Optical characterization based on temperature of inkjet-printed CsPbBr$_3$ thin film

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Abstract: Metal halide perovskites possess exceptional optical properties and can be deposited onto a substrate through inkjet-printing technique. This combination has been demonstrated to be highly effective in the fabrication of optoelectronic devices. The optical properties of the caesium lead bromide (CsPbBr$_3$) perovskite nanocrystals are reported in a temperature range from 77 to 393 K. The obtained results show that CsPbBr$_3$ nanocrystals present great emissive properties. The bandgap energy and photoluminescence (PL) energy are demonstrated to increase from low to high temperatures. The increasing temperature manifests an unusual blueshift in the bandgap energy, and it is also observed reversible PL loss and a widening of the full width at half maximum. Concerning the effect of the exciton, it is shown that the exciton binding energy remains relatively constant with changes in temperature. The results obtained in this study of these perovskites make CsPbBr$_3$ a promising candidate for optoelectronic applications.

I. INTRODUCTION

Perovskite is a material characterized by a specific crystal structure, represented by the formula ABX$_3$. This structure comprises two cations, A and B, which are often significantly different in size and may be monovalent or divalent, and an anion, X, that bonds to both positively charged ions. According to the chemical formula, A is monovalent and B is divalent. [1]

Metal halide perovskites (MHPs) have been of interest to many studies in recent years due to their outstanding optical properties [2]. MHPs present a broad absorption spectrum and high photoluminescence quantum yield (PLQY), making this kind of semiconductor a good candidate for the manufacture of new and improved optoelectronic devices with high efficiency, including light-emitting diodes and solar cells. Perovskite-based colloidal CsPbX$_3$ (X = Cl$^-$, Br$^-$, I$^-$) nanocrystals (NCs) are a type of MHPs with noteworthy properties for light emission. The inorganic nature of CsPbX$_3$ is crucial for ensureing the non-degradation of the material. Perovskite NCs are commonly synthesized through the hot-injection method, which consists of reacting caesium carbonate with oleic acid in a metal halide solution [3]. CsPbX$_3$ NCs have been found to exhibit significantly more efficient and narrow photo-luminescence compared to organic polymers, as well as sharper and tunnable emission peaks [3]. PL is the result of the radiative recombination mechanism, in which a coherent light is used to excite the samples and cause an electron from the valence band to move to the conduction band. In addition, CsPbX$_3$ NCs are direct band-gap semiconductors that their band-gap energy can be tuned by changing the combination of cations and anions present in the structure. This property also makes MHPs promising candidates for a range of optoelectronic and photovoltaic applications. On account of low non-radiative recombination processes,

this type of semiconductors show a high photolumines-cence quantum yield. A crucial feature of lead halide perovskite NCs is their elevated defect tolerance, this outstanding property is a key factor for their bright PL. It has been demonstrated that these materials possess exceptional electronic properties, including high carrier mobility and lifetime, strong broadband absorption, long carrier diffusion lengths, tunable band-gap energy, and low exciton binding energies [4].

Another point worth mentioning is the high exciton binding energy. Excitons are neutral quasi-particles caused due to the excitation of an electron from the valence band to the conduction band. When an electron transitions from one band to the other, it leaves a "hole" behind. This hole is essentially the absence of the electron and has opposite charge. The electron and the hole are attracted through the Coulomb interaction. This attraction between the electron and the hole is an important factor in the electrical and optical properties of semiconductor materials. This whole combination is the so-called exciton, and its energy is relatively smaller than the free electron and hole and the band-gap energy. At low temperatures, the exciton has a stronger effect. The understanding and study of their properties are crucial for the development and optimization of optoelectronic devices [4].

Stokes shift refers to the difference in the positions of the absorption and emission peak. In nanocrystal electronic structures, it is intrinsic, and it is not a consequence of extrinsic effects such as impurities or solvent-related effects [5]. Particularly, in CsPbBr$_3$ NCs, it is the result of transitions from the valence band edge state to the conduction band edge state and the conduction band edge state to the confined hole state. Hence, it is mainly caused by the band edge emission and absorption, and it is conditioned by the energy difference between the valence band edge state and the confined hole state [6].

