Crystalline-Size Dependence of Dual Emission Peak on Hybrid Organic Lead-Iodide Perovskite Films at Low Temperatures

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ABSTRACT: In this work, we have investigated the crystalline-size dependence of optical absorption and photoluminescence emission of CH$_3$NH$_3$PbI$_3$ films, which is necessary to identify the potential practical applications of the gadgets based on perovskite films. This study was carried out at low temperatures to minimize the extra complexity induced by thermal effects. The purpose was to clarify the origin of the dual emission peak previously reported in the literature. We found that the grain size is responsible for the appearance or disappearance of this dual emission on CH$_3$NH$_3$PbI$_3$ at low temperatures, whereas we have inferred that the thickness of the perovskite layer is a much more important factor than the size of the grains in the location of the energy of the band gap. Moreover, the increase in the grain size allows slowing down the phase transition. Additionally, we evidence a decrease in the effective Rydberg energy of the exciton in several samples, from 23−25 meV at 7 K to 12−13 meV at 165 K, by fitting to Elliott–Toyozawa theory. We have extracted other important physical parameters of perovskites from the photoluminescence-data deconvolution, such as the band gap, exciton–phonon interaction, and exciton binding energy. A new phase transition at 45.5 K was determined by the temperature dependence of full width at half-maximum and the integrated intensity of the photoluminescence, and it was confirmed by the radiative lifetime obtained from the time-resolved photoluminescence emission by means of time-correlated single-photon counting at different temperatures, excitation fluencies, and emission energies.

1. INTRODUCTION

Recently, a significant effort to understand the photophysical processes occurring in perovskites has been carried out because of the potential that these materials offer to practical applications, such as solar cells, field effect transistors, lasers, batteries, or light-emitting devices. In particular, the organic–inorganic metal-halide perovskite has been widely investigated because of the extraordinary improvement shown on the efficient solar cells. The unique properties of CH$_3$NH$_3$PbI$_3$, such as band gap modulation or long-range balanced electron- and hole-diffusion lengths, make it a promising photovoltaic material. The structural stability and polymorphism of this material as a function of temperature (T) has been previously reported: cubic−tetragonal (327 K) and tetragonal−orthorhombic (165 K). However, there are still unsolved questions about important photophysical processes occurring in CH$_3$NH$_3$PbI$_3$ films that need to be clarified, such as the origin of the dual emission peak already observed at low temperatures. Although its existence was previously shown, the scientific community has not come to an agreement about the origin of this dual emission. For example, Xing reported three emission peaks, which have been assigned to bound-exciton emissions and a free exciton; however, Fang attributed the low- and high-energy emission peaks to free and bound excitons, and Kong attributed them to a donor−acceptor pair (DAP) (low energy) and free-exciton transitions. Last, Panzer and Wehrenfennig ascribed the existence of this dual emission to the presence of tetragonal inclusions in the orthorhombic phase at low temperatures, whereas Dar attributed it to the coexistence of CH$_3$NH$_3$I-ordered and CH$_3$NH$_3$I-disordered orthorhombic domains. Hence, despite the current effort, an understanding of the essential characteristics of perovskite films is still evolving.

Moreover, it has been studied how the thickness of the perovskite films affects the absorbance and the photocurrent. The absorption coefficient curve of the organometal-halide perovskites (CH$_3$NH$_3$PbX$_3$, X = halogen) at room temperature showed not only an unusual sharp shoulder near its reported
band gap value (~1.57 eV) but also that this shoulder occurs at higher absorption coefficients than most other comparable semiconductors. This fact clarifies why very thin absorber films are sufficient for perovskite solar cell manufacture.\textsuperscript{15,16} Moreover, because of the purely exponential trend of the Urbach tail, any traces of absorption by deep levels are observed below the absorption band edge. This influences such high open-circuit voltage ($V_{oc}$) values\textsuperscript{17} (up to 1.13 V) comparable to the perovskite band gap.

In the present study, we focus on the nature of the exciton recombination channels below/above the orthorhombic–tetragonal phase transition (165 K), depending on the crystalline size of perovskite films, to clarify the origin of the dual emission peak already observed at low temperatures. Previously, it has been verified in other kind of structures that periodicities of the order of 250 nm can produce duplication of bands.\textsuperscript{18} To that end, we have studied the dependence of the periodicities of the order of 250 nm can produce duplication of bands.\textsuperscript{18} To that end, we have studied the dependence of the periodicities of the order of 250 nm can produce duplication of bands.\textsuperscript{18} To that end, we have studied the dependence of the periodicities of the order of 250 nm can produce duplication of bands.\textsuperscript{18} To that end, we have studied the dependence of the periodicities of the order of 250 nm can produce duplication of bands.\textsuperscript{18}

