

Exciton and Bandgap Energies of Hybrid Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Abstract

Exciton and bandgap energies of organic-inorganic hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ were investigated by reflection and absorption spectroscopy on a single crystal and a high-quality planar-type thin film. We have shown that exciton binding energy is 28 meV indicating excitons are stable and dominate the optical spectra around the absorption edge even at room temperature. The bandgap energy determined using a polycrystalline thin film is 1.70 eV at room temperature.

1. Introduction

Organic-inorganic hybrid perovskite crystals $\text{CH}_3\text{NH}_3\text{PbX}_3$ [X is Cl, Br or I] are of great interest as materials of high-efficiency and low-cost solar cells. In 2009, Kojima et al. [1] first reported the development of a solar cell using a perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. Efficiencies of perovskite solar cells have increased rapidly and are approaching those of Si thin film solar cells [2].

Although the efficiencies of perovskite solar cells are increasing, fundamental optical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are still unclear. Whether excitons exist at room temperature is also controversial. In this paper, we report exciton characteristics and bandgap energies of $\text{CH}_3\text{NH}_3\text{PbI}_3$ investigated by reflection and absorption spectroscopic measurements on single crystals and polycrystalline thin films.

2. Experimental

Single crystals were prepared using a technique reported in ref. [3]. $\text{CH}_3\text{NH}_3\text{I}$ reacted with an stoichiometric amount of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ in a HI aqueous solution. Single crystals of about 1 mm³ in size were grown by slow evaporation method.

We prepared polycrystalline thin films of $\text{CH}_3\text{NH}_3\text{PbI}_3$ using a vapor deposition method. We used PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ as vapor sources evaporated in a vapor deposition chamber with an ultimate pressure of 10⁻⁷ Pa. 660-nm-thick polycrystalline thin films were deposited on flat glass substrates under deposition rates as low as 0.1 nm/s. We confirmed that the obtained thin film samples are of high qualities. An X-ray diffraction pattern of a high-quality thin film is shown in Fig. 1. It should be noted that no traces of

impurities or unreacted materials are found and that the deposited polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ is preferentially oriented so that (110) plane is parallel to the substrate surface.

We measured reflection spectrum of a single crystal at room temperature and absorption spectra of a polycrystalline thin film from 6.4 to 300 K.

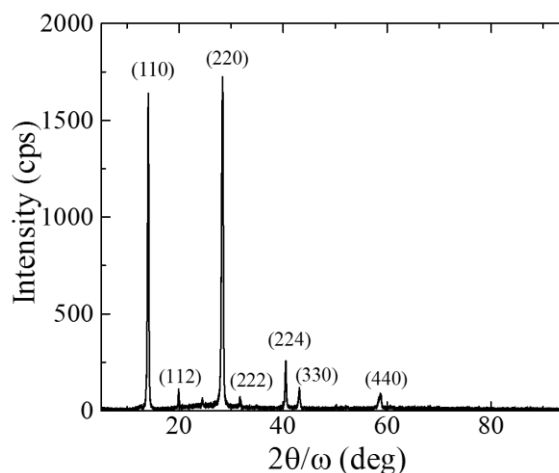


Fig. 1 $2\theta/\omega$ X-ray diffraction pattern of a polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film.

3. Results and discussion

Figure 2 shows a reflection spectrum of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystal and optical absorption spectra of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film. The reflection spectrum depicted with a black dash-dotted line in Fig. 2 is of a typical Lorentzian shape. Since the reflection spectrum is well fitted with a simple Lorentzian model function (shown with an orange line in Fig. 2) as in the case of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ [4], we conclude that excitons dominate the reflection around the absorption edge even at room temperature.

Fundamental absorption edges around 1.6–1.7 eV continuously blue-shifted with increasing temperature except for the discontinuous jump below 160 K which is believed

to be accompanied by a structural phase transition.