An interesting approach to consider is the temperature effect on this kind of material. It is known that temperature changes electronic properties, among others [7]. For instance, the electrical conductivity of a semiconductor material changes when the temperature increases. At low temperatures, the electrons in a semiconductor material are more strongly bound to their respective atoms. There is also a large energy gap between the valence band and the conduction band, which is responsible for electrical conduction. As a result, the valence band electrons need a relatively high amount of energy in order to transition to the conduction band. However, as the temperature increases, the bonds that hold the electrons in place begin to break due to thermal energy, causing there to be more free electrons. The band-gap becomes narrower, too. This makes it easier for the valence band electrons to transition to the conduction band, leading to an increase in the material's electrical conductivity [7]. Examining the effect of the exciton in such materials by temperature changes is worthwhile taking into account.

The inkjet-printing technique is efficiently used for the fabrication of low-cost and large-area perovskite structures, it consists of the deposition of thin film layers of perovskite. It takes advantage of the drop-on-demand inkjet method and uses piezo inkjet printing, which uses a piezoelectric ink injection system with a piezoelectric transducer activated via voltage pulses. This leads to the generation of pressure waves, which propagate within the ink channel resulting in droplets being generated at acoustic frequencies. Additionally, the technique features the injection of droplets emanating from the nozzle. [8]

In this study, the optical properties of inkjet-printing CsPbBr$_3$ NCs are investigated through absorbance, transmittance, reflectance and photoluminescence measurements at temperatures ranging from 77 to 393 K.

II. EXPERIMENTAL PROCEDURE

Lead halide perovskites (LHPs) have been used in order to carry out this project. In particular, CsPbBr$_3$ nanocrystals. The LHPs have been deposited by the inkjet printing technic. Additionally, the used ink has been developed by the research group *Advanced semiconductors* lead by Ivan Mora and it has been elaborated from colloidal CsPbBr$_3$ NCs [9]. Several samples under different conditions, such as the number of layers printed and the time and temperature of annealing, were prepared and studied. The best results have been obtained from the samples with three MHPs layers with a post-processing annealing at 95ºC for 10 minutes under N$_2$ atmosphere. The perovskite was printed over silicon (Si) and fused silica substrates. The optical properties have been studied using Optical Absorption

(OA) and Photoluminescence (PL) Spectroscopy. On the other hand, this research was divided into two parts: the analysis of optical properties at ambient temperature and as a function of temperature.

The OA measurements were possible thanks to the *Bentham PV300 EQE system* which consists of an integrating sphere that uses a monochromatic light from a dual xenon and quartz halogen source. At room temperature, transmittance and reflectance measurements were required to obtain the absorbance spectra. However, absorbance was easily computed using the following equation:

$$1 = A + T + R \tag{1}$$

Temperature dependence measurements (both PL and OA) have been done inside a Linkam cryostat, from 77 K up to 393 K using liquid nitrogen. The absorbance was evaluated using a Matlab script that is based on Elliott fits [10], considering the reflectance as a second order polinomic and latter introduced as fitting parameters. The generalized formula of Elliott is:

$$\alpha(\hbar\omega) \propto \frac{1}{\hbar\omega} \sum_j \frac{2E_B sech\left(\frac{\hbar\omega - E_j^B}{\Gamma}\right)}{j^3} + \int_{E_B}^{\infty} \frac{sech\left(\frac{\hbar\omega - E}{\Gamma}\right)}{\hbar\omega} \cdot$$
$$\cdot \frac{1}{1 - exp\left(-2\pi\sqrt{\frac{E_B}{E - Eg}}\right)} \cdot \frac{1}{1 - \frac{8\mu^2 b}{\hbar^4}(E - Eg)} \tag{2}$$

The first part of the equation represents the sum of discrete excitonic peaks, while the second one is the continuum contribution [10]. The discrete part reflects a series of excitonic resonances with energy levels equal to $E_j^B = E_g - \frac{E_B}{j^2}$. The remainder of the formula is made up of continuum states and it is the result of the correlation between electrons and holes due to Coulomb interaction. Elliott fit is based on the interaction between the bandgap energy E_g and the exciton binding energy E_B. This method offers the possibility to compute both energies. In order to accurately determine the E_g, it is necessary to have an understanding of E_B, as excitonic effects can significantly influence the interpretation of the absorption spectra even at room temperature. For this reason, Elliott fit has also been used to determine E_g and E_B at room temperature. [10]

Regarding PL measurements at room temperature, the samples have been excited with the 325-nm line from a helium-cadmium laser. The light emitted by the samples, once it has crossed through a monochromator, is studied with a detector connected to a data processing system. The result of these measurements is the PL peak in the visible range. The PL characterization based on temperature was made using the same system as for the transmittance measurements modifying some components of the system. For instance, an ultraviolet laser was em-

ployed for exciting the sample, working at 405 nm, with a power on the sample abut 1 mW.