2. METHODS AND MATERIALS

2.1. Sample Preparation and Description. Sample preparations have been previously explained.\textsuperscript{19} Fluorine-doped tin oxide (FTO) coated glass was carefully cleaned with ultrapure water and ethanol. Then, the substrates were dried using a N$_2$ stream. A ≈ 40 nm-thick layer of TiO$_2$ was deposited on the FTO-coated glass by spin-coating anhydrous ethanol solution of titanium isopropoxide and heated at 500 °C for 30 min under room atmospheric conditions. On this TiO$_2$ buffer layer was deposited a 200 nm TiO$_2$ mesoporous layer. Halide perovskite CH$_3$NH$_3$PbI$_3$ (“cuboidlike”) films of 350 nm (S1) and 300 nm (S2) thickness were deposited inside a glovebox by spin-coating 30 μL of a 1.082 M solution of PbI$_2$ in dimethylformamide at 500 rpm for 5 s and 6000 rpm for 20 s, followed by heating at 40 °C for 3 min and 100 °C for 10 min on a hot plate. The PbI$_2$ film was then dipped for 1 min in a CH$_3$NH$_3$I solution in isopropanol (0.044 M or 0.063 M depending on the grain size), spun at 500 rpm for 5 s, 1500 rpm for 10 s, and 3000 rpm for 20 s, and heated at 40 °C for 3 min and at 100 °C for 10 min on a hot plate. Scanning electron microscopy (SEM) images of the substrate were obtained using a JSM-7000F JEOL 216 FEG-SEM system using secondary and retrodispersed electron beams (Figure 1).

2.2. Experimental Setup. Samples have been characterized by placing them in the cold finger of a commercial closed cycle, compressed helium cryostat (ARS DE-202). This cryogenerator has a heating resistance and a thermometer, with which the temperature can be controlled from 10 K to room temperature. For time-integrated PL measurements we used a continuous wave laser diode at 405 nm. In time-resolved PL (TRPL) experiments we used for excitation a 200 fs pulsed Ti:sapphire (Coherent Mira 900D, 76 MHz of repetition rate) laser doubled to 400 nm with a BBO crystal. The backscattered PL signal was dispersed by a double 0.3-m focal length grating spectrograph/spectrometer (1200 g/mm with 750 nm blaze) and detected by an Andor Newton 970 EMCCD camera (for time-integrated PL spectra) and by a Si Micro Photon Device (MPD) single photon avalanche diode (SPAD) photodetector connected through a multimode optical fiber to the monochromator (for time-resolved PL spectra); the SPAD was attached to a time correlated single photon counting electronic board (TCC900 from Edinburgh Instruments).\textsuperscript{20,21} Absorbance spectra were registered by using a halogen lamp focused on the sample and an Ocean Optics spectrophotometer.

3. RESULTS AND DISCUSSION

To reach a deeper understanding of the underlying physical mechanisms of CH$_3$NH$_3$PbI$_3$ (hereafter MAPbI$_3$) films, we have investigated the crystalline-size dependence of optical absorption and PL emission. It has been previously seen that this is an important factor in absorption phenomena.\textsuperscript{22,23} The accurate control of the crystalline size and shape of particles that constitute the perovskite films helped us to eliminate the random signals due to the surface morphology of spatially inhomogeneous samples.\textsuperscript{22,24,25} Moreover, the dependence of PL spectra on temperature and excitation wavelengths was also determined.

3.1. Optical Absorption: Exciton Binding Energy and $E_g$ in MAPbI$_3$. The evolution of the absorbance curves in small- and large-grain samples with temperature, that is, for grains of two different average sizes (352 and 103 nm, hereafter also denoted as S1 and S2, respectively), of MAPbI$_3$ was measured.
As shown in Figure 2, the material with smaller grains transforms from the tetragonal into orthorhombic phase at $T_c$ = 150 K, and both phases undoubtedly coexist below $T_c$ down to approximately 110 K (see the inset of Figure 2a). The absorbance spectra clearly show an excitonic absorbance resonance in both phases:

(i) For the orthorhombic low-$T$ phase, the exciton resonance is clearer and fairly narrower as temperature decreases (down to 7 K). It has Lorentzian rather than Gaussian broadening.

(ii) In the case of the tetragonal high-$T$ phase, the excitonic resonance remains up to about 220 K; above this temperature, it is being only observed as a shoulder (shallow maximum).

It must be noted that the low-energy part of the spectrum is purely excitonic, whereas the high-energy part presents the continuous excitonic absorbance or band—band.

