

Influence of defects on photoluminescence from $\text{Cu}_2\text{ZnSnS}_4$ thin films

J. P. Teixeira^{1, #}, R. A. Sousa¹, J. P. Leitão¹, M. G. Sousa¹, A. F. da Cunha¹, P. A. Fernandes^{1, 2}, P. M. P. Salomé³

(1) Departamento de Física and I3N, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

(2) Departamento de Física, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal

(3) International Iberian Nanotechnology Laboratory for Nanostructured Solar Cells, Av. Mestre José Veiga 4715-330 Braga, Portugal

#jenniferpassos@ua.pt

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) presents promising properties for thin film photovoltaics (PV) technology [1]:

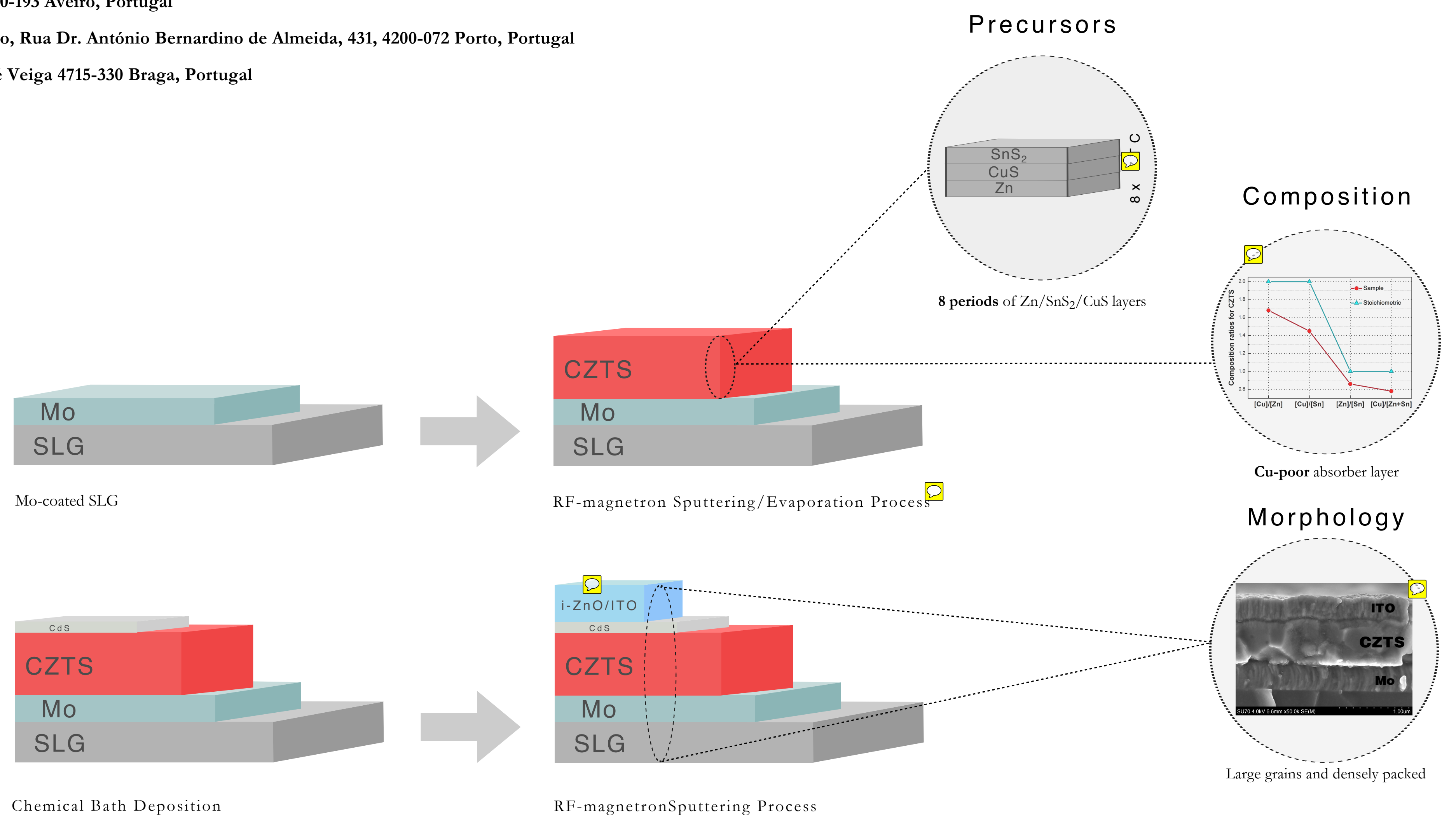
- non toxic character and availability of the constituents;
- high absorption coefficient ($>10^4 \text{ cm}^{-1}$) in the near-infrared and visible spectral regions;
- almost optimal direct bandgap energy (1.5 eV).

