

Optical characterization of CsCu_2I_3 and $\text{Cs}_3\text{Cu}_2\text{I}_5$ metal halide perovskites

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Abstract: Ternary copper halide compounds, where copper presents oxidation state +1 (Cu^+), have been of great interest because of their optoelectronic properties. In particular, cesium copper halide nanostructures with composition either CsCu_2I_3 or $\text{Cs}_3\text{Cu}_2\text{I}_5$ are materials with excellent emission properties within the visible range, driven by self-trap exciton mechanism. In this work we study the optical properties of two copper based halide perovskites, CsCu_2I_3 and $\text{Cs}_3\text{Cu}_2\text{I}_5$, first at room temperature and later with dependence on temperature. We found that the excitation of the PLE is occurring in the UV region, in agreement with the absorption edge. As a function of the temperature, the band gap decreases with the temperature for both composition, however the emission behaviour exhibits an apparent anomalous behaviour with temperature. The results are discussed in terms of the excitation energy and the bandgap dependence with temperature.

I. INTRODUCTION

Perovskite materials have attracted great interest in the last years because of their outstanding physical properties like piezoelectricity, superconductivity, colossal magnetoresistance or ferroelectricity, among others, that can be exploited in a wide range of applications.

Since the late 2000s, perovskites also began to be studied due to their excellent optical properties, related to their semiconducting nature. They have shown great potential in devices like displays, sensors, LEDs and solar cells. For instance, these materials have shown an extraordinary evolution in solar cells, reaching values as high as 29% when there are combined with silicon in a tandem solar cell [1].

Perovskites are a family of materials with the formula ABX_3 , where A and B are monovalent and divalent cations respectively. In this structure, the electronic properties of the perovskite are mainly driven by the B-X bond, while the A cation has a minor influence but can also modify the B-X bonds. In particular, halide perovskites offer a direct bandgap that can be tuned over the whole visible range by changing its composition or its particle size, and outstanding photoluminescence quantum yield (PLQY) that almost reaches 100% (due to their low non-radiative recombination processes), and very sharp emission, with narrow emissions (10-40 nm). In addition, they also exhibit interesting electronic properties, such as ambipolar carrier transport, long carrier diffusion lengths, high carrier mobility and lifetime, and tuneable bandgap energy. These compounds also show very high defect tolerance. This is attributed to vacancy defects, still being abundant because of their low formation energy, only generate intraband states or very shallow trap states close to the valence and conduction band. Because there is no states in the middle of the gap that would act as traps for carriers, recombination time is not diminished and consequently there is no detriment in the optical properties of the material. On the other hand, antisites and interstitial point defects that would generate mid gap states and act as traps for the carriers have very high formation energy, so they rarely happen at all [2], [3]. This results in a

crystal with a fair number of defects but no trap energy levels. Very different to the usual extremely pure and defect free semiconductor. This also results in easier, low cost, low temperature fabrication process.

In particular, lead halide perovskites (LHP) have been extensively studied. With structure APbX_3 , A being an inorganic or organic cation, lead in the B position and X being a halide anion, most frequently Cl^- , Br^- or I^- . These materials can be easily synthesized into nanocrystal (NC) structure in the form of colloidal solution and can be transferred to a substrate by different physical means (being spin coating the most employed). In this form they show very bright photoluminescence with an easily tuneable emission wavelength by changing the ratio of the halide components [2].

The results with LHP are very promising, but they have the inherent problem of the toxicity of lead, which is quite problematic when designing commercial devices. The perovskite itself is not toxic but is not very stable, and the lead salts in which it decomposes to are highly toxic.

Recently, a simple way of avoiding the lead toxicity has arisen: avoiding this element in the perovskite structure. A lot of research has begun on lead-free halide perovskite where lead is substituted by another element [4]. Different approaches can be found in the literature: from changing lead to lighter elements from the same group IV like tin or germanium, or substituting it by bismuth and antimony from group V, and employing transition metals such as copper, iron, titanium or manganese also show potential.

