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Time Resolved Photoluminescence and Trap Density Measurements in DJ Phase 2D Perovskite

Abstract

With the reported high stability of DJ phase 2D perovskites, bringing to light its characteristics and properties of photophysics will aid the development for their usage in optoelectronics. This work attempts to find the slow surface and fast bulk traps density values in DJ phase 2D perovskites with 0.75 ligand length and a DDA added into it to help uncover the recombination mechanism of their charge carriers. We found that the amount of data samples and the TRPL feature both samples exhibit prevents the obtainment the precise trap density values. However, the non-radiative recombination rate values from PLQY measurements still implies the consistency with the observed TRPL data.

Introduction

In the recent years, organic-inorganic perovskite has become one of the materials in the spotlight for its efficient photovoltaics and light-emitting applications [1]. It experiences a tremendously fast development within just 11 years of progress, surging to over 25% of efficiency in the present day for solar cells applications [2]. Unfortunately, although possessing a high efficiency, organic-inorganic perovskites are still yet to be commercialized due to challenges in their stability against moisture, heat, and light illumination [3].

This is where Two-Dimensional (2D) perovskite structures come to play as a potential solution [1,3]. The superiority in stability of 2D perovskites compared to the usual 3D perovskites comes due to the additional larger organic cations (L) which are appended between two inorganic metal halide octahedra layers with its hydrophobic nature, creating a Ruddlesden-Popper (RP) phase and causing the 2D perovskite to be able to fend off water

molecules that would likely to infiltrate into the perovskite lattice [1,3]. However, RP phase 2D perovskite is still yet at the peak of stability [3].

The weak Van der Waals interaction between two inorganic layers with their adjacent organic cations layer attached to it creates a gap that could spawn a structural instability in the 2D perovskite structure [3,4] as shown in figure (1). Elimination of this gap could be done by adding Diamene compounds creating what we call the Dion-Jacobson (DJ) phase 2D perovskites [3]. To uncover their potential for optoelectronics applications, understanding their photophysics characteristics will be crucial [5].