Huge increase of the efficiency of CZTS based solar cells: 0.66% (1996) to 8.4% (2013) [2,3]. This record is far from the one obtained for CIGS (20.9%) and multicrystalline silicon (20.4%) [4,5].

The efficiency limits of CZTS based solar cells may be due:

- fluctuations of stoichiometry along the thin film;
- heavily doping and high compensation values;
- local disorder at grain boundaries.

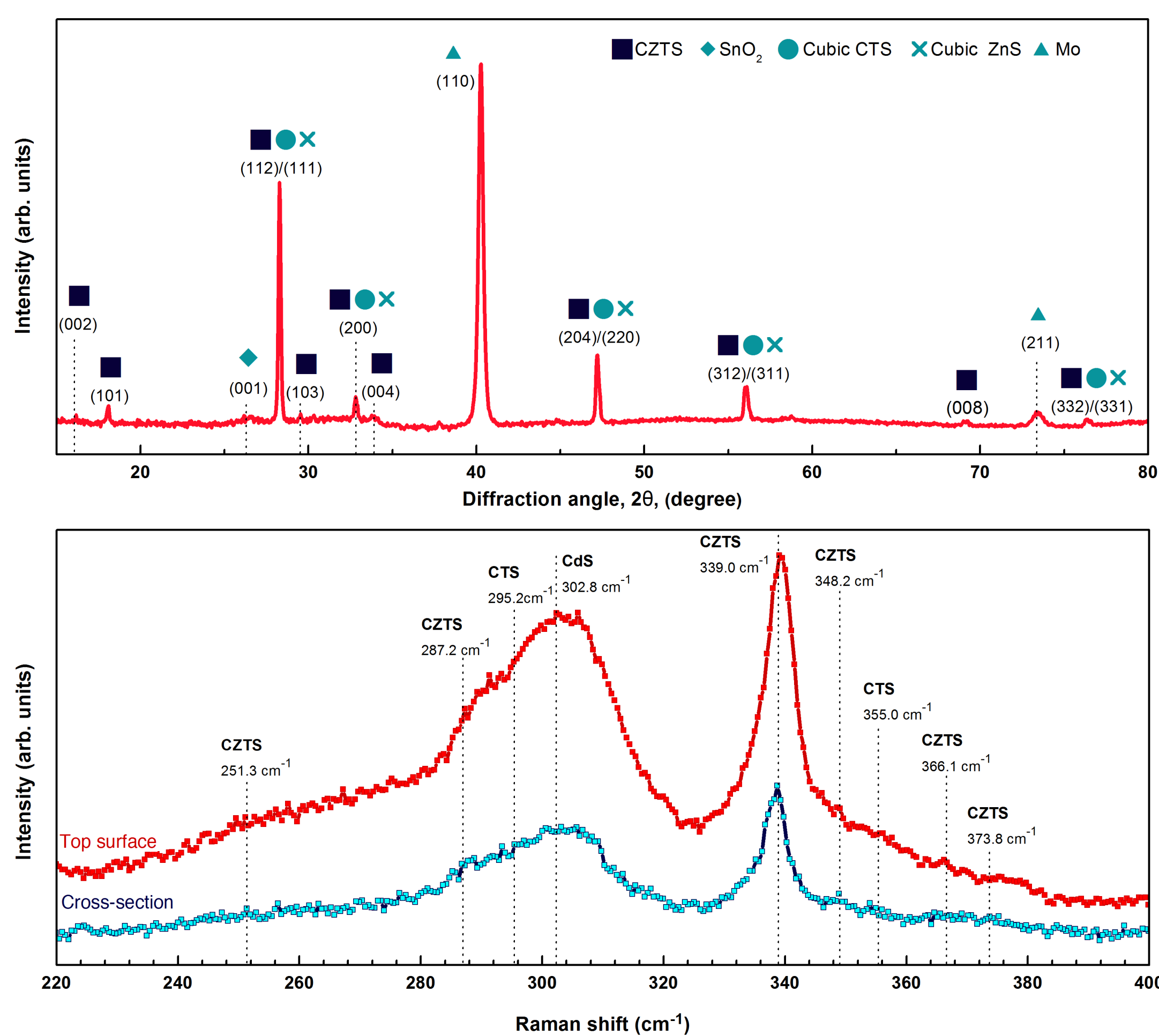
All these issues will strongly affect the electronic levels structure.



