THE RECOMBINATION MECHANISM AND TRUE GREEN AMPLIFIED SPONTANEOUS EMISSION IN CH$_3$NH$_3$PbBr$_3$ PEROVSKITE

Thesis by
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ABSTRACT

The recombination mechanism and true green amplified spontaneous emission in CH₃NH₃PbBr₃ perovskite

Davide Priante

True-green wavelength emitters at 555 nm are currently dominated by III-V semiconductor-based inorganic materials. Nevertheless, due to high lattice- and thermal-mismatch, the overall power efficiency in this range tends to decline for high current density showing the so-called efficiency droop in the green region (“green gap”). In order to fill the research green gap, this thesis examines the low cost solution-processability of organometal halide perovskites, which presents a unique opportunity for light-emitting devices in the green-yellow region owing to their superior photophysical properties such as high photoluminescence quantum efficiency, small capture cross section of defect states as well as optical bandgap tunability across the visible light regime.

Specifically, the mechanisms of radiative recombination in a CH₃NH₃PbBr₃ hybrid perovskite material were investigated using low-temperature, power-dependent (77 K), temperature-dependent photoluminescence (PL) measurements. We noted three recombination peaks at 77K, one of which originated from bulk defect states, and another two from surface defect states. The latter were identified as bound-excitonic (BE) radiative transitions related to particle size inhomogeneity or grain size induced surface...
state in the sample. Both transitions led to PL spectra broadening as a result of concurrent blue- and red-shifts of these excitonic peaks. The blue-shift is most likely due to the Burstein-Moss (band filling) effect. Interestingly, the red-shift of the second excitonic peak becomes pronounced with increasing temperature leading to a true-green wavelength of 553 nm for CH$_3$NH$_3$PbBr$_3$. On the other hand, red-shifted peak originates from the strong absorption in the second excitonic peak owed to the high density of surface states and carrier filling of these states due to the excitation from the first excitonic recombination.

We also achieved amplified spontaneous emission around excitation threshold energy of 350 $\mu$J/cm$^2$ when optically pumped using 475 nm laser pulses, thus supporting the assignment of carrier absorption and re-excitation mentioned above.
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<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>MAPbBr$_3$</td>
<td>CH$_3$NH$_3$PbBr$_3$</td>
</tr>
<tr>
<td>MAPbI$_3$</td>
<td>CH$_3$NH$_3$PbI$_3$</td>
</tr>
<tr>
<td>MAPbI$_{3-x}$Cl$_x$</td>
<td>CH$_3$NH$<em>3$PbI$</em>{3-x}$Cl$_x$</td>
</tr>
<tr>
<td>MAPbBrI$_3$</td>
<td>CH$_3$NH$_3$PbBrI$_3$</td>
</tr>
<tr>
<td>CB derived</td>
<td>Conduction band derived states</td>
</tr>
<tr>
<td>VB derived</td>
<td>Valence band derived states</td>
</tr>
<tr>
<td>E$_F$</td>
<td>Fermi level</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full with at half maximum</td>
</tr>
<tr>
<td>SE</td>
<td>Spontaneous emission</td>
</tr>
<tr>
<td>ASE</td>
<td>Amplified spontaneous emission</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>TDPL</td>
<td>Temperature-dependent photoluminescence</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>CCT</td>
<td>Correlated color temperature</td>
</tr>
<tr>
<td>CRI</td>
<td>Color rendering index</td>
</tr>
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1. Introduction

1.1 – Perovskite, a new challenging material for light emitting devices

The term Perovskite comes from the Russian mineralogist Lev Aleksevich von Perovski even though the compound (CaTiO$_3$) was discovered in 1839 by the German Gustav Rose. Properties such as high conductivity$^{1,2}$, high carrier mobility$^3$ and ferroelectricity$^{4,5}$ in these oxides, should have attracted great attention in terms of absorbing/emitting device fabrication, however they started receiving consideration only when layered organometal-based halide perovskite were first demonstrated to exhibit a semiconductor-to-metal transition with increasing dimensionality. For the present interest, the A cation represents the methylammonium (CH$_3$NH$_3^+$) ion, B represents lead (Pb) and X is the halogen (I, Cl, Br and also mixture are frequently used).

Organic-inorganic halide perovskites emerged first in the photovoltaic field as they have been demonstrating quick efficiency boost in just few years. High efficiency is not the only factor that revolutionized solar cells; flexibility in material growth as well as architectures plays an important role in this emerging material. Recently, researchers started to focus also on perovskite-based light emitting devices and many studies have been performed thanks to the discovery of interesting optoelectronic properties.$^6,7$ These compounds naturally form quantum well structures$^8$ in which the barrier correspond to the organic layer, having a larger bandgap, and the well to the inorganic part. Hence, remarkable optical properties have been demonstrated.$^9,10,11,12$ For example, photoluminescence can be tuned from blue, green to ultraviolet varying the
halogen ion, I, Br, Cl respectively.\textsuperscript{13} Table 1 summarizes the main optical characteristics of such perovskites. The strong photoluminescence observation owned to electron-hole recombination comes from the large exciton binding energy caused by the alternating of inorganic-organic parts as well as dielectric confinement effect. This enhancement of the Coulomb interaction comes from reduction on the screening phenomena for the carriers due to the smaller dielectric contestant\textsuperscript{8}.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bandgap (eV)</th>
<th>Structure at RT</th>
<th>Carrier diffusion length</th>
<th>CB (eV)</th>
<th>VB (eV)</th>
</tr>
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<tbody>
<tr>
<td>MAPbBr\textsubscript{3}</td>
<td>2.32\textsuperscript{14}</td>
<td>Cubic</td>
<td>&gt; 10 μm\textsuperscript{15}</td>
<td>-3.36</td>
<td>-5.58</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3}</td>
<td>1.5–1.61\textsuperscript{16}</td>
<td>Tetragonal</td>
<td>&gt; 8 μm\textsuperscript{15}</td>
<td>-3.93</td>
<td>-5.3</td>
</tr>
<tr>
<td>MAPbCl\textsubscript{3}</td>
<td>3.1\textsuperscript{10}</td>
<td>Cubic</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3-x}Cl\textsubscript{x}</td>
<td>1.55–1.64\textsuperscript{17}</td>
<td>Tetragonal</td>
<td>&gt; 1.9 μm\textsuperscript{18}</td>
<td>-3.75</td>
<td>-5.43</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3-x}Br\textsubscript{x}</td>
<td>1.5–2.32\textsuperscript{19}</td>
<td>Tetragonal/cubic, turnover x ~ 0.2</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Since the strong light emission, perovskite-based materials have attracted much attention and important progresses have followed the first demonstration of amplified spontaneous emission (ASE)\textsuperscript{7} in such materials leading to state-of-the-art single crystals\textsuperscript{15, 20} , microdisks\textsuperscript{21} and nanowires lasers\textsuperscript{22}. Furthermore, studies on the physics behind this compound have attracted the attention of many scientists that seized the opportunity of having a new field to explore. Electron-hole diffusion lengths\textsuperscript{23, 24} , carrier
recombination\textsuperscript{25,26,27}, carrier lifetimes\textsuperscript{28} and quantum confinements\textsuperscript{29} are just few of the multiple aspects of the still not well-known perovskite area.

