Supplementary material

## Identification of High-Temperature Exciton States and Their Phase-Dependent Trapping Behaviour in Lead Halide Perovskites

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Figures



**Figure 1.** (a) Distribution of the particle size of the perovskite dispersed in the EA/EC solution (0.002 M), which was measured by a light scattering method. (b and c) Examples of perovskite particles observed by an optical microscope. For this observation, the perovskite dispersion was firstly diluted and then deposited onto a glass slide. The particle size was estimated by just comparing the darker contour to the scale bar. In our opinion, the surface and the bulk regions of these small perovskite grains play comparable roles in determining the physics properties of the sample. Notably, for these particle size measurements, a high concentrated perovskite dispersion was firstly prepared and then diluted, just the same to that used for the absorption properties measurements. For the dispersion preparation and dilution

processes, only the magnetic stirring was used. It is expected that the perovskite grains and their size would not be influenced by the macroscopic low-energy stirring process. Thus, the perovskite dispersion with different concentrations should have the similar grain size as evaluated here.



**Figure 2.** (a) Steady-state photoluminescence (PL) of the perovskite dispersions with different concentrations. (b) A comparison of the measured PL peak energy to the estimated one by considering the photon reabsorption effect. A good agreement is achieved, confirming that the energy state for radiative recombination keeps unchanged regardless of the concentration. (c) Transient PL of the perovskite with different concentrations, probed at the same energy of 2.28 eV. They exhibit almost the same decay process, confirming the similar photophysics properties between different samples.



Figure 3. Two examples of theoretical simulations of the light absorption spectra according to the Tauc model including the contributions of both indirect and direct bandgap absorption. (a) The light absorption is modeled as  $Abs \sim a \times (E-1.52)^2 + (E-1.6)^{1/2}$ , where the 1.52 and 1.6 are assumed to be the indirect and direct bandgap width, and (a) is a relative prefactor reflecting the relative probability of indirect bandgap transition. To obtain a continuous absorption spectrum without any singularity, two formulas, including  $a(E-1.52)^2 = (E-1.6)^{1/2}$ and  $2a(E-1.52)=1/2(E-1.6)^{-1/2}$ , need be satisfied in math, yielding a=14.3525, as shown with the open black square plot, red and green lines. This theoretical simulation may resemble the experimental spectra of the  $CH_3NH_3PbI_3$  absorption. However, the value of (a) means that the probability of indirect bandgap transition is much larger than that of the direct bandgap transition, which is obviously contradictory with the basic principles of photoelectric interactions of a semiconductor<sup>1</sup>. By decreasing the a to 1 or another smaller value, an obvious transition between the indirect and direct bandgap absorption can be observed, as the open pink circle plot shows; while no such a transition has been found in experiment. (b) The light absorption is modeled as Abs~ $a \times (E-2.2)^2 + (E-2.3)^{1/2}$ . Similarly, a large a of 10.3 is needed to obtain a continuous absorption spectrum, while the excitonic feature cannot be reflected.



**Figure 4.** (a) Fittings of the CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> absorption spectra with the indirect bandgap and bound exciton model, respectively. The solid black square plot is the residual absorption spectra by subtracting the continuum term (Abs<sub>continuum</sub>), as Abs<sub>total</sub>-Abs<sub>continuum</sub>. The green line is the free exciton absorption (Abs<sub>FE</sub>), and the open red circle plot is derived as Abs<sub>total</sub>-Abs<sub>continuum</sub>-Abs<sub>FE</sub>, which can be well fitted by the bound exciton absorption model as the red line shows. The dash blue line gives a fitting of the absorption tail below 2.22 eV with the indirect bandgap model, as Abs.~(*E*-*E*<sub>g</sub>)<sup>2</sup>, yielding the *E*<sub>g</sub> of 2.138 eV. The orange line is the single Gaussian peak fitting of the Abs<sub>total</sub>-Abs<sub>continuum</sub> spectrum. The residuals of the single exciton model, the broadening is significantly increased, and a large residual exists. (c) Energy level diagram of the perovskite if adopting the indirect bandgap model. The indirect bandgap model may give emissions below 2.138 eV (e.g. >580 nm).



**Figure 5.** (a) Fittings of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> absorption spectra with the continuum band and double excitons model, yielding an  $E_g$  of 1.645 eV, a free exciton binding energy of 17 meV and a bound exciton binding energy of 67 meV. (b) Steady-state PL of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and the double-peak fitting. The lower-energy emission (1.572 eV) is located at the similar energy position to that of the bound exciton, while the higher-energy emission (1.635 eV) may come from both the continuum band and free exciton states. The PL data is reorganized from reference 2.



