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Charge Carrier Recombination Dynamics in MAPb(Br_{1−y}I_y)₃ Single Crystals

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Abstract: Studying the carrier recombination process in MAPb(Br_{1−y}I_y)₃ single crystals (SCs) is important for its application in the optoelectronic field. In this work, a series of MAPb(Br_{1−y}I_y)₃ SCs with varied Br/I compositions have been studied. Steady-state photoluminescence (PL) spectra, time-resolved photoluminescence (TRPL) spectra and time-resolved microwave photoconductivity (TRMC) were used to understand the radiative and non-radiative recombination processes of MAPb(Br_{1−y}I_y)₃ SCs. By comparing the dynamics of TRPL and TRMC, we conclude that the dynamics of TRPL is dominated by the electron trapping process, which is in accordance with the fast decay component of TRMC kinetics, whereas the slower decay component in TRMC is dominated by the hole trapping process. Moreover, we find both the electron and hole trapping rates in mixed-halide perovskite MAPb(Br_{1−y}I_y)₃ (0 < y < 1) SCs are higher than that of mono-halide perovskite MAPbBr₃ SCs and MAPbI₃ SCs. This suggests mixed-halide crystals could introduce additional electron and hole trapping densities, which could be related to the fluctuation of Br/I compositions in the crystals. This work is helpful for understanding carrier recombination process in mixed-halide perovskite SCs.

Keywords: mixed-halide perovskite; time-resolved spectroscopy; single crystal



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1. Introduction

Organic–inorganic hybrid perovskite has shown great application prospects in solar cells [1–4], light-emitting diodes [5,6], X-ray detectors [7–9], biomedicine [10,11] and other fields in recent years due to its advantages such as high absorption coefficient, long carrier diffusion length and adjustable bandgap [1,12–15]. The bandgap of MAPb(Br_{1−y}I_y)₃ single crystals (SCs) can be adjusted in the range of 1.49–2.28 eV by changing the Br/I compositions [16–18], which are very suitable for applications in light-emitting diodes, detectors and solar cells [19,20]. Compared with polycrystalline perovskite materials, single-crystal perovskite can eliminate the grain boundary defects, and would thus exhibit different optical and electrical properties [21–24]. Moreover, the altered Br/I compositions in mixed-halide perovskite would also affect the photophysical properties such as carrier recombination process [16,17,20,25]. Currently, the photophysical properties of MAPb(Br_{1−y}I_y)₃ SCs are not fully understood.

Understanding the photophysical properties in mixed-halide perovskite SCs is essential for their applications. In this regard, many studies have been conducted for studying the photophysical properties of mixed-halide perovskite in the past few years. For example, Rehman et al. studied carrier mobilities of FAPb(Br_{1−y}I_y)₃ single-crystal films by time-resolved Terahertz photoconductivity, and found that the carrier mobility of the

mixed-halide perovskite was lower than that of mono-halide perovskite and reached the lowest value when $y = 0.6$ [25]. Hoke et al. found that photoexcitation of $\text{MAPb}(\text{Br}_{1-y}\text{I}_y)_3$ single-crystal films could form iodine and bromine rich domains, and the former acts as trap centers [17]. Jeffrey et al. observed ion migration and phase segregation phenomenon in $\text{MAPbBr}_{1.5}\text{I}_{1.5}$ SCs by transient absorption measurements [20]. While Junsang et al. found that introducing Cl atom into $\text{MAPb}(\text{Br}_{1-y}\text{I}_y)_3$ SCs could effectively inhibit its phase segregation [16]. Although extensive studies have been carried out for mixed-halide SCs, there are still some aspects of research that are not very clear. For example, most of the studies are focused on the process of phase segregation, and correlations between I compositions and the carrier recombination process; in particular, the relationship between the non-radiation recombination process and Br/I compositions is still not very clear.