![Figure 1](image.png)

\textbf{Figure 1.} External and internal quantum efficiency versus peak wavelength showing the efficiency droop in the green gap\textsuperscript{30}.

To date, most of light emitters are dominated by III-V / II-VI semiconductor-based inorganic materials thanks to their abundance and well known technology. Nevertheless, drawbacks such as relatively high price and material flaws that lower the applicability are still present. For instance, high lattice- and thermal-mismatch as well as Auger recombination in such material-based light emitting diodes tend to decline the overall power efficiency for high current density showing the so-called efficiency droop in the
blue-green region (Fig. 2), a well-known problem that affects both external and internal quantum efficiency (IQE).

IQE is the ratio between the number of photon emitted per unit time and the number of carriers injected per unit time and can be considered as

\[
IQE = \frac{Bn^2}{An + Bn^2 + Cn^3 + k(n - n_0)^m + \frac{I_{LK}}{qV_{QW}}}
\]

where \( An \) is Shockley-Read-Hall rate, \( Bn^2 \) is the radiative recombination rate, \( Cn^3 \) is Auger recombination rate, \( k(n - n_0)^m \) is the non-radiative mechanism loss related to delocalization of carriers (\( n_0 \) is the threshold carrier density that gives delocalization and \( k \) is a constant), \( m \geq 2 \). \( I_{LK} \) is electron leakage current, \( q \) is the elementary charge and \( V_{QW} \) is the volume of the active region. Hence the numerator corresponds to the number of photons emitted and the dominator to the number of photons injected. The ideal case occurs when all the injected carriers are converted into light so that IQE = 1. A representation of the electron flow in a standard quantum well structure is shown in Fig. 3.
As mentioned before, Auger recombination and Shockely-Read-Hall recombination are some of the principal causes of the efficiency droop but these internal non-radiative recombination processes are not the only ones. For example, some of the carriers survive the recombination in the active region but they leak from it so that no radiative recombination occurs as those appear as lost electrons. Several other mechanisms influence the IQE of the active region such as polarization charges, wells asymmetry, electron overfly and defect-assisted tunnelling (Fig. 4).

Hence organic-inorganic halide perovskite, thanks to its low cost and simple solution process may be the key to solve these issues and to realize a new era based on solid-state organic-inorganic light emitting devices.
1.2 – Structure and impurities in organometal halide perovskite

1.2.1 – Basic perovskite structure
Perovskite refers to the class of compound having the same formula of calcium titanate, more in general ABX₃ where A and B represent two cations with different dimensions and X represents the anion. In Figure 1 is shown the octahedral perovskite structure where 6 X anions, at the face centered positions, lie around the B atom (body center position). Therefore, any materials with the same crystal structure of CaTiO₃ have, by definition, a perovskite structure. The A atom can be Ca, Na, K, Cs whereas B atom can be Sn, Ti, Sr, Si etc.
As mentioned briefly above, the perovskite structure is rather simple forming the ABX$_3$ octahedra. Ideal cubic cells are generally formed of A ions sitting at the corners of the cube, at $(0, 0, 0)$ position, B ions at the body centers, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ position, and X ions at the face centers, $(\frac{1}{2}, \frac{1}{2}, 0)$ position. Different distortion mechanisms have been studied and have been identified as principal causes of properties variation in these oxides compounds$^{31,32}$, such as:
- BX$_3$ octahedron distortion
- B ions off-center displacement
- Octahedron framework tilting
- Vacancies or A, B, X ion ordering in the octahedron

However, an ideal structure with a group cubic space $Pm3m$, shows the ions perfectly packed with a relationship of their ionic radii following the formula:

$$r_A + r_X = \sqrt{2} (r_B + r_X)$$

where $r$ is the radius of ion A, B and X.
Considering the organic-inorganic perovskite, we said that the A is an organic ion but, due to the space available in the cubic cell, only small ions can fit inside the 3D structure. Usually A ions are formed of three C-C or C-N bonds and the most used one is CH$_3$NH$_3$. For lower dimensionality (2D) the structure can be seen as a 3D one cut along the <100> or <110> plane into a single layer-thick and A and X ions are split into halves. The 2D structure is then formed substituting the organic ions and the inorganic molecules are embedded within the organic ones. The resulting structure can be represented by the formula (R-NH$_3$)$_3$BX$_3$ where (R-NH$_3^+$) is the ammonium cation (in our case R = CH$_3$), B the metal ion and X the halogen. In Figure 4 is shown the octahedral perovskite structure.

1.2.2 – **Intrinsic defects in perovskite materials**

One of the most significant properties of organometal halide perovskite compounds is the long lifetime and carrier diffusion length that attracted attention for solar cell technologies notwithstanding its defective nature mostly due to unintentionally doping, i.e. intrinsic defects.$^{33,34}$

One of the methods to analyze these impurities is to use the density functional theory (DFT) that helps on describing the electronic structures of many systems through a quantum mechanical approach.

Some works have been performed on organolead trihalide perovskites$^{23,35}$ such as on CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ (MAPbBr$_3$ and MAPbI$_3$ henceforth) cubic structure approximating well the experimental values. A bandgap of 2.2 eV (1.89 eV experimentally) for MAPbBr$_3$ have been obtained showing only shallow defect levels as
shown in Fig 5. Only four deep levels have been noticed and these are Pb$_i$ (Pb interstitial), Pb$_{Br}$ (Pb antisite substitution on Br), Br$_{MA}$ (Br antisite substitution on CH$_3$NH$_3$) and Br$_{Pb}$ (Br antisite substitution on Pb). Calculating the formation energies of these four deep levels, it has been figured that they are not dominant defects as they show high formation energies.

MAPbI$_3$ shows a bandgap of 1.5 eV and comparable electronic properties, for instance similar conduction band minima curvatures with MAPbBr$_3$. Although intrinsic defects follow similar trend, it is noted that during growth, PbI$_2$ or CH$_3$NH$_3$I vacancies (Schottky defects) having low formation energies are present and vacancies of Pb, I and CH$_3$NH$_3$ (Frenkel defects) form only shallow levels as in MAPbBr$_3$.

![Figure 5. Energy levels showing shallow defects on MAPbBr$_3$. (a) donor-like defects and (b) acceptor-like defects $^{25}$](image)
1.2.3 – *Introduction to surface states*

In 1932 Igor Yevgenyevich Tamm proposed the existence of surface states, i.e. energy states found at the edges of materials that differs from the well-known bulk states.

In a perfect crystal the electron wave function are described by Bloch theorem which asserts that the energy states for electrons can be written as Bloch waves that are solution of the Schrödinger equation:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r) = E\psi(r)
\]

where \( r \) is the position, \( V(r) \) is the crystal potential, \( \psi(r) \) is the wave function and \( E \) is the electron energy

\[
\psi(r) = u(r)e^{ikr}
\]

where \( \psi(r) \) is the Bloch wave with periodic potential, \( u \) is a periodic function with the same periodicity of the crystal, \( k \) is the wave vector and \( e^{ikr} \) is the plane wave, i.e. the electron travels in the crystal like a free particles.

However, at the edges of the crystals, the situation is different as the perfect periodicity is no longer maintained hence a deviation of electron behaviors are expected compared to that in the bulk as well as for the electronic structure.