For the sake of comparison, Figure 2b shows the absorbance curves of the samples with different grain sizes at two temperatures, 7 and 152 K (temperature at which the orthorhombic to tetragonal transition occurs). It can be clearly seen that the excitonic front is somewhat wider and shifted toward a high energy in sample S1 (larger grains) in relation to sample S2 (smaller grains), which is consistent with the corresponding larger photocurrent measured on the cell, due to light trapping effect by scattering (Figure 2c). The smaller open circuit voltage measured in S1 might be due to a greater disorder in this film.

By fitting the absorbance spectra using the Elliott—Toyozawa theory with Lorentzian (low $T$ region) and Gaussian (high $T$ region) broadenings (see Figure 2a), the evolution for the orthorhombic phase represented by blue circles and the evolution for the tetragonal phase represented by red squares (the points between 240 and 300 K are less precise because the maximum cannot be unequivocally distinguished) can be obtained. The shift of the excitonic peak with $T$ has a positive rate (contrary to that observed in Si, Ge, and III–V semiconductors and II–VI) on the order of 0.4–0.5 meV/K in both phases (see Figure 3a for exact fitted values). These values are very similar to those measured in PbS and PbSe semiconductors and are due to Pb orbitals contributing to the valence band of these materials. Fits of spectra in Figure 2a also confirms the decrease in the effective Rydberg energy of the exciton from 29(6) to 13(5) meV after the phase transition temperature, which is consistent with recent estimations. In old reports, 35–50 meV was estimated from magneto-PL measurements.

After Toyozawa, Lorentzian/Gaussian broadening is related to weak/strong phonon coupling. By fitting the full excitonic curves, we could also determine the dependence of the energy of the band gap, $E_g$, on $T$ for both phases (see Figure 3b). The observed variation is fairly linear, and the values of the $E_g$ slopes are shown in the figure. The slopes are lower than those obtained for the excitonic binding energy but similar to those observed in some IV–VI semiconductors.

3.2. Time-Integrated PL: Band Studies. Figure 4 shows the time-integrated PL spectra of a perovskite (MAPbI$_3$) film consisting of larger grains (average size 352 nm) at temperatures ranging from 15 K up to 293 K and using...
three different excitation fluences. As previously reported in
the literature, we observed two bands in the spectra, and their
behavior can be described as follows:

(i) Traditionally, the higher energy band has been
associated with the orthorhombic phase (O). This
higher energy emission peak “O” can only be observed at
high-fluence excitation (see Figure 4a), and it gradually
appears below 140 K, although it is almost imperceptible
throughout the whole low-temperature range. This band
is placed nearby the corresponding absorption onset.14
According to the polaronic mechanism, the spectral
width of this band does not decrease with temperature,
leading to a characteristic and enduring finite line width,
even at very low temperatures.30,31

(ii) The low-energy band, on the other hand, has been
associated with the tetragonal phase and high-fluence
excitation; it is perceptible throughout the whole
measured temperature range, even at a low temperature
range, causing the appearance of dual emission (see
Figure 4). There is a remarkable predominance of the
low-energy PL band for \( T = 140 \) K (23.8 nJ/cm\(^2\)) as well
as for the transition region at \( T = 115 \) K (370 nJ/cm\(^2\)).
However, the shape of the PL emission in this tetragonal
phase (“T”) is independent of the fluence excitation,
excluding contributions of defect broadening. Some
authors have assigned the lower energy band of this dual
emission at high-fluence excitation: (i) to a DAP around the
transition15 and (ii) to the inclusion of the tetragonal phase
(\( T_u \)) at temperatures below the phase transition.
13,14,26,34 Therefore, residual tetragonal MAPbI\(_3\)
crystals could coexist and be responsible for this dual
emission. One of the arguments in favour of the
inclusion of the tetragonal phase at high-fluence excitation
is that at temperatures below the phase transition, we still detect emission centered on the same
energy as in the room-temperature phase.14 Recently, it
has been pointed out about the importance of the nature
of the organic cation \((\text{CH}_3\text{NH}_3)^+\) on the appearance of
dual emission, 6,33 whereas the nature of the halide ion (I,
Br) is supposed to have a negligible impact.6 In other
words, the atomic ordering in the organic cation takes
place progressively when cooling down.

(iii) Last, the S1 sample at low-fluence excitation (see Figure
4b,c) shows important differences with respect to the
high-fluence excitation previously reported. We have
measured a new sublow-energy band labelled “M.” For
the lowest excitation power used (1.43 nJ/cm\(^2\)), there is
a strong red shift at \( T < 115 \) K of the “M” band (see
Figure 5); whereas the energy at which the “T” and “O”
emissions are centered almost does not change with
decreasing fluence excitation. Moreover, there also exists
a strong red shift with decreasing power, the detected
emission of “M” being no longer centered on the similar
energy as the room-temperature “T” phase. Therefore,
the band gap energy strongly depends on the fluence
excitation on this region.