In this work, we studied carrier recombination dynamics of $\text{MAPb}(\text{Br}_{1-y}\text{I}_y)_3$ SCs with Br/I compositions by using steady-state photoluminescence (PL) spectroscopy, time-resolved photoluminescence (TRPL) spectroscopy and time-resolved microwave photoconductivity (TRMC). First, the $\text{MAPb}(\text{Br}_{1-y}\text{I}_y)_3$ SCs with the dimensional sizes of 4~10 mm were successfully grown by inverse temperature crystallization (ITC) method. Then, TRPL and TRMC measurements were conducted for understanding carrier recombination dynamics of the crystals. By comparing the dynamics of TRPL and TRMC, we concluded that the dynamics of TRPL is dominated by electron trapping process, which is in accordance with the fast decay component of TRMC kinetics. While the slower decay component in TRMC is dominated by hole trapping process. Moreover, both the electron and hole trapping rates of mixed-halide perovskite $\text{MAPb}(\text{Br}_{1-y}\text{I}_y)_3$ ($0 < y < 1$) SCs are higher than that of mono-halide perovskite SCs, indicating that Br/I mixing could introduce new trap states. This work is helpful for understanding carrier recombination process in mixed-halide perovskite SCs.

2. Materials and Methods

2.1. Chemicals and Reagents

N, N-Dimethylformamide (DMF, 99.5%), gamma-butyrolactone (GBL, 98%), lead bromide (PbBr_2 , 98%), methylammonium bromide (MABr, 99%), lead iodide (PbI_2 , 99%), methylammonium iodide (MAI, 98%) were purchased from Aladdin. All materials were used as received without further purification.

2.2. Growth of $\text{MAPb}(\text{Br}_{1-y}\text{I}_y)_3$ Perovskite Single Crystals

The specific parameters of growing $\text{MAPb}(\text{Br}_{1-y}\text{I}_y)_3$ SCs are shown in Table 1. First, the solute was dissolved into solvent with the specific molar ratio, and the precursor solution was obtained by stirring at 800 rpm for 24 h at room temperature. Next, the stirred precursor solution was filtered with a 0.22 μm microporous filter membrane to obtain a clear solution. After that, the precursor solution was heated at a specific temperature (Table 1) for 3 days to obtain the seed crystals with 1~2 mm in size. The seed crystals were then placed into the new clear precursor solution, and the above steps were repeated until the crystal grew to over 4 mm in size.

Table 1. Growth conditions of $\text{MAPb}(\text{Br}_{1-y}\text{I}_y)_3$ crystals with varied I compositions.

y	Molar Ratio of Solute	Solvent	Concentration [M]	Growth Temperature [°C]
0	MABr:PbBr ₂ = 1:1	DMF	1.60	50
0.73	MABr:PbBr ₂ :MAI:PbI ₂ = 2:2:1:1	GBL	1.67	55
0.82	MABr:PbBr ₂ :MAI:PbI ₂ = 1:1:2:2	GBL	1.67	55
1	MAI:PbI ₂ = 1:1	GBL	1.23	90

2.3. Steady-State and Time-Resolved Photoluminescence Measurements

The steady-state PL and TRPL measurements were collected by time-correlated single photon counting (TCSPC) mode in a fluorescence spectrometer (FS5, Edinburgh Instru-

ments, Livingston, UK). Its light source was a picosecond laser (EPL-375, Edinburgh Instruments, Livingston, UK) with the pulse duration of 100 ps and operating wavelength of 375 nm. The repetition rate of the picosecond laser can be varied in the range of 20 KHz~20 MHz.

2.4. Time-Resolved Microwave Conductivity Measurements

The photoconductance transients of samples were measured by a homemade TRMC measurement system. The exciting light source is a Ti: Sapphire femto-second laser (Spfire ACE-100F, Spectra Physics, Santa Clara, CA, USA) at 800 nm with a pulse duration of ~100 fs. The frequency doubled laser pulse (~400 nm) were employed for exciting the samples. The TRMC setup uses a home-built microwave source with output frequency of 35.4 GHz and output power of 22.8 dBm. The microwave is first divided into signal channel and reference channel. The microwave in signal channel transmits the sample twice due to reflection by an FTO glasses. The reflected microwave and reference microwave are added in the magic Tee to reduce the microwave power reaching a low noise amplifier (TRLA-180400G40B, Gain 40 dB). The amplified microwave is converted to a voltage signal by a diode detector (R422C, Keysight, Santa Rosa, CA, USA) and collected by an oscilloscope (DPO 4104B, Tektronix, Beaverton, OR, USA).

In contrast to cavity-perturbation-type TRMC [26], TRMC kinetics in this work were measured in an open cell model, i.e., without resonant cavity. In perturbation case, the reflected microwave power change is proportional to carrier concentration. Furthermore, the microwave power change is detected by the Schottky diode, whose voltage output is proportional to the input microwave power. Thus, TRMC in this work probe the photocarrier concentration by the voltage-output-type Schottky diode.

