Exciton–exciton scattering in perovskite CH$_3$NH$_3$PbBr$_3$ single crystal

Hideyuki Kunugita$^{1*}$, Yuki Kiyota$^1$, Yosuke Udagawa$^1$, Yuco Takeoka$^1$, Yuiha Nakamura$^2$, Junro Sano$^2$, Tomonori Matsumi$^{shita}$$^{2,3}$, Takashi Kondo$^{2,3}$, and Kazuhiro Ema$^1$

$^1$Faculty of Science and Technology, Sophia University, Chiyoda, Tokyo 102-8554, Japan
$^2$Department of Materials Engineering, The University of Tokyo, Bunkyo, Tokyo 113-8654, Japan
$^3$Research Center for Advanced Science and Technology, The University of Tokyo, Meguro, Tokyo 153-8904, Japan

$^*E$-mail: h-kunugi@sophia.ac.jp

Received February 10, 2016; accepted March 11, 2016; published online May 17, 2016

We have measured photoluminescence spectra in CH$_3$NH$_3$PbBr$_3$ at low temperatures and found a nonlinear emission at the lower energy side of the exciton resonance. Considering that this signal shows a rapid decay, we have assigned it as originating from the exciton–exciton inelastic scattering process called P-emission. The energy difference between this P-emission and the free exciton resonance is 20–30 meV, which is consistent with recent studies of the exciton binding energy.

© 2016 The Japan Society of Applied Physics

---

R ecent studies of three-dimensional (3D) lead-halide perovskites CH$_3$NH$_3$PbX$_3$ (X = Cl, I, Br) have demonstrated the great potential of such perovskites for use as photovoltaic materials. A photovoltaic power conversion efficiency of more than 21% has been already achieved. Although the physical and chemical mechanisms that allow such a high performance have not been fully clarified thus far, free-carrier (nonexcitonic) generation is often considered as one of the key properties. On the other hand, in two-dimensional (2D) lead-halide perovskites, excitons have shown to be stable even at room temperature and there are many studies discussing possible applications of such perovskites for light-emitting or nonlinear optical devices.

For CH$_3$NH$_3$PbI$_3$, there have been many studies that searched for an answer to this question, in which the exciton binding energies were estimated by several methods, which insist that the photogenerated carriers are mainly free carriers.

For CH$_3$NH$_3$PbBr$_3$, on the other hand, there are few studies that discuss the exciton binding energy. Recently, we have investigated the temperature dependence of the reflection spectra of CH$_3$NH$_3$PbBr$_3$ single crystals and showed that the photoexcited carriers have excitonic properties even at room temperature.

In the present work, we have measured photoluminescence (PL) spectra of CH$_3$NH$_3$PbBr$_3$ at low temperatures. As the excitation intensity increased, we have found a new spectral peak that appears at the lower side of the free exciton energy. Since the new spectral peak shows a nonlinear dependence on the excitation intensity and appears only just after the excitation, we can assign it to the exciton scattering process called P-emission. The observation of P-emission indicates that CH$_3$NH$_3$PbBr$_3$ can be regarded as a stable excitonic system like inorganic wide-gap semiconductors.

The samples used in this study were grown by the evaporation of DMF solutions at 100°C and kept in a cryostat (Iwatani CryoMini CRT-HE05-TOP) for low-temperature measurements. The excitation light source for PL experiments was the second harmonic of a pulse from an amplified mode-locked Ti:Al$_2$O$_3$ laser at a repetition rate of 10kHz (Coherent RegA). For reflection experiments, we used a halogen lamp and signals were detected by a spectrometer equipped with a charge-coupled detector (Horiba iHR320+Synapse).

Figure 1 shows reflection and PL spectra of a CH$_3$NH$_3$PbBr$_3$ single crystal at 5 K. The observed reflection spectrum is well reproduced by the excitonic Lorentz model, and the estimated free exciton resonance is 544 nm (2.28 eV). As with our previous results, the excitonic PL peak was clearly observed at the free exciton resonance, accompanied by a broad peak on the lower energy side. In many semiconductors, the photogenerated excitons at low temperatures are trapped at impurity levels or defects and form bound excitons. Such a bound exciton luminescence often dominates the PL spectrum. In our experiments, however, we observed free exciton PL signals in all samples, although our samples were grown by a simple evaporation method. This may originate from the unique properties of defect states in CH$_3$NH$_3$PbBr$_3$, which will lead to a long lifetime of photoexcited carriers and a high photovoltaic performance.