Moreover, below 45 K, this sublow-energy band labelled
“M” seems to change its tendency and present a blue shift with
decreasing temperature. Thus, the behavior of this sublow-
energy band, which does not appear in the small-grain
perovskite film and reaches the maximum in PL intensity at
the temperature of 15 K for the power of 1.43 nJ/cm\(^2\), might
be explained as bound-state excitons10 rather than an inclusion
of the tetragonal phase.

Hence, a more detailed study of the grain structure should be
carried out to gain deeper insight into the dependence of
the fundamental properties and processes taking place in this
perovskite on the crystalline size.

Figure 5 shows the energy values of the bands as a function
of temperature obtained from the PL spectra. By decreasing
the temperature, the PL peak energy of the tetragonal band
decreases linearly until \( T = 165 \) K. Table 1 summarizes the
values of the temperature coefficient \( \alpha = \partial E / \partial T \) obtained
for different fluence excitations.

| Power (nJ/cm\(^2\)) | Sub-Low | High = Orthorhombic | Low = Tetragonal |
|--------------------|---------|---------------------|-----------------|
| 23.8               | −86(12) | 24(4)               | −86(9)          |
| 370                | −38(7)  | 370(50)             | −38(5)          |
| 370                | −38(70)| 1.4(0.2)            | −388(60)        |

Moreover, the comparison between the calculated14 and
measured energy band gaps of MAPbI\(_3\) is collected on Table 2.
In the temperature range 165 K > \( T > 115 \) K, there exists a
transition behaviour before arriving to the orthorhombic
structure. Below the tetragonal-to-orthorhombic phase transi-
tion, there is a strong dependence of the PL spectra on the
fluence excitation, as shown in Figure 4. As the excitation
power is decreased, the intensity of the lower energy band
remarkably drops, broadens, and shifts to lower energy,
whereas the higher energy band nearly vanishes (see Figure
4). Because two coexisting crystallographic phases15−35 in
several inorganic perovskite materials of mixed38−40 and
pure41−43 composition, including MAPbI\(_3\), have been already
observed, we suggest that the measured emission in the low-
temperature phase could be explained by supposing a very
small relative volume fraction of low-energy sites attributable
to small embodiments of individual tetragonal phase
crystallites, where photoexcited carriers can be trapped.14
Therefore, the subgap sites in the tetragonal crystallites can
only be partially filled under weak excitation by the few free
carriers. On the other hand, the emission observed at higher
energy under strong excitation could be caused by the
remaining carriers in the orthorhombic phase after saturating
the tetragonal crystallites. Moreover, other arguments in favour
of the inclusion of the tetragonal phase at high-fluence excitation
are as follows: (i) At temperatures below the phase

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**Figure 5.** Temperature-dependent data of the PL peak energy of the
three bands obtained from the PL spectra. The sample is the larger
grain (352 nm) perovskite film (thickness 350 nm). The uncertainty
of the data is less than the size of the symbol.
Table 2. Band gap Energy (identified as the PL peak energy from Gaussian deconvolution) of CH3NH3PbI3

| crystal structure | calculated $E_g$ (eV) | measured $E_g$ (eV) |
|------------------|----------------------|--------------------|
|                  |                      | 370 nJ/cm²         | 23.8 nJ/cm²       | 1.43 nJ/cm² | deconvolution |
| low-symmetry     | 1.564(7)             | 1.524(3)           | 1.505(5)          | 1.491(13)  |
| orthorhombic     | 1.634(7)             | 1.628(4)           | 1.633(3)          | 1.613(4)   |
| tetragonal       | 1.5274(12)           | 1.529(2)           | 1.5286(14)        | 1.535(3)   |
| cubic            | 1.3                  |                    |                   | 1.415(8)   |

Figure 6. PL intensity depending on the wavelength for three different powers and for a temperature of 40–50 K, well below the phase transition temperature. It corresponds to the sample of a 600 nm, 300 nm and 100 nm thick continuous CH3NH3PbI3 “cuboidlike” film. The grain sizes are <80 nm, 103 nm and 352 nm. The PL intensity was normalized at the higher energy band. Inset: SEM images of the three spatially homogeneous and conformal films of CH3NH3PbI3 perovskite with corresponding crystal sizes.