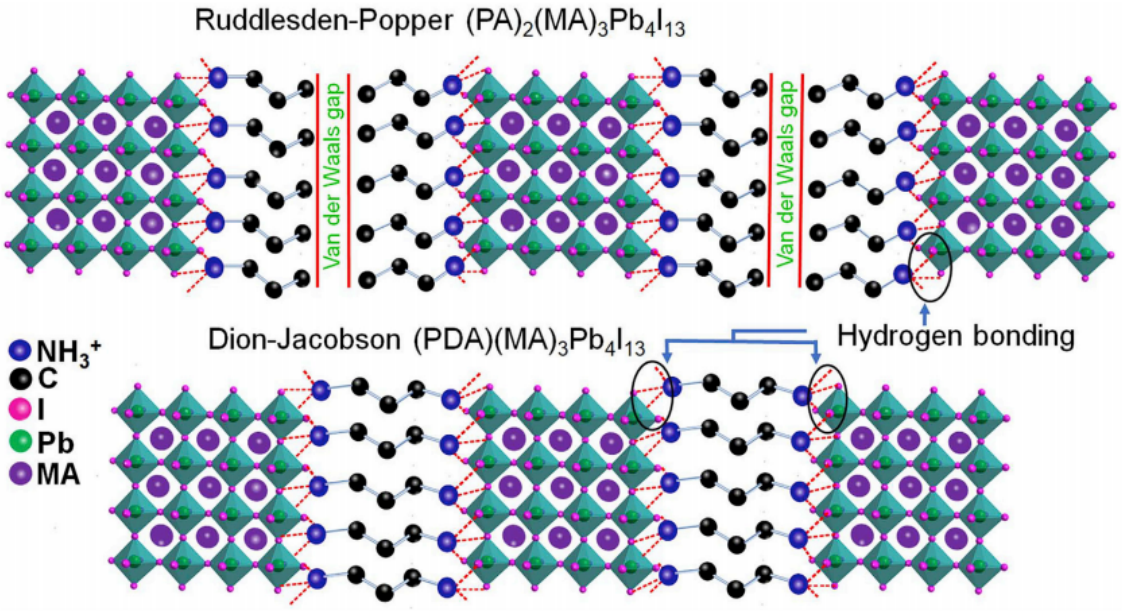

***Figure 1**. The illustration for the structural form of the RP phase and DJ phase of 2D perovskites [3]*

One of the main factors affecting the photophysical properties of perovskites includes their number of defects or traps which influence the recombination process. There generally exist three ways of electrons and holes recombining with each other which are bimolecular radiative, bimolecular non-radiative, and trap-mediated recombination [6]. However, multiparticle and auger recombination is minimized when using a low-power laser to excite the perovskite samples, leaving the charge carriers to recombine through the band edge by spontaneous emission or mediated by the traps [6,7,9,10]. Therefore, by knowing the

equation of how the carrier density and traps change with time and the time-integrated band edge PL intensity, the initial charge carrier density generated by the laser pulse equals to,

$$n_c(t=0) = \sum_i n_{TP}^i(0) \cdot \left(1 - e^{-a_i \cdot \tau_0 \cdot \frac{I_{PL}}{k}}\right) + \frac{I_{PL}}{k} \quad (1)$$

in which $n_{TP}^i(0)$ is the ith type of trap density when time (t) amounts to zero, a_i is the trapping cross section times the carrier velocity, τ_0 is the lifetime of the PL decay, and k is a constant [7,9,10].

With perovskite thin films having a thickness less than 200nm, the photoexcited charge carriers could be assumed to be uniformly distributed since carrier diffusions are faster than the recombination process [6]. In effect, the initial charge carrier density of a perovskite film excited by a laser pulse with a fluence of I_0 (photons / cm^2) could be also obtained by the equation,

$$n_c(t=0) = \frac{I_0 \cdot A}{D} \quad (2)$$

where A is the absorbance of the film and D is the thickness of the film [6]. In addition, for caution, this theory for the approximation of the concentration of the two kinds of trap upholds when the lifetime of the radiative recombination is much faster than the other trap-mediated recombination [10]. With the above being said, this project aims to understand and find the values of trap density in two samples of DJ phase 2D perovskites where one has a ligand length of 0.75 and the other with DDA added into it.

Experimental Methods

Time-Resolved Photoluminescence (TRPL) measurements were done to discover the emission decay lifetime from recombination mechanisms in the two samples. The TRPL measurement utilized the Time-Correlated Single Photon Counting or TCSPC method where

the data collection of a single photon emission was acquired from many periodic excitations caused by the incoming laser pulses [8]. This method works only if the probability that a photon being emitted per excitation cycle is low [8]. The laser pulses being used to excite the samples are ultrafast lasers which have a wavelength of approximately 390nm and a period between pulses of 250ns, where a varying power from 25nW to 400nW was tested with each value of power illuminated the sample for 15 seconds, while the light emission with a wavelength of 515nm was gathered as the data. The two samples have a diameter of approximately 1000 μm and 40nm in thickness.

The first attempt to extract the trap density value were done by fitting the plot of carrier density versus Time-Integrated PL intensity from Xie, et al. paper [9] shown in figure (2) with the purpose of understanding the meaning and the intuition behind Eq (1). The data from the plot were extracted by employing a "data grabber" application available on the internet which then utilized for the plot fitting with the application and programming language of OriginLab and Python. From there on, we measure the trap density of both the DDA and 075 sample using the TRPL data and the initial charge carrier densities which we calculated by using Eq (2).