Some of those perovskites have an unusual photoluminescence mechanism in the form of self-trapped excitons (STE) [5], [6]. The most typical way for carriers to recombine and emit light is through inter-band luminescence, that is the electron in the conduction band recombines with a hole in the valence band generating a photon with energy being that of the gap of the material (E_{gap}). At low enough temperatures an electron and a hole can attract to each other by Coulomb interaction and form a bound state known as an exciton. The exciton behaves as a quasiparticle neutral in charge. In the process of binding some energy (E_b) is lost, so

latter when the exciton recombines and emits a photon, it has a slightly lower energy than that of the bandgap energy. An unusual type of exciton can happen in materials with soft lattice and with strong electroacoustic interaction. In this case the interaction is so strong that excited electrons and holes considerably deform the lattice around them and with this the exciton has a more stable state staying immobile at the place of the deformation than continue moving and dragging the deformation along. This causes another energy loss for the exciton know as self-trapping energy (E_{ST}). When recombination finally happens, it is from the STE level to a modified valence band consequence of the deformation of the lattice caused by the exciton. This new level is closer by a quantity know as deformation energy (E_d). The final energy of the generated photon can be summarized with following expression:

$$E_{PL} = E_{gap} - E_b - E_{ST} - E_d \quad (1)$$

In this work we are going to study and characterize the optical properties as a function of the temperature of two copper-based metal halide perovskites, CsCu₂I₃ and Cs₃Cu₂I₅. Both have STE as their photoluminescence mechanism.

II. EXPERIMENTAL PROCEDURE

Perovskites containing CsCuI with two different stoichiometries have been employed for this final project: CsCu₂I₃ and Cs₃Cu₂I₅. Colloidal solutions of quantum dots with sizes in the range of some tens of nanometers were fabricated by either the one-pot method or hot injection, respectively, using different proportions of CsI and CuI. The solutions were drop-casted on fused-silica substrates and annealed in a furnace at 100 °C in a controlled atmosphere (humidity levels below 1 ppm). All samples were provided by the *Electrophotonics group* in the context of the European Project Drop-it.

To analyse the optical properties, in this work we used three different procedures. Optical absorption (OA), Photoluminescence (PL) and photoluminescence excitation (PLE). Initially, all measurements were done at room temperature and, in a second step, only PL and OA were studied as a function of the temperature, from 10 K to 290 K.

Optical absorption at room temperature was evaluated by measuring the transmittance and reflectance spectra, by using an integrating sphere (Bentham PV300 EQE system), using monochromated light from a Xe and quartz halogen dual lamp source, and collecting the transmitted (or reflected) light with an InGaAs photodetector. For evaluating the absorption as a function of the temperature, the samples were illuminated using a deuterium lamp and the transmittance was collected by an optical fibre and analysed by an Ocean Optics spectrometer. For both cases, the absorption coefficient was evaluated using the following relation [7]:

$$T = (1 - R)e^{-\alpha d} \quad (2)$$

The reflectance was not measured as a function of temperature and was assumed constant, as a free parameter to be adjusted for determining the band gap energy.

The PL and PLE at room temperature were done using the Xe and quartz halogen dual lamp as an excitation source, whereas the emitted light was analysed using the Ocean Optics spectrometer. The PLE measurements correspond to the integrated intensity of the emission peak as a function of the excitation wavelength (i.e., the PL spectrum for each point was collected and individually analysed to determine the PLE intensity).

Finally, temperature dependence PL measurements were done by exciting the samples with the line 325-nm from a HeCd laser and analysing the emitted light with a single-grating monochromator coupled to a GaAs photomultiplier.

For cooling down the samples, they were introduced inside a closed cycle He-cryostat. First the sample was placed in its position, then the cryostat was closed and a system consisting of a primary pump and a turbomolecular pump generated a high vacuum on the cryostat. Finally, we turned on the compressor which generated a flow of liquid helium around the sample lowering its temperature (close to 10 K). We started our measures at the lowest temperature possible, after that the compressor was stopped and the temperature started to rise slowly. With a temperature sensor close to the sample and monitored by a Matlab script that also controls either the PL or OA acquisitions, the measurements were repeated every time the temperature reached the set value (steps of ≈ 10 K).