energy band (orthorhombic phase) at 40 K (for the 352 nm thick-grain film), 50 K (for the 103 nm thick-grain film), and 50 K (for the <80 nm thick-grain film), respectively. From the comparison to the excitation spectra (Figure 2a) at this temperature, it can be inferred that photoexcitation takes place entirely through the band gap of the orthorhombic phase (at about 1.69 eV), even though the dominant emission is related to the band gap of the tetragonal phase (at about 1.60 eV). That is because quantifiable excitation through this transition at about 1.6 eV is not possible as the comparison of the emission and excitation spectrum suggests.14 This implies that despite the small relative volume fraction of low-energy states, these sites offer the predominant radiative exciton recombination pathway.14 From the comparison of the emission and excitation spectra, it can be deduced that small individual crystallites could cause a high density of subgap states at the phase boundaries. In fact, we can infer from Figure 6 that the grain size determines which band has more weight for a fixed high power. Thus, increasing the grain size from 80 to 352 nm, it is possible to enhance the tetragonal band versus the orthorhombic band. Indeed, for grain sizes greater than 352 nm, we would be able to eliminate the orthorhombic band. At the same time, a grain size of 100 nm is the optimum size to obtain the same weight in both bands (for a high power). This dependence on the grain size of the structure stability has been already observed in other materials.45 Hence, although traditionally the temperature of 165 K has been associated as the tetragonal-to-orthorhombic phase transition temperature, we can see in Figure 6 that the increase in the grain size allows slowing down the phase transition. On the other hand, the thickness of the perovskite layer has no influence on the appearance or disappearance of the dual emission. However, the thickness of the layer is a much more important factor than the size of the grains in the location of the energy of the band gap (see Figure 6).

3.3. Deconvoluted Gaussian Fitting. 3.3.1. Band Gap Energy. A fundamental key to improving the conversion efficiency is to better understand the yet unclear exciton recombination pathways.30 For this reason and due to the still existing contradictions when trying to interpret the PL emissions, a detailed Gaussian fitting deconvolution is necessary. This can help to give insight not only into the origin of the dual emission peak but also into the existence or not of phonon-assisted indirect transitions causing the tetragonal emission. It has been observed that the intensity of the orthorhombic band decreases with increasing temperature, whereas the intensity of the tetragonal band progressively increases. Some authors have interpreted that the PL tetragonal-band emission stems from phonon-assisted indirect transitions during the exciton recombination process, whereas the PL orthorhombic-band emission originated from direct transitions.47 Other authors, however, defend that the PL emission of the tetragonal band, which is observable for the entire temperature range, cannot be ascribed to the indirect band gap emission affected by a quantum confinement effect.38 In this context, the thorough deconvolution of our time-integrated temperature-dependent PL bands into Gaussian peaks could provide information on the exact number of PL emissions of CH3NH3PbI3 perovskite films and their characteristics and allow to correctly interpret them.

Keeping that in mind, we have deconvoluted the measured time-integrated PL spectra profiles by using a Gaussian fitting, as shown in Figure 7. The spectra at a few selected temperatures for each fluence are shown. The typical PL profile for the large-grain film can be divided into several Gaussian peaks, as illustrated in Figure 7. The different colors used for each of the deconvolution peaks are associated with the different symmetries defining the perovskite structures (see...
Temperature-dependent data of the (a) fwhm and (b) band gap energy of the different peaks obtained from the PL spectra by using deconvoluted Gaussian fitting. Note that the orthorhombic structure has a larger band gap than the tetragonal structure, as theoretical calculations have already revealed. The uncertainty of the data is less than the size of the symbol.

Figure 7. Deconvoluted time-integrated PL spectra profiles for the large-grain film by using Gaussian fitting. Each row shows the profiles, depending on the power, at a given temperature associated with each of the four different phases of the perovskite. Peaks assignment: pink (orthorhombic), red (tetragonal), green (low-symmetry monoclinic/rhombohedral), and yellow (C).

Figure 8. Temperature-dependent data of the (a) fwhm and (b) band gap energy of the different peaks obtained from the PL spectra by using deconvoluted Gaussian fitting. Note that the orthorhombic structure has a larger band gap than the tetragonal structure, as theoretical calculations have already revealed. The uncertainty of the data is less than the size of the symbol.

(i) At low temperatures ($T < 45.5$ K), we would obtain the inhomogeneous broadening contribution ($\Gamma_0 = 74.4$ meV). This term dominates at relatively low temperatures, and a nearly constant broadening was expected. This result is larger than that obtained in a less precise way, where a value of 38 meV was obtained, whereas it is much more similar to the behavior described more recently by Dar et al. (ii) While raising the temperature from 45.5 to 165−218 K, it was found that the line width decreases (increases) almost linearly with temperature. Hence, the existence of the latter low-symmetry phases below 45.5 K cannot be discarded. Moreover, our results suggest that PL is as a suitable method to explore the structural phase transitions in organometal-halide perovskites.