The above one-dimensional single-electron Schrödinger equation gives two solution as can be seen in Figure 6. The first solution has a Bloch character and represents the bulk states that exponentially decay reaching the vacuum. This can be obtained for both metals and semiconductors although for the latter the eigenenergies have to reside within the allowed bands and have a real \( k \)-vector. The second solution represents localized electron wave function at the crystal surface showing decaying tails at both the bulk and the
vacuum. This particular solution corresponds to the so-called surface states where the
eigenenergies reside in the forbidden energy gap showing an imaginary $k$-vector.

These surface states are mostly expressed as dangling bonds, namely chemical bonds that
terminate in free space not joining a second atom forming localized states. These alter the
charge balance of the material causing an unfavorable situation.

Two types of surface states are present in the energy gap and are called conduction band
derived (CB derived – acceptor states) and valence band derived (VB derived – donor
states) states depending on whether they lie below the conduction band or above valence
band respectively. When CB derived are occupied they are negatively charged whereas
neutraly charged if empty. Similarly happens for VB derived being positively charged
when empty and neutral when *doubly* occupied (spin degeneracy). Therefore, when
electrons fill the acceptor states, the surface is charged and the most favorable option
would be to push the Fermi level ($E_F$) below these states so that the can be emptied.
Unfortunately the energy of these states is fixed at the surface hence no energy shifting
are possible. The band edges bend either upwards (for n-type semiconductor) or
downwards (for p-type semiconductor) so that the $E_F$ is crossed by the states and they can

---

**Figure 6.** Two qualitatively different types of Schrödinger equation solution: (a) Bulk states-like Bloch
wave and (b) localized wave function at the crystal surface.
be emptied (Fig. 7). A space charge region is then formed due to different charges at the interface. The band bending keeps on going until the equilibrium between the negative charges at the acceptor levels and the positive charges in the near surface region is reached:

\[ Q_{SC} + Q_{SS} = 0 \]

where \( Q_{SC} \) is the space charge and \( Q_{SS} \) is the surface state charge. This causes the so-called Fermi level pinning at surface state energy.

Figure 7. N-type semiconductor band bending due to space charge formation and Fermi level pinning.
1.2.4 – Excitons in perovskite

It is possible that at the surface as well as in the bulk, some states are filled with neutral quasiparticles that do not transport electric charge. These particles are called excitons and consist on electron-hole pairs bonded by a Coulomb interaction. An exciton is formed when the system absorbs a photon such that an electron is excited to a higher energy state forming a hole and these are attracted by the Coulomb force (Fig. 8). Two types of excitons exist: excitons that stay close to donor, acceptor or neutral atom (bound excitons) and free excitons. Since the coulomb interaction is quite easy to be screened by free carriers, excitons are found only in pure semiconductor materials and due to their low energy, sharp emission peaks are usually noticed at low temperature at energy below the energy gap.

Unlike inorganic semiconductors, where light amplification is generally due to electron-hole recombination in conducting plasma and lasing emission occurs when a population inversion is created, in organic materials, as a result of light absorption, non-coherent exciton population is formed and lasing emission needs the consumption of the exciton with the subsequent formation of a vibrational state.

Since perovskite is an organic-inorganic semiconductor, researchers have not addressed yet the light emission dynamics to the organic excitonic effects or to electron-hole plasma as in inorganic materials. However, MAPbI$_3$ and mixed methylammonium lead iodide-chloride (MAPbI$_{3-x}$Cl$_x$) have shown binding energies in the range of 20-60 meV$^{36,37,38}$ with negligible bound excitons under solar light, hence only free carriers are generated at room temperature. On the other hand strong excitonic peaks have been observed in temperature-dependent photoluminescence experiment on thin film perovskite showing
the normal Wannier-type excitons owned to structural phase transition from orthorhombic to tetragonal. MAPbBr$_3$ shows sharp peaks at 2.258 eV, 3.329 eV and 3.9 eV whereas MAPbI$_3$ shows peaks at 1.633 eV, 2.8 eV and 3.6 eV.$^{28}$ Differences between types of perovskite are consequences to halogen substitution.

![Figure 8. Schematic representation of exciton.](image)

### 1.3 – Light emission processes

#### 1.3.1 – Spontaneous emission

When light having energy larger than the bandgap is absorbed by a semiconductor material, electrons gain energy and travel from the ground state (valence band - VB) to the excited state (conduction band - CB) leaving behind holes. These excited carriers do not reside in the CB for long (lifetime) but they tend to relax and release their energy through electron-hole recombinations returning to thermal equilibrium. When this
happens a photon is released as consequence of energy relaxations; furthermore, if it occurs spontaneously, the process is called spontaneous emission (SE) as electrons move randomly from the CB to the VB having a random phase (Fig. 9). Transitions do not occur only from CB to VB but also from defects states, donor levels etc. and non-radiative recombination processes are also possible, but this will not be discussed here as not the main focus of the thesis and because it has been demonstrated that these types of recombinations are minimal in perovskites.

For direct bandgap materials the emitted photon wavelength ($\mu$m) is given by

$$\lambda = \frac{hc}{E_g} \approx \frac{1.24}{E_g}$$

While for indirect bandgap materials we have

$$\lambda = \frac{hc}{(E_g - E_{phonon})} \approx \frac{1.24}{(E_g - E_{phonon})}$$

where $h$ is Planck’s constant, $c$ is the speed of light in vacuum, $E_g$ is the energy gap and $E_{phonon}$ is the phonon energy in eV.

Spontaneous emission is the main process light-emitting diodes (LEDs) are based on. Recently organometal halide perovskite-based LEDs have been demonstrated showing bright electroluminescence\textsuperscript{39,40} and optical tuning from 517 nm using MAPbBr\textsubscript{3}, 630 nm using MAPbBrI\textsubscript{3} all the way to 773 nm with MAPbI\textsubscript{3-x}Cl\textsubscript{x}.\textsuperscript{41,42} The full width at half
maximum (FWHM) for MAPbBr$_3$ was as small as 25 nm, less than half of FWHM of P8BT-based LEDs$^{43}$ and circa half of that of standard InGaN-based LEDs$^{44}$. LEDs structures will be described later.

![Figure 9](image.png)

**Figure 9.** Spontaneous emission process. (a) Electron in an excited state; (b) electron-hole recombination and (c) electron in the ground state with photon emission.

### 1.3.2 – Amplified spontaneous emission

Amplified spontaneous emission (ASE) is usually considered as the prelude of lasing action, also called stimulated emission. In a standard L-I characteristic (power-current) of semiconductor lasers, light output slowly increases linearly with the current, quite similar to that of LEDs (spontaneous emission range) until a threshold value where gain overcomes the losses (stimulated emission exceeds spontaneous emission) and the light output increases steeper.

ASE is defined as the process wherein photons, spontaneously emitted, are amplified by stimulated emission processes, i.e., when a medium is pumped hard, population inversion
is reached and carrier recombinations occur at higher rate compared to low pumping energies (Fig. 10). The emitted photons have good special coherence but low temporal coherence which makes ASE an unwanted process in lasers as can limit the gain and sometimes prevent lasing.

ASE is significant in random lasing applications where no cavity is required. Some works on free-cavity configuration-based perovskite working in this regime have been reported\textsuperscript{7,19,45} showing a distinct SE-ASE transitions and proving their high absorption coefficient and low Auger recombination as well as demonstrating gain values similar to colloidal quantum dots\textsuperscript{46,47} and conjugated polymers\textsuperscript{48}.