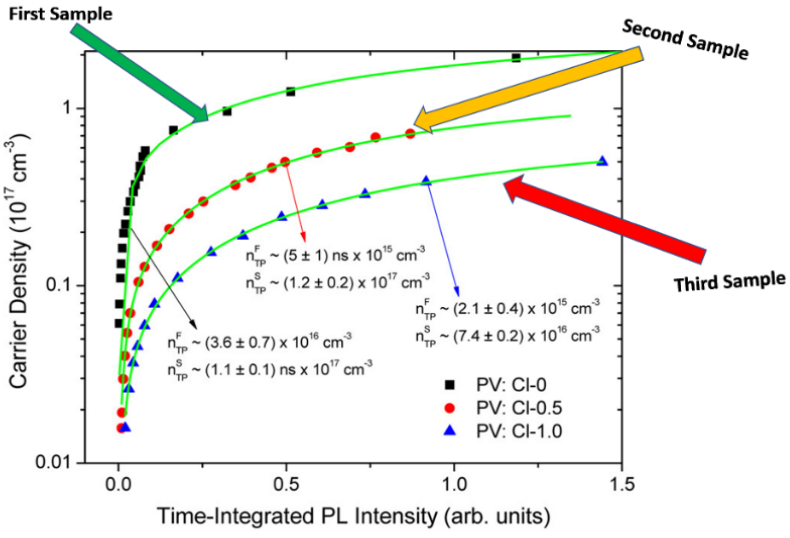

***Figure 2**. The data plot of the carrier density versus time-integrated PL from Feng Xian Xue's, et al. paper which are used to try to fit Eq (1) [9].*

Experiments on measuring the Photoluminescence quantum yield (PLQY) of the 075 and DDA sample were then executed to further see the connection between the PL lifetime, radiative and non-radiative recombination rates, and the PLQY itself. To find the PLQY, an integrated sphere, which is a hollow sphere with a diffusely high reflecting material covering the surface within, is used to provide an isotropic light scattering distribution [12]. To obtain the PLQY value, many measurements inside the integrated sphere with different configurations were conducted. One of the measurements were done without the samples and with only the laser aimed at the sphere's inner wall, while the other configurations consisted with the sample inside but with different exposure time and with the laser directed at different spots, being the inner wall of the surface and directly to the sample itself [12]. The background noise detected by the spectrometer in the integrated sphere are also measured.

Results and Discussion

Both samples' TRPL plot in figure (3) were fitted with a bi-exponential function which implies that there are two mechanisms affecting the recombination process [6]. One of the processes lifetimes labeled as *t1* represents the shorter lifetime of the trap-mediated recombination, while *t2* depicts the longer lifetime of the radiative recombination [6]. Its values of t1 and t2 can be seen in table (1) where it indicates that the 075 sample has a longer lifetime (slower decay) compared to the DDA sample. However, the PL decay lifetime between the different values of fluences that we use for each sample does not display any

significant difference as observed in figure (2) and table (1) where the values of t1 and t2 are listed.