2.5. X-ray Diffraction Measurements

The X-ray diffraction (XRD) measurements were completed by an X-ray diffractometer (DX-2700BH, Haoyuan, Dandong, China) whose light source was 1.54 Å X-ray generated by a copper target. The samples were single crystals crushed into powder, and measured at room temperature in the air.

2.6. Steady-State Absorption Measurements

The steady-state absorption measurements were measured by an ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer (UV-3600i Plus, Shimadzu, Kyoto, Japan). The samples were placed inside the integrating sphere (ISR-603, Shimadzu, Kyoto, Japan), and measured at room temperature in the air.

3. Results and Discussions

As shown in Figure 1a, MAPb(Br_{1-y}I_y)₃ SCs at sizes of 4~10 mm were grown successfully by ITC method. All the crystals exhibit a ladder structure, except for MAPbBr₃ SCs with a cubic structure. With the increase in I compositions, the color of the MAPb(Br_{1-y}I_y)₃ SCs starts to change from orange to black, which suggests that the absorption characteristics change with the I compositions. From X-ray diffraction (XRD) measurements (Figure 1b), we observe that MAPbI₃ SC has two diffraction peaks at $2\theta = 27.96^\circ$ and 28.26° , whereas the other crystals exhibit a single diffraction peak in the range of $27^\circ < 2\theta < 32^\circ$. According to the Bragg diffraction relationship, the two diffraction peaks at $2\theta = 27.96^\circ$ and 28.26° should belong to (004)_T and (220)_T crystal face of the tetragonal phase in MAPbI₃ SC, whereas the single diffraction peak in the range of $27^\circ < 2\theta < 32^\circ$ of other crystals should belong to (200)_C crystal face of cubic phase [27]. According to the position of the diffraction angle [27–29], the lattice parameters of the MAPb(Br_{1-y}I_y)₃ SCs can be calculated, as shown in the supplementary materials, Table S1. Based on the correlations between lattice parameter and the I compositions [27–30], the I composition in MAPb(Br_{1-y}I_y)₃ can be determined. This is shown in Figure 1c and Table 1, which the tetragonal phase of MAPbI₃ SCs should be treated as the pseudo-cubic phase. By comparing the I composition determined by

XRD measurements and in reactants, it can be found that the I composition in the crystal is higher than the ratio of I in the reactant, as shown in Figure 1c. This suggests that the I^- anion in the reactant is more likely to occupy the anion site in the crystal, which is possibly due to the complex interaction between the solute and the solvent, resulting in different probability of the halogen anions merging into the crystal during the formation of the crystal [19,31]. In this work, steady-state PL, TRPL and TRMC were used to measure MAPb(Br_{1-y}I_y)₃ SCs to understand their carrier recombination process.

