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Strain and Optoelectronic Tuning in Mixed Halide Perovskites

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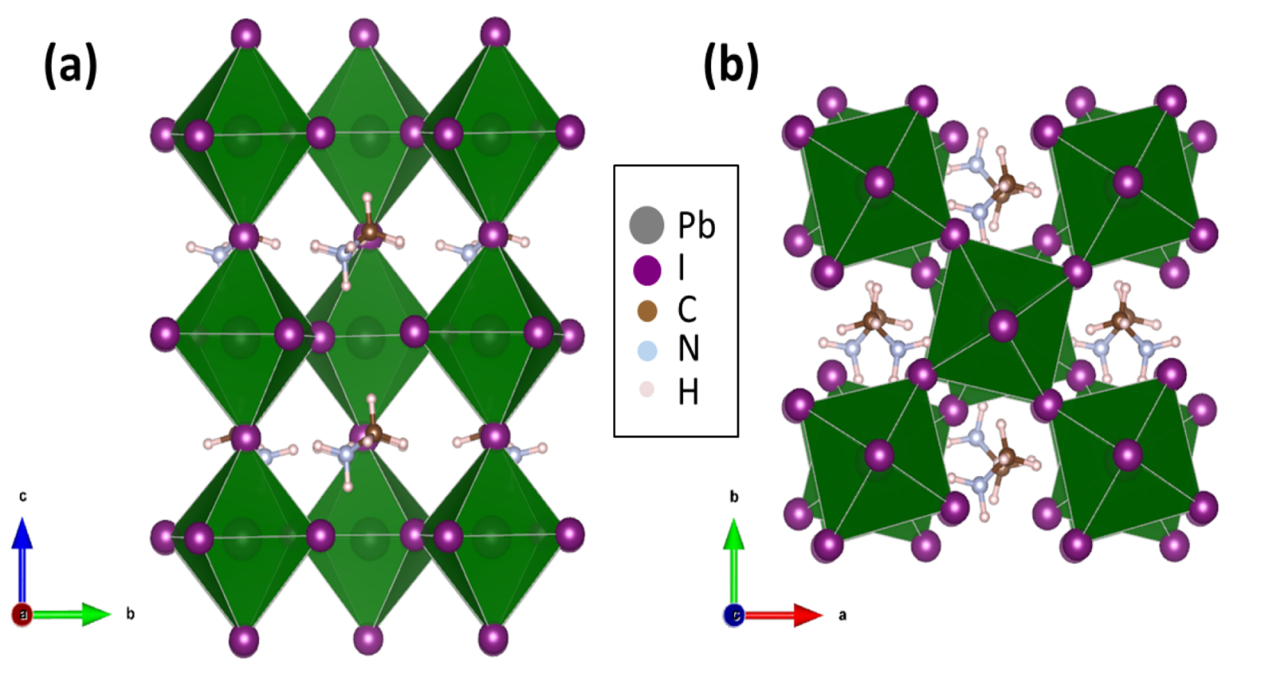
Objective: Defects in hybrid perovskite are actually a critical challenge in emerging hybrid perovskite materials to understand better the instabilities issue and to improve their opto-electronic properties. In this project, we address the key issue of such as, are point defects favorable to control materials' properties? Do structural defects play a role in the photo-induced phase separation (halide mobility, kinetics of phase separation)? [2-3] Therefore, we introduced on purpose different defect concentrations with 1 MeV proton ion irradiation into triple cation" (FA, MA, Cs) based $(MA_{0.83}\ FA_{0.17})_{0.95}Cs_{0.05}$ Pb $(I_{0.83}\ Br_{0.17})_3$ hybrid perovskite (TCMHP) films. The irradiation induced point defects affecting the residual strain in perovskite film and influence the excitonic dynamics (types and timescales) and optical emission and absorption properties [3, 4]. Study shows how we can learn about the role of defects and strain in these halide perovskites using time resolved and temperature dependent photoluminescence. The PL temperature dependence gives some insight into electron-phonon coupling mechanism and their modification with ion irradiation.

Hybrid perovskites



- ☐ High absorption coefficient
- ☐ Semi-conductor with direct band gap
- ☐ long carrier lifetimes (ms)
- ☐ long carrier diffusion lengths [1]

