Influence of Crystallization Temperature on the Optical Properties of MAPbBr₃ Single Crystals

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ABSTRACT

Optical properties of methylammonium lead bromide (MAPbBr₃) perovskite single crystals grown using a seed-induced inverse temperature crystallization method were studied using photoluminescence (PL) and time-resolved PL measurements. Crystallization rate was observed to be faster with an increasing crystallization temperature. The highest crystal quality was recorded for a sample crystallized at 85 °C, and it exhibited the strongest X-ray diffraction peaks and PL intensity. The PL spectra for all samples crystallized at room temperature showed an asymmetric shape with a shoulder in the low energy side; this can be attributed to a photon recycling effect caused by re-emission inside the single crystal. We confirmed that the structural and optical properties of MAPbBr₃ single crystals can be manipulated by modifying the crystallization temperature.

Keywords: Perovskite, Photoluminescence, Single crystal, Time-resolved photoluminescence

1. Introduction

In recent years, methylammonium lead halide perovskites have emerged as viable semiconductor materials in applications such as solar cells, light-emitting diodes, laser, and photodetectors [1–4]. In particular, organometal halide MAPbX₃ (MA = CH₃NH₃, X = Cl, Br, or I) single crystals exhibit excellent optoelectronic properties including high carrier mobility, high absorption coefficient, and tunable emitting wavelength [2,5,6]. To realize large-scale, high-quality, and rapid growth rate perovskite single crystals, several methods including anti-solvent vapor-assisted crystallization, seed-induced method, and inverse temperature crystallization (ITC) have been studied [5–7].

Most of these studies focused on device characteristics and efficiency of perovskite single crystals, and little attention is given to the fundamental properties of single crystals [5–7]. To develop high-quality single crystals, asymmetrical photoluminescence (PL) emission spectra occurring in MAPbBr₃ single crystals must be addressed. Yang *et al.* reported band-to-band transitions from surface regions and carrier diffusion from the surface to the interior regions [8]. Chen *et al.* attributed asymmetrical PL spectra of the low-energy side to defect-related bound exciton transition at low temperatures [9]. Wang *et al.* demonstrated changes in PL spectra caused by the phase transition of perovskite single crystals with temperature, and low-energy PL peaks caused by the formation of vacancy for Br ions [10].

In this study, MAPbBr₃ perovskite single crystals were synthesized using seed-induced and ITC methods at various crystallization temperatures to achieve rapid growth rates and high crystallinity. Subsequently, optical properties were evaluated using PL and time-resolved PL (TRPL) spectroscopy. With increasing crystallization temperatures, the rate of microcrystal formation increased. Thus, high-

quality single crystals were synthesized with a high growth rate at 85 °C. The PL spectra showed asymmetrical shapes at room temperature, which may be attributed to the photon recycling effect that occurs inside the single crystal.

2. Experimental details

For the synthesis of MAPbBr₃ perovskite single crystal samples, a 1 M solution of MA and PbBr₂ was prepared in *N,N*-dimethylformamide (DMF) at room temperature. The MAPbBr₃ precursor solution was then filtered using a PTFE filter with a 0.2-μm pore size. To synthesize the seed crystal, 2 ml of the filtrated solution was placed in a beaker, and the beaker was kept in an oven at crystallization temperatures until the observed seed crystal was approximately 1 mm in size. The seed crystal was then placed in 5 ml of fresh precursor solution and baked in an oven at different crystallization temperatures between 80 to 100 °C. All seed induced crystals were then allowed to grow for 180 min.

X-ray diffraction (XRD) measurements were conducted using X'pert Pro X-ray diffractometer (Malvern Panalytical). Temperature-dependent PL measurement was performed using a spectrometer (DM500i, Dongwoo Optron Co., Ltd.) with a He-Cd laser (λ = 325 nm, Kimmon) as the excitation source. The PL spectra were recorded using a charge-coupled device detector (ANDOR DV420-BU2). The samples were mounted on a closed-cycle cryostat (CCS-150, Janis Research Co., Inc.) with the temperature ranging from 10 to 300 K. The TRPL was measured using a FLS 920 spectrometer (Edinburgh Instruments Ltd.), and a picosecond pulsed diode laser (λ = 375 nm, pulse width = 48.4 ps, EPL-375, Edinburgh Instruments Ltd.). The TRPL spectra were recorded using a time-correlated single-photon

counting system.