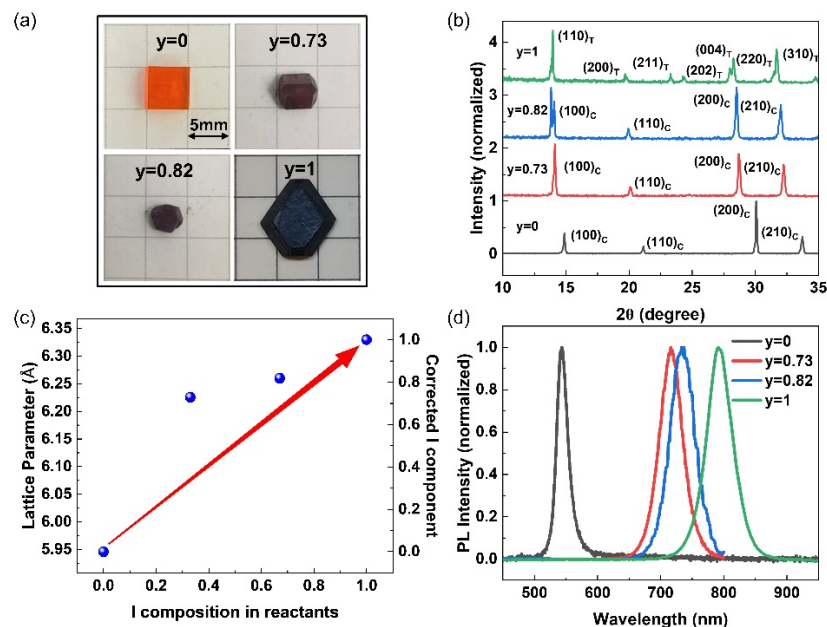


Figure 1. (a) Photos of MAPb(Br_{1-y}I_y)₃ SCs with varied I compositions grown by ITC method. (b) XRD of MAPb(Br_{1-y}I_y)₃ SCs in the range of $10^\circ < 2\theta < 35^\circ$. (c) The correlation between lattice parameter and I compositions in reactants for MAPb(Br_{1-y}I_y)₃ SCs. The corrected I composition was determined by lattice parameter and the tetragonal lattice was treated as pseudo-cubic. (d) PL emission spectra of MAPb(Br_{1-y}I_y)₃ SCs with indicated I compositions at room temperature.

We have measured the UV-VIS-NIR absorption spectra of MAPb(Br_{1-y}I_y)₃ SCs by integrating sphere method in this work (as shown in Figure S1), and analyzed the bandgaps by using Tauc analysis [27,32]. The bandgaps of MAPb(Br_{1-y}I_y)₃ SCs are determined as 1.49 eV, 1.62 eV, 1.70 eV, 2.15 eV for $y = 1, 0.82, 0.73, 0$, respectively. The emission characteristics of MAPb(Br_{1-y}I_y)₃ SCs were studied by steady-state PL measurement. Figure 1d shows the PL spectra of MAPb(Br_{1-y}I_y)₃ SCs grown with different I compositions at room temperature. All the measured MAPb(Br_{1-y}I_y)₃ SCs show only one PL emission peak, which can be attributed to the emission from free carrier recombination [33]. With the increase in I compositions, a red shift of the PL peak and a nearly linear correlation between PL emission peak energy and I compositions were observed (as shown in Figure S1c).

TRPL of MAPb(Br_{1-y}I_y)₃ SCs were measured to understand the carrier recombination process. In general, the carrier recombination dynamics in semiconductors is mainly composed of charge trapping, bimolecular recombination and Auger recombination, which can be described by the following equation [34,35]

$$\frac{dn(t)}{dt} = -kn(t) - \gamma n(t)^2 - An(t)^3, \quad (1)$$

where k , γ and A are charge trapping, bimolecular recombination, and Auger recombination coefficients, respectively. We observed that the carrier recombination dynamics in MAPb(Br_{1-y}I_y)₃ SCs showed a non-single exponential decay trend, as shown in Figure 2. According to Equation (1), in the case of low trapped state concentration, the carrier recombination process may be dominated by bimolecular recombination or Auger recombination,

which could cause the decay of kinetics to become faster with the increase in excitation fluence. However, the carrier recombination dynamics in MAPb(Br_{1-y}I_y)₃ SCs showed a trend that was independent of the excitation fluence, as shown in Figures 2b and S2. This strongly suggests that the TRPL kinetics are mainly dominated by the charge trapping process in the range of measured excitation fluence, even though the kinetics in MAPb(Br_{1-y}I_y)₃ SCs exhibit non-single exponential decays. For the PL originated from free carrier recombination, either electron trapping or the hole trapping can induce the decay of TRPL. Since MAPb(Br_{1-y}I_y)₃ SCs are more similar to p-type semiconductors [36], we would expect most of the hole trap states could be filled by background free holes, and accordingly we deduce TRPL kinetics are dominated by electron trapping process.

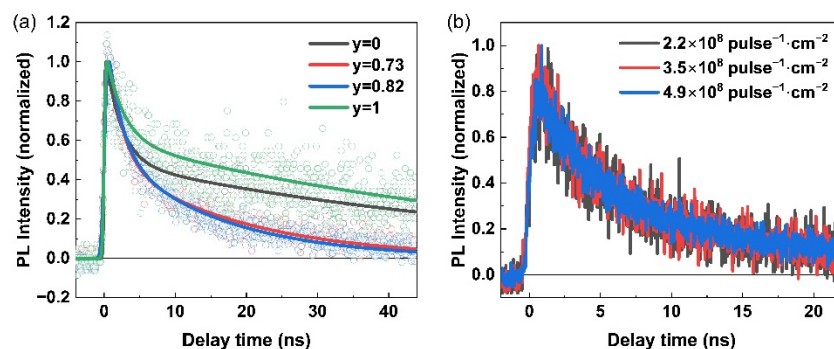


Figure 2. (a) TRPL kinetics of MAPb(Br_{1-y}I_y)₃ SCs with indicated I composition after photoexcitation at 375 nm with an excitation fluency of $4.9 \times 10^8 \text{ pulse}^{-1} \cdot \text{cm}^{-2}$. The solid lines are fitting curves based on multi-exponential decay functions, and the detailed fitting parameters are shown in Table 2. (b) TRPL kinetics of MAPb(Br_{0.18}I_{0.82})₃ SCs at different excitation fluencies.