Solar cell: **SLG/Mo/CZTS/CdS/i-ZnO/ITO**

CZTS thin film was obtained through rapid thermal processing (RTP) of hybrid multiperiod precursors layer

STRUCTURE



XRD X'Pert MPD Philips diffractometer equipped with a Cu-K α source

- Two peaks with origin in the Mo layer.
- The reflections on the planes (002), (101), (103), (004), (008) can be related only to CZTS phase.
- The attribution of a few of the most intense reflection peaks is not clear
- Due to quite similar structure and unit cell size of different crystalline phases, including CZTS, just XRD analysis do not allow the distinction between CZTS, Cu_2SnS_3 (CTS) and ZnS: the presence of ZnS and CTS can not be excluded.

The combination of XRD with Raman spectroscopy is mandatory.

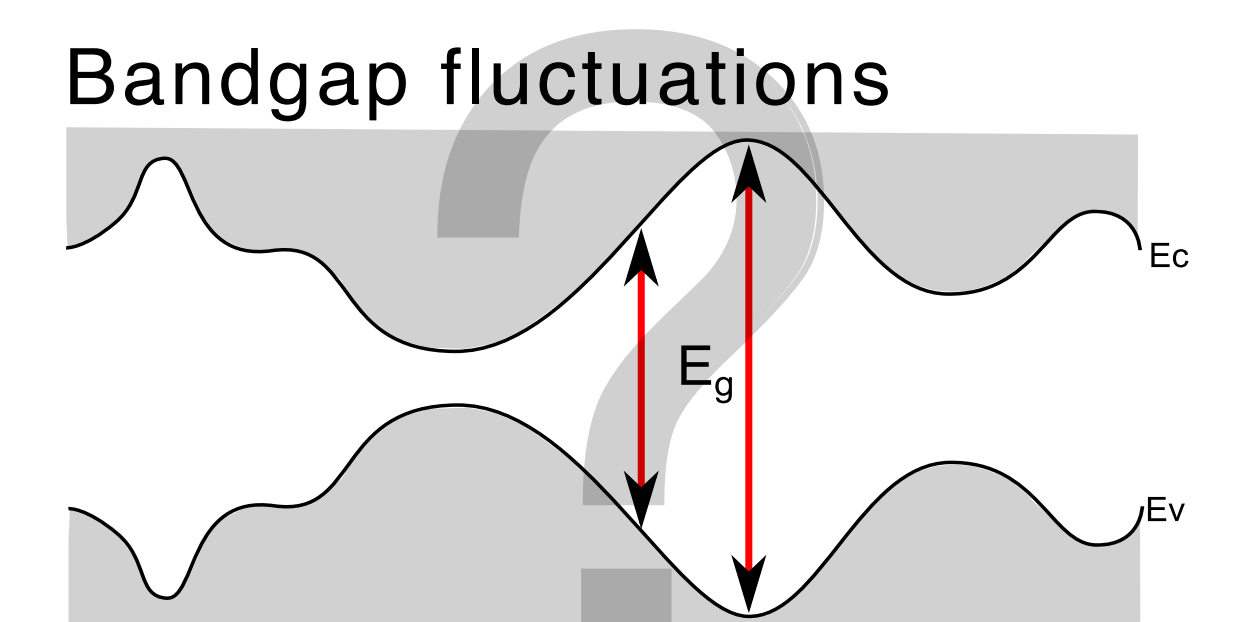
RAMAN LabRam Horiba HR800 UV spectrometer, excitation line at 532 nm

- CZTS is the dominant phase due to the A mode (kosterite phase) at 339 cm^{-1} and few other modes with much lower relatively intensities.
- Trace of CTS phase
- The $E_1(\text{LO})$ mode of the CdS phase is also a dominant peak in all spectra due the measurements carried out in solar cells.