- ❖ Tetragonal phase at room temperature
- ❖ Cubic phase for T>330 K

Ion Irradiation

1 MeV Proton irradiation the ARAMIS facility at IJClab, Orsay.

- ❖ Beam size: ~ 1 mm, Current: below 2 μA.cm^{-2}

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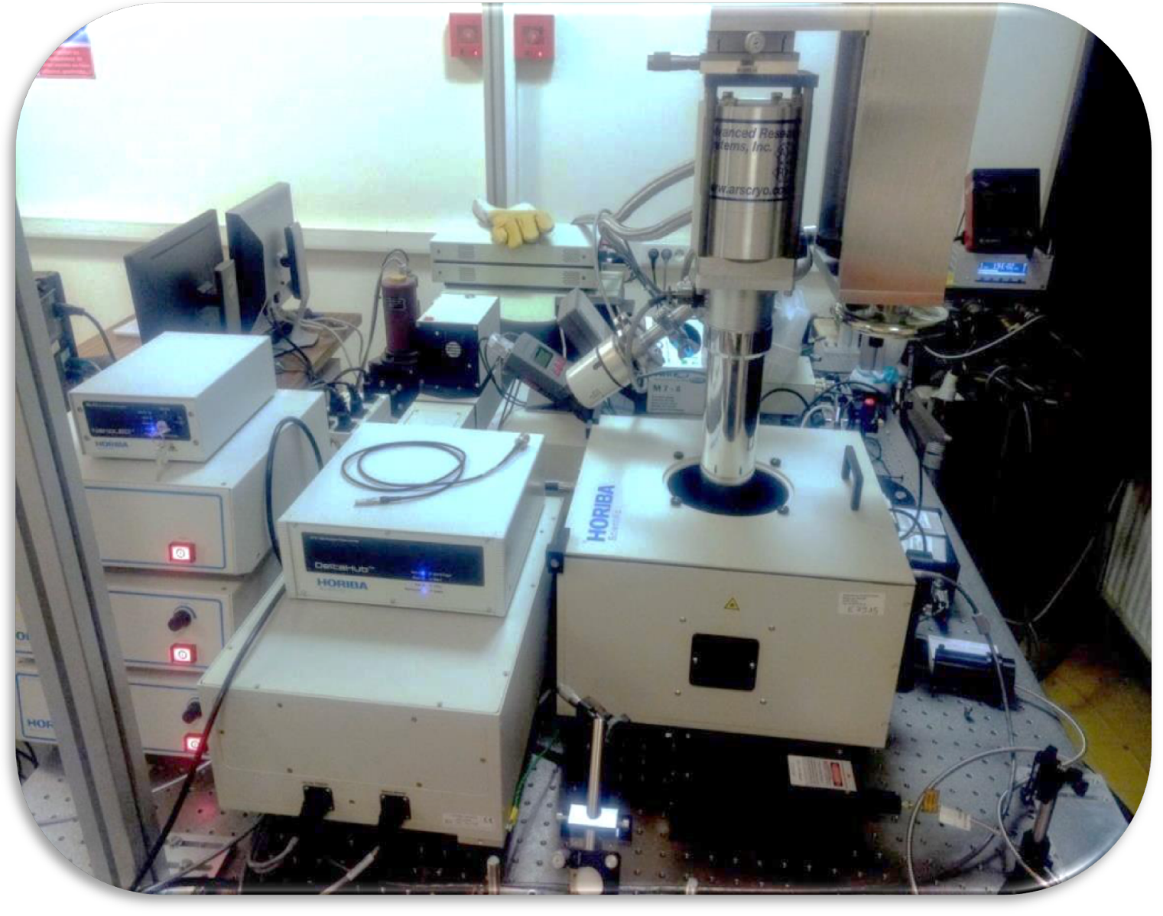
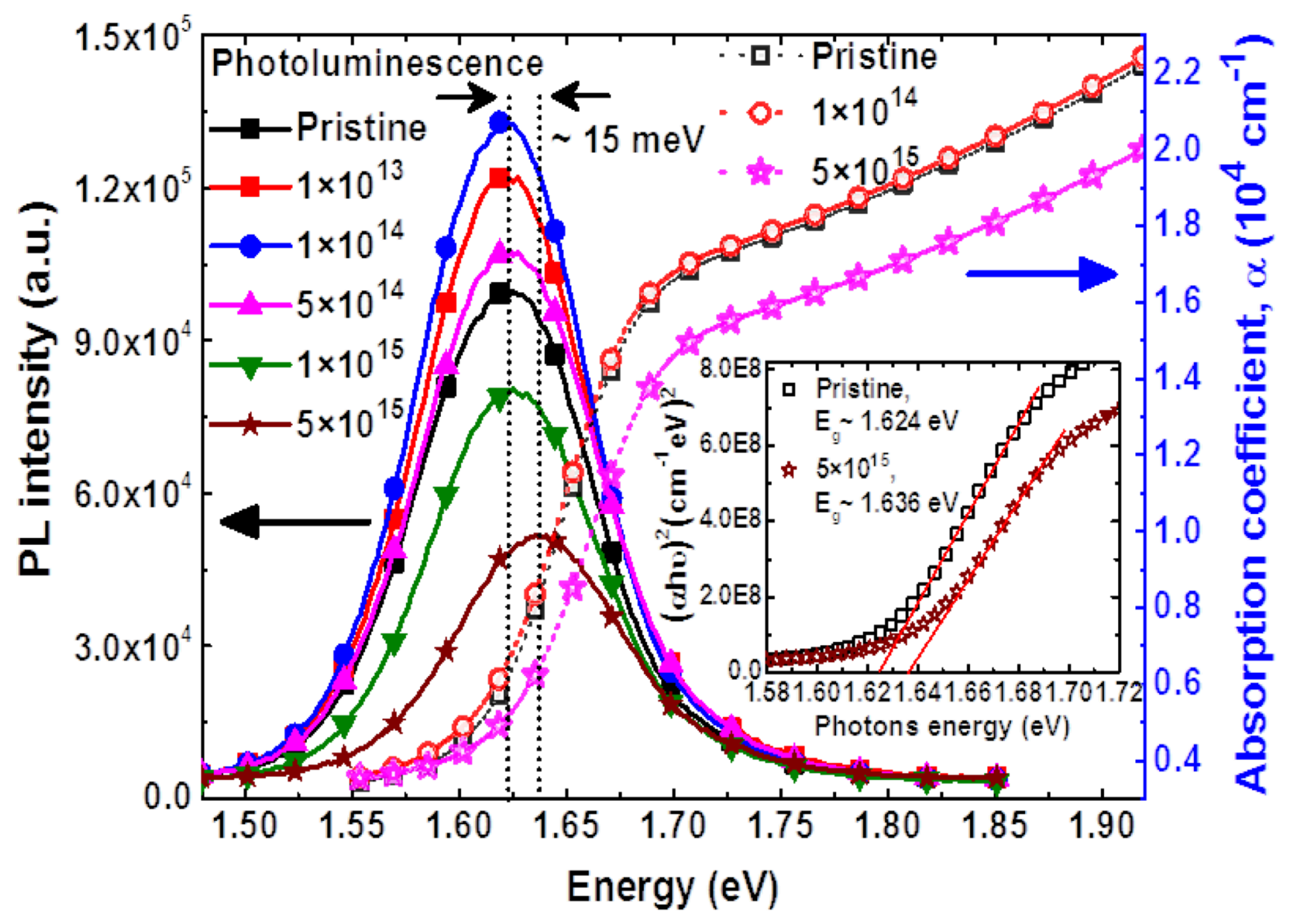
CNRS Installation 07/2018