Table 2. Fitting parameters for TRPL and TRMC kinetics of MAPb(Br_{1-y}I_y)₃ single crystals with different Br compositions.

y	TRPL					TRMC					$k_{\text{trap-e}}$ [$\times 10^6 \text{ s}^{-1}$] ^b	$k_{\text{trap-h}}$ [$\times 10^6 \text{ s}^{-1}$] ^c	
	A_1	τ_1 [ns]	A_2	τ_2 [ns]	τ_A ^a [ns]	A_1	τ_1 [ns]	A_2	τ_2 [ns]	A_3			τ_3 [ns]
0	0.54	2.2	0.46	59.4	28.5	0.13	2.2	0.26	59.4	0.61	1720	35.1	0.6
0.73	0.59	2.0	0.41	18.4	8.7	0.06	2.0	0.66	18.4	0.28	1182	114.9	0.8
0.82	0.55	2.0	0.45	15.5	8.1	0.43	2.0	0.49	15.5	0.08	809	123.5	1.2
1	0.45	2.4	0.55	60.7	34.5	0.01	2.4	0.80	60.7	0.19	9554	29.0	0.1

^a τ_A is the average life of TRPL; ^b $k_{\text{trap-e}}$ is the trapping rate of the electron, calculated from τ_A of TRPL; ^c $k_{\text{trap-h}}$ is the trapping rate of the hole, calculated from τ_3 of TRMC.

The non-exponential decay of TRPL may be caused by the uneven distribution of trap states [37]. Trap states with different energy values could lead to different carrier capture rates, and the distribution of trap states at different positions in space will also lead to the probability of carriers encountering trap states. To compare the influence of I composition on electron trapping rates, TRPL kinetics are fitted by double exponential decay functions, and the average lifetime (τ_A) were calculated as $(A_1 \tau_1 + A_2 \tau_2) / (A_1 + A_2)$, as shown in Table 2. We find that, the average TRPL lifetime of MAPb(Br_{0.27}I_{0.73})₃ SCs (~8.7 ns) is close to that of MAPb(Br_{0.18}I_{0.82})₃ SCs (~8.1 ns), and much shorter than that of MAPbBr₃ SCs (~28.5 ns) or MAPbI₃ SCs (~34.5 ns) (as shown in Table 2), suggesting that the mixture of Br and I will lead to the increase in the electron trapping rate.

Different from TRPL, TRMC reflects the change of semiconductor photoconductivity, which depends on the change of carrier mobility and carrier concentration. Thus, TRMC will be sensitive to the change of free carrier concentration when the carrier mobility is assumed to be constant. Herein, there are two main channels for the decay of free charge concentrations. One is the reduction in free carrier concentration caused by the radiation recombination between free electrons and holes. The other is that the free electrons (holes) are captured by the immovable electron (hole) defects. The decay of photoconductivity kinetics may be dominated by one or both paths.

Figures 3a and S3 shows the comparison between TRPL and TRMC of MAPb(Br_{1-y}I_y)₃ SCs. The decay of TRMC can be divided into two parts: fast decay and slow decay processes. The fast decay process of TRMC is similar with that of TRPL, whereas the slow decay does not occur in TRPL. As discussed above, TRPL kinetics is more likely to be dominated by electron trapping process. Thus, the fast decay component in TRMC can be attributed to the decay of free electron concentration due to charge trapping process. For the slower decay component of TRMC, there are two possible explanations. Firstly, the slower decay component of TRMC is induced by the recombination between de-trapped electron and holes. In this explanation, the amplitude of TRMC in long timescale is contributed by the free carrier concentrations origin from de-trapped electrons and holes, and the recombination between de-trapped electrons and holes led to the decay of TRMC amplitude. The other explanation is that the slower decay component of TRMC is actually dominated by hole trapping processes. In this explanation, the amplitude of TRMC in long timescale is contributed by the free holes, and the trapping of free holes reduced the free charge concentrations and consequently resulted in the decay of TRMC amplitude. For the first explanation, the decay of TRMC would be determined by both the concentrations of de-trapped electrons and de-trapped holes, is thus a second order carrier recombination process. In other words, an excitation fluency dependence of the slower decay component is expected. However, we observe that TRMC is independent with the excitation fluency (Figures 3b and S4), suggesting the de-trapped charge recombination model does not fit our observations. Therefore, we attribute the slower decay component of TRMC to the hole trapping process.