At this point, we will analyze the evolution of the line width (fwhm; $\Gamma$) with the temperature (see Figure 8a), keeping in mind that the independent Boson model is no longer valid:

- At low temperatures ($T < 45.5$ K), we would obtain the inhomogeneous broadening contribution ($\Gamma_0 = 74.4$ meV). This term dominates at relatively low temperatures, and a nearly constant broadening was expected. This result is larger than that obtained in a less precise way, where a value of 38 meV was obtained, whereas it is much more similar to the behavior described more recently by Dar et al. (ii) While raising the temperature from 45.5 to 165−218 K, it was found that the line width decreases (increases) almost linearly with temperature. Hence, the existence of the latter low-symmetry phases below 45.5 K cannot be discarded. Moreover, our results suggest that PL is as a suitable method to explore the structural phase transitions in organometal-halide perovskites.

In conclusion, the study of the temperature-dependent PL spectra reveals the existence of different phases in the orthorhombic, tetragonal, and monoclinic structures, as well as the possible presence of new phases in the temperature range studied. These results are consistent with previous theoretical and experimental studies, and provide valuable insights into the structural and electronic properties of organometal-halide perovskites.
can be neglected, and the optical phonon energy takes a value of $\Gamma_{\text{opt}} = 27.0$ meV. This outcome is consistent with the Raman scattering experiment on CH$_3$NH$_3$PbI$_3$, which revealed optical phonons with an energy of $25 - 42$ meV for the torsion mode of the organic cations, whereas the vibration of the inorganic cage and the vibration of the organic cations are associated with much smaller energies.

Moreover, it can be demonstrated that the shift of the line width ($\Delta \text{fwhm}$) scales with the fwhm, although this dependence varies in each one of these three already exposed regions. It is necessary to note that $\Gamma_T = 74.4$ meV is the inflection value that causes the line width to decrease or increase with temperature. For a linewidth <74.4 meV (>74.4 meV), the line width will increase (decrease) with increasing temperature. This variation will be larger as we move away from fwhm.

As shown in Figure 5, when studying the band gap energy, we have distinguished three blocks (high, low, and sublow). Further in-depth analyses of the PL spectra reveal that they can be better described by five to six peaks, as obtained from Gaussian fit deconvolution (Figure 8b and Table 2). These peaks will be here labelled orthorhombic, tetragonal, low-symmetry monoclinic/rhombohedral, and “C”, from higher to lower energies and are shown in Figure 8b. All these peaks behave similarly during heating. Both the lower energy emission peak attributable to the tetragonal phase (T) and the highest energy emission peak attributable to the orthorhombic phase (O) of CH$_3$NH$_3$PbI$_3$ experience twice the blue shift previously reported. Additionally, a continuous blue shift for temperatures higher than 165 K has also been observed. Both the blue shifts can be described by a temperature coefficient $\alpha = \partial E/\partial T$ (see Table 3).

\begin{table}[h]
\centering
\caption{Temperature Coefficient of CH$_3$NH$_3$PbI$_3$ Obtained for Different Temperature Regions}
\begin{tabular}{|c|c|c|c|c|}
\hline
$T$ (K) & orthorhombic & tetragonal & low-symmetry & C \\
\hline
45.5 & 396(30) & 455(14) & 291(30) & 147(20) \\
165 & -164(50) & -168(30) & 13(60) & \\
300 & 535(50) & 235(13) & 147(17) & 236(19) \\
\hline
\end{tabular}
\end{table}

Figure 9. Temperature-dependent data of integrated intensity at the laser excitation power of 1.43 nJ/cm$^2$. Phase transitions are associated with the local minima. The uncertainty of the data is less than the size of the symbol.

\begin{equation}
I_T = \frac{I_0}{1 + A e^{-E_b/k_B T}}
\end{equation}

in which $I_0$ is the intensity at 0 K, $A$ the rate constant of the exciton dissociation process and $k_B$ is the Boltzmann constant.

First of all, we made the fitting obviating the difference of behavior before and after the transition temperature. In that way, we have estimated the fluorescence dependence of $E_b$ for three of these peaks: tetragonal-, orthorhombic-, and low-symmetry-structures. Thus, an increase in $E_b$ is observed with the decrease in power. The values obtained for the orthorhombic phase are concentrated between 42 meV (370 nJ/cm$^2$) and 56 meV (1.43 nJ/cm$^2$), whereas for the tetragonal phase, they vary between 25 meV (370 nJ/cm$^2$) and 61 meV (1.43 nJ/cm$^2$). The highest values obtained for the tetragonal phase are close to those published by some authors. For example, for the CH$_3$NH$_3$PbI$_3$ film, the published $E_b$ values are 62.3 meV from the PL measurements and 55 meV from the absorption data. Nevertheless, we should note that this exciton binding energy was obtained without taking into account the two different behaviors before and after the transition temperatures; therefore, this exciton binding energy may be overestimated, being the upper bound for $E_b$ of halide perovskites.