3. Results and discussion

Figure 1(a) shows images of the grown MAPbBr₃ single crystal at different crystallization temperatures. The size of the crystals obtained when using the added seed-induced method was larger compared with that obtained using the general ITC method [11,12]. The largest crystal size obtained was $\sim 63 \times 59 \times 25 \text{ mm}^3$ at 85 °C. However, at crystallization temperatures greater than 90 °C, the spontaneous formation of smaller multiple crystals was observed; moreover, the crystals appeared stacked. This may be attributed to the decreasing solubility of MAPbBr₃ in DMF with increasing temperature [11]. At higher crystallization temperatures, the precursor solution becomes supersaturated, thereby producing a large number of small crystals. This prevents the seed-induced crystal from growing further. To confirm crystallinity, we performed XRD measurements at room temperature. Figure 1(b) shows the XRD spectra obtained with diffraction angles (10° to 80°). The narrow and strong diffraction peaks at 15.3°, 30.5°, 46.3°, and 63.0° correspond to the (100), (200), (300), and (400) planes of the cubic phase, respectively [12]. As shown in Fig. 1(b), the sample crystallized at 85 °C exhibits stronger (~ 10 times) diffraction peaks compared to those of other samples. The full width at half maximum (FWHM) of the diffraction peaks is shown in the inset of Fig. 1(b). Except for the (100) plane, the FWHM of the diffraction peaks is the lowest in the 85 °C sample. The strong intensities and narrow linewidths are indicative of high crystallinity. Thus, we experimentally confirm that high-quality MAPbBr₃ single crystals with a high growth rate can be grown using the seed-induced ITC method at 85 °C.

Figure 2(a) illustrates the room temperature PL spectra of the MAPbBr₃ single crystal samples. The PL peak positions of all samples are located at around 534 nm; for the sample obtained at 85 °C, the peak intensity is approximately three times stronger compared to that of the sample obtained at 90 °C. Thus, the PL results are in good agreement with the XRD data. However, we observed variations in the PL spectrum with changing irradiation positions of the excitation laser beam. Two spots (center of sample: spot A and edge of sample: spot B) with differences in PL peak positions are illustrated in the inset of Fig. 2(b). In the PL peak position, spot A is located at a shorter wavelength range than spot B, and the difference between the two PL peak positions is about 5 nm. To identify the change caused by the difference in the laser irradiation position, an excitation power-dependent PL experiment was performed at the two spots. The variations in the PL characteristics

(peak position and relative intensity) corresponding to the power of the excitation source at the two spots showed a similar tendency (not shown here).

The PL spectra for all samples exhibit asymmetric shapes, with the shoulder located in the long-wavelength (low energy) side at room temperature. The temperature-dependent PL measurements were performed to investigate the low-energy state of PL emission. Figure 3(a) shows the temperature-dependent PL spectra measured at spot A of the 85 °C sample for the selected temperatures. MAPbBr₃ single crystals are well known for phase transitions to cubic ($T > 230 \text{ K}$), tetragonal ($145 \text{ K} < T < 230 \text{ K}$), and orthorhombic ($T > 145 \text{ K}$) phases as the temperature decreases. Our XRD measurement was performed only at room temperature, and thus, we could not directly confirm the phase transition with the change in temperature; however, the temperature dependence of the PL peak in Fig. 3(b) shows a similar tendency to the reported results [9,10].

The obtained PL spectra can be separated into three Gaussian peaks ($T \leq 70 \text{ K}$) and two Gaussian peaks ($T > 80 \text{ K}$). The PL peak

Figure 2. (Color online) (a) Room-temperature PL spectra of MAPbBr₃ single crystal samples. (b) PL spectra of the sample obtained at 85 °C in different irradiation regions. The inset shows the laser irradiated region of the sample.

Figure 3. (Color online) Temperature-dependent (a) PL spectra, (b) PL peak positions, and (c) FWHM of the 85 °C sample on laser irradiation spot A.

Figure 1. (Color online) (a) MAPbBr₃ single crystal images at different crystallization temperatures. (b) X-ray diffraction patterns at room temperature. The inset shows the full width at half maximum (FWHM) of (100), (200), (300), and (400) planes.

Figure 4. (Color online) (a) PL decay curves of spot A and PL decay times of (b) spot A and (c) spot B as a function of emission wavelength. The measured PL spectrum and fitted PL peaks are also shown.

energies and FWHM extracted from Gaussian fitting results are shown in Figs. 3(b) and 3(c), respectively. Similarly, a change in FWHM with increasing temperature was observed at the two peaks. This is consistent with the excitation power-dependent PL results, which suggest that the two PL emission origins are the same. The sub-peaks appearing in low-temperature regions can be attributed to the phase transition from the orthorhombic phase. At high temperatures, the main peak (Peak1) originates from band-to-band transition [10]. However, the origin of the low-energy peak (Peak2) observed in the PL spectra at high temperatures is unclear [8,10,13].

To investigate the carrier dynamics of the shoulder peak (Peak2), TRPL measurement was conducted as a function of wavelength at room temperature. Figure 4(a) presents the PL decay curves of spot A (85 °C sample). With an increase in the emission wavelength from 515 to 563 nm, the PL decays become slower. The PL decay times of the 85 °C sample were calculated using the bi-exponential decay function $I(t) = \sum A_i \exp(-t/\tau_i)$, where A_i is the pre-exponential constant and τ_i is the decay time shown in Figs. 4(b) and 4(c). At the PL peak of spot A, the PL decay times of τ_1 and τ_2 are 0.42 and 2.1 ns, respectively. Fast and slow PL decay times, τ_1 and τ_2 , are attributed to recombination centers present on the surface defects (Br vacancy) and the bulk of the MAPbBr₃ single crystal, respectively [13,14].