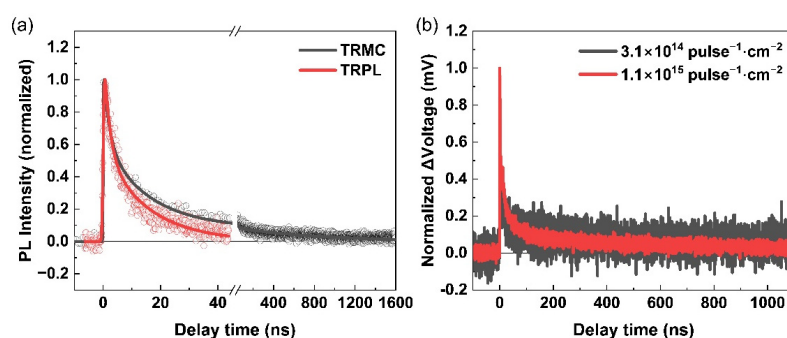


Figure 3. (a) Comparison between TRMC and TRPL kinetics of MAPb(Br_{0.18}I_{0.82})₃ SCs at room temperature. The TRPL (TRMC) solid lines are fitting curves based on multiple-exponential decay functions, and the detailed fitting parameters are shown in Table 2. (b) TRMC kinetics of MAPb(Br_{0.18}I_{0.82})₃ SCs at different excitation fluencies.

Figure 4 shows the TRMC of MAPb(Br_{1-y}I_y)₃ SCs with different I compositions. The kinetics are fitted by two lifetimes of τ_1 and τ_2 , that occurs in TRPL, and an additional long lifetime (τ_3). This long lifetime (τ_3) is the hole trapping lifetime. It can be found that the long-lived decay component (τ_3) of MAPb(Br_{0.27}I_{0.73})₃ SCs (1182 ns) and MAPb(Br_{0.18}I_{0.82})₃ SCs (809 ns) decay faster than the mono-halide perovskite of MAPbBr₃ SCs (1720 ns) and MAPbI₃ SCs (9554 ns) (as shown in Table 2). Combined with the results of TRPL, we conclude that both the electron and hole trapping rates in mixed-halide MAPb(Br_{1-y}I_y)₃ SCs are higher than that of mono-halide perovskite of MAPbBr₃ SCs and MAPbI₃ SCs. In other words, the mixed-halide perovskite introduces both additional electron and hole traps comparing with that of mono-halide perovskite. For the nature of the additional traps in the mixed-halide perovskite, it is still not clear yet. One possibility is that the inhomogeneous distribution of Br/I in crystal could induce the fluctuation in energy for the conduction and valence bands [16,24], and some deep energy states could act as the additional trap states.

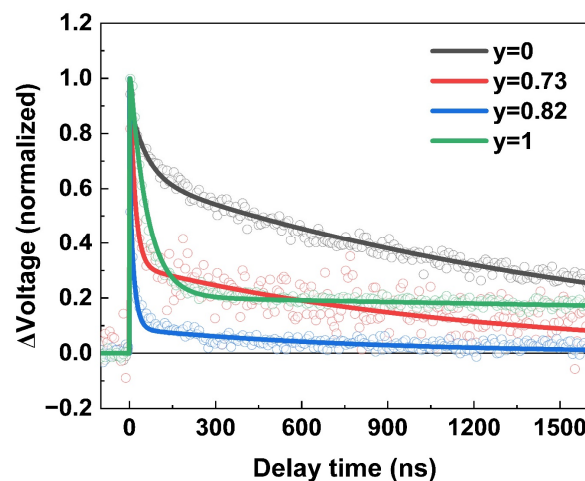


Figure 4. TRMC kinetics of MAPb(Br_{1-y}I_y)₃ SCs with indicated I compositions. The solid lines are fitting curves based on multi-exponential decay functions, and the detailed fitting parameters are shown in Table 2.