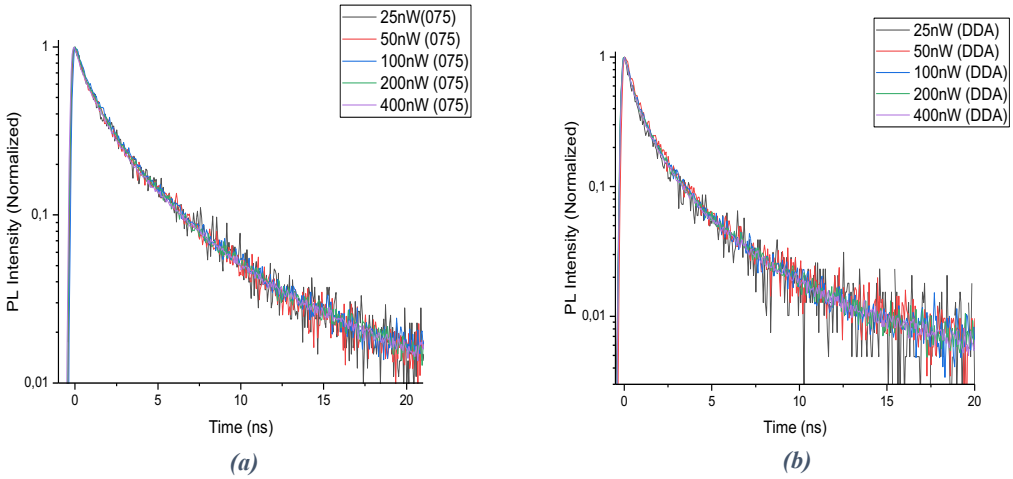

***Figure 3**. The TRPL measurement plot for the (a) 075 sample and (b) DDA sample with laser power from 25nW to 400nW.*

Power (nW)	τ_1 075 (ns)	τ_2 075 (ns)	τ_{avg} 075 (ns)	k_{rad} 075 (ns^-1)	k_{nonrad} 075 (ns^-1)	τ_1 DDA (ns)	τ_2 DDA (ns)	τ_{avg} DDA (ns)	k_{rad} DDA (ns^-1)	k_{nonrad} DDA (ns^-1)
25	0,89	4,00	2,32	0,019	0,41	0,57	2,74	1,23	0,015	0,80
50	0,86	3,85	2,29	0,019	0,42	0,60	2,60	1,25	0,014	0,78
100	1,02	3,99	2,33	0,018	0,41	0,60	2,65	1,29	0,014	0,76
200	0,87	3,69	2,24	0,019	0,43	0,57	2,56	1,27	0,014	0,77
400	0,94	3,97	2,31	0,019	0,41	0,58	2,61	1,26	0,014	0,78

***Table 1.** The values of the lifetime of trap-mediated recombination (τ_1), the lifetime of radiative recombination (τ_2), the weighted average of the lifetime (τ_{avg}), the radiative and non-radiative recombination rate (k_{rad} and k_{nonrad}), for both 075 and DDA samples.*

For the fitting of the charge carrier density PL versus Time-Integrated PL plot from Xie et al. paper [9] using Eq (1), the process was not quite linear. There exist an amount of trial and error and guessing of the unknown values to achieve the correct fitting. The initial fitting was done for the second sample (PV: Cl-0.5) by employing only one term of Eq (1) (one kind of trap) since many of the parameter's values are not known yet. This yields us the fitting plot where the fitting strays up until a certain point pointed by the arrow in figure (4a),

indicating that there are two types of traps affecting the recombination process in which a single type of trap dominates in the region from the middle to the end data points where another type of trap prevails in the early to middle data points. The two types of traps exist here are the fast and slow trap which occur in the bulk and the surface, respectively, in which the fast bulk trapping take place in a period of fs to ps while the slow surface trapping occurs in a timescale of 100 ps or more since longer time is needed for the charge carrier to travel through the couple nm thickness of the perovskite film [9,10].