**Figure 6.** (a) Top-view scanning electron microscope image and (b) X-ray diffraction pattern of the MAPbBr<sub>3</sub> film.



**Figure 7.** An example of steady-state PL of the MAPbBr<sub>3</sub> films in the temperature regime from 70 to 130 K. A strong broad emission centered at about 620 nm can be assigned to the trap emission and the sharp PL peak located at about 550 nm is the exciton emission.



**Figure 8.** Temperature-dependent steady-state PL (850 nm is the wavelength upper limit of the instrument) of MAPbI<sub>3</sub>. At temperatures higher than 130 K, two emission bands can also be distinguished, similar to that of MAPbBr<sub>3</sub>.



**Figure 9.** An example of the PL spectrum fitting to derive the intensity of different emission bands. (BE: bound exciton, FE: free exciton)



**Figure 10.** X-ray diffraction pattern of the CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> single crystal, which has a cuboid shape as shown in the left inset. For the top surface, the (100) lattice plane is mainly exposed. The bulk (100) crystal plane is exposed by directly cleaving the single crystal. The right inset gives the microscope photograph of the cleaved surface, which is ultra-smooth without any physical crack and grain boundary.



**Figure 11.** Two dimensional pseudocolor (normalized PL intensity) plots of transient PL spectra for the MAPbBr<sub>3</sub> single crystal as functions of emission wavelength and time delay (200 K). Even when the temperature is increased to 200 K, the single crystal still gives two PL centers corresponding to the free and bound excitons emissions.



**Figure 12.** Transient PL of the perovskite single crystal (165 K) probed at 542 and 554 nm, respectively. These two emission centers exhibit different decay dynamics, thus excluding the possibility of light scattering effect in causing the double-peak PL.



Figure 13. PL spectra of the perovskite film and single crystal at room temperature by increasing the excitation intensity ( $I_{exc}$ ). They give the similar emission features.



**Figure 14.** Transient PL (probed at 550 nm) of the perovskite film measured at 90, 145 and 300 K, respectively, where the monomolecular recombination lifetime is derived to be 27, 730 and 351 ns, respectively.



**Figure 15.** Scheme of the simplified charge processes between the exciton and trap states. The blue arrow depicts the formation of free exciton (FE) and the arrow 1 depicts the formation of bound exciton (BE). These two processes are ultrafast, which have little influence on the PL properties in the nanosecond time scale. Arrow 2: Trapping of FE; 3: Trapping of BE; 4: FE radiative recombination; 5: BE radiative recombination; 6: Trap emission.



**Figure 16.** (a) Transient PL of the FE and BE emissions of the film at 70K and 145K, respectively. (b) Temperature dependent PL intensity of the FE and BE emissions. These results indicate that both the free and bound exciton could be fast captured by the trap states.



**Figure 17.** Excitation intensity-dependent PL spectra of the perovskite single crystal at 70 K. The trap emission shows a blue-shift when increasing the excitation, and the free and bound exciton emissions can also be observed.



**Figure 18.** Room-temperature PL properties and stimulated emission of the MAPbBr<sub>3</sub> film. The stimulated emission is realized by pumping the film (at 450 nm) with a femtosecond amplifier (Coherent Astrella) and a OPA system (Opera-solo). At room temperature, the free exciton is mainly dissociated into free carriers while the bound exciton keeps stable.

Note 1. Modeling the thermal-induced exciton transfer



**Figure 19.** Schematic diagram of the energy states of the exciton and trap state. In the thermal-induced charge transfer process, an energy barrier need be overcome. For the exciton-to-trap (i.e. trapping), the energy barrier is  $E_1$ , while  $E_2$  for the opposite transfer process (i.e. de-trapping). Obviously,  $E_1 > E_2$  since the energy of the trap state is lower than that of the exciton state.

For the charge transfer between different localized states, energy barriers are usually need be overcome, as schematically shown in Figure 19. Here, we consider the exciton trapping process, and a single trap state is assumed. The complicated interactions and charge transfer between multiple exciton states and trap states are ignored. In this case, the rate equation of the charge transfer under low excitation can be modeled as

$$\begin{cases} \frac{dn_1}{dt} = -An_1N_2 \exp\left(-\frac{E_1}{K_BT}\right) + BN_1n_2 \exp\left(-\frac{E_2}{K_BT}\right) \\ \frac{dn_1}{dt} = -\frac{dn_2}{dt} \\ n_1(0) = n_0 \\ n_2(0) = 0 \end{cases}$$

where *t* is the time following the exciton formation,  $n_0$  is the initial exciton density,  $n_1$  is the exciton density,  $N_1$  is total density of the exciton state,  $n_2$  is the occupied trap density,  $N_2$  is the total density of the trap state, *A* and *B* are the dynamic constants,  $K_B$  is the Boltzmann constant and *T* is the temperature. By solving this rate equation, the influence of the

temperature on the exciton transfer process can be estimated. For clarity, here we give some examples of the exciton decay at different temperature by the numerical calculations, as in Figure 20. With these results, it can be confirmed that the higher temperature would accelerate the exciton trapping process.



