of the spectra.
- PLQE and PL:
  - Calculate the quantum efficiency from the three experiments for all your samples.
  - Determine the lifetime of the excited state of each sample from the time resolved PL measurements.
  - Find  $k_{\text{rad}}$  and  $k_{\text{nonrad}}$  for the excitonic sample(s) and compare them.
  - Find  $k_1$  and  $k_2$  for the free carrier sample(s) and compare them.
- Try to find out which sample is MAPI, which sample is BAPI and which sample is another perovskite by comparing the results of your samples.

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