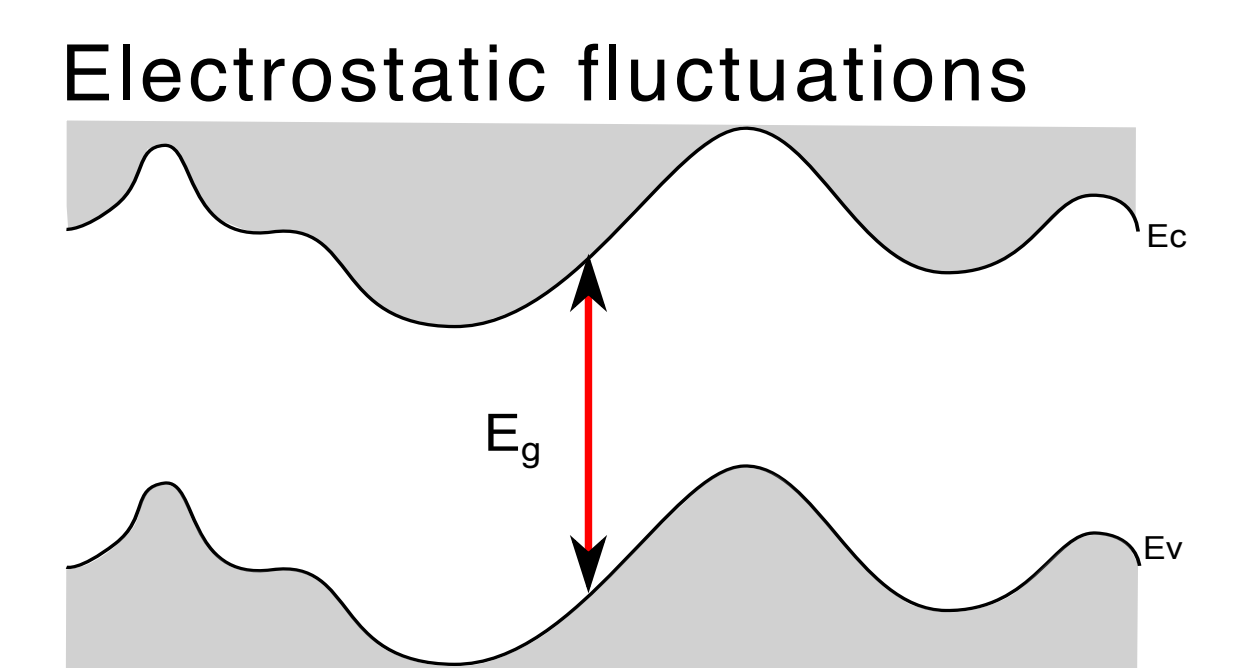
POTENTIAL FLUCTUATIONS

Structural and electronic inhomogeneities create potential fluctuations that affect the conduction and valence band edge with strong influence on the solar cells efficiency.

In CZTS will be expected the presence of both fluctuations.



- Variations of alloy composition;
- Stress;
- Stoichiometry.



