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Temperature-Dependent Amplified Spontaneous Emission Across Crystalline Phase Transitions in Solution-Processed $MAPbBr_3$ Thin Films

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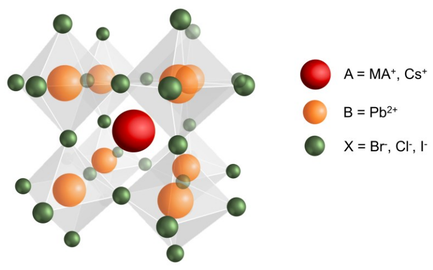
INTRODUCTION & AIM

Over the past decade, hybrid metal-halide perovskites have attracted great interest for optoelectronic and photonic applications due to their excellent light-emission properties—such as high photoluminescence quantum yield, optical gain, and amplified spontaneous emission—making them promising materials for LEDs, light-emitting transistors, and lasers.
Despite extensive studies, the fundamental photophysical mechanisms underlying ASE in these materials are still not fully understood.



This work aims to provide an in-depth analysis of the fundamental photophysical mechanisms governing amplified spontaneous emission (ASE) in $MAPbBr_3$ perovskite films. To this end, we carried out a comprehensive investigation of the temperature-dependent evolution of ASE and photoluminescence (PL) in a $MAPbBr_3$ thin film over the 20–300 K range, under both nanosecond-pulsed and continuous-wave (cw) excitation."

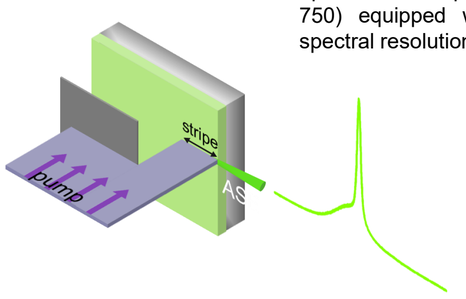
METHOD

Sample Fabrication

The MAPbBr3 film was synthesized from a solution prepared by dissolving MABr and $PbBr_2$ in a DMF:DMSO cosolvent and deposited by spin-coating onto a quartz substrate.

Absorption, Photoluminescence and Amplified Spontaneous Emission

ASE properties have been explored by pumping the film with a LBT MNL100 Nitrogen laser @ 337 nm (3 ns pulses, 10 Hz).
To compare the ASE properties with the characteristic photoluminescence, **PL experiments** have been performed at low energy density by exciting the sample with a cw solid state laser, @ 405 nm, with a power of 1 mW.



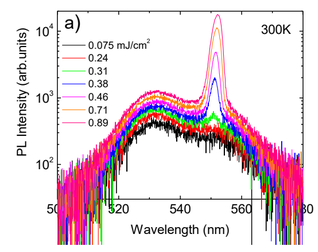
All the measurements were performed by collecting the signal, in waveguide configuration, from the edge of the film irradiated with the beam focused in a rectangular stripe (4 mm × 80 μm). The emission was acquired by means of an optical fiber coupled to a spectrometer (ACTON SpectraPro-750) equipped with a Peltier cooled-CCD (Andor). The spectral resolution was about 0.5 nm.

The measurements have been performed in vacuum (at about 10^{-2} mbar), from 300 K down to 20 K in steps of 20 K, by using a closed cycle He cryostat.

UV−Vis absorption spectrum was acquired by using a spectrophotometer (PerkinElmer Inc., Waltham, MA, USA, model UV−Vis Lambda 900).

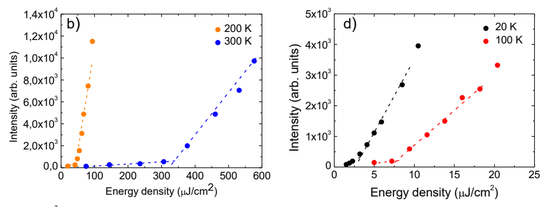
RESULTS

Amplified Spontaneous Emission



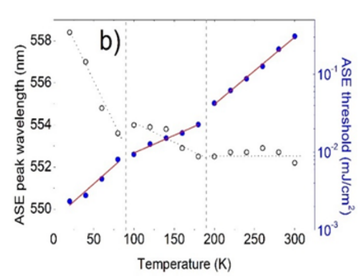
PL spectra vs the excitation density at 300 K

The PL spectra at 300 K show the appearance of the ASE peak for increasing excitation density.
Similar results are obtained at lower temperatures with the corresponding ASE threshold decreasing with temperature (from 300 μJ/cm² down to 43 μJ/cm², 9.4 μJ/cm² and 2.3 μJ/cm², for T = 200 K, 100 K, and 20 K, respectively.