III. RESULTS AND DISCUSSION

A. Optical properties at room temperature

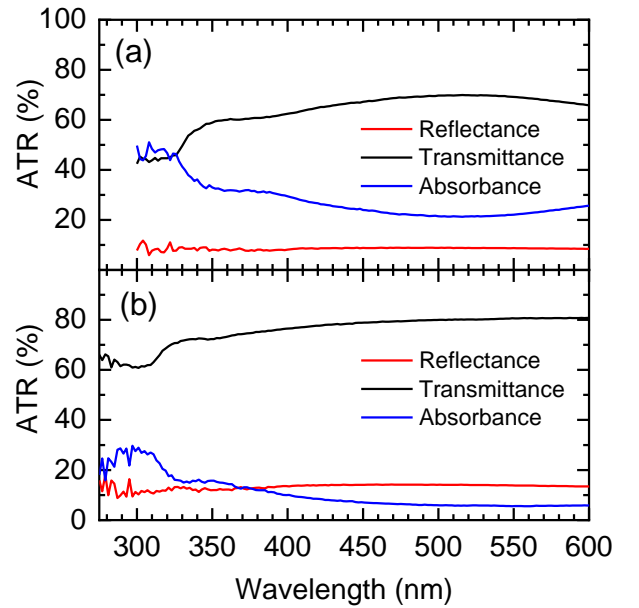


FIG. 1: Transmittance, reflectance and absorbance spectra obtained for the (a) CsCu₂I₃ and (b) Cs₃Cu₂I₅ samples.

In order to determine the absorbance of the CsCuI samples, the transmittance and reflectance spectra were measured. Then the absorbance can be directly obtained from conservation of energy:

$$1 = A + R + T \quad (3)$$

We then calculate absorption coefficient using Eq. (2) and using Tauc's formalism [7], we can get the optical gap of the sample fitting the absorbance to the next equation.

$$(\alpha \cdot d \cdot E)^{1/n} = B(E - E_{gap}) \quad (4)$$

Both compounds have a direct band gap so n is 1/2 in this case. Using this procedure, we were able to extract the band gap energy of each compound, finding 3.65 eV and 3.79 eV for samples CsCu₂I₃ and Cs₃Cu₂I₅, respectively. These values are consistent with the reported in the literature for similar compounds [8].

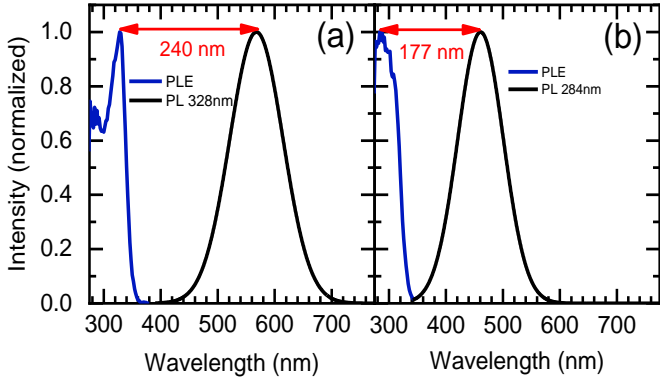


FIG. 2: PL and PLE spectra for the (a) CsCu₂I₃ and (b) Cs₃Cu₂I₅ samples. The represented PL spectra were recorded using the excitation wavelength with the maximum PLE, 328 nm and 284 nm for the CsCu₂I₃ and Cs₃Cu₂I₅ samples, respectively.

Comparing the PL and PLE spectra we can extract the Stokes shift of the compounds (see FIG. 2). To do so, we used the PLE spectra and the PL spectra from the wavelength where the excitation is maximum. We can see that CsCu₂I₃ has very large Stokes shift of around 240 nm that, converted into energy, is about 1.6 eV. On the other hand, the Cs₃Cu₂I₅ compound display also a large Stokes shift, about 177 nm, that converted in energy is around 1.68 eV, quite similar in both samples.

