Complexity of Perovskites Absorption Measurements

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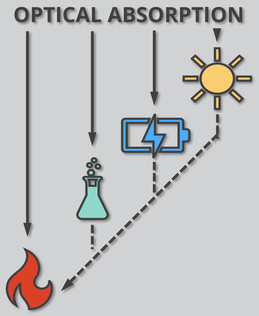
1. The Methods

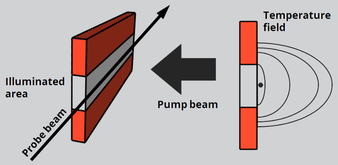


The absorbed light can be transformed to different forms.

- Light, electrons and holes, chemical energy or thermal energy.

We used the three following methods to determine an absorption spectra of the $MAPbBr_3$ single crystal.

1. Confocal Photoluminescence Spectroscopy (PL):
   - Detects the optically active transitions only.
2. Fourier Transform Photocurrent Spectroscopy (FTPS) [1]:
   - Measurement was performed on single crystal with ITO contacts on the upper (illuminated) side of the sample. Or with gold contacts on sides of the sample.
3. Photothermal Deflection Spectroscopy (PDS):
   - Uses conversion of absorbed light to thermal energy.
   - This creates a temperature field close to the sample surface and thus changes a refractive index of surrounding liquid. This change deviates the probe beam.
   - From the deviation of the probe beam, the absorption spectra can be computed.



2. The Challenge

Comparing the results obtained by PL, FPTS and PDS measurements we can clearly see significant differences in absorption spectra, see Fig. 2.

The information obtained from confocal PL originates mainly from the surface area where the 442 nm excitation laser is strongly absorbed. Therefore this method gives by geometry unaffected absorption spectra and correct position of optical band gap.

On the other hand, the FTPS and PDS methods are using white light to obtain the absorption spectra. This causes that the absorption spectra measured on thick single crystal contains the information from different depths. This can be easily proven by changing the contact geometry in FTPS measurement, see Fig. 1. Or comparing the thin layer and single crystal spectra in case of PDS, see inset of Fig. 2.

Our future goal is to extract/analyze the bulk and surface contribution to the absorption spectra using these methods.

Besides that, we use the absorption spectra determined by PL to extract material parameter often referred as Urbach Energy.

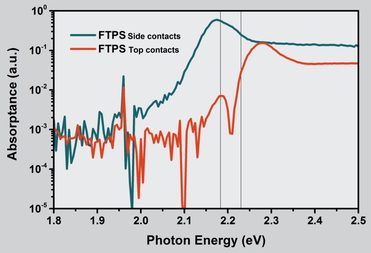


Fig. 1: Comparison of static FTPS measurements with different geomteries.

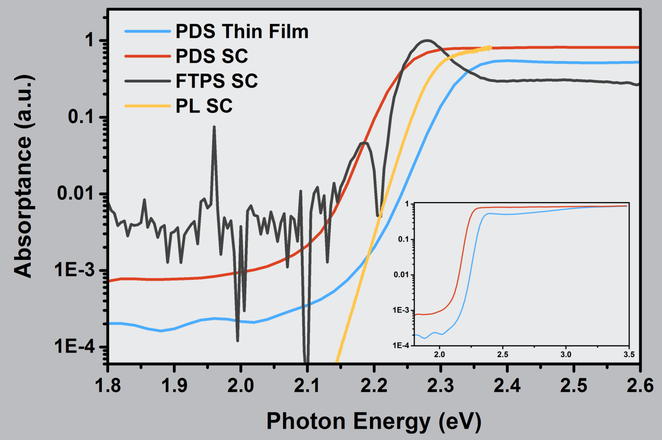


Fig. 2: Comparison of $MAPbBr_3$ absorptance spectra determined using different methods.

3. Introduction to Urbach Energy

The exponential slope of absorption edge is often referred as Urbach Energy, E_U.

$$\alpha(E) = \alpha_0 \, exp\left(\frac{E-E_C}{E_U}\right),$$

where E is the photon energy, and α_0 and E_C are material constants.

Urbach Energy relates to structural disorder of the material.

Its temperature independent (static) part is related to a density of defects.

$$E_U(T) = E_U(0) + \frac{2E_U(0)}{exp(E_P/kT)-1}$$

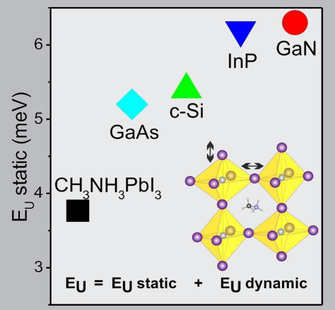


Fig. 3: Comparison of static Urbach energy of typical PV absorbers. [2]

In comparison with other semiconductors, perovskite thin films has lower values of Urbach energy, which suggests a great electronic properties, see Fig. 3.

4. Link to the Photovoltaic Device Performance

Open circuit voltage losses (of optimized PV device) scale with Urbach energy $E_U(T)$ of the absorber material.

Urbach energy can serve as easily accessible material parameter used for pre-selecion of promising photovoltaic absorbers.

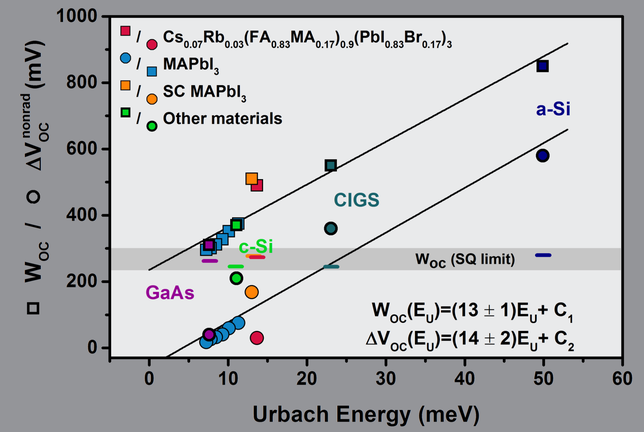


Fig. 4: Connection between Urbach energy computed from PL spectra and non-radiative open circuit voltage losses ΔV_{OC}^{nonrad}.

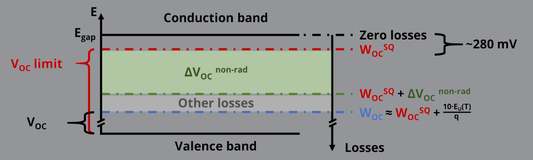


Fig. 5: Diagram of basic contributions to the V_{OC} losses of photovoltaic device.

Summary

- Perovskite structural disorder (Urbach Energy) is comparable with high quality single crystalline semiconductors.
- Urbach energy can be used to predict potential of newly developed photovoltaic absorbers.

We acknowledge the support of Czech Science Foundation Project No. 17-26041Y, Operational Programme Research, Development and Education financed by the European Structural and Investment Funds and the Czech Ministry of Education, Youth and Sports (Project No. CZ.02.1.01/0.0/0.0/16_019/0000760 - SOLID21 and No. CZ.02.1.01/0.0/0.0/15_003/0000464 - Centre of Advanced Photovoltaics). This contribution was partially supported by Grant Agency of the Czech Technical University in Prague No. SGS16/244/OHK4/3T/14.

[1] Poruba, A.; Holovsky, J.; Purkrt, A. and Vanecek, M. Advanced optical characterization of disordered semiconductors by Fourier transform photocurrent spectroscopy. *J. Non-Cryst. Solids*. **2008**, 354(19-25), 2421-2425.

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