Figure 20. Numerical results of the exciton decay at different temperatures, where  $E_1=0.1$  eV and  $E_2=0.25$  eV was taken as an example here.

## Note 2. Explanation of the multiphonon transition model.

For any solid or semiconductor system, the total energy is composed of the electronic and lattice terms. The Hamiltonian of the system can be written as  $\hat{H}=\hat{H}_{e}+\hat{H}_{L}+\hat{H}_{eL}$ , where  $\hat{H}_{e}$ ,  $\hat{H}_{L}$ and  $\hat{H}_{eL}$  are the Hamiltonians of the electron, lattice and electron-lattice interaction. By the linear approximation, the  $\hat{H}_{eL}$  can be written as  $\hat{H}_{eL} \sim \sum_{s} u_{s}Q_{s}$ , where  $u_{s}$  is the coupling parameter of electron-lattice interaction and  $Q_{s}$  is the lattice position in the normal coordinate. With this Hamiltonian, the total energy of the system can be derived as  $U(Q)=E(Q)+1/2M\omega^{2}Q^{2}$ , where the first term is the electronic energy including the electronlattice interaction and the second one is the elastic energy of the lattice. For the nonirradiative charge transition process, the total energy is conservative. According to the multiphonon transition scenario, the charge capture activation energy ( $E_{\rm B}$ ) is

$$E_{B} = \frac{\left(E_{ji} - S\overline{h\omega}\right)}{4S\overline{h\omega}},$$

where 
$$S = \sum_{s} \frac{\omega}{2h} \left( \frac{1}{\omega^2} \int (\varphi_j - \varphi_i) u_s(r) \varphi_s dr \right)^2$$
,  $\overline{h\omega} = \frac{1}{S} \sum_{s} \frac{\omega}{2h} \left( \frac{1}{\omega^2} \int (\varphi_j - \varphi_i) u_s(r) \varphi_s dr \right)^2 h\omega$ ,  $E_{ji}$ 

is the energy difference between state *j* and *i*,  $\varphi_{(ijs)}$  is the wave function of state *i*, *j* and *s*, respectively, and  $\omega$  is the frequency of the lattice vibration. Thus, the  $E_B$  would be increased if decreasing the electron-lattice interaction (i.e.  $u_s$ ) when the  $\omega$  keeps unchanged. For the perovskite, this decrease due to the orthorhombic-tetragonal phase transition is indicated from the decrease in the elastic constant.<sup>3</sup>

## Note 3. Modeling the relationship between the trap emission peak and intensity

We assume that the trap states have an exponential distribution in the energy space, that is,  $N_t(E)=N_0exp[(E-E_0)/\varepsilon_0]$ , where  $N_t$  is the trap density,  $N_0$  is a pre-factor,  $E_0$  is the bottom of the trap state and  $\zeta_0$  is a parameter reflecting the trap distribution. We also assume that the emission energy peak ( $\Delta E$ ) is the energy difference between the highest occupied trap state ( $E_2$ ) and the valence band ( $E_1$ ). The highest occupied trap state can be derived from the trapped charge density, that is,

$$n_t(E) = \int N_0 \exp((E_2 - E_{20})/\xi_0) dE = N_0 \xi_0 \left[ \exp((E_2 - E_{20})/\xi_0) - 1 \right].$$

Under the low excitation, the charge decay rate is usually independent to the  $n_t$ . The emission intensity ( $I_{PL}$ ) is proportional to  $n_t$ , that is  $I_{PL}=f \times n_t$ , where f is a proportional parameter. Thus, the  $E_2$  can be derived as  $E_2=\xi_0 \times ln[1+I_{PL}/(fN_0\xi_0)]+E_{20}$ , where  $E_{20}$  is the bottom of the trap states. Therefore,  $\Delta E = \xi_0 \times ln[1+I_{PL}/(fN_0\xi_0)]+\Delta E_0$ , where  $\Delta E_0 = E_{20}-E_1$ .

## References

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