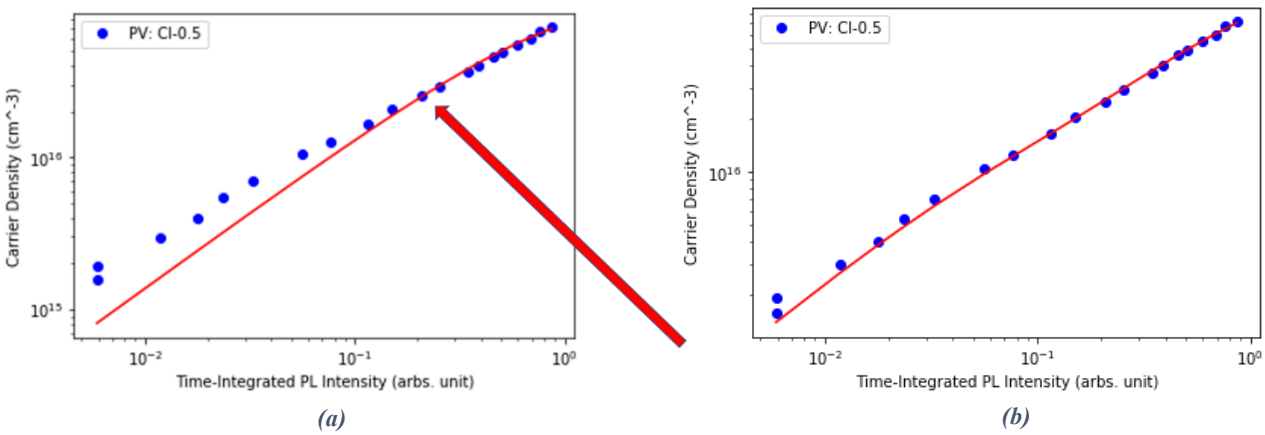

Figure 4. *(a) The initial fitting using only one type of trap term for the second sample plot with the data extracted from figure (2) where both the x-axis and y-axis are in a log scale. The red arrow signifies the point in the plot where the fitting line starts to diverge. (b) The final fitting of the second sample plot with the both the slow and fast trap term in Eq (1).*

To get the density value of each type of trap, we divide the plot into two sections at the point where the initial fitting starts to diverge and fit each part individually with only a single term of Eq (1). The result for the latter fitting gives us a trap density of 1.18836 x $10^{17} cm^{-3}$ which is close to what Xie's et al. paper had also come to for the slow trap density which amounts to 1.2 x $10^{17} cm^{-3}$ [9]. Unfortunately, the fitting plot of the former data sets produce a different value than the mentioned value in the paper due to the curve is supposed to be fitted with two types of traps as in equation (1). This prompts for the fitting of the whole curve with Eq (1) but an educated guessing for the a_i, τ_0, and k values are needed to get the same result as stated in the paper which their value emerges to be 5.2 for $a_{slow} \cdot \tau_0$, 304.3 for

$a_{fast} \cdot \tau_0$, and 28.71 for k. Fitting the plot with the aforementioned values will generate us the fitting line in figure (4b), where the slow and fast trap density for the second sample amounts to 1.1 x $10^{17} cm^{-3}$ and 4.1 x $10^{15} cm^{-3}$, respectively, which are close to the values in the paper by Xie, et al. [9]. It indicates that the fast traps in the bulk start to quench the radiative recombination process at lower fluences while the traps in the surface come into play when higher fluences are reached. The same routine was done for the third samples and yields a similar result with the paper used for the plotting. However, for the first sample, due to the data also not being too clean, the fitting does not converge easily, and some bugs still appear which are still unsolved to date.

Applying the same fitting routine for the charge carrier density versus the Time-Integrated PL of 075 and DDA sample plots gives us figure (5a) and (5b) where the extracted trap density value amounts to 1.05 x $10^{15} cm^{-3}$ and 1.16 x $10^{15} cm^{-3}$, respectively, which has a similar values to each other and corresponds to be the density of the fast surface traps [6,10]. This seemingly comparable trap density values of the two samples does not correspond to the faster lifetime of the DDA sample, however, this is due to the data samples not having a large range of fluences values which also causes the fitting to only be able to extract a single type of trap density.