![Figure 10. Amplified spontaneous emission process, (a) Population inversion and (b) incoherent photon emissions.](image)

### 1.3.3 – Stimulated emission

Following Boltzmann statistics the ratio between an excited state (1) and a low energy state (2) is give as
\[
\frac{n_2/\rho_2}{n_1/\rho_1} = \exp\left[-\frac{(E_2 - E_1)}{k_B T}\right]
\]

where \(n_1\) and \(n_2\) are the electron densities at energy levels \(E_1\) and \(E_2\), \(\rho_1\) and \(\rho_2\) are the electron densities of states, \(k_B\) is the Boltzmann’s constant and \(T\) is the temperature.

In order to have stimulated emission the following relation has to be fulfilled

\[
\frac{\left(n_2\right)}{\left(\rho_2\right)} > \frac{\left(n_1\right)}{\left(\rho_1\right)}
\]

which means that population inversion is reached where the electron densities at the excited states is larger than the one in the lower state. Similarly, this condition can be obtained considering \(T < 0\) (negative temperature). In other words, the stimulated emission rate (rate of electron transition from CB to VB) has to be larger than the absorption rate (rate of electron transition from VB to CB):

\[
r_{stim}(E_{21}) > r_{abs}(E_{12})
\]

When a photon interacts with a system that have \(\left(n_2/\rho_2\right) > \left(n_1/\rho_1\right)\), it stimulates the emission of another photon with the same phase and same frequency hence two coherent photons are formed. This is a chain reaction that stimulates the emission of other photons having a cascade emission as shown in Fig. 11.
The first demonstration of lasing in perovskite comes from a vertical cavity optical structure where $\text{MAPbI}_{3-x}\text{Cl}_x$ is confined within a dielectric distributed Bragg reflector and a gold mirror. Low threshold of 0.2 $\mu$J/pulse, narrow FWHM (1.6 nm) and suppression of photon bunching under high excitation energies confirms the lasing action. Different microcavities have also been explored such as whispering gallery mode lasing, microdisk lasers, nanowire lasers and lasing from spherical resonators showing promising results and opening alternatives of III-V semiconductor lasers.

Figure 11. Stimulated emission process. (a) Electron in the excited state; (b) stimulation of a second photon and (c) electron in the ground state with two coherent photons emitted.

### 1.4 – Random lasing

Since Letokhov reported the first laser with non-resonant feedback in 1966, random lasers have become of great interest thanks to their simple structure and low cost stimulated emission applications and these triggered scientists to study the lasing mechanisms and the complex physics that surrounds such process.
A random laser is a laser that consists in a highly disordered gain medium, like powders or small particles that act as scattering centers as well as laser resonator (having sizes larger than the emission wavelength) such that light is trapped in a close-loop and amplification of the gain material can be achieved (Fig. 12). One of the most material studied as random laser medium is ZnO owned to its optical properties, simple growth process and different obtainable structures\textsuperscript{54,55,56,57}.

As I mentioned above, ASE is a noteworthy process related to random lasers since such devices do not need mirror cavities (also called “mirrorless laser”) and incoherent feedback is obtained from the light scattering, hence similar to ASE process. However, it is important to distinguish ASE and lasing regarding incoherence and coherence random lasing emission respectively. When the photon average path length within the medium is equal to the gain length (path a photon treads before producing another photon), incoherent emission is obtained as every photon creates another photon along its path. On the other hand, with increasing the number of scatterings, a close-loop can be formed such that light returns to the same scattering center where it was scattered before and when the gain overcomes the losses lasing occurs. In other words

\[ l_t \leq \lambda \]

where \( l_t \) is the mean free path and \( \lambda \) is the optical wavelength. This is also called Anderson localization regime where in theory no radiation can escape from the cavity.
Different from standard semiconductor lasers that exhibit single mode resonance, in random lasers several resonant modes appear due to diverse loops of light scattering.

**Figure 12.** Schematic random laser with amplification from scattering centers.

### 1.5 – Thesis outline

In chapter 1 I present the background of the thesis work and a short literature review describing the organic-inorganic perovskite structure, optical properties and light-emitting device-based perovskite applications. I also introduce what type of defects can be found in this organometal halide perovskite as well as excitons states that can help to better understand the further discussion. In chapter 2 an overview on the characterization tools such as XRD, SEM, photoluminescence and optical pumping set up. A literature review on the fabrication of light-emitting device-based perovskite is also presented.

In chapter 3 the full CH$_3$NH$_3$PbBr$_3$ photoluminescence at both room and low temperature is presented in order to address the observation of excitons and defects. I also describe the
optical pumping characterization to show the SE-ASE transition in such material and to confirm the excitons theory emerging from the RT photoluminescence measurement. Room and low temperature XRD results to check phase purity and SEM analysis to distinguish different photoluminescence behaviors on three perovskite structures are also provided.

In chapter 4 I conclude the thesis work summarizing the results and giving an outlook on the possible future studies and applications that surround this highly attractive material.

1.6– Significant research contributions

– Understood the defect signatures in different CH$_3$NH$_3$PbBr$_3$ structures.
– Discovered the excitonic features in CH$_3$NH$_3$PbBr$_3$ powders and their role in the recombination mechanisms.
– Achieved amplified spontaneous emission through optical pumping
– Proposed a solution to the efficiency roll over and “green gap” in semiconductor emitting devices.
– Mixed CH$_3$NH$_3$PbBr$_3$ powders in yellow phosphor in order to obtained different colors temperatures suitable for various applications.
– Mixed CH$_3$NH$_3$PbBr$_3$ powders in red phosphor in order to achieve white light.
2. Experimental methods and details

2.1 – Overview of perovskite based light emitting devices fabrication

Being organometal halide perovskite a pretty much new material, not many devices have been developed, however LEDs and some optical pumped lasers have been reported. To date no electrical injection-based perovskite laser has been demonstrated, hence there is still a long way to go before making such material useful for applications. However promising studies have been carried on. The fabrication process of an optically pumped laser is different from the standard photolithography technique used in electrically injected ones, nevertheless a minimum design is needed. As anticipated previously, the first lasing demonstration by R. H. Friend\textsuperscript{8} in 2014 comes from a simple vertical cavity surface emitting laser as shown in Fig. 13. The active medium (MAPbI\textsubscript{3-x}Cl\textsubscript{x}) is embedded between a gold mirror and a dielectric DBR (95\% reflectivity). A 1 \( \mu \)m-PMMA spacer is added to the cavity in order to attach the gold mirror ending up with a total cavity thickness of 8 \( \mu \)m. Regarding the other perovskite lasers, no cavity or fabrication is needed as as-grown samples are optically pumped. Whispering gallery nanolasers with different shapes (triangular, hexagonal, spherical and cubic)\textsuperscript{15,39,40,42}, microcrystals random lasers\textsuperscript{35, 58} and nanowire lasers offering photoluminescence quantum yields close to 100\%\textsuperscript{16} represent the perovskite state-of-the art lasers. In Figure 10 are presented the up-to-date lasing devices.
Figure 13. Schematic representation of up-to-date perovskite-based lasers. (a) VCSEL, (b)-(e) whispering gallery mode of as-grown perovskite lasers.