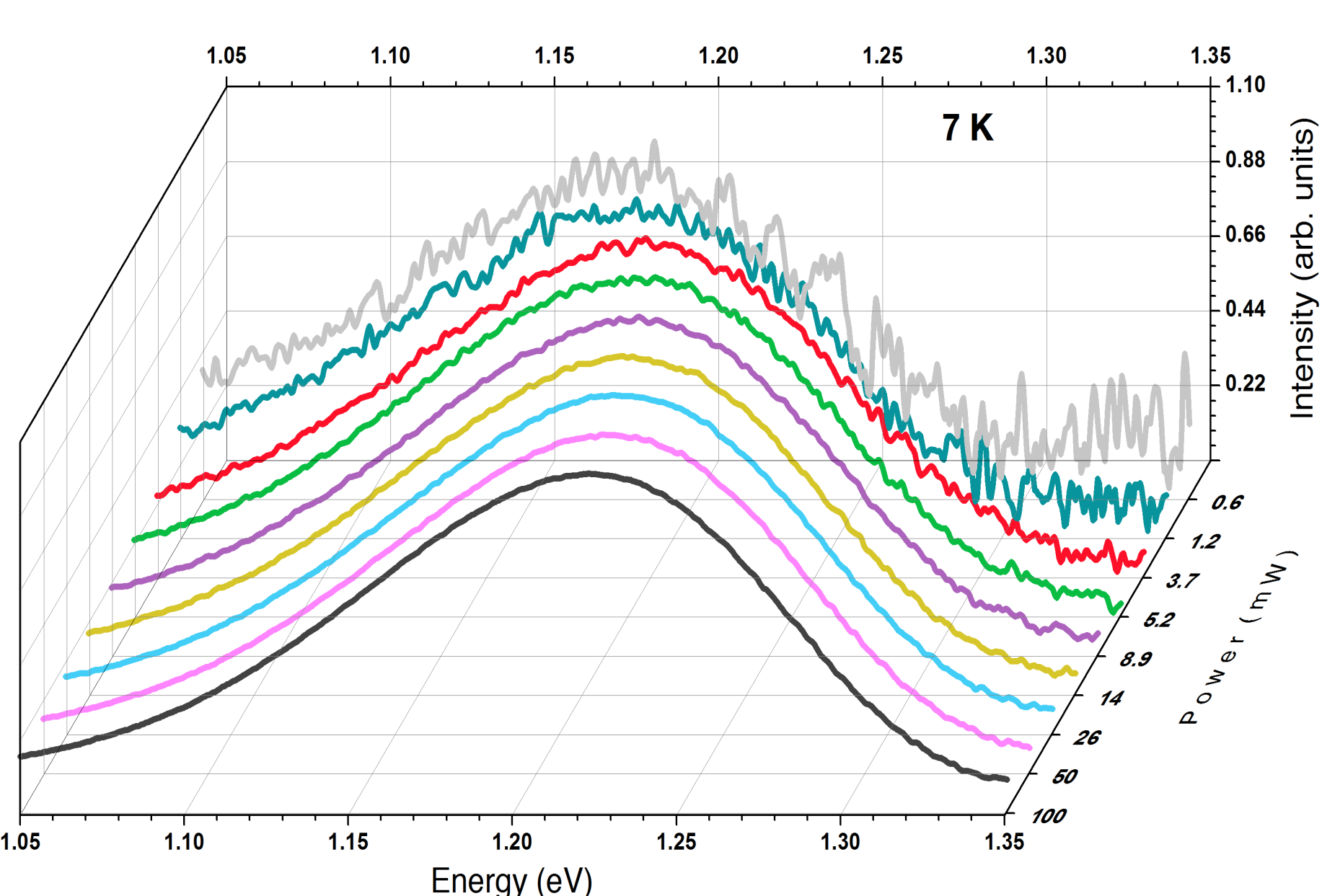
- Inhomogeneous distribution of charges.

Evidence for the existence of electrostatic fluctuations.

ELECTROSTATIC FLUCTUATIONS

PL Bruker IFS 66v FTIR spectrometer, Ge detector and excitation with Ar⁺ ion laser (514.5 nm)

