Exciton fine structures in $CH_3NH_3PbBr_3$ single crystals studied by temperature-dependent photocurrent and photoluminescence excitation spectroscopy

Kyoto Univ. [1], Chiba Univ.[2]

○L. Q. Phuong[1], T. Yamada[1], T. Aharen[1], Y. Yamada[2], A. Wakamiya[1], and Y. Kanemitsu[1]

E-mail: le.phuong.46c@st.kyoto-u.ac.jp

Methylammonium lead halide perovskites ($MAPbX_3$, X = I, Br and Cl) have emerged as a potential class of materials for advanced optoelectronic applications including solar cells, light-emitting diodes, lasers, and photodetectors [1]. The dominant type of excitations, i.e., charge carriers or excitons, in perovskite thin films has a decisive role in determining the performance of perovskite-based devices. Therefore, it is of great significance to comprehend the nature of excitations and their fundamental photoelectrical properties in $MAPbX_3$ perovskites. Thus far, the binding energy of excitons in $MAPbBr_3$ has not been well assessed yet, and reported to fluctuate from 15 to 60 meV [2]. These scattered values of the reported exciton binding energies lead to discordant opinions on the nature of excitation in $MAPbBr_3$. In order to reconcile this debate, further work is required. Utilizing different spectroscopic techniques simultaneously and single crystals provides a powerful routine to achieve thoroughly optoelectronic properties in organic-inorganic lead halide perovskites [3].

Here we examined the fundamental properties of excitons in $MAPbBr_3$ single crystals using a combination of temperature-dependent photocurrent excitation (PCE) and photoluminescence excitation (PLE) spectroscopy. Steady-state photoluminescence (PL) measurements for $MAPbBr_3$ at 16 K revealed a sharp emission band peaking at 2.247 eV. On the other hand, multiple peak structures appeared in both PCE and PLE spectra, and the energy position of the lowest peak is identical to that of the sharp PL band. We ascribed the sharp PL band to the emission of the free excitons at the ground state, and the high-energy peak structures in the PCE spectra to the excited states of the free excitons. The binding energy of excitons in $MAPbBr_3$ then was evaluated to be about 20 meV at low temperatures. The temperature dependence of the exciton binding energy in $MAPbBr_3$ will be discussed.

Part of this work was supported by JST-CREST (JPMJCR16N3) and JSPS KAKENHI (16F017).

[1] Y. Kanemitsu, J. Mater. Chem. C **5**, 3427 (2017).

[2] Y. Yamada, T. Yamada, and Y. Kanemitsu, Bull. Chem. Soc. Jpn (2017) to be published.

[3] Y. Yamada *et al.*, J. Am. Chem. Soc. **137**, 10456 (2015); L. Q. Phuong *et al.*, J. Phys. Chem. Lett. **7**, 2316 (2016); L. Q. Phuong *et al.*, J. Phys. Chem. Lett. **7**, 4905 (2016).