We fitted the absorption spectra assuming a Gaussian-shaped exciton resonance absorption and a continuous absorption band due to interband transition, and obtained binding energies and bandgap energies. In Fig. 2, the decomposed excitonic and the interband absorptions are depicted with green broken lines for room temperature. The obtained exciton binding/bandgap energies were 28 meV/1.70 eV at 300 K and 47 meV/1.74 eV at 6.4 K, respectively. The relatively large exciton binding energies are consistent with our previous report [5] (binding energy of the exciton was measured to be 50 meV at 4.2 K). This is also consistent with the value reported by D’Innocenzo et al. (35-75 meV) [6], and much higher than that reported by Yamada et al. (6 meV) [7]. This strongly suggests that excitons are stable in $\text{CH}_3\text{NH}_3\text{PbI}_3$ even at room temperature.

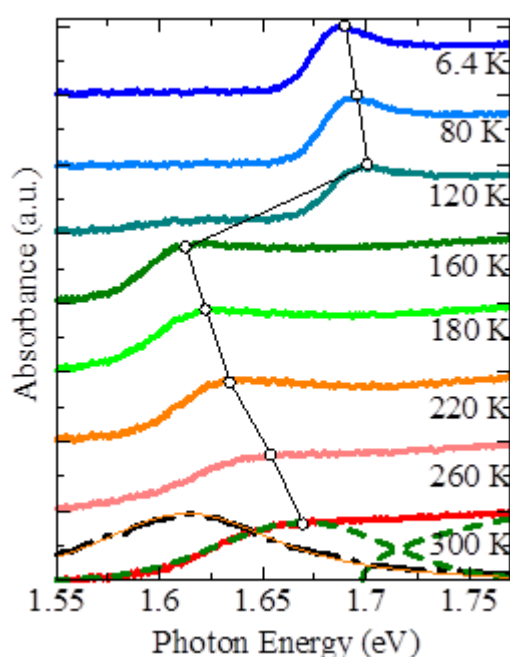


Fig. 2 Temperature-dependent absorption spectra of a polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film. Small circles represent exciton resonance energies. A reflection spectrum of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystal at room temperature is shown with a black dash-dotted line.

Almost all the previous reports on $\text{CH}_3\text{NH}_3\text{PbI}_3$ rely on the absorption spectra measured using polycrystalline films formed on mesoporous TiO_2 layers for which no exciton resonance peaks have been observed around the absorption edges even at low temperatures as pointed out by D’Innocenzo et al. [6]. This is presumably due to rapid dissociation of excitons at the perovskite/ TiO_2 interfaces in mesoporous samples. However, we would like to suggest that the absorption edges of mesoporous samples are still dominated by the excitonic absorption because the reported absorption edge energies of mesoporous samples are almost the same as those of the high-quality planar-type thin films

reported in this paper. It should be emphasized that the bandgap energies (about 1.5–1.6 eV) determined based on the location of the absorption edges (for example, the Tauc plot used in refs. [8, 9]) might be incorrect because they ignore the effects of the excitonic absorption below the bandgap.

Finally, it should be noted that the exciton resonance energy of the polycrystalline thin film was larger than that of the single crystal as shown in Fig. 2. The same discrepancy between single crystals and polycrystalline thin films have been observed for $\text{CH}_3\text{NH}_3\text{PbBr}_3$, too [10]. The reason for this anomalous discrepancy is unclear at the present stage of our investigation.

4. Conclusions

We have determined the exciton binding energy and the bandgap energies of $\text{CH}_3\text{NH}_3\text{PbI}_3$ based on absorption spectra measured using a high-quality planar-type polycrystalline films. The exciton binding energy and the bandgap energy at 300 K (6.4 K) was 28 meV (47 meV) and 1.70 eV (1.74 eV), respectively. This large binding energy of excitons indicates that excitons are stable even at room temperature and the fundamental absorption edges are dominated by the excitonic effects. Ignoring the excitonic effects in bandgap determination would lead to incorrect results. We suggest that the obtained large bandgap energy may contribute relatively high open-circuit voltages in solar cells fabricated with $\text{CH}_3\text{NH}_3\text{PbI}_3$.

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