It would be more accurate to differentiate for temperatures lower and higher than the transition temperature. Thus, lower exciton binding energy values are obtained for the tetragonal phase (see Table 4). In the region where the orthorhombic phase dominates, the activation energy at high fluorescence excitation (24 meV) is similar to the exciton binding energy obtained from the optical absorption measurements, 29(6) meV (see section 3.1). Similarly, in the region where the tetragonal phase dominates, the binding energy (6 - 11 meV)
also agrees with the value deduced from optical absorption in section 3.1 (13(5) meV). These results also agree with values of 18–24 meV\textsuperscript{27} or 32 meV\textsuperscript{14,59} already reported for the tetragonal structure by using microwave photoconductance and PL experiments. The present study suggests that for the same composition, the exciton properties of hybrid perovskites are sensitive to the fluence, temperature, synthesis, and structure details, such as the grain size. As probed, at high temperature, the exciton screening (due to collective orientational motion of the MA\textsuperscript{+} cations) produces a large population of free carriers.\textsuperscript{27} Another possibility for the interpretation of the activation energies listed in Table 4 for sub-low and orthorhombic phases is to consider that they are associated to a carrier detrapping mechanism, instead of exciton dissociation.

3.3.3. Excitonic Character of the Peaks. The fluorescence–PL dependence was additionally conducted in the range of 0.06–370 nJ/cm\textsuperscript{2}. The position and intensity of the different PL bands/peaks also vary with laser fluences because the inherent band gap of MAPbI\textsubscript{3} increases with the accumulation of charges during photoexcitation.\textsuperscript{6,61} With increasing fluence at temperatures below 90 K, a continuous blue shift of the low-energy emission band (tetragonal- and low-symmetry-phase) is observed because of the tetragonal band-filling effect.\textsuperscript{61} Deconvolution shows how the tetragonal peak fills with fluence excitation, whereas the low-symmetry peak “M” decreases (see Figure 7a–c), causing the blue shift of the low-energy emission band. Indeed, once the tetragonal peak has been filled, the orthorhombic peak begins to increase. At high fluence, the coexistence of the tetragonal phase and the orthorhombic phase is observed. Figure 8b shows the different peaks that undergo a blue shift with the fluence increase, being greater for the peaks assigned to smaller $E_b$. By contrast, only at higher fluences (>200 nJ/cm\textsuperscript{2}), the orthorhombic peak shows a blue shift. This could be explained if the dynamic charge transfer from the orthorhombic to tetragonal structure takes place at lower fluences (<200 nJ/cm\textsuperscript{2}). Hence, the band-filling effect dominates at higher fluences (>200 nJ/cm\textsuperscript{2}).

At temperatures lower than 45.5 K, a perceptible sublinear dependence of the integrated PL intensity on the fluence was detected in the $E_b$ position of the “C” peak obtained by deconvolution, whereas the low-symmetry peak “M” was almost linear (see Figure 10). This sublinear dependence observed for $T < 40$ K can be produced by the inefficient diffusion of the photogenerated carriers and suggests the presence of nonradiative recombination at low temperatures (see Figure 11). By contrast, the rest of the peaks display an overlinear relationship between the fluence and the integrated PL intensity. At higher temperatures, the “C” peak disappears, whereas the rest of the peaks go closer to a biexcitonic behavior, as shown in Figure 10. An increment in the carrier density yields the saturation of nonradiative recombination centers, getting better effective internal quantum efficiency and suggesting that Auger recombination plays a minimal role under this fluence.\textsuperscript{57}

### Table 4. Binding Energy

| power (nJ/cm\textsuperscript{2}) | sub-low | orthorhombic | tetragonal |
|-------------------------------|---------|--------------|------------|
|                               | $T < 165$ K | $T > 165$ K | $T < 165$ K | $T > 165$ K |
| 370                            | 39(12)   | 5(6)         | 24(16)     | 3(4)        |
| 23.8                           | 147(30)  | 9(5)         | 57(14)     | 3(2)        |
| 1.43                           | 482(80)  | 12(5)        | 70(20)     | 2(2)        |
|                               | $T < 115$ K | $T > 115$ K |
| 370                            | 7(5)     | 11(7)        |
| 23.8                           | 13(7)    | 9(4)         |
| 1.43                           | 30(11)   | 6(4)         |

Figure 10. Excitonic character of the peaks: “C” (exciton, X), tetragonal (biexciton, 2X), low-symmetry “M” (Trion+, X+), and orthorhombic (2X*) peaks. Inset: Excitation fluency-dependent data of integrated intensity at the temperature of 40 K; this was used to determine each of the values of the slopes plotted in Figure 10.

