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# Comparative study on the excitons in lead-halide-based perovskitetype crystals CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>

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## Abstract

Optical absorption and magnetoabsorption spectra of the lead-halide-based perovskite-type crystals,  $CH_3NH_3PbX_3$  (X = Br, I) have been investigated. The lowest-energy excitons in these crystals are normal three-dimensional Wannier-type excitons. Bohr radii, binding energies, reduced masses, effective *g* factors, and oscillator strengths of the excitons have been determined with satisfactory accuracy. A larger bandgap and more tightly bound nature of the excitons in  $CH_3NH_3PbBr_3$  compared to those in  $CH_3NH_3PbI_3$  are a natural consequence of the halogen substitution.

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Excitons confined in a low-dimensional structure are subjects which have been extensively studied because of their enhanced binding energies, oscillator strength, and nonlinear optical responses. The large family of the leadhalide-based perovskite-type crystals has been studied recently, since these crystals exhibit distinctive optical properties due to their unique crystal structures. They are self-organized low-dimensional crystals, where [PbX<sub>6</sub>] (X = I, Br) octahedra form zero, one, two, or threedimensional (3D) networks [1-3]. Among them, the twodimensional (2D) crystal group (R-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> has been most intensely investigated, because these crystals exhibit a number of fascinating characteristics, such as huge nonlinearity with ultrafast response [4-6], bright electroluminescence [7], and outstanding scintillation characteristics [8]. In addition, we have shown recently [9] that the excitons

in a 2D crystal  $(C_6H_{13}NH_3)_2$  are Wannier-type ones with comparatively strong 2D character, whose binding energies are enhanced by the spatial confinement and the image charge effect [10,11].

On the other hand,  $CH_3NH_3PbX_3$  (X = I, Br) are perovskite-type crystals, where corner-sharing [PbX<sub>6</sub>] octahedra form 3D networks. Since they can be regarded as a 3D analogue of the 2D crystals [12], the knowledge of their excitonic and electronic properties is necessary for better understanding of those in lower-dimensional counterparts. There have been some reports on their fundamental optical properties [13-16], and it has been found that their electronic structures are essentially the same as those of  $CsPbX_3$  [17,18]. On the other hand, there have been a limited number of reports on their detailed excitonic parameters such as binding energies, Bohr radii, and reduced masses [15,16,19,20]. For example, Ishihara determined the binding energy of the lowest-energy exciton in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> to be 45 meV from the temperature dependence of its luminescence intensity [15]. On the

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other hand, Hirasawa et al. reported the optical and magnetoabsorption (MA) study of  $CH_3NH_3PbI_3$  [19,20], and estimated the binding energy, Bohr radius and reduced mass of its lowest-energy excitons to be 37 meV, 28 Å and 0.12 $m_0$ , respectively. However, Hirasawa's values seem rather unreliable, because their MA spectra taken on microcrystalline samples suffer from magnetic-field-induced photoluminescence which apparently shifts exciton absorption peaks to the higher energy side. We have remeasured MA spectra of  $CH_3NH_3PbI_3$  with much improved accuracy, and compared with those in  $CH_3NH_3$ -PbBr<sub>3</sub> in order to clarify the effects of halogen substitution.

Samples used in our MA study were randomly oriented polycrystalline thin films prepared by simultaneous deposition of CH<sub>3</sub>NH<sub>3</sub>I(Br) and PbI<sub>2</sub>(Br<sub>2</sub>) on quartz substrates. We have confirmed that optical properties of the samples are almost identical with those of single crystals. Optical absorption spectra of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> were obtained by transforming reflection spectra of a single-crystalline sample using the Kramers–Kronig relation. A single crystal of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>,  $5 \times 5 \times 3$  mm<sup>3</sup> in size, were grown by slow evaporation from a dimethylformamide solution where stoichiometric amounts of PbBr<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>Br were dissolved.