Summarizing the discussions above, carrier recombination process in MAPb(Br_{1-y}I_y)₃ SCs can be described by Figure 5. For MAPb(Br_{1-y}I_y)₃ SCs, there are still electron traps and hole traps. Since MAPb(Br_{1-y}I_y)₃ SCs are more similar to p-type semiconductors, most of the hole trap states are expected to be filled by background free holes, leading to less hole trap density than the electron trap density in the crystal. As a result, the electron trapping rate is much higher than the hole trapping rate and dominates the decay of TRPL kinetics. The great difference between the electron trapping rate and the hole trapping rate leads to the fast decay and the slow decay of photoconductivity dynamics. Compared with MAPbBr₃ SCs and MAPbI₃ SCs (Figure 5a,b), the mixed-halide perovskite MAPb(Br_{1-y}I_y)₃ SCs exhibit faster electron and hole trapping rates, due to the introduced additional traps (Figure 5c).

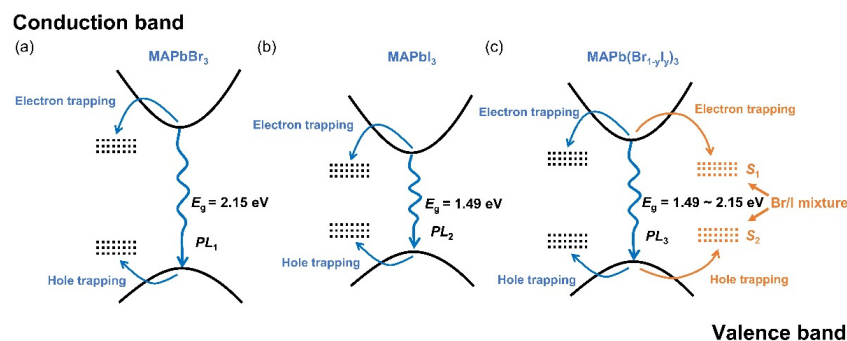


Figure 5. Schematic of carrier recombination dynamics in (a) MAPbBr₃, (b) MAPbI₃, and (c) MAPb(Br_{1-y}I_y)₃ SCs.

4. Conclusions

In summary, the carrier recombination process of MAPb(Br_{1-y}I_y)₃ SCs have been studied in this work. A series of MAPb(Br_{1-y}I_y)₃ SCs with different Br/I compositions were measured by steady-state photoluminescence spectra, time-resolved luminescence spectra and time-resolved microwave photoconductivity to explore the radiative and non-radiative recombination processes. By comparing the dynamics of TRPL and TRMC, we conclude that the dynamics of TRPL is dominated by electron trapping process, whereas the slower decay component in TRMC is dominated by hole trapping process. We find both the electron and hole trapping rates in mixed-halide perovskite MAPb(Br_{1-y}I_y)₃ SCs are higher than that in MAPbBr₃ SCs and MAPbI₃ SCs, which suggests mixed-halide crystals could introduce additional electron and hole trap densities. The increased trap densities in

mixed-halide perovskite MAPb(Br_{1-y}I_y)₃ SCs could be related to the fluctuation of Br/I compositions in the crystals.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12101425/s1>, Absorption spectra; Relationship between I compositions and PL peak energy; TRPL; TRMC; Fitting parameters (PDF). Figure S1: (a) Absorption spectra of MAPb(Br_{1-y}I_y)₃ single crystals measured by integration sphere method. (b) Bandgap energy obtained by Tauc analysis. (c) The correlation between PL peak energies and I compositions for MAPb(Br_{1-y}I_y)₃ single crystals, Figure S2: TRPL kinetics of MAPb(Br_{1-y}I_y)₃ single crystals with (a) y = 0; (b) y = 0.73; (c) y = 0.82; (d) y = 1 under different excitation fluencies, Figure S3: Comparison between TRMC and TRPL kinetics of MAPb(Br_{1-y}I_y)₃ single crystals with (a) y = 0; (b) y = 0.73; (c) y = 0.82; (d) y = 1 at room temperature. The solid lines are fitting curves based on multiple exponential decay functions, and the detailed fitting parameters are shown in Table 2. Figure S4: TRMC kinetics of MAPb(Br_{1-y}I_y)₃ single crystals with (a) y = 0; (b) y = 0.73; (c) y = 0.82; (d) y = 1 under different excitation fluencies, Table S1. Lattice parameters of MAPb(Br_{1-y}I_y)₃ single crystals with different I compositions.

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