These Stokes shifts are considered large for these types of materials. This is due to the STE excitation mechanism described in Section I. The carriers excited with E_{gap} , first lose energy (E_b) in the formation of the exciton. Then, through the process of self-trapping, they lose energy (E_{ST}) again. And finally, they do not decay to the valence band but to a deformed ground state which is E_d closer. So, when recombination finally happens the decay is at a much lower energy (E_{PL}), which can be calculated with Eq. (1), resulting in these large Stokes shifts. Knowing this, we can express the Stokes shift in energy with following Eq. (5):

$$\Delta E_{Stokes} = E_{excitation} - E_{emission} = E_b + E_{ST} + E_d \quad (5)$$

Also, from the activation curve of the photoluminescence effect we can get a rough estimate of the bandgap energy of the sample. To do so, we take the lower energy side of the PLE curve (in this case the right side with longer wavelengths) and fit it to a sigmoid function using the

Levenberg-Marquardt least squares algorithm. From the resulting fitted function, we can get the activation energy of the photoluminescence effect that corresponds to the optical gap. This method is not regarded as a good way to obtain the optical gap but with it we can get a rough determination of the band gap energy. The adjusted sigmoid function provided a band gap energy of $E_{gap} = 3.65$ eV and $E_{gap} = 3.87$ eV for the CsCu₂I₃ and the Cs₃Cu₂I₅ samples, respectively, that are close to the ones obtained by OA analysis.

B. Optical properties as a function of temperature

The PL spectra of both compounds have been measured as a function of the temperature. The obtained data was adjusted to a gaussian to characterize the emission of the material. From the parameters of the fitted gaussian we were able to obtain their central energy position of the emission, their full width at half maximum (FWHM) and the integrated PL intensity as a function of the temperature.

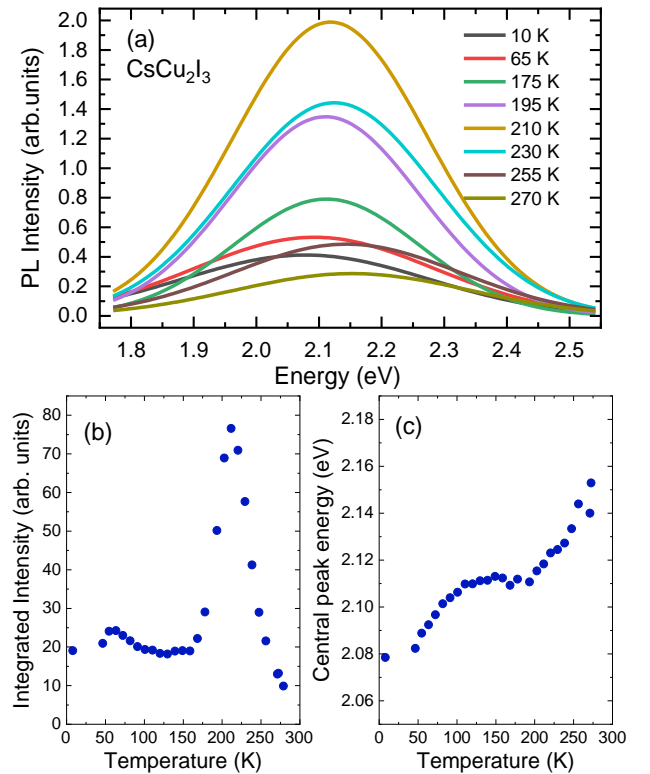


FIG. 3: (a) Selected PL spectra at different temperatures for the CsCu₂I₃ sample. (b) Evolution of the integrated PL intensity of the emission peak and (c) evolution of the emission peak with the temperature.

In FIG. 3 we present the acquired spectra at different temperatures for the CsCu₂I₃ sample [FIG. 3(a)], together with their integrated intensity and the central peak position [FIG. 3(b) and FIG. 3(c), respectively] as a function of the temperature. One can observe that the emission peak increases 4 times its intensity from 10 K to 210 K, temperature in which the peak starts to decrease to a similar level than at low temperatures. Its FWHM increases with temperature from 0.12 eV to 0.17 eV within the range of

studied temperatures. Regarding the peak position, its energy monotonically increases with the temperature, from 2.09 eV at 10 K up to 2.15 eV at room temperature.