Excitation density dependence of the emission intensity at the ASE peak wavelength

Below ASE threshold the peak at 530 nm is ascribed to **Free Exciton (FE)** emission, while the broad peak at 544 nm to **Bound Excitons (BE)**

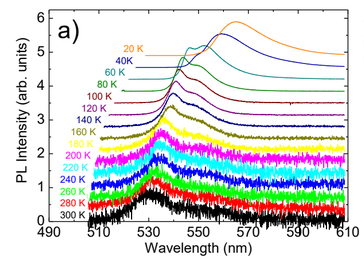


Temperature dependence of the ASE peak wavelength and ASE threshold

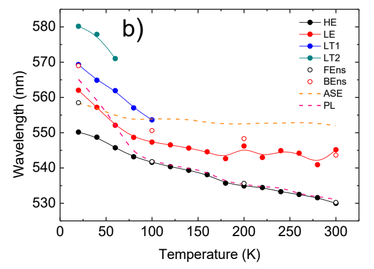
A gradual shift of the ASE peak as a function of temperature is observed, indicating the occurrence of three distinct emission regimes, with transition points around 190 K and 90 K.

Likewise, the temperature dependence of the ASE threshold exhibits a progressive exponential decrease upon cooling, with slope discontinuities again at 190 K and 90 K.

Photoluminescence and comparison with ASE



PL spectra as a function of the temperature under continuous wave pumping



Peak wavelength vs temperature of all the peaks contributing to emission spectra.

In the range from RT to 120 K, the cw-PL spectra are well fitted by two Gaussian peaks (**HE- high energy and LE- low energy**), with a peak position and linewidth comparable to the ones observed for FE and BE emission under nanosecond pumping below threshold.
The line-shape variation observed below 100 K is due to the appearance of a third peak (**LT1** between 100 K and 80 K) and of a fourth peak (**LT2** between 60 K and 20 K).

DISCUSSION

Under both nanosecond and continuous excitation, the spontaneous emission reveals contributions from free excitons (FE), bound excitons (BE), and trap states, with their relative prominence varying with temperature and excitation conditions.The difference between the emitting states observed under nanosecond and cw pumping can be ascribed to the different excitation regime .
Anyway, both the ASE and the cw-PL temperature dependence demonstrate that three different emission regions are present, with transition temperatures at about 190 K and 90 K related to the **orthorhombic-tetragonal and tetragonal-cubic phase transitions,.**

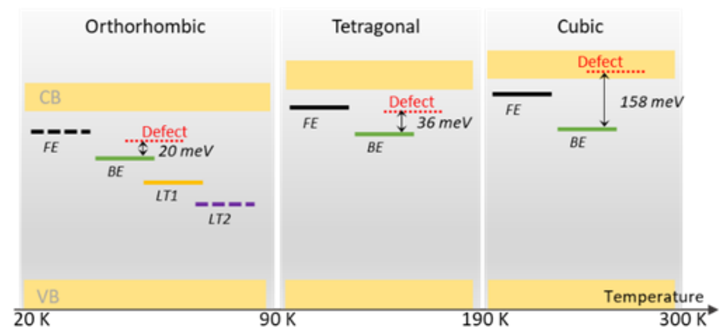
The ASE temperature dependence is quantitatively investigated by modelling the sample as a three levels laser system. The progressive PL intensity increase as the temperature decreases is the typical signature of the presence of a thermally activated non radiative processes, described by:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{0nr}} e^{-\frac{E_a}{kT}}$$

where E_a is the activation energy of non radiative process

Moreover, also ASE threshold temperature dependence is demonstrated to be due to the thermal activation of a non radiative process, as the temperature increase, whatever is the crystalline phase of $MAPbBr_3$.

A reasonable scheme of the energy levels as a function of the temperature is depicted alongside



CONCLUSION

- The film spontaneous emission under nanosecond and continuous wave pumping shows the **interplay of emission of Free Excitons (FE), Bound Excitons (BE), and trap states** (visible only below 100 K), with relative contributions depending not only on the temperature, but also on the excitation regime.
- ASE threshold is strongly temperature dependent, due to the thermal **activation of non-radiative processes**.
- The ASE temperature dependence shows clear discontinuities around 90 K and 190 K, related to the **orthorhombic-tetragonal** and **tetragonal-cubic phase** transitions leading to different activation energies and coupling rates of the non-radiative process.
- **ASE comes from BE** in the whole temperature range and, among the three phases, the orthorhombic one shows the intrinsically best ASE properties, with the lowest ASE values and the smallest temperature dependence.

FUTURE WORK

The results, beyond providing a detailed understanding of the basic optical properties of $MAPbBr_3$ thin films, evidence a strong dependence of the intrinsic ASE properties on the crystalline phase, suggesting that a proper control of the crystalline phase showing gain at room temperature can provide a powerful way to optimize the ASE and lasing properties of hybrid lead halide perovskites.