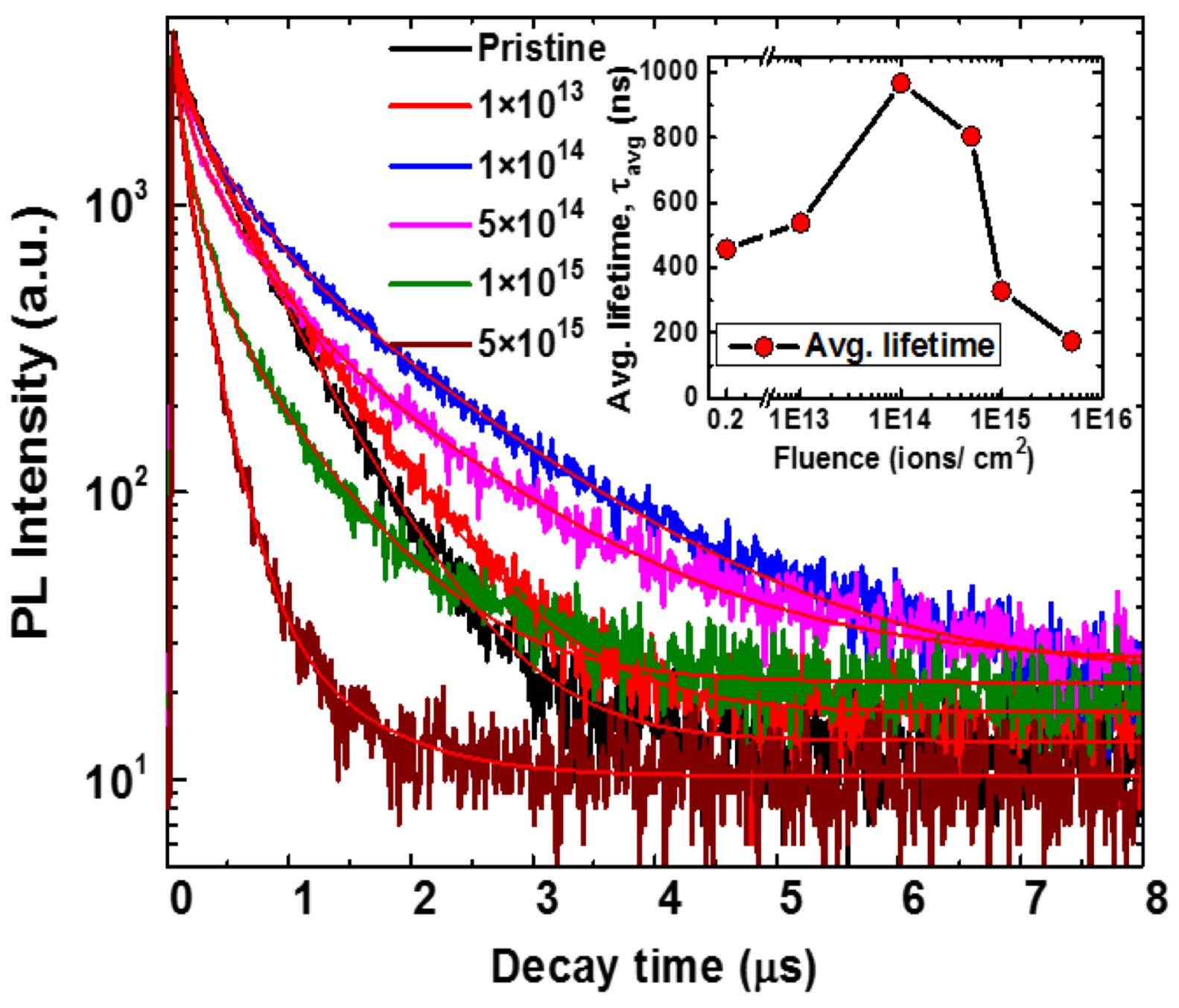


PL measurements

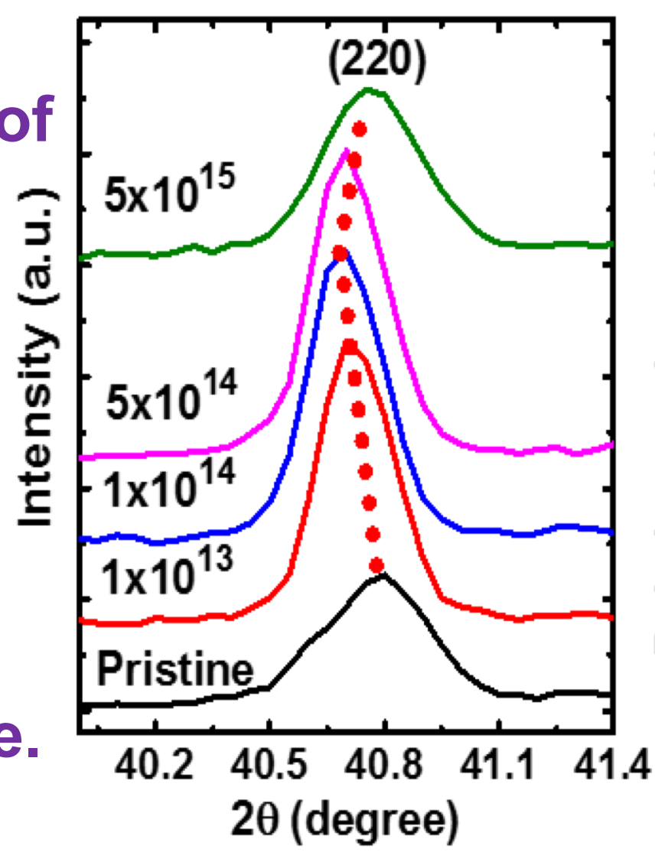
PL measurement: Reflection geometry at 45°
Excitation Laser: Argon laser (λ=488nm)
Spectrometer: TRIAX320 (Horiba-JY equipped with R928 photomultiplier (Hamamatsu)
TCSPC: Picoquant laser ~440 nm, max. freq. 100 MHz
Optical closed-cycle cryostat from ARS : T=10 K