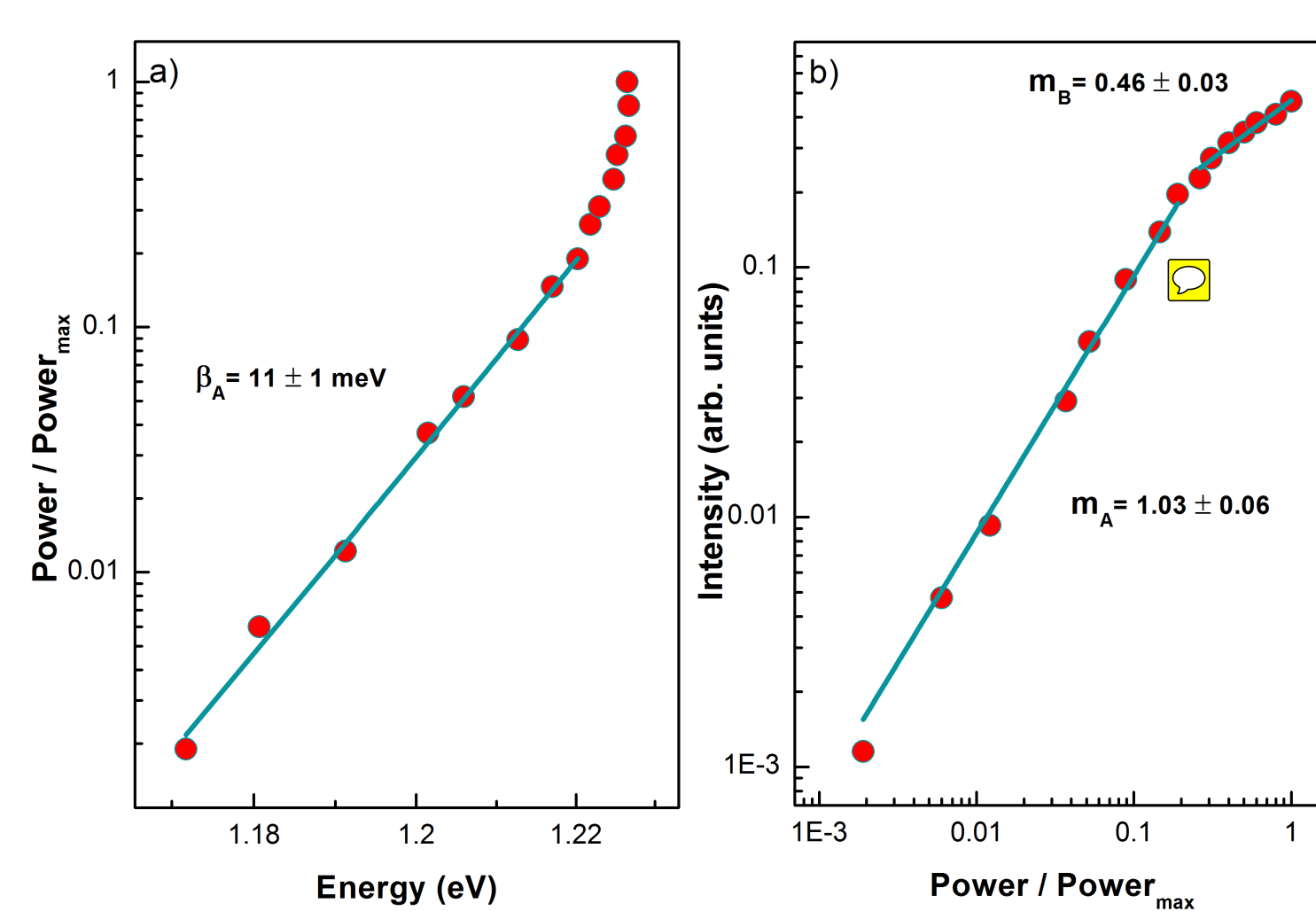
The discussion of the nature of the radiative transitions requires the study of the influence of temperature and excitation power on the PL.



- At lower temperatures the luminescence is dominated by an asymmetric band with peak energy (E) at 1.22 eV.