Fang *et al.* demonstrated the photon recycling effect caused by the re-emission originating from the edge of the bulk after self-absorption and internal reflections [15]. After PL is generated at the surface of single crystal, part of the PL emission penetrates into the single crystal and is absorbed by itself. Reabsorbed photon represents re-emission with a red-shifted PL peak due to the stoke shift. These behaviors were well explained by the PL and TRPL results of this study. All optical properties in spot A, including the excitation power-dependent PL, temperature-dependent PL, and TRPL characteristics were similar to those in spot B, thereby indicating that the PL emission origins of the two spots could be the same. In Fig. 4(a), slower decay with an increase in the emission wavelength of the MAPbBr₃ single crystal can be explained by the photon recycling effect. The accumulation of PL emissions penetrating inside the surface of the single crystal continues the process of resorption and re-emission, which results in an increase in decay time owing to an increase in the emission wavelength. In

Figs. 4(b) and 4(c), the slow decay time τ_2 at the low-energy side PL peak position is 4.9 and 8.4 ns for spots A and B, respectively. The longer lifetime at spot B can be explained by more active resorption and re-emission occurring at the single crystal edge.

4. Conclusions

We investigated the influence of crystallization temperatures on the optical properties of MAPbBr₃ perovskite single crystals using PL and TRPL measurements. It was found that an increase in the crystallization temperatures (from 80–100 °C) led to the formation of multiple microcrystals. We confirmed that the optimal crystallization temperature was 85 °C in the seed-induced ITC method. All samples exhibited asymmetric PL spectra at room temperature; moreover, the two separated PL emissions showed similar characteristics as a function of excitation laser power and temperature. The PL peak on the low energy side at high temperatures was explained by the re-emission originating at the edge of the crystal due to the self-absorption and reflection inside the bulk.

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References

- [1] C. Aranda, A. Guerrero, and J. Bisquert, *ChemPhysChem* 20, 2587 (2019).
- [2] Z. K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, and F. Hanusch, *Nat. Nanotechnol.* 9, 687 (2014).
- [3] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, and T. C. Sum, *Nat. Mater.* 13, 476 (2014).
- [4] B. R. Sutherland, A. K. Johnston, A. H. Ip, J. Xu, V. Adinolfi, P. Kanjanaboos, and E. H. Sargent, *ACS Photon.* 2, 1117 (2015).
- [5] D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, and Y. Losovyj, *Science* 347, 519 (2015).
- [6] Y. Liu, Z. Yang, D. Cui, X. Ren, J. Sun, X. Liu, J. Zhang, Q. Wei, H. Fan, F. Yu, and X. Zhang, *Adv. Mater.* 27, 5176 (2015).
- [7] M. I. Saidaminov, A. L. Abdelhady, B. Murali, E. Alarousu, V. M. Burlakov, W. Peng, I. Dursun, L. Wang, Y. He, G. MacUlan, and A. Goriely, *Nat. Commun.* 6, 1 (2015).
- [8] B. Yang, X. Mao, S. Yang, Y. Li, Y. Wang, M. Wang, W. Deng, and K. Han, *ACS Appl. Mater. Interfaces* 8, 19587 (2016).
- [9] C. Chen, X. Hu, W. Lu, S. Chang, L. Shi, L. Li, H. Zhong, and J. B. Han, *J. Phys. D: Appl. Phys.* 51, 045105 (2018).
- [10] K. H. Wang, L. C. Li, M. Shellaiah, and K. W. Sun, *Sci. Rep.* 7, 1 (2017).
- [11] M. I. Saidaminov, A. L. Abdelhady, G. Maculan, and O. M. Bakr, *Chem. Commun.* 51, 17658 (2015).
- [12] H. Zhang, Y. Liu, H. Lu, W. Deng, K. Yang, Z. Deng, X. Zhang, S.

- Yuan, J. Wang, J. Niu, and X. Zhang, [Appl. Phys. Lett.](#) 111, 103904 (2017).
- [13] H. H. Fang, S. Adjokatse, H. Wei, J. Yang, G. R. Blake, J. Huang, J. Even, and M. A. Loi, [Sci. Adv.](#) 2, e1600534 (2016).
- [14] D. Priante, I. Dursun, M. S. Alias, D. Shi, V. A. Melnikov, T. K. Ng, O. F. Mohammed, O. M. Bakr, and B. S. Ooi, [Appl. Phys. Lett.](#) 106, 081902 (2015).
- [15] Y. Fang, H. Wei, Q. Dong, and J. Huang, [Nat. Commun.](#) 8, 14417 (2017).