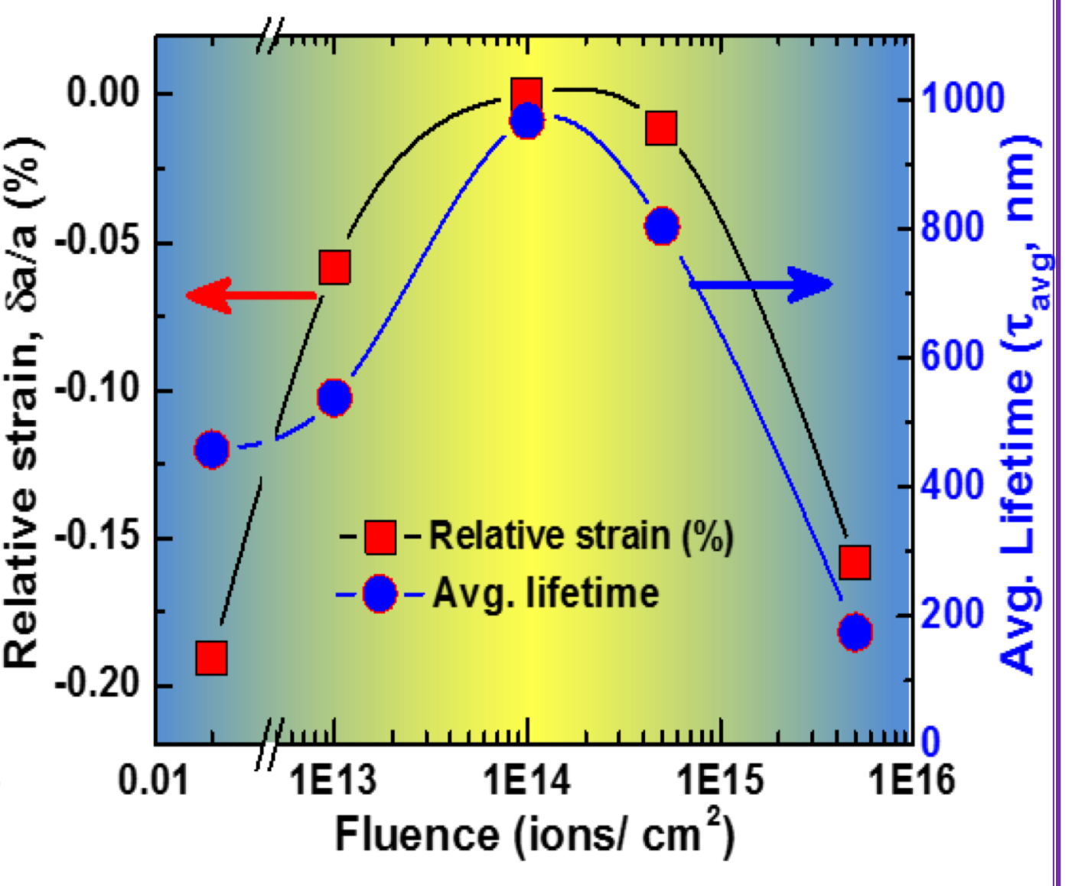
Optical absorbance and PL emission



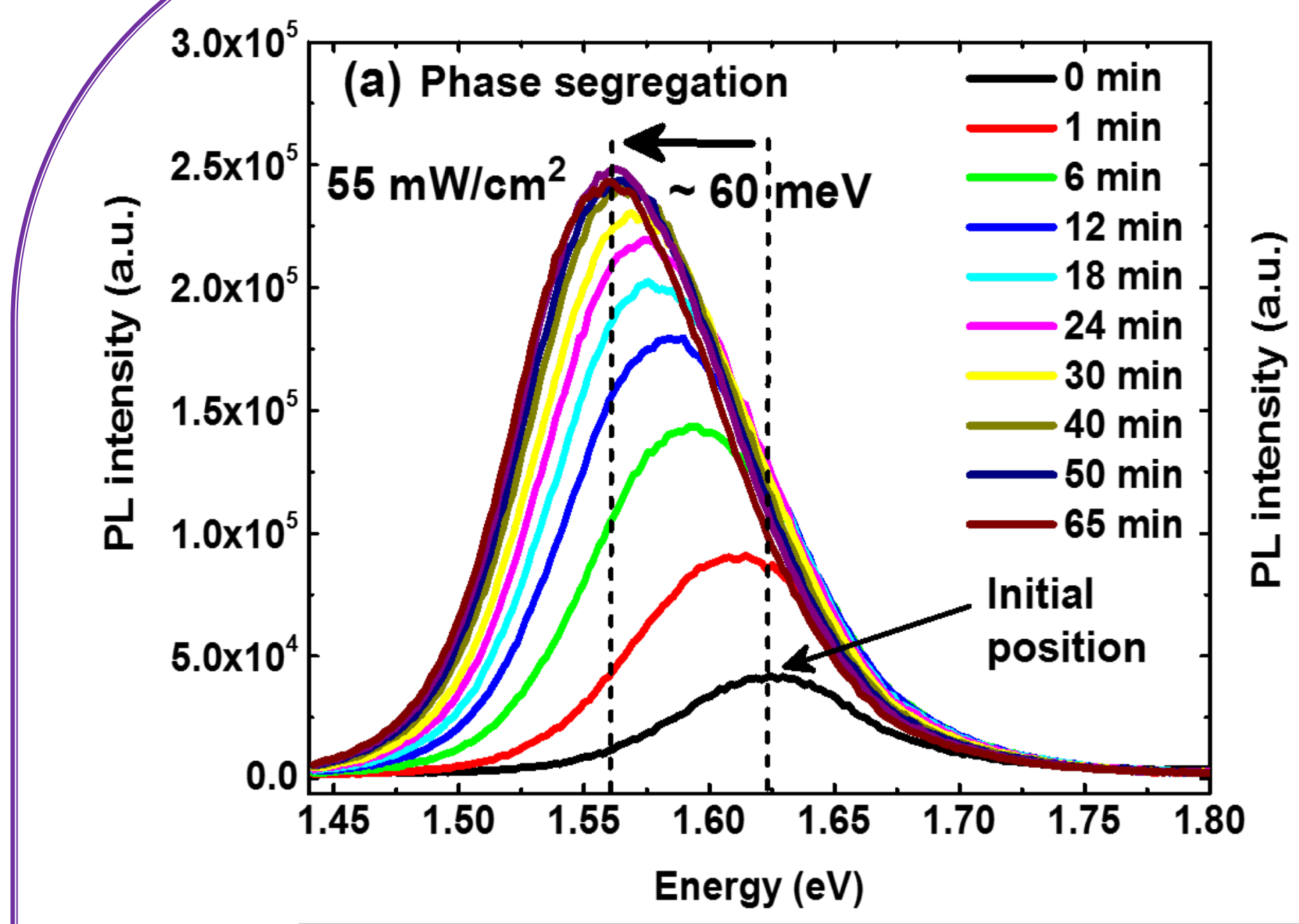


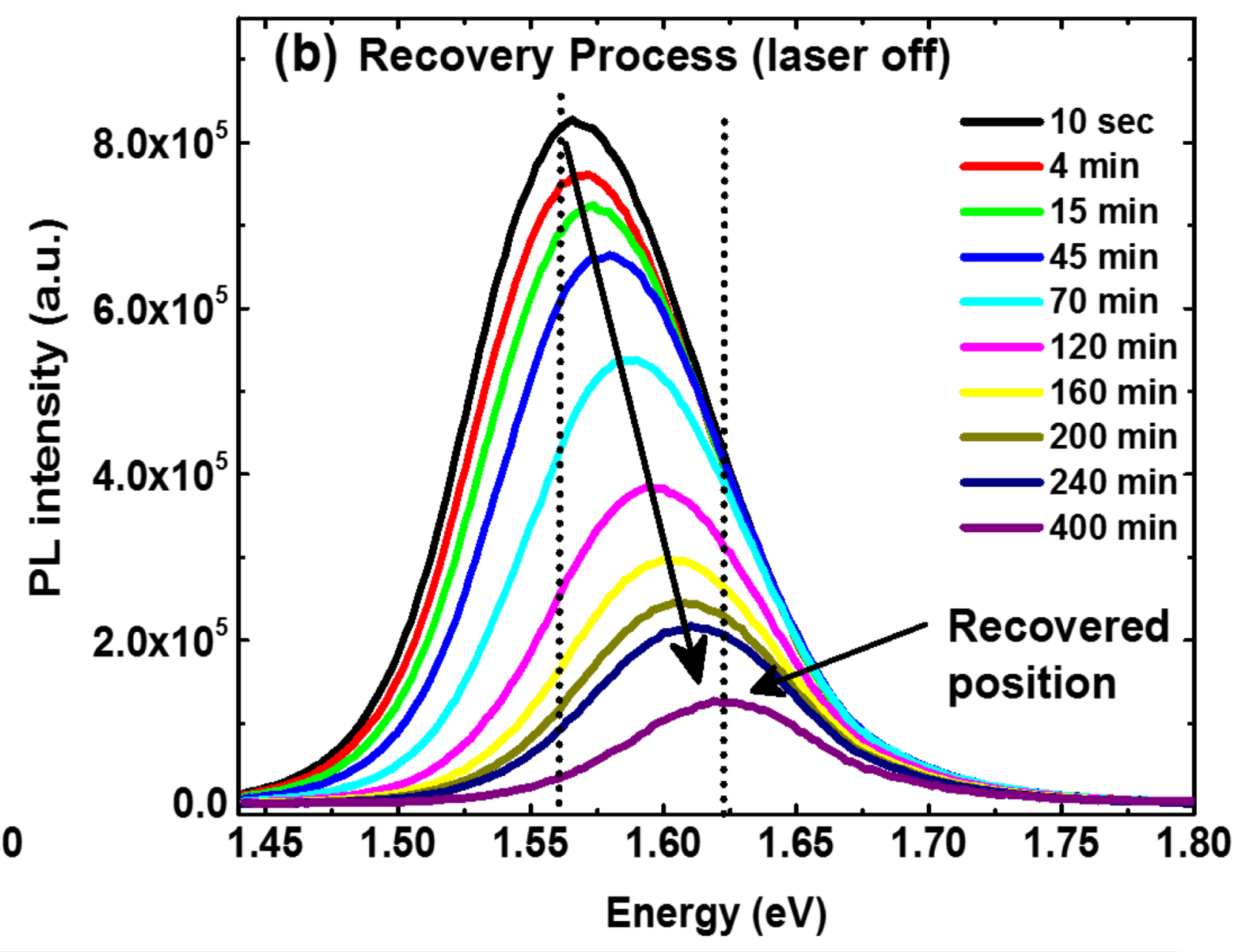
- ❖ Optical absorbance and PL emission spectra as a function of irradiation fluence.
- ❖ Lifetime change with irradiation fluence.
- ❖ Strain relaxation at moderate fluence and compressive strain formation at high fluence.
- ❖ Lifetime follow the strain behavior with irradiation fluence.