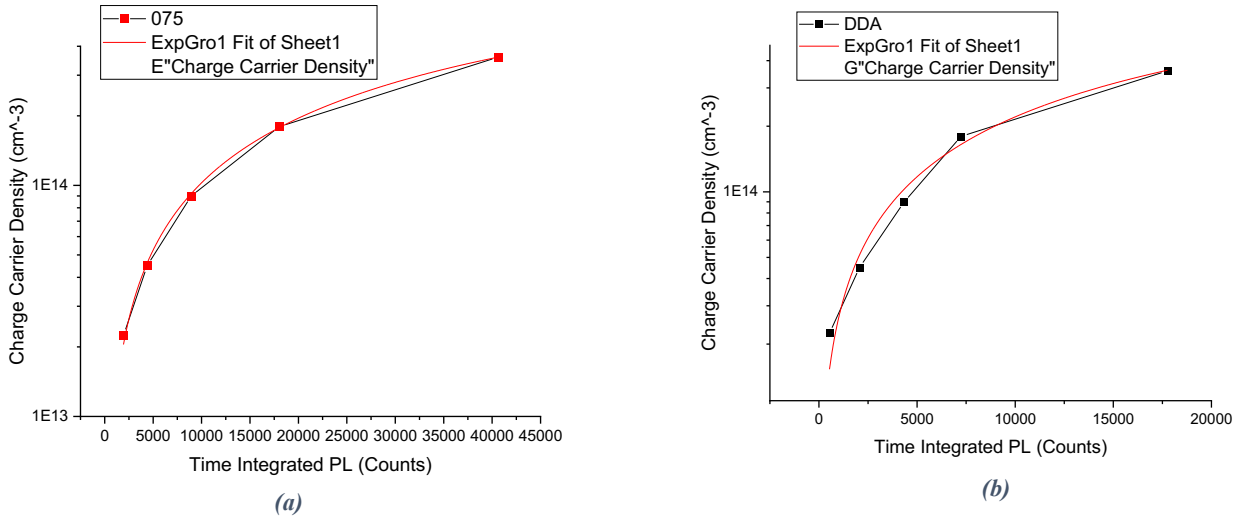

Figure 5. *The fitting of the carrier density vs time-integrated PL using only a single type of trap for both (a) the 075 sample and (b) the DDA sample.*

From the PLQY measurements, we attained the PLQY value (η) of 4.3% and 1.8% for the 075 and DDA sample, respectively. Together with the decay lifetime result from the TRPL measurements we could built a conjunction which connects and shows how much the trap-mediated recombination affects the charge carrier density overtime (the non-radiative recombination rate) [13]. We first calculated the weighted average of the lifetime of τ_1 and τ_2 (τ_{avg}) using the amplitude for each lifetime from the TRPL experiments, in which τ_{avg} equals to,

$$\tau_{avg} = \frac{1}{k_{rad}+k_{nonrad}} \tag{3}$$

where k_{rad} and k_{nonrad} are the radiative and non-radiative recombination rates [12]. However, to find k_{rad} and k_{nonrad}, the following equations are needed,

$$k_{rad} = \frac{\eta}{\tau_{avg}} \tag{4}$$

$$k_{nonrad} = \frac{1-\eta}{\tau_{avg}} \tag{5}$$

which gets us the values of τ_{avg}, k_{rad}, and k_{nonrad} stated in table (1) for both 075 and DDA sample [13]. In particular, the obtained results of k_{nonrad} for DDA amounts to a higher value for approximately 0.4 more than the 075 sample which supports and indicates that the DDA sample has a larger trap density compared to the 075 sample [13]. This is consistent with the TRPL plot where the DDA sample has a faster lifetime decay than the 075 sample.

Having the relatively low PLQY for both samples, this means that noises could easily affect the PL signal detected significantly creating data samples which has a low quality for it to be analysed [11]. In effect, it might be the origin of the similarity of the two samples trap density value from the fitting. This calls for higher power laser to be used in future

experiments, however, having high value of fluences could initiate Auger recombination where the theory breaks down which means more care and caution should be [6,7,9,10].

Conclusion

All in all, we learned how to do TRPL measurement and understand the process of fitting the charge density equation (Eq (1)) to be able to find the traps density in the 075 and DDA sample of DJ phase 2D perovskite. From the TRPL measurements were found that DDA has a shorter lifetime than the 075 sample which is consistent with the DDA sample values of the non-radiative recombination rates (k_{nonrad}) being larger than the 075 sample, indicating that indeed the DDA sample has a higher amount of trap density and thus a faster lifetime. However, the fitted trap values from the TRPL measurement have a very similar fast surface trap density value between each other. This similarity from the fitting arises due to not having a large range of data samples and the fact that the low efficiency of PL yield of the samples prompts the proportion of PL emitted from the samples to the noise to be not ideal causing inadequate data quality. Therefore, more experiments to acquire adequate data samples should be done and analyzed.

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