III.   RESULTS AND DISCUSSION

A.   Optical properties at room temperature

The data presented in this section serve as a basis for the measurements as a function of the temperature.

Absorbance, transmittance and reflectance are shown in Fig. 1, which exhibits the optical properties of the CsPbBr$_3$ NCs on fused silica. The absorbance and transmittance spectra show an edge at about 520 nm, while reflectance remains approximately constant in the whole studied range. Previous studies have indicated that the absorption edge is at around 524 nm [9]. In comparison, the current results indicate a value that is deemed satisfactory. The absorption edge represents the point at which the strong short-wavelength absorption changes to weak long-wavelength absorption according to literature [2]. The relation between absorbance, transmittance and reflectance can also be observed: these quantities must satisfy equation (1), the absorbance and transmittance have a symmetrical profile and reflectance remains fairly constant.
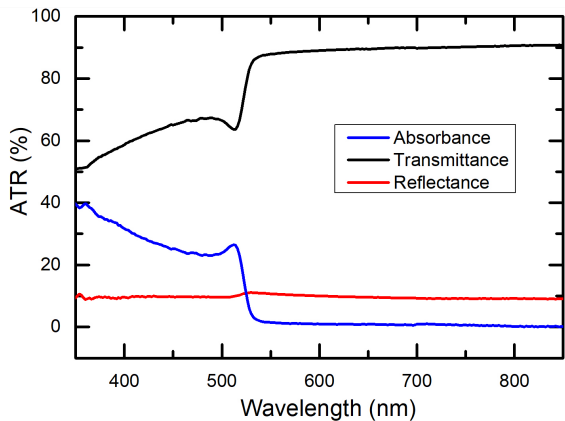

FIG. 1: Absorbance, transmittance and reflectance (ATR) spectra of the sample of CsPbBr$_3$ film on fused silica at room temperature.

Furthermore, using the Elliot fitting, E_g and E_B were determined. These energies are 2.437 eV and 29.72 meV, respectively. The confidence bounds of these findings are 95% according to the used method. As shown in Fig. 2, the beginning of the interband absorption may be identified as an edge positioned at about 2.35 eV, consistent with the data obtained in Fig. 1. With regard to the sum of excitonic peaks, the excitonic peak is well distinguished because it reaches a value well below the absorbance of the experimental data. Nevertheless, the

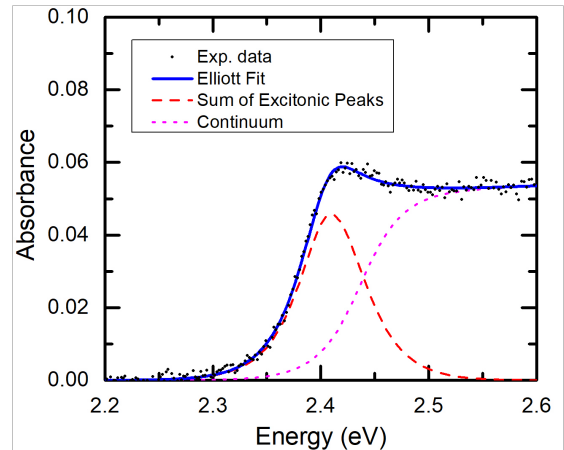absorption increase is mainly caused by the continuum contribution [10].