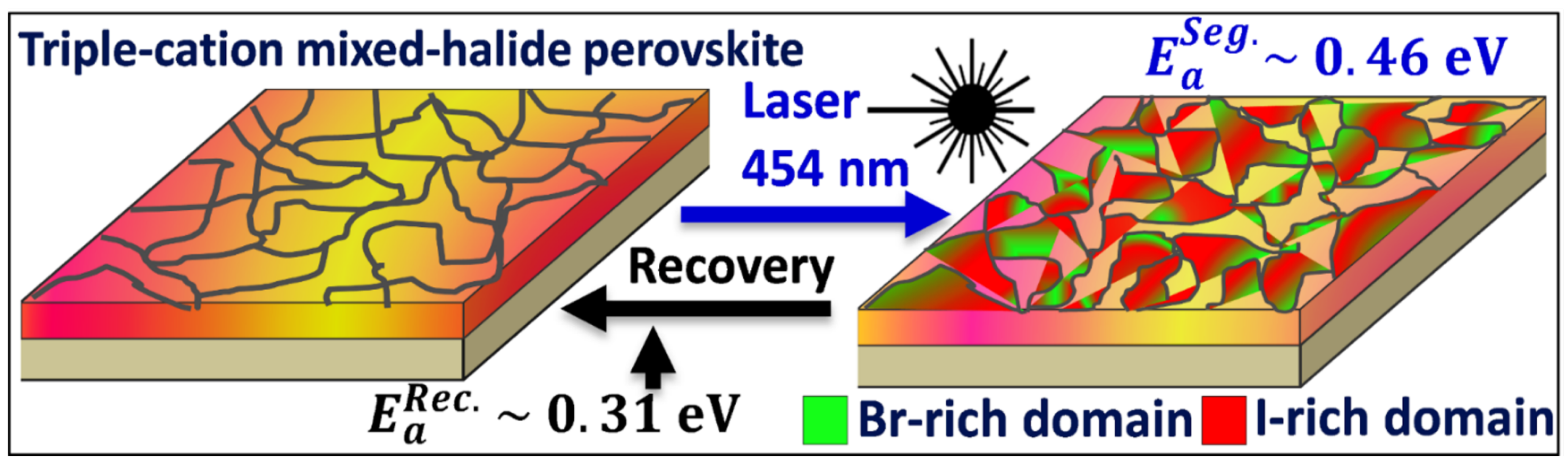




Photoluminescence and PL Decay







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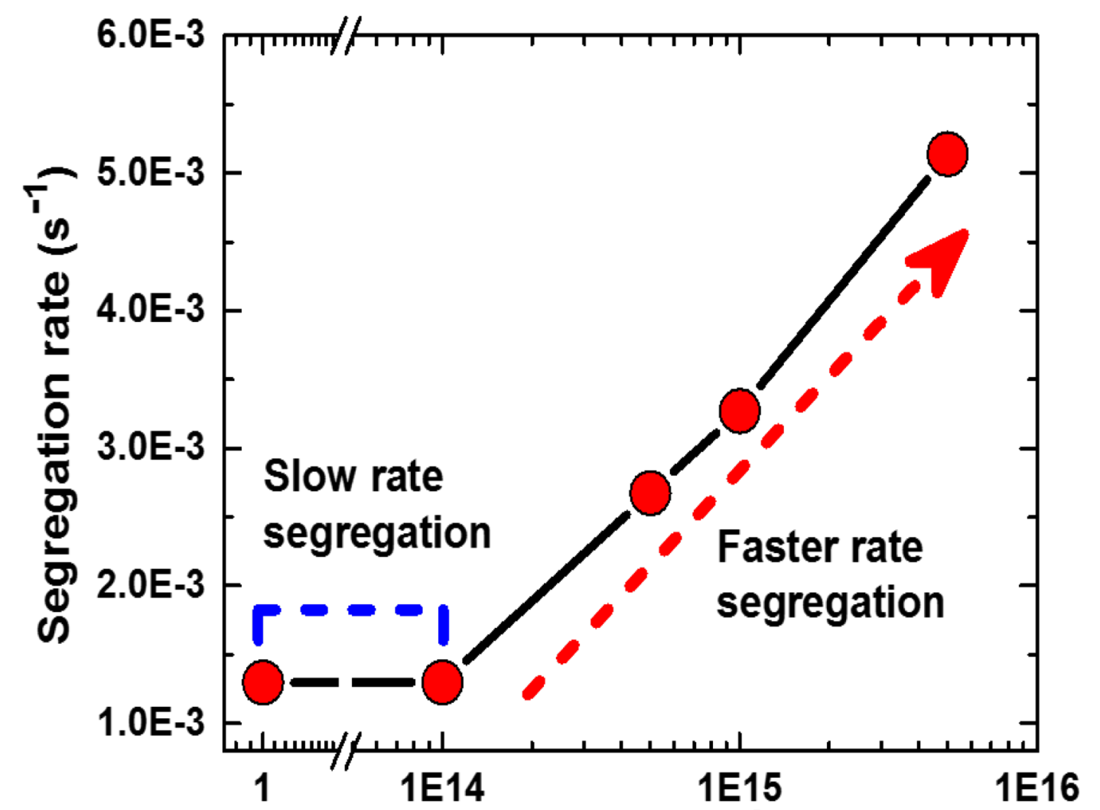
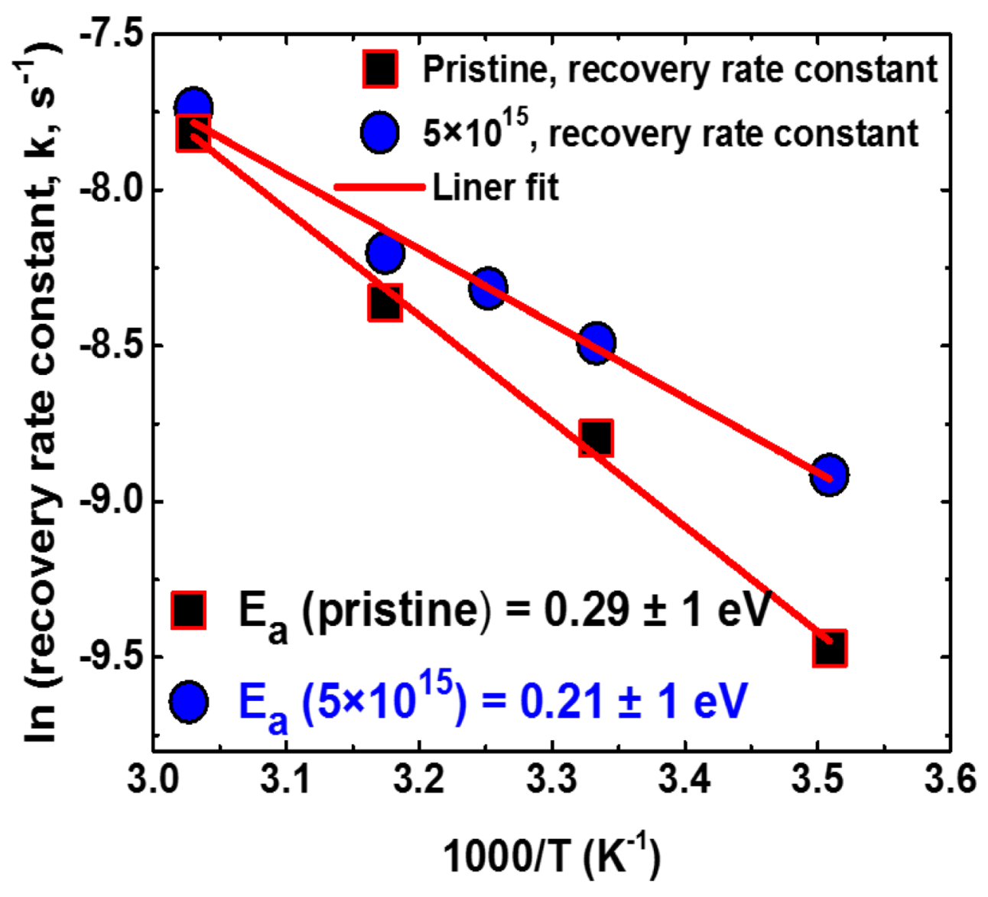