Note that the free exciton resonance energy reported above is different from the one in our previous report. There was some variation in resonant energy, although all of our samples were single crystals. To obtain larger single crystals, we used a growth in hot solution method. However, a difference in growth condition often produces differences in the macroscopic shape and surface condition of the samples. Such differences will change an internal strain of the crystals, which probably causes a shift in excitonic resonant energy.
Figure 2 shows the excitation intensity dependence of the PL spectra, where a new luminescence peak at the lower energy side of the free exciton resonance appears with increasing excitation intensity. Since the new peak grows nonlinearly compared with the exciton emission, its origin can be considered to be a result of interactions between excitons, such as biexciton formation or exciton–exciton scattering. In 2D perovskite materials, biexciton-originated luminescence was clearly observed, therefore the observed nonlinear peak seems to originate from a biexciton at first glance. However, the assignment to biexciton formation is unlikely because of the following reason. In general, biexciton binding energies roughly range from 1/10 to 1/5 of the corresponding exciton binding energies. The energy difference between the observed peak and the exciton resonance, which corresponds to the biexciton binding energy if the peak is assigned to the biexciton emission, is about 20–30 meV. This value is inconsistent with the range from 1/10 to 1/5 of the reported exciton binding energy of 36–76 meV. Although the reported values have some inaccuracy, the value of 20–30 meV is too large to be assigned to the biexciton binding energy.

Figure 3 shows time-resolved PL spectra at the highest excitation intensity shown in Fig. 2. We can see that the signal we focused on above is only observed just after excitation. The spectral shape at 60 ps after the excitation became similar to the PL spectra at weak excitation in Fig. 2. This result means that the new peak decays very rapidly compared to the free exciton signals, indicating that it can be emitted only at high exciton densities. Therefore, we can assign this peak as originating from an exciton–exciton inelastic scattering process. In this scattering process, an exciton is scattered into a higher exciton state ($n \geq 2$), while another is scattered on the photon-like branch of the polariton dispersion producing a luminescence photon called “P-emission”.

As shown above, the energy difference between the P-emission and the exciton resonance was 20–30 meV. This difference corresponds to the transition energy from the $n = 1$ exciton state to the $n = 2$ or higher exciton states, and the energy of the $n$th exciton is given by $E_n = (E_g/n^2)$, where $E_g$ and $E_n$ are the bandgap and exciton binding energy, respectively. Therefore the excitonic binding energy can be estimated to be 20–40 meV. Note that the obtained binding energy is directly estimated from the energy difference in excitonic emissions, without using any other material parameters. The estimated values are similar to those obtained in recent absorption studies using spin coated films. According to past magnetoabsorption results, however, the binding energy was estimated to be 76 meV, which is larger than the present estimation. Although the reason for this contradiction is unclear at this moment, it may be necessary to reconsider the material parameters such as the dielectric constant or carrier effective mass used for estimation in the magnetoabsorption study.

The estimated binding energies are consistent with our previous results showing that excitonic properties exist even at room temperature. Considering that an efficiency of more than 10% was reported using this material, our results suggest that the thermal dissociation of excitons at room temperature is not essential for high-performance photovoltaic cell materials. For a deeper understanding of the photovoltaic mechanism present in lead-halide perovskite materials, it is necessary to evaluate the carrier recombination loss with detailed information of the excitonic properties.

Besides being a promising candidate for photovoltaic applications, recent studies hold out the possibility that CH$_3$NH$_3$PbBr$_3$ will be useful for a light-emitting diode. Since stimulated emissions by the exciton–exciton scattering process have been discussed in some semiconductors, lead halide perovskites may also have a potential for lasing gain materials.

In conclusion, we have observed a new photoluminescence signal in CH$_3$NH$_3$PbBr$_3$ that shows a nonlinear increase in excitation intensity. Considering that this peak shows a rapid
decay compared with the free exciton signals, we have assigned this peak as a result of the exciton–exciton inelastic scattering process called P-emission. From the energy difference between the P emission and the free exciton luminescence, we can estimate the exciton binding energy to be 20–40 meV, which is in good agreement with the results of recent studies.

Acknowledgements This research was supported by the Japan Science and Technology Agency (JST) Advanced Low Carbon Technology R&D program (ALCA), and partly supported by JSPS KAKENHI (25286072 and 26600119) and The Science Research Promotion Fund.