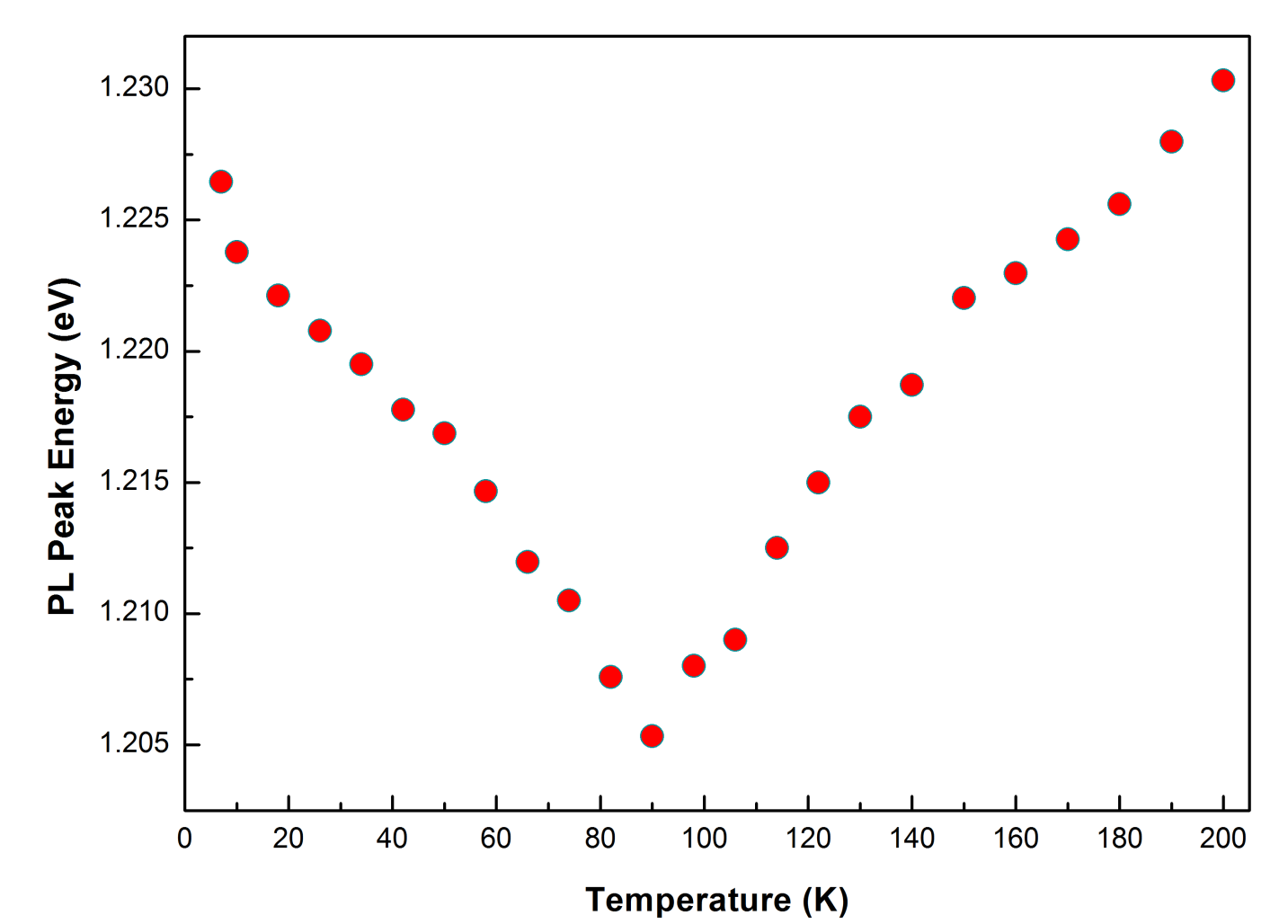
- The power excitation (P) was varied from 0.6 to 100 mW.

- With the increase of the excitation power:
 - slight increase of FWHM;
 - no significant change of the shape;
 - blue shift of the peak energy.



- The dependence on P of E was fitted with $I = I_0 \exp(E/\beta)$ [7].
- A value of 11 meV was estimated for β .
- The estimated value for β is typical for heavily doped and highly compensated materials.

- The dependence on P of the PL intensity (I) was fitted with $I \propto P^m$ [8].
- Two different regions were identified (A and B).
- In region of the lower excitation power values, the estimated suggest some localization degree of the charge carriers.



- The temperature (T) was varied from 7 to 200 K.

- Red shift of 21.1 meV for the range 7 < T < 98 K followed by a blue shift of 25.0 meV until 200 K.
- The temperature dependence of the E is ascribed to the influence of mainly of electrostatic potential fluctuations model [6].

The luminescence is dominated by an asymmetric band with peak energy at 1.22 eV. The excitation power and temperature dependencies can be explained just considering electrostatic potential fluctuations in both conduction and valence bands.

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