From Figure 10, it can also be deduced that one C-exciton (“C” peak) exists in our larger grain perovskite film. On the one side, the spin–orbit splitting of the valence band could produce another different exciton, M-exciton (low-symmetry peak “M”). Because of Figure 8b, in which the optical gap for C-exciton is smaller, the hole of the C-exciton (M-exciton) should be situated in the upper (lower) branch of the valence band. However, this M-exciton (low-symmetry peak “M”) also could be understood as a positive Trion, in which the exciton is bound to a hole. In our PL spectrum of Figure 7b,c, it can be observed that the low-symmetry “M” (Trion, X*) peak is stronger than the “C” (exciton, X) and tetragonal (biexciton, 2X) peaks (see Figure 10). This could be a signature of an intrinsic doped monolayer, arising from the charged trap states present in the SiO\textsubscript{2} substrate. The orthorhombic phase, which has been detected at higher temperature and excitation fluence, is associated with 2X*.

3.4. Time-Resolved PL. TRPL emission was measured by means of time-correlated single-photon counting at different temperatures, excitation fluences, and emission energies. From these measurements, the life time is calculated that can be seen in Figure 11. At an excitation fluence of 370 nJ/cm\textsuperscript{2} (see Figure 11), the radiative emission of the lower energy band (red line/circle) and the higher energy band (orthorhombic peak, purple line/square) has been calculated. The radiative
emission shows clearly three drops of the lifetime with the temperature, which confirm the temperatures of the three phase transitions already determined by time-integrated PL. In addition, there is a concordance with the temperatures at which the minimum values are observed in the integrated intensity versus $1/T$ of Figure 9. From Figure 11, it can also be seen that in all phase transitions (at 165 K and around 280 K), only the radiative emission takes place, with the exception of the transition that takes place at the temperature close to 45.5 K (in which both the radiative and nonradiative emissions could be involved, as suggested from Figure 10). As aforementioned, our results suggest that a phase transition from a low-symmetry to an orthorhombic phase occurs at that temperature where the symmetry of the anionic sublattice is modified, whereas no ostensible modification of the cation dynamics is suggested. By using a three-level model with thermal activation energies ($E_{\text{act}}$) of 53.63(12), 45.67(15), and 50.86(14) meV, depending on the PL components, we can explain a possible nonradiative emission at 45.5 K by PL quenching due to the thermal escape of electrons. This would explain why when increasing the temperature to 140 K there is a decrease in the intensity of the peaks associated with 2X' (orthorhombic) and X' (monoclinic/rhombohedral) versus the increase observed for 2X (tetragonal) (see Figure 7). Additionally, dark states of photoexcited carriers are revealed with the activation energies due to thermal excitation ($E_{\text{th}}$) of 41(2), 30.5(7), and 35.06(14) meV. By contrast, these activation energies are too low if we compare it to the onset 41(2), 30.5(7), and 35.06(14) meV. By contrast, these

4. CONCLUSIONS
We have reported the optical absorption and PL emission characteristics of CH$_3$NH$_3$Pbl$_3$ perovskite as a function of several important parameters such as the grain size, temperature, excitation fluencies wavelength, and time (in the case of TRPL measurements). This systematic and detailed study allows us to clarify the nature of the not well-known dual emission peak, finding absorption and emission tendencies and suggesting the existence of a novel low-temperature phase with symmetry reduction. Sometimes, for convenience, it can be assumed that the vibration of each group of bands is independent of the rest of the molecule or compound, but we should bear in mind that those vibrations can be strongly coupled. This fact makes techniques such as Raman and IR spectroscopies or transient PL measurements suitable sources of information of the atomic local environment and therefore sensitive to structural phase transitions. Thus, for instance, TRPL emission data collected in Figure 11 evidence a phase transition for this CH$_3$NH$_3$PbI$_3$ compound at temperatures close to 45 K. (More other evidences are given along the manuscript). X-ray diffraction measurements, which provide the average structure of the sampled compound, are limited for systems such as that of this perovskite because the fixing of the atomic coordinates of the light elements of the cation are responsible of the symmetry lowering at low temperatures. This reduction of symmetry below 45 K would also explain the increase of the number of bands.

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Notes
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