1) H. J. Snaith, J. Phys. Chem. Lett. 4, 3623 (2013).
2) T. Miyasaka, Chem. Lett. 44, 720 (2015).
3) Web [http://www.nrel.gov/nepc/images/efficiency_chart.jpg].
4) T. Ishihara, J. Takahashi, and T. Goto, Phys. Rev. B 42, 11099 (1990).
5) K. Tanaka, T. Takahashi, T. Kondo, T. Umebayashi, K. Asai, and K. Ema, Phys. Rev. B 71, 045312 (2005).
6) K. Tanaka, T. Takahashi, T. Kondo, K. Umeda, K. Ema, T. Umebayashi, K. Asai, K. Uchida, and N. Miura, Jpn. J. Appl. Phys. 44, 5923 (2005).
7) M. Era, S. Morimoto, T. Tsutsui, and S. Saito, Appl. Phys. Lett. 65, 676 (1994).
8) T. Fujita, Y. Sato, T. Kuitani, and T. Ishihara, Phys. Rev. B 57, 12428 (1998).
9) G. Lanty, J. S. Lauret, E. Deleporte, S. Bouchoule, and X. Lafosse, Appl. Phys. Lett. 93, 081101 (2008).
10) I. Ishi, H. Kunugita, K. Ema, T. Ban, and T. Kondo, Appl. Phys. Lett. 77, 3487 (2000).
11) Y. Yamada, T. Nakamura, M. Endo, A. Wakamya, and Y. Kanemitsu, IEEE J. Photovoltaics 5, 401 (2015).
12) A. Miyata, A. Mitoglu, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith, and R. J. Nicholas, Nat. Phys. 11, 582 (2015).
13) H. Kunugita, T. Hashimoto, Y. Kiyota, Y. Udagawa, Y. Takeoka, Y. Nakamura, J. Sano, T. Matsushita, T. Kondo, T. Miyasaka, and K. Ema, Chem. Lett. 44, 852 (2015).
14) Y. Yang, Y. Yan, M. Yang, S. Choi, K. Zhu, J. M. Luther, and M. C. Beard, Nat. Commun. 6, 7961 (2015).
15) Y. Yang, M. Yang, Z. Li, R. Crisp, K. Zhu, and M. C. Beard, J. Phys. Chem. Lett. 6, 4688 (2015).
16) M. A. Green, Y. Jiang, A. M. Souifani, and A. Ho-Baillie, J. Phys. Chem. Lett. 6, 4774 (2015).
17) K. Galkowski, A. Mitoglu, A. Miyata, P. Plochocka, O. Portugall, G. E. Eperon, J. T.-W. Wang, T. Stergiopoulos, S. D. Stranks, H. Snaith, and R. J. Nicholas, Energy Environ. Sci. 9, 962 (2016).
18) T. Shi, W.-J. Yin, F. Hong, K. Zhu, and Y. Yan, Appl. Phys. Lett. 106, 103902 (2015).
19) X. Qin, H. Dong, and W. Hu, Sci. China Mater. 58, 186 (2015).
20) Y. Kato, D. Ichii, K. Ohashi, H. Kunugita, K. Ema, K. Tanaka, T. Takahashi, and T. Kondo, Solid State Commun. 128, 15 (2003).
21) C. Klingshirn, Semiconductor Optics (Springer, Heidelberg, 2012) Chap. 20.
22) K. Tanaka, T. Takahashi, T. Ban, T. Kondo, K. Uchida, and N. Miura, Solid State Commun. 127, 619 (2003).
23) T. Kobayashi, Y. Segawa, and S. Namba, Solid State Commun. 31, 253 (1979).
24) H. Ichida, Y. Kanematsu, T. Shimomura, K. Mizoguchi, D. Kim, and M. Nakayama, Phys. Rev. B 72, 045210 (2005).
25) M. Bamba, S. Wakaiki, H. Ichida, K. Mizoguchi, D. Kim, M. Nakayama, and Y. Kanematsu, Phys. Rev. B 91, 235205 (2015).
26) J. H. Heo, D. H. Song, and S. H. Im, Adv. Mater. 26, 8179 (2014).
27) Y.-H. Kim, H. Cho, J.-H. Heo, T.-S. Kim, N. Myoung, C.-L. Lee, S. H. Im, and T.-W. Lee, Adv. Mater. 27, 1248 (2015).
28) C. Klingshirn, Semiconductor Optics (Springer, Heidelberg, 2012) Chap. 22.
29) F. Deschler, M. Price, S. Pathak, L. E. Klintberg, D. D. Jarauusch, R. Higler, S. Hütter, T. Leijtens, S. D. Stranks, H. J. Snaith, M. Attari, R. T. Phillips, and R. H. Friend, J. Phys. Chem. Lett. 5, 1421 (2014).