On the other hand perovskite light emitting diodes require an engineering fabrication. Similar to organic LEDs, the active medium is sandwiched between two large bandgap materials (TiO$_2$ or PEDOT:PSS and F8) so that a quantum well-like layer is formed and electrons and holes are trapped for the subsequent recombination. Finally ITO and MoO$_3$/Ag are used as cathode and anode respectively. Fig 14 shows the perovskite LED structure$^{31,32}$. Analogous three-layered structures can be employed where the active material is embedded within the usual hole injection layer PEDOT:PSS and tetrafluoroethylene-perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid copolymer (PFI)$^{29}$ or ZnO$^{30}$ instead of F8.
2.2 – Material preparation

The perovskite material that most has been studied is MAPbI$_3$ as it shows the highest photovoltaic efficiency$^{59,60}$. Several techniques$^{61,62}$ have been developed based on the desired structure even though polycrystalline thin film process is the most used since it is simple, inexpensive with a good match for solar cell requirements. Obviously single crystal thin films would increase most of the material properties but such structure has not been reported yet although studies on single crystal cubic millimeters and micrometers reporting crack-free and extremely low defect densities, but with difficult real applications, have been demonstrated$^{15,18}$.

The thin film preparation process we used is depicted in Fig. 15a where a PbBr$_2$ precursor solution is spin-coated on a substrate and through a vapor assisted solution process technique we evaporated the second organic precursor (CH$_3$NH$_3$Br).

Similar method was used for powder preparation where MAPbBr$_3$ was condensed out of solution evaporating the solvent from a solution of equimolar PbBr$_2$ and CH$_3$NH$_3$Br in DMF (N,N-dimethylformamide). In order to confine the powders we cured them with
polydimethylsiloxane (PDMS), we spin-coated it onto a $\text{Al}_2\text{O}_3$ substrate and we then placed another sapphire layer on top so that the active material results embedded within two transparent substrates to obtain a flat layer for the subsequent photoluminescence and optical pumping measurement (Fig. 15b).

**Figure 15.** MAPbBr$_3$ preparation. (a) thin film using vapor-assisted solution process; (b) powders/PDMS spin-coating process on sapphire substrate; (c) powder/PDMS mixture and thin membrane.
2.3 – Photoluminescence in perovskite materials

Photoluminescence (PL) is the emission of light from any form of matter after electromagnetic radiations are absorbed. Excitation occurs by means of a source, such as a laser, having energy larger than the sample bandgap so that several relaxation processes, as described in chapter 1.3 (SE, ASE, stimulated emission), may happen. PL includes both fluorescence (light emission after photon absorption) and phosphorescence (emission of radiation with certain delays due to “forbidden” energy states transitions) and important information can be detected from this measurement. Materials band structures, crystal defects such as vacancies and substitutional atoms as well as internal stresses are only few studies related to PL.

Temperature-dependent PL (TDPL) is also considered a powerful technique to study the carrier transport, localized states, excitonic states and to remove the phonon noise and better analyze the material structure. The intensity obtained from TDPL is well fitted employing Arrhenius’ formula:

\[
I(T) = \frac{1}{1 + C_1 \exp\left(\frac{-E_{A1}}{k_B T}\right) + C_2 \exp\left(\frac{-E_{A2}}{k_B T}\right)}
\]

where \(I(T)\) is the normalized photoluminescence intensity, \(C_1\) and \(C_2\) are two non-radiative recombination constants, \(E_{A1}\) and \(E_{A2}\) are the non-radiative recombination activation energies\(^{63,64}\) and \(k_B\) is Boltzmann’s constant.

In Fig. 16 is shown the schematic PL setup we used for the measurement. A 473 nm laser, passing through a mirror, is used as excitation source. The light coming from the
sample is then collected using a photodetector and a monochromator to separate and transmit a portion of the signal. Finally, a computer plots the signal collected from the photodetector. The same setup was used for the TDPL with the only different that we integrated the liquid nitrogen chamber to cool down the sample.

In Fig. 17 is shown the photoluminescence from MAPbBr$_3$ powders/PDMS in plastic cuvette and spin-coated on sapphire substrate when we excited with 266 nm pulse laser. Green light can be observed from both suspended (Fig. 17 (a)) and deposited (Fig. 17 (b)) powders. The blue light is due to phosphorescence from the plastic cuvette.

![Figure 16. Schematic photoluminescence setup.](image)

Regarding perovskite, several temperature-dependent studies have been performed, especially on MAPbI$_3$, providing significant information on the phase changing in this material$^{65,66}$. Above 330 K, the structure is cubic whereas at RT a phase transition towards a tetragonal structure is involved where the PbI$_6$-octahedra rotates around the c-axis$^{67}$. Continuing decreasing the temperature, another phase transition is observed at
approximately 160 K\textsuperscript{49,58,68} (tetragonal-to-orthorhombic transition) involving a tilting of the PbI\textsubscript{6}-octahedra.

Similar results have been reported for thin film MAPbI\textsubscript{3-x}Cl\textsubscript{x} showing slight differences on absorption edge shifts moving from one phase to the other\textsuperscript{21} and free excitonic peaks\textsuperscript{69} due to coexistence of orthorhombic and tetragonal phases. Moreover increasing the temperature, a blue shift has been also observed, even though the bandgap of orthorhombic structure is larger than the tetragonal one. This has been attributed mostly to electron-phonon interactions and thermal expansion having opposite effects on the bandgap energy compared to conventional semiconductors.

Not many studies on MAPbBr\textsubscript{3} are available, however theoretical electronic structures and TDPL measurement showed three-dimensional Wannier excitons\textsuperscript{29} and larger bandgaps compared MAPbI\textsubscript{3} or MAPbI\textsubscript{3-x}Cl\textsubscript{x} due to the substitution of the halogen.

The crystal structures and transition temperatures of CH\textsubscript{3}NH\textsubscript{3}PbX\textsubscript{3} (X = Cl, Br or I) are enlisted in Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>MAPbCl\textsubscript{3}</th>
<th>MAPbBr\textsubscript{3}</th>
<th>MAPbI\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystal system</strong></td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td><strong>Transition temperatures (K)</strong></td>
<td>177</td>
<td>236</td>
<td>330</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td><strong>Transition temperatures (K)</strong></td>
<td>172</td>
<td>149~154</td>
<td>161</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

Table 2. Crystal structures and transition temperatures of perovskites\textsuperscript{70}. 

42
Figure 17. Green photoluminescence from MAPbBr₃ using 266nm pulse laser. (a)-(b) emission from suspended particles and from deposited particles in the cuvette; (c) strong green emission from powders/PDMS spin-coated on sapphire.
2.4 – *X-ray diffraction and scanning electron microscope*

In order to verify the crystal structure and the orientation of MAPbBr$_3$, X-ray diffraction has been utilized whereas for morphology information we used the standard scanning electron microscope (SEM).

The main concept in XRD is the constructive interference of X-rays and the sample where the first are produced by a cathode ray tube that is collimated on the sample and filtered to obtain a monochromatic ray. The law that rules this phenomenon is given by

\[ n\lambda = 2d \sin \theta \]

and it is called Bragg’s Law where $n$ is an integer, $\lambda$ is the wavelength, $d$ is the gap between the atomic planes and $\theta$ is the diffraction angle. Hence, constructive interference happens when the difference in the ray travel path is equal to $n$-times the radiation wavelength and a X-ray beam escapes the material at the same angle of the incident ray.