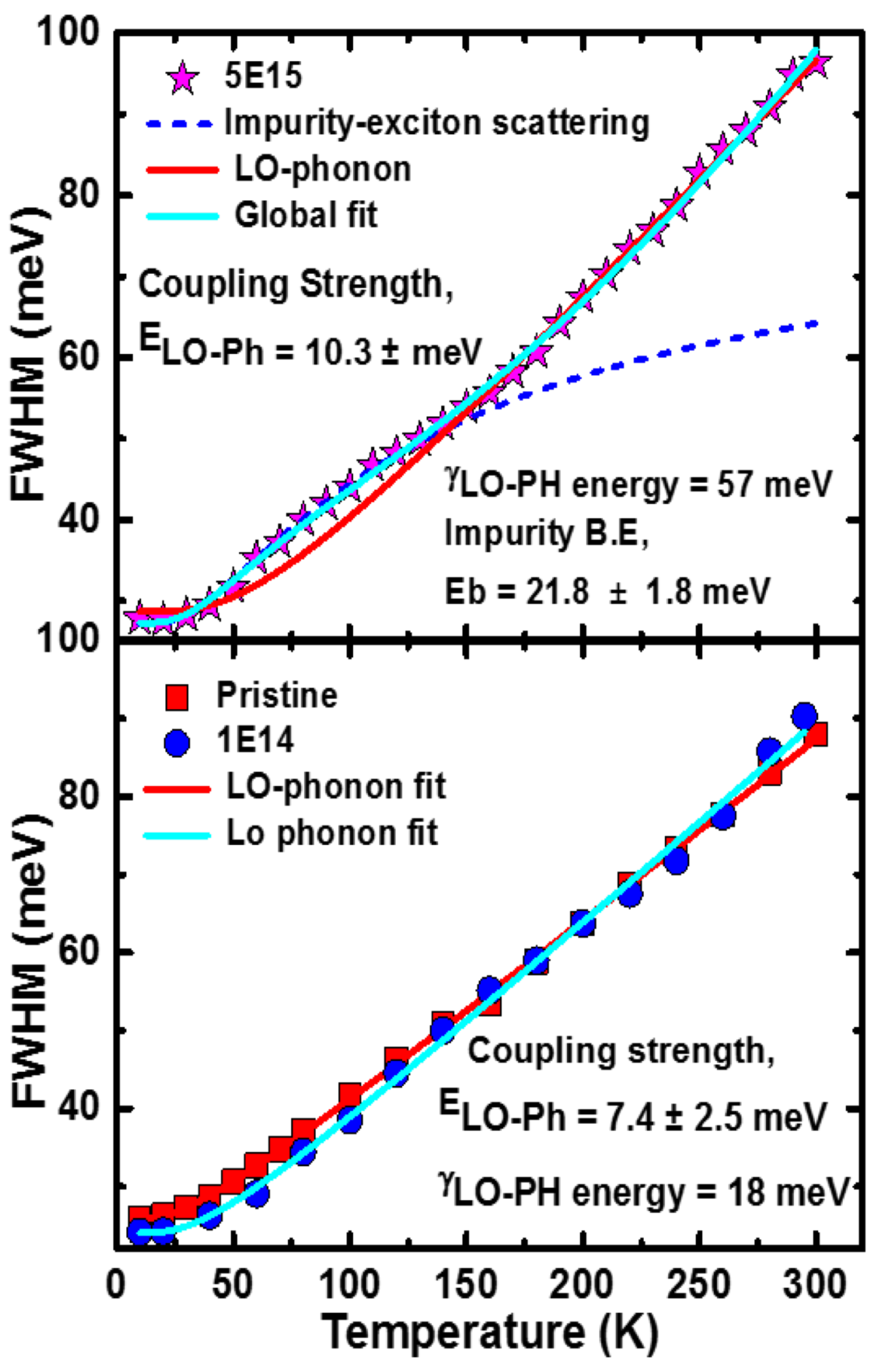
Temperature dependent Photoluminescence

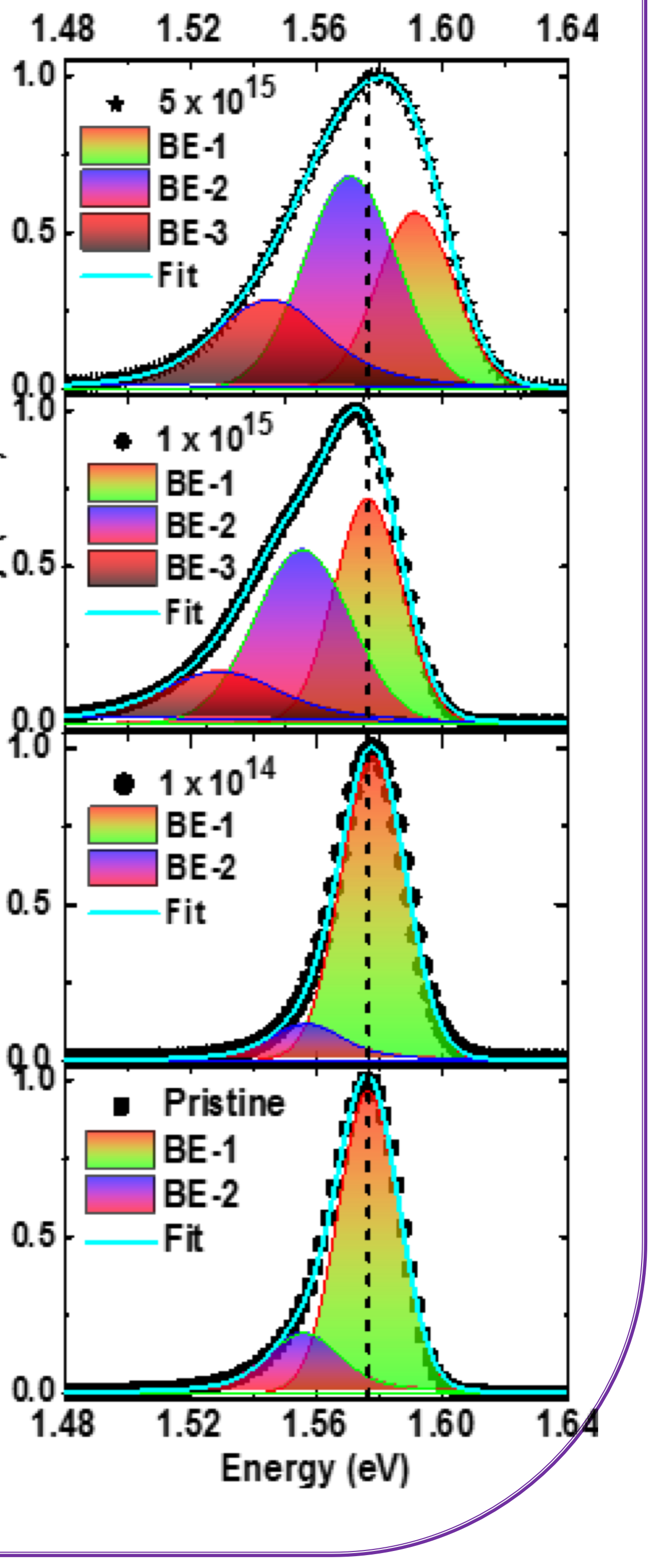
Temperature dependence of the PL spectra of different irradiated film at T=10 K.

- ❖ The irradiation defects are revealed with low temperature photoluminescence (PL) through bound exciton radiative recombination mechanisms.

- ❖ Temperature dependence PL linewidth gives some insight into electron-phonon coupling mechanism and their modification with ion irradiation.
- ❖ Segall's expression:

$$\Gamma = \Gamma_{inh} + \gamma_{ac}T + \frac{\gamma_{LO}}{exp(\hbar\omega_{LO}/k_B T)-1}$$





- ❖ Increase in defects mediated segregation rate with high proton irradiation fluence.
- ❖ Lowering in activation energy of halide migration in presence of high defect concentration.

Pending Issues: This work opens new possibilities for the use of defects engineering to understand the degradation pathways and residual strain role in optical properties of hybrid perovskite films. Study of Irradiation defects are useful for developing a new generation of metal halide absorbers materials with improved radiation stability to enable potential space applications.

Conclusion: We have studied the 1 MeV proton irradiation effect in triple cation based mixed halide perovskites film. The exciton lifetime improvement from about 400 ns to ~900 ns for a fluence of 10^{14} cm^{-2}. Higher irradiation fluence is shown to restore compressive strain and leads to sample degradation, with lower lifetimes values (200 ns). We observed that phase stability and activation energy of halide migration is correlated with residual lattice strain and defect concentration induced by proton irradiation.

References: [1] [Wolf et al., J. Phys. Chem. Lett .5 (2014) 1035], [2] D.A. Egger et al., Adv. Mat. 30 (2018) 1800691, [3] O. Plantevin, et al., *Phys. Status Solidi B* (2019) 1900199. [3] S.K. Gautam and O. Plantevin, et al., Adv. Funct. Mater. 2020, [4] Hui-Seon Kim et al, NPG Asia Material-12, (2020) 78

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