Fig. 1 shows the optical absorption spectrum of  $CH_3NH_3PbBr_3$  at 5 K. Rather sharp excitonic lines are located at 2.258 eV(I), 3.329 eV(II), and around 3.9 eV(III). We have measured the temperature dependence of its optical absorption spectrum. The lowest-energy exciton line (I) shifts to higher energy as the temperatures increase, and it is located at 2.337 eV at room temperature. The observed exciton peak energy at room temperature agrees well with that in the previous report [13,14]. These excitonic structures (I–III) are similar to the absorption spectrum of  $CH_3NH_3PbI_3$  (1.633 eV(I), 2.8 eV(II), 3.6 eV(III) [19]), indicating that fundamental electronic structures of both crystals are essentially the same. Blue shift of the whole structures in  $CH_3NH_3PbBr_3$  as compared to  $CH_3NH_3PbI_3$  is due to the halogen substitution.

Electronic structures of the 3D crystals have been



Fig. 1. Optical absorption spectrum of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> at 5 K.

analyzed in terms of group theoretical considerations (see Fig. 2). A first-principles band calculation [21] shows that the sixfold conduction band is mainly composed of Pb 6p orbitals (with a small amount of contribution from I 5s (Br 4s) orbitals), whereas the valence band is the Pb 6p-I 5p (Br 4p) antibonding state. The direct bandgap is located at the R[111] point, where the conduction band and valence band have  $\Gamma_4^-$ (p-like) and  $\Gamma_1^+$ (s-like) symmetry, respectively. After introducing the spinorbital interactions, the valence band transforms as  $\Gamma_6^+(J=1/2)$ , while the sixfold conduction band splits into the fourfold  $\Gamma_8^-$  state (J = 3/2) and the twofold  $\Gamma_6^$ state (J = 1/2), respectively. Here J represents the total angular momentum. The absorption peaks I correspond to the excitons which come from the  $\Gamma_6^+ \rightarrow \Gamma_6^-$  space transition at the *R* point. The direct product  $\Gamma_6^+ \times \Gamma_6^-$  transforms according to  $\Gamma_1^- + \Gamma_4^-$  representations, where the sixfold  $\Gamma_4^-(J=1)$  is dipole allowed, while the twofold  $\Gamma_1^-(J=0)$  is a spin triplet and thus dipole forbidden; the observed lowest-energy excitons I are attributed to  $\Gamma_4^-$  excitons. On the other hand, the absorption peaks II correspond to a  $\Gamma_6^+ \rightarrow \Gamma_8^-$  transition at the R point (spin-orbit split-off band). Higher energy structures III are associated with the interband transition at the M[110] point [19,21]. The energy difference between these structures of CH<sub>3</sub>NH<sub>3</sub>PBr<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>-PbI<sub>3</sub> is a direct consequence of the halogen substitution. Replacement of I with Br shifts the  $\Gamma_1^+$  valence band to lower energies thus resulting in the increase in the bandgap.

MA measurements have been carried out on



Fig. 2. Schematic energy diagram of 3D crystals at the R[111] point of the Brillouin zone. (a) The conduction band and valence band have  $\Gamma_4^-$  and  $\Gamma_1^+$  symmetry, respectively. (b) With the spin–orbit interaction, the conduction band splits into fourfold  $\Gamma_8^-$  and twofold  $\Gamma_6^-$  states, while the valence band transforms as twofold  $\Gamma_6^+$  in double representation. (c) The lowest-energy exciton is split by the Coulomb and exchange interactions into sixfold  $\Gamma_4^-$  and twofold  $\Gamma_1^$ states and transitions to these states are optically allowed and forbidden, respectively.



Fig. 3. Magnetoabsorption spectra of (a) CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and (b) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> in the Faraday configuration at 4.2 K. The spectra are shown for  $\sigma^+$  polarization (solid lines) and  $\sigma^-$  polarization (dashed line).