All the diffraction directions can be measured by moving the incident beam within a 2\(\theta\)-angle range (diffraction pattern) and by converting this to the d-spacings and comparing them to a reference material; the desired sample phase is then obtained. Fig. 18 shows the XRD schematic phenomenon based on Bragg’s law.
Regarding the topography of the sample, the signal we used is based on secondary electrons; however, SEM also provides other type of electron collection such as backscattered electrons, X-rays, Auger electrons and transmitted electrons. In short, an electron beam is shined onto the sample interacting with its surface and the electrons are then collected by a detector that reproduces the image in the monitor.

2.5 – Femtosecond laser for optical pumping

As described above, photoluminescence is the process of light emission from a material. To excite the electrons in a higher energy state, an amount of energy is required and this can occur in two ways: electrical injection (the emission of light process is called electroluminescence) and optical pumping. The latter consists in light excitation from a source, usually a laser, and this technique is usually used in semiconductor lasers in order to reach population inversion increasing the power input. In this field, ultrashort pulse
lasers such as picosecond ($10^{12}$ second) and femtosecond lasers ($10^{15}$ second) are used due to their high peak intensity and these short pulses are usually achieved using the passive mode locking technique that briefly consists on incorporating a semiconductor saturable absorber that absorbs low-intensity light and transmits high-intensity light. In a laser cavity this continually happens and after many rounds this brings to selective pulses. Femtosecond laser setup can be very complicated as much optics is required. An illustration of the optical pumping setup used in our experiment is shown in Fig. 19. PL information was collected using an Ultrafast Systems Helios spectrometer integrated with femtosecond laser pulsing at 475 nm where the pulses were produced in a 900mW Ti:sapphire regenerative amplifier operating at 800 nm with 35 femtosecond pulses an 1kHz repetition rate.
2.6 – *Color temperature and phosphor applications*

All the light in the visible range can be represented by a color, also called “color temperature”. For instance, lamp filaments or candles show a red/orange color and this is associated to a “warm” look. On the other hand, the blue sky shows the standard blue/white color that’s why it is associated to a “cool” color. The color temperature unit is Kelvin and can vary from 2000 K (for warm colors) to 7000 K (for cool colors).

More scientifically, color temperature is the temperature that a black body has when it is stimulated with a source and emits a radiation at similar wavelength to the light source.
Taking the example of the lamp filament, if it gets heated, at a certain point it will start glowing changing its hue from red to yellow. If it gets even hotter, white light can be noticed. These sources are called incandescent radiators and they emit light in all the visible range. Fig. 20 shows the Kelvin color temperature scale from warm to cool colors.

![Kelvin color temperature scale](image)

**Figure 20.** Kelvin color temperature scale.

An important definition is the correlated color temperature (CCT) that is the color temperature of a black body that better matches the light for the human eyes. Several light sources do not emit light through thermal radiation (fluorescence lamp, LEDs) and this means that they do not follow the black body behavior.

The CCTs can be observed in the CIE 1931 $x,y$ chromaticity space that helps to link the colors to the human vision (Fig. 21). The curved edges of the plot represent the monochromatic light (single wavelength) whereas the curved line in the middle denotes the white light. Mixtures of colors can be formed selecting any two points in the plot and drawing a straight line. All the colors within this range can be obtained as a combination of the selected two colors. Similar concept works for 3 colors by drawing a triangle and all the combinations can be obtained within it.

Another significant term is the color rendering index (CRI) that is a measure that compares the natural colors from a light source to references sources. The lower is the
CRI, the more the color is unnatural. The highest value is 100 and it is given only to sources that are equal to daylight or to a black body.

![CIE 1931 x,y color space chromaticity diagram.](image)

**Figure 21.** CIE 1931 x,y color space chromaticity diagram.

The most important application regarding the color temperature measurement concerns the white light emission as this reduces the global power, the usage of fossil fuels and at the same time mimics the sunlight. Building interiors lighting, backlighting for LCD displays and automotive headlights can be some of the many applications. Regarding that, it is important to consider the color temperature of illumination in different places, for example in public areas where warmer colors are used to promote relaxation and in closed areas where cool colors are used to promote concentration.

Devices can be created by combining phosphor materials with the selected chips with the advantage of easy fabrication and low cost. For example white-light LEDs are usually
made of blue chips integrated with YAG (Ce$^{3+}$:Y$_3$Al$_5$O$_{12}$) (Fig. 22) although they demonstrate unstable light color under different current\textsuperscript{72}. The blue light emitted from the LED is absorbed by the phosphor material that converts it into yellow light. White light is obtained combining the yellow fluorescence with the transmitted blue light.

![Figure 22](image_url)

**Figure 22.** (a) Schematic white light LED structure based on yellow phosphor material and (b) Ce:YAG phosphor chromaticity points\textsuperscript{73}

Another way to get different hues is the combination of red, green and blue (RGB) colors. Specially, when the intensity of these three hues is maximum, white light is obtained. Standard TVs and cellphones use RGB to create images in the screens we usually say in day life.

The current setup we used for our measurement is described in Fig. 23. A 405 nm blue laser is shined onto the MAPbBr$3$/Ce:YAG sample being first collimated by a quartz lens. The laser is then filtered by a 405 nm filter in order to remove the signal from the detector. The light is then collected using Mc Science L5000 LED containing a 3.3 inch integrated sphere connected to a spectrometer (range: 250 nm – 850 nm).
3. Characterization of CH$_3$NH$_3$PbBr$_3$ structures

3.1 – X-ray diffraction and scanning electron microscope characterization

In order to confirm the room temperature MAPbBr$_3$ cubic structure$^{55,58,74}$ and to demonstrate the complete phase purity of the powder material, XRD has been examined. Fig. 24 shows the RT X-ray diffraction plot where strong diffraction peaks define the cubic-CH$_3$NH$_3$PbBr$_3$ perovskite structure.

For powder XRD measurements we used a Cu Ka$_1$ excitation (=8047.8) whereas for data collection a STOE IPDS2 diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) was employed. In order to confirm the material cubic structure, we measured the unit cell with 606 reflections from 48 measured frames (a =5.9152 Å).

Unlike the method we used for powder preparation explained in Chapter 2.2, the material was grinded to obtained small particles and it was not mixed with PDMS.
The difference between the transmitted and the scattered beam corresponds to 2θ-diffraction angle from which value one can derive the atomic planes d-spacing. The numbers above the peaks indicate the Miller indices. As can be noticed, the main peaks are due to X-ray diffraction from the \{100\}, \{110\}, \{200\}, \{210\}, \{211\}, \{220\} and \{300\} planes. Crystallographic analysis reveals that the crystal structure of MAPbBr$_3$ belongs to the cubic system with the space group Pm3m (no. 221) at room temperature, which is in agreement with the reported ones.

We also performed temperature-dependent XRD (Fig. 25) to confirm that in the PL measurement described in Chapter 3.2 the different peaks did not come from phase changing and despite the reported phase change temperature in MAPbBr$_3$, our XRD measurement did not show evidence of it.