FIG. 2: Absorbance spectra with Elliot fitting of the sample of CsPbBr$_3$ film on fused silica at room temperature.
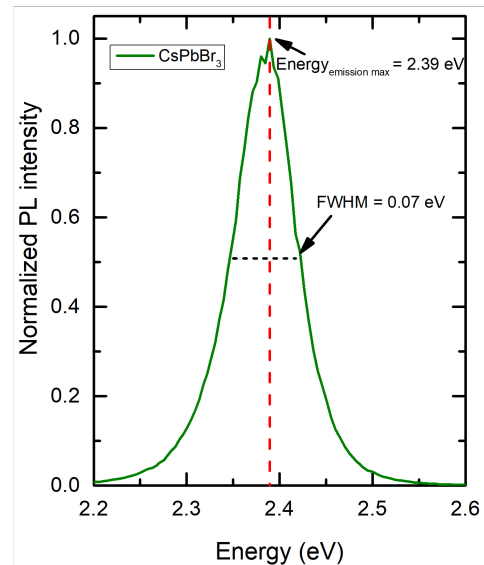

FIG. 3: PL spectra of the sample of CsPbBr$_3$ NCs film on silicon at room temperature.

PL measurements at room temperature show that the sample emits in the visible range from 2.2 to 2.55 eV approximately (Fig. 3). The PL peak is centered at around 2.39 eV, which corresponds to an emission wavelength of 519 nm. In other words, the maximum emission intensity of a sample occurs at this single wavelength, while lower intensity is observed at wavelengths both below and above this peak. The full width at half maximum

(FWHM) is only about 0.07 eV (16 nm). This data is coherent with the previous results and with literature [2].

B.   Optical properties as a function of temperature

The absorbance at different temperatures has been obtained directly from the measurement of the transmittance (introducing the effect of the reflectance as a background in the absorbance in the fitting procedure with the Elliot formula). In the Fig. 4 we present the absorbance evaluated in this way, for different temperatures. As the temperature increases, the absorption edge shows a decrease in pronunciation and it is reached at higher energies. Therefore, at higher temperatures the wavelength blueshifts. This small blueshift can also be seen by comparing Fig. 4 with the room temperature absorbance shown in Fig. 2. The increasing prominence of low temperatures in the absorption profile is caused by the presence of recognizable excitonic absorption characteristics in the samples. The results are consistent with the existing research on this subject [11].
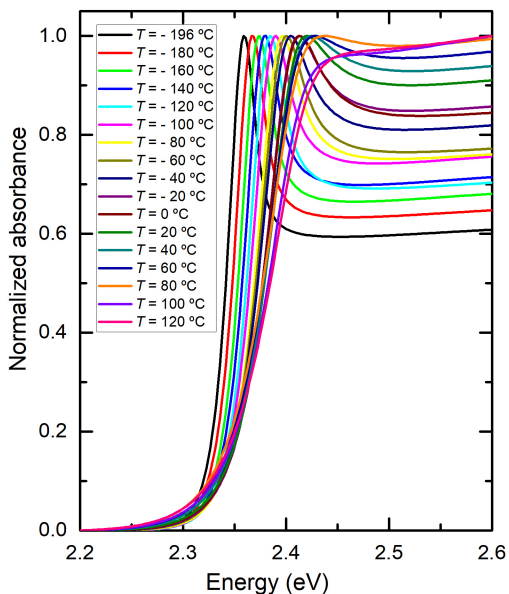

FIG. 4: Normalized absorbance profile as a function of temperature of CsPbBr$_3$ film on fused silica. The temperature range goes from T = -196 ºC to T = 120 ºC.

In Fig. 5, it is presented the temperature dependence of the CsPbBr$_3$ sample. As the temperature increases, the PL intensity decreases and it gets broader. Thus, the peak becomes less definite. Previous researches suggest that this PL loss is reversible upon cooling [12].

Fig. 6 illustrates the temperature dependence of the bandgap and PL energies, as well as the exciton binding energy and the Stokes Shift. It is exhibited that temperature leads to an increase in the E_g. It should be noted
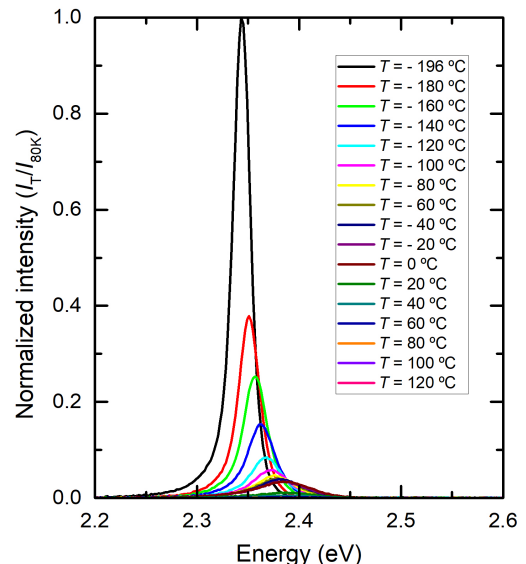