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> at 4.2 K in pulsed magnetic fields up to 45 T in the Faraday configuration  $(\mathbf{k} || \mathbf{B})$ , where **k** is the direction of the incident light and **B** is the magnetic field. The samples were both 1-µm-thick films deposited on 4-mm-diameter quartz substrates. They were immersed in liquid helium in a specially designed cryostat where a coil made of Nb/Ti superconducting wires was installed in a liquid-nitrogen bath. Magnetic fields up to 45 T were generated by discharging a condenser bank into the coil. The light from a xenon lamp was introduced into the sample through an optical fiber, a polarizer and a quarter-wavelength plate. The light transmitted through the sample was guided through another optical fiber to an optical multichannel analyzer (OMA). The xenon flash started at almost the same time the gate of the OMA was opened. MA spectra were taken while the gate of the OMA was open, for about 1 ms, when the magnetic field reached its peak value.

Fig. 3(a) and (b) shows the MA spectra around the

lowest-energy excitons of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, respectively, in the Faraday configuration for the lefthanded circular ( $\sigma^+$ ) polarization. The MA spectra for the right-handed circular ( $\sigma^-$ ) polarization are displayed only for the highest magnetic field by dashed lines for comparison. Note that no magnetic-field-induced photoluminescence is observed for both samples. The peak energies of the absorption lines are plotted as functions of the magnetic field, by closed circles for  $\sigma^+$ , and open circles for  $\sigma^-$  polarizations in Fig. 4. The solid lines in Fig. 4 are theoretical curves fitted with the method of least-squares by the formula

$$E = E_0 \pm \frac{1}{2} g_\perp \mu_{\rm B} B + c_0 B^2, \tag{1}$$

where  $E_0$ , the energy of the absorption line at B = 0,  $g_{\perp}$ , the effective *g* factor,  $c_0$ , the diamagnetic coefficient, and  $\mu_B$ , the Bohr magneton. The second term in Eq. (1) is the Zeeman term and the third term the diamagnetic shift. The



Fig. 4. Energy shifts as functions of the magnetic field in the Faraday configuration for (a) CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and (b) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Closed circles and open circles represent the experimental values for  $\sigma^+$  and  $\sigma^-$  polarization, and solid lines show the theoretical fitting with the method of least-squares.

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Table 1

Determined exciton parameters of the three-dimensional crystals CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Previously reported data are included in parentheses

CH <sub>3</sub> NH <sub>3</sub> PbBr <sub>3</sub>	CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub>
20 (14.5 <sup>a</sup> )	22 (28 <sup>b</sup> )
76 (150 <sup>a</sup> )	50 (37 <sup>b</sup> , 45 <sup>c</sup> )
$0.13m_0 (0.12m_0^{a})$	$0.15m_0 (0.09m_0^{a}, 0.12m_0^{b})$
2.03	1.72
0.03	$(0.02^{\circ})$
	$\begin{array}{c} CH_{3}NH_{3}PbBr_{3}\\ \hline \\ 20~(14.5^{a})\\ 76~(150^{a})\\ 0.13m_{0}~(0.12m_{0}^{\ a})\\ 2.03\\ 0.03\\ \end{array}$

<sup>a</sup> Koutselas et al. [16].

fitting was quite satisfactory. The values of  $g_{\perp}$  and  $c_0$  of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> were determined to be 1.72 and 1.35 × 10<sup>-6</sup> eV/T<sup>2</sup>, respectively; those of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> are obtained to be  $g_{\perp} = 2.03$ ,  $c_0 = 1.28 \times 10^{-6} \text{ eV/T}^2$ , respectively. We believe the obtained diamagnetic coefficient  $c_0$  of the excitons in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is more accurate than the previously reported value [19].

Since the excitons in both crystals are considered to be 3D Wannier excitons, we can express

$$\frac{a_{\rm B}}{a_{\rm H}} = \left(\varepsilon \frac{c_0}{c_{\rm H}}\right)^{1/3}, \qquad \frac{E_{\rm B}}{R_{\rm y}} = \left(\frac{1}{\varepsilon^4 (c_0/c_{\rm H})}\right)^{1/3}, \\
\frac{\mu}{m_0} = \left(\frac{\varepsilon^2}{c_0/c_{\rm H}}\right)^{1/3},$$
(2)

respectively, assuming simple 3D hydrogenic envelope functions and isotropic media. In these equations,  $c_{\rm H} = 1.23 \times 10^{-10} \text{ eV/T}^2$ ,