![X-ray diffraction profile of MAPbBr$_3$ powders.](image)

**Figure 24.** X-ray diffraction profile of MAPbBr$_3$ powders.
Figure 25. Temperature-dependent XRD profile of MAPbBr₃ powders showing no significant phase changes.
We analysed two structures (powders and thin film) under SEM to compare the two different techniques. As shown in Fig. 26 the powder sample presents cracks and very inhomogeneous particles due to the irregular grinding of the particles. No PDMS was used for the SEM measurement.

On the other side, the thin film image shows more uniform and homogeneous particles owned to the vapour-assisted growth method.

![Figure 26. MAPbBr$_3$ SEM pictures of (a) powders (high inhomogeneity) and (b) thin film (more homogeneity).](image)

3.2 – *Photoluminescence characterization*

As mentioned before, a continuous wave 473 nm laser was used for the PL measurement. Fig. 27 shows the PL spectra at 77K (-196 °C) at different powers (0.8 – 80 µW) for powder sample. We noted that the radiative recombination processes were dominated by an asymmetric narrow peak (left) at 552 nm (2.246 eV) and broad hump (right) with
center wavelength at 590 nm (2.102 eV). We addressed these two peaks to emissions from surface defect states and bulk defect states respectively.

At low power (0.8 µW) the peak intensity difference between the two peaks, δ, is approximately zero, meaning that the recombination process occurs strongly through bulk defects. At 8 µW δ is as large as 17 a.u., i.e., the narrow peak increases faster than the broad hump that starts saturating as most of the bulk defect states get filled. At high excitation power (80 µW) all of the bulk defect states are filled and most of the recombination processes occur from the surface states as δ becomes as large as 1700 a.u.. A slight blue-shift can also be observed increasing the power and this is mostly due to the band filling effect in which most of the states near the bulk defects result occupied so that the absorption edge is raised to larger energies and recombination occurs at smaller wavelengths.

![Figure 27. Power-dependent PL of MAPbBr₃ powders at 77K.](image)
Regarding the asymmetric narrow peak, we deconvoluted the spectrum at 80 µW with a Gaussian peak fit and this originated two peaks at 552 nm and 544 nm with FWHM of 12 nm and 5 nm other than the broad hump with FWHM of 54 nm (Fig. 28). These narrow peaks are attributed to inhomogeneity as shown in SEM picture and different surface states in the powder sample.

![Multiple peak fitting](image)

**Figure 28.** Multiple-peak Gaussian fitting of MAPbBr₃ PL spectrum at 80 µW showing two surface state-related peaks.

To ascertain this theory we test a MAPbBr₃ single crystal having low trap-state density⁵ and no defect hump was observed hence supporting our attributions of the broad hump to defect states in powder material. Fig. 29 shows the absorbance and photoluminescence of MAPbBr₃. 480 nm excitation wavelength was used for PL measurement. A clear band
edge cutoff can be noticed and the absence of excitonic peak further supports the lack of defect states.

Similarly, we tested the thin film perovskite and as expected, due to less crystallinity compared to the powders, only one narrow peak (higher homogeneity) and a stronger broad peak related to surface states and bulk defects respectively were observed. δ Value is -10 supporting the less sample crystallinity assertion (Fig. 30).

Figure 29. (a) Single crystal MAPbBr$_3$ absorbance and PL spectrum; (b) single crystal picture
In order to verify that the broad hump is determined by bulk defect states recombinations, TDPL was performed sweeping the temperature from 77K to RT. As shown in Fig. 31 at low temperature the bulk defects peak is pronounced compared to higher temperatures where slowly disappears until RT where no peak is visible indicating an irrelevant role of the bulk defects.

We also noted that the two peaks at 544 nm and 552 nm showed different behaviors with temperature. The first one blue-shifted whereas the second one moved towards higher energies. We then fitted the spectra using Gaussian functions to better represent the phenomena (Fig. 32). This two peaks related to surface states were denoted as bound excitons 1 and 2 (BE$_1$ and BE$_2$) consistent with the grain size inhomogeneity discussed.
Figure 31. Temperature-dependent PL spectra of MAPbBr$_3$ showing bulk defect states at low temperature and surface states shifting towards RT. Blue and red lines act as guide for the eyes.
Figure 32. Peak wavelength as function of temperature showing surface states temperature-dependent blue and red shift.

before. Moreover, BE values of 20-60 meV for MAPbI₃ were reported²⁸⁻²⁹,⁷⁵ confirming our assumption of BE surface states recombination.

The blue-shift trend observed can be explained considering the band filling dynamic (Burstein-Moss effect⁷⁶) that happens due to two main energy sources: optical excitation (laser) and thermal excitation (temperature). In fact, increasing the temperature most of the states near the conduction band result occupied so that the absorption edge is raised to larger energies showing the blue-shift trend. At the same time, the laser excites the carriers that start filling up the surface states emitting at shorter wavelengths, hence contributing to the blue-shift observed in BE₁.

This mechanism can be modelled using the following equation⁷⁷:

$$\Delta E_{BM}^B = \frac{\hbar^2}{2m_e^*} \left(3\pi^2 n\right)^{2/3}$$
where $\Delta E_{g}^{BM}$ is the energy due to Burstein-Moss band filling, $\hbar$ is the reduced Plank constant, $m_{eh}^{*}$ is the reduced effective mass and $n$ is the carrier concentration.

The overall surface state energy can be defined as $E_{g} = E_{g}^{0} + \Delta E_{g}^{BM}$, considering $E_{g} = 2.28$ eV that corresponds to the energy of BE$_{1}$.

Unlike our explanation, a recent study encountered the same behaviour and addressed it to the electron-phonon interaction and thermal expansion in which the standard semiconductor Varshni and Bose-Einstein models employed to describe the temperature-dependent PL. They claimed that this model cannot be applied to such material as they show opposite effects on bandgaps\textsuperscript{60}. Furthermore, the second excitonic peak, showing red-shift behaviour, becomes prominent with raising the temperature, showing a wavelength of 553 nm. The strong absorption of the second excitonic peak, due to high density of surface states, originates the red-shift as BE$_{1}$ acts as an optical pump for the narrower bandgap BE$_{2}$.

The single crystal TDPL (Fig. 33) supports again the statement of the free-bulk defects and the absence of surface states in such structure. In fact no broad peaks are observed around 600 nm and neither multiple peaks as noticed in the powders sample. However a slight blue shift was observed from 87K to RT of 4 nm. The different emission wavelength at RT showed in Fig. 29 and Fig. 33 is mostly due to material degradation. In fact we noticed that with time, the PL emission shifts from longer wavelengths to shorter ones.
Figure 33. Temperature-dependent PL spectra of MAPbBr$_3$ single crystal showing a stable evolution. The blue is drawn to show the slight blue shift (4 nm).
We also demonstrated true green ASE from MAPbBr$_3$/PDMS sample when optically pumped with 475 nm pulse laser. The spontaneous emission peak dominates at low excitations and results at 535 nm consistent with BE$_1$ in PL data. When we increase the power a peak centered at approximately 550 nm raises and keeps red-shifting until 553 nm. The evolution of the PL spectrum can be seen in Fig. 34.

This can be explained considering that ASE peak coincides with BE$_2$ hence supporting the explanation given for the TDPL measurement in which BE$_1$ recombination pumps the smaller bandgap BE$_2$.

The evolution from SE to ASE occurs at 350 µJ/cm$^2$ that is the point where the 550 nm-peak starts appearing in Fig. 25 (light blue line).