FIG. 5: Temperature dependent PL spectra taken from -196 ºC to 120 ºC of the sample of CsPbBr$_3$ film on fused silica.
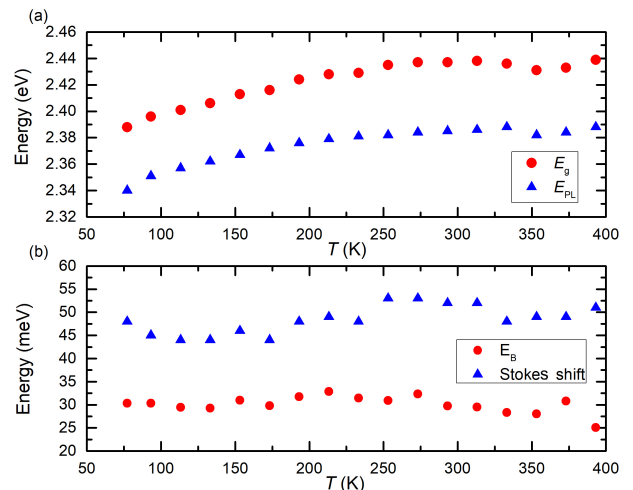

FIG. 6: (a) Temperature evolution of the bandgap energy and PL energy for the CsPbBr$_3$ film on fused silica. (b) Exciton binding energy and Stoke's shift as a function of temperature for the sample of CsPbBr$_3$ NCs inkjet-printed on fused silica.

that most semiconductors do not have such behaviour. This finding is atypical, but according to literature, similar results have been observed in low temperature measurements of plumbotrihalide perovskites [11]. As it has been shown, E_{PL} and E_g increase from low to high temperature, which can also be observed at Fig. 6a. While the E_g shows values between 2.388 and 2.437 eV, the E_{PL} from 2.34 to 2.39 eV. The energy variation of the bandgap is approximately 49 meV. Although this variation is not very large, it affects other optical properties.

For instance, it is sufficient for explaining the absorption edge variation. In relation to Fig. 6b, it is observed that E_B fluctuates from 30 to 35 meV. In comparison to the bandgap, one might say that E_B remains constant through temperature changes. These values were obtained by the Elliot fitting with a 95% of confidence bounds. These nanocrystals present a small Stokes shift, as it is shown in Fig. 6b, which might suggest that the peaks of absorption and emission are narrowly spaced. It spans from approximately 45 to 55 meV when modifying the temperature. The presence of this small Stokes shift in CsPbBr$_3$ has a negative impact on the applications since it transfers Förster resonant or re-absorption energy [6]. The energy values presented in Fig. 6b do not change much through temperature and are three orders of magnitude below the E_g and E_{PL}. Therefore, in comparison, it could be said that they remain constant in the face of temperature changes.

IV. CONCLUSIONS

In conclusion, temperature-dependent of optical properties of CsPbBr$_3$ NCs have been presented. The findings were in excellent agreement with the reported values in the literature. Furthermore, the samples present an emission wavelength around 520 nm at room temperature which corresponds to the green light in the visible range. This value does not remain constant throughout temperature changes. In addition, using Elliott fitting, the bandgap and the exciton binding energies were directly determined. It is shown an increase of the bandgap and PL energies in the range of 77 to 393 K. Both PL and absorption measurements manifest an atypical blueshift with increasing temperature which might be related to the bandgap increase. Reversible PL loss and a widening of the FWHM are observed upon temperature variation from low to high. The sample presents a small Stokes shift, which might suggest that the absorbance and the emission peaks are closely positioned. Also, the temperature-dependent behaviour of the exciton binding energy is relatively constant. These results demonstrate that CsPbBr$_3$ NCs show potential for optoelectronic applications.

In further investigations, it might be interesting to study the other two perovskites, CsPbI$_3$ and CsPbCl$_3$, to gain a more comprehensive understanding of the optical properties of lead-based inorganic perovskites.

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