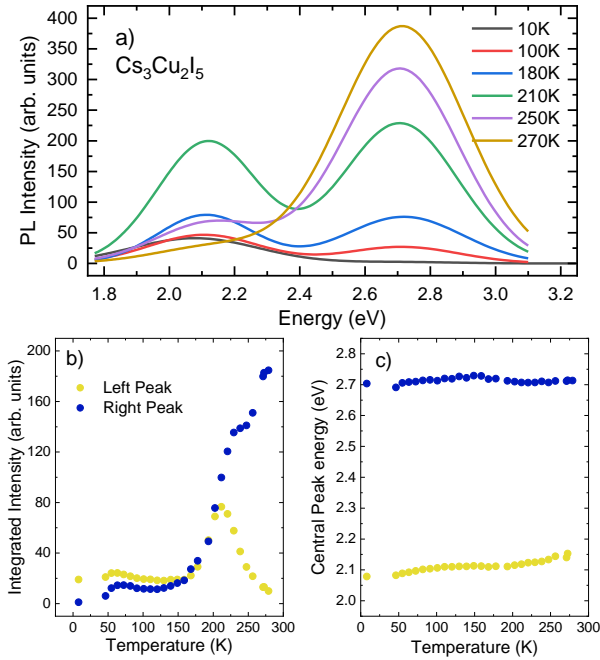


FIG. 4: (a) Selected PL spectra at different temperatures for the Cs₃Cu₂I₅ sample. (b) Evolution of the integrated PL intensity of the emission peak and (c) evolution of the emission peak with the temperature.

In FIG. 4 we show the acquired spectra at different temperatures for the Cs₂Cu₂I₅ sample [FIG. 4(a)]. In this case, there are two emission peaks that evolve differently with the temperature. The peaks were fitted in the energy domain to analyse them independently. Their integrated intensity and their central peak positions are represented as a function of the temperature [FIG. 4(b) and FIG. 4(c), respectively]. These two emissions are centred around 2.1 eV and 2.7 eV, located in the yellow and blue ranges, respectively. The *blue peak* increases monotonically its integrated intensity, almost 30 times from 10 K to room temperature, whereas its energy position is practically constant, with a variation between 2.69 eV and 2.72 eV in the whole range of temperatures. Its FWHM increases with temperature from 0.16 eV to 0.20 eV within the range of studied temperatures. On the other hand, the *yellow peak* exhibits the same behaviour as the emission found for the CsCu₂I₃ sample, showing also a maximum integrated intensity at 210 K and practically the same energy shift with temperature (from 2.08 eV at 10 K up to 2.17 eV at room temperature). The observation of this yellow emission and the fact that it evolves with temperature in a similar way than the emission from the CsCu₂I₃ sample suggest that this sample is presenting a mixture of compositions, in agreement with Ref. [5]. Nevertheless, further analysis needs to be done for corroborating this hypothesis.

In order to clarify the intensity behaviour from both samples, transmittance measurements as a function of the

temperature were performed. In FIG. 5 we display the transmittance spectra for the CsCu₂I₃ and Cs₃Cu₂I₅ samples. We found that the transmittance shows a similar trend than the one observed at room temperature: a suddenly decreases at around 340 nm and 325 nm for CsCu₂I₃ and Cs₃Cu₂I₅ samples, respectively. At lower temperatures, this change in the transmittance is also observed but at slightly shorter wavelengths.

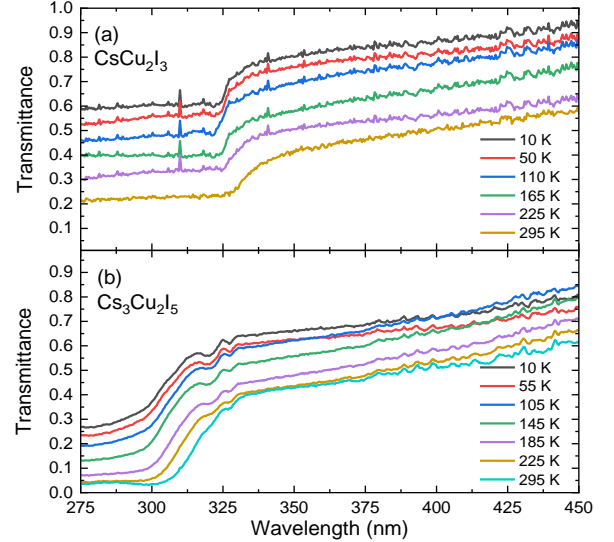


FIG. 5: Selected transmittance spectra at different temperatures for (a) CsCu₂I₃ and (b) Cs₃Cu₂I₅ compounds.

For determining the band gap energy as a function of the temperature, we applied the same methodology than for the measurements at room temperature, supposing that the reflectance is constant at a value around 10%. The results are plotted in FIG. 6 for the two different samples. The bandgap energy values obtained at room temperature by PLE and optical absorption by this method are in good agreement with the ones obtained at similar temperatures.