At the threshold a significant spectral narrowing occurs showing a drop in the FWHM from 44 nm to 6 nm and the sudden increase in peak wavelength from 535 nm to 553 nm (Fig. 35,36).

![Figure 34. PL emission spectra of MAPbBr$_3$/PDMS varying the optical power. Spontaneous emission and amplified spontaneous emission peaks can be noticed at 535 nm and 553 nm.](image-url)
Figure 35. Pump fluence versus PL intensity showing a clear threshold at 350 µJ/cm² from SE to ASE.

Figure 36. Plot of FWHM and peak wavelength versus pump fluence showing a the drop in linewidth and increase in peak wavelength
Since we did not design a specific cavity no coherent feedback could be achieved hence no lasing action. The optical feedback could be formed via random scattering in the medium formed by inhomogeneous particles. Furthermore, in order to get random lasing the mean free path has to be smaller than the emitted wavelength and the average path length equal to the gain length so that enhancement via optical loop can be achieved. But as shown in Fig. 26a, the distance the light has to travel between the particles is too big and the gain length is still larger than the average path length, hence no spatial resonance and optical gain could be fulfilled.

3.3 – Color temperature characterization
Since the range of phosphor materials suitable for LEDs is narrow, we studied the color temperature of MAPbBr₃ in order to use it as a phosphor material and see the response in term of different colors.

We measured the color temperature of either MAPbBr₃ and mixture MAPbBr₃/Ce:YAG to see if the data matches the Planckian locus. The closer the data to the Planckian locus are, the better, as we may covert the green light emitted from the perovskite and the yellow from Ce:YAG into different colors suitable for several applications. Fig. 37a shows the CIE plot of both MAPbBr₃ and MAPbBr₃/Ce:YAG mixture. Varying the weight percentage from 0% to 100% of perovskite we obtained different value of CCT. We obtained data around 5500K for MAPbBr₃ only, meaning that this material might be suitable for Compact fluorescent lamp and phone screens as they work in this range of the Kelvin Color Temperature Scale.
Moreover, we noticed that combining Ce:YAG with MAPbBr$_3$ and decreasing the concentration of the latter the color temperature shifted from cooler colors to warmer colors allowing the development of a large choice of different applications (Fig. 37b).

Furthermore, in order to prob whether perovskite can be suitable to be used for white light emitting devices, we combined a nitrate-based red phosphor with MAPbBr$_3$ and mixed it wit PDMS creating an homogeneous combination (Fig. 38a). The mixture was then poured into a LED cap mold, to give the proper shape, containing a commercial blue LED chip that had been attached beforehand to a jig and wire bonded with gold wires to the jig pads. Finally it was place in an oven and kept at 150 °C to solidify the cap. Fig. 38b shows the white light emitted from the device once voltage was applied to the LED, proving that the perovskite is a suitable phosphor material that can be used in RGB white emitting devices.

![Color temperature data on CIE color space chromaticity diagram.](image)

**Figure 37.** Color temperature data on CIE color space chromaticity diagram.
Table 3. Color temperature data for different MAPbBr$_3$ percentage.

<table>
<thead>
<tr>
<th>MLB percentage (%)</th>
<th>Color Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4141</td>
</tr>
<tr>
<td>50</td>
<td>3305</td>
</tr>
<tr>
<td>60</td>
<td>2762</td>
</tr>
<tr>
<td>100</td>
<td>5770</td>
</tr>
</tbody>
</table>

Table 4. CCT related applications.

<table>
<thead>
<tr>
<th>CCT (K)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>Daylight CFL</td>
</tr>
<tr>
<td>4100</td>
<td>Moonlight</td>
</tr>
<tr>
<td>2700-3300</td>
<td>Incandescent lamps/warm white</td>
</tr>
</tbody>
</table>

Figure 38. (a) Schematic RGB-based perovskite integration and (b) white light emission
4 – Conclusion and Recommendation

4.1 – Conclusion
Organometal perovskite presents an unprecedented opportunity for low cost solution processibility of lasers with optical bandgap tunability across the visible light regime. Its photophysics properties resemble that of a direct bandgap inorganic semiconductor with small excitonic binding energies and small capture cross section of defect states. Hence, the organometal perovskite material can be custom designed for efficient light emitters in the green-yellow gap.

In this thesis we explained the radiative recombination mechanisms of methylammonium lead bromide (CH$_3$NH$_3$PbBr$_3$) using low and room temperature photoluminescence. Powders, thin films and single crystals have been investigated and compared to better understand the different properties. Twofold bound excitonic transitions have been identified in the powders sample leading to a concurrent blue- and red-shift in the temperature-dependent photoluminescence measurement.

We eventually observed amplified spontaneous emission from the same sample when optically pumped with a pulse laser. Clear spontaneous emission-amplified spontaneous emission transition can be noticed at approximately 350 µJ/cm$^2$ with a simultaneous steep drop of the bandwidth. The final emission wavelength hits the true green color at 553 nm.

To date lighting technologies are based on GaN inorganic materials to produce violet, blue and green colors. Ce:YAG phosphor is also used in conjunction with violet color light emitters to generate white light and at the same time white light can be obtained
combining red, green and blue light emitters. Here we have demonstrated the color temperature tunability using CH$_3$NH$_3$PbBr$_3$ as a phosphor material. By changing the amount of perovskite and mixing it with yellow phosphor several color temperature have been obtained suitable for different applications. White light was also achieved integrating the phosphor to a blue LED.

4.2 – Outlook and future applications

Important works can still be done to better understand the recombination mechanisms and for future applications. The outlook is stated below:

First of all the study of transient absorption and time-resolved PL could help to determine the carrier lifetime and the electron-hole population in the bulk and at the surface of such material (powders), after excitation. This studies will contribute to better understand the material properties for realizing light emitting devices.

In term of photonics-related devices, the field is still pretty much unexplored. MAPbBr$_3$ VCSEL has not been reported yet due to difficulties on getting single crystal thin films, accurate thickness and stable refractive index, though this work is in progress in our laboratory. Fabry-perot laser based on optical excitation of DBR (distributed Bragg reflector) cladded CH$_3$NH$_3$PbBr$_3$ film is under production as well as the cavity design.

Similarly, random lasing demonstration needs a better medium design as explained in Chapter 1.4. Although measurements have not been taken, we integrated high reflective BaSO$_4$ nanoparticles in microcrystals perovskite to act as scattering medium increasing the disorder and to reach the lasing oscillations.
Electrical-pumping devices (LEDs) have already been demonstrated although they are still in early stages. The most challenging goal is represented by electrical-pumping lasers as they can be designed for more efficient use of electrical energy than an LED and the targeted laser-based technology will provide significant energy savings in current electricity production. However, the main issue perovskite community keeps facing is the material instability that brings to degradation of optical properties.

VLC (visible light communication)-based perovskite is another uncharted field. Such devices not only can provide illumination but can also send data using the same light source. Important here is how fast the signal respond is and the availability of a receiver able to receive such information. Measurements are ongoing in our lab.
Publication list

  DOI: 10.1063/1.4913463


- D. Priante, et al., “The recombination mechanisms leading to amplified spontaneous emission at the true-green wavelength in CH3NH3PbBr3 perovskites”. KFUPM-KAUST Third International Workshop on Photonics.
References