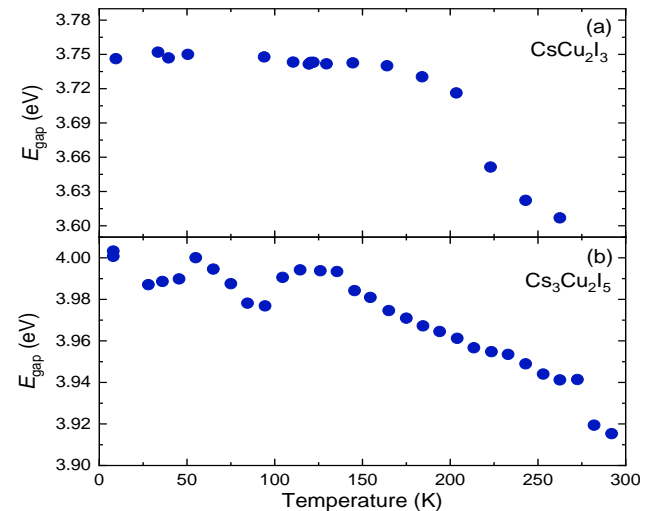


FIG. 6: Calculated bandgap energies as a function of the temperature from Tauc plots (a) CsCu₂I₃ and (b) Cs₃Cu₂I₅ compounds.

Regarding the bandgap energy evolution with the temperature, both samples present a decrease of the bandgap energy at higher temperatures, with a total variation of about 0.15 eV and 0.1 eV for CsCu₂I₃ and Cs₃Cu₂I₅ samples, respectively. This variation in the bandgap energy is not very large but it is enough for affecting the optical behaviour at wavelengths between 310 nm and 340 nm (4 eV and 3.65 eV, respectively), where the absorption edge is located.

This variation of the absorption edge with temperature could explain the intensity reduction at low temperatures of the blue emission for the Cs₃Cu₂I₅ sample. Actually, the temperature dependence PL measurements were done using a single excitation wavelength of 325 nm (3.81 eV) from a HeCd laser that it is absorbed at room temperature providing a good PL emission (as shown by PLE). At low temperatures, the bandgap energy increase implies a lower absorption at this excitation energy. Because of this lower absorption, there is also a lower generation of electro-hole pair and, in consequence, lower PL emission.

In the case of the CsCu₂I₃ sample (or phase for the yellow emission of the Cs₃Cu₂I₅ sample), the situation is slightly different: the excitation from HeCd laser (3.81 eV) is always above bandgap energy of this compound in the studied range of temperature. However, there is a maximum integrated emission at temperatures around 210 K, which is compatible with a resonant excitation condition. Nevertheless, the bandgap energy and the excitation energy differ to each other, so there must be another particle involved in the process that fulfils the resonant condition.

Considering that the self-trap exciton mechanism is driven the PL emission, the formation of the excitons has an energetic cost (E_b). It has been reported in the literature that the exciton binding energy is about 128 meV at room temperature [8]. In our case, the resonance take places at 210 K, where the CsCu₂I₃ sample has a band gap energy of around 3.69 eV. Considering that the excitation energy is

3.81 eV, it results in an energy difference of about 120 meV, in good agreement with the reported values for similar samples at room temperature.

IV. CONCLUSIONS

The emission position, Stokes shifts and bandgap energies at room temperature were determined in this work, finding an excellent agreement with reported values in the literature.

On the other hand, the results we had for PL as a function of the temperature are apparently anomalous compared to the expected behaviour of conventional semiconductors: the CsCu₂I₃ sample presents a yellow emission around 460 nm, with a resonance around 210 K, whereas the Cs₃Cu₂I₅ sample shows two emissions, one around 460 nm and another one at 560 nm that could be ascribed to a CsCu₂I₃ phase, with relative intensities that depend on the temperature. Temperature dependence of OA experiments were performed to determine the evolution of bandgap energy with temperature, helping to explain the temperature dependence of the PL results. The analysis of the data allows also determining the binding energy of the exciton in CsCu₂I₃ compound, obtaining a value of 120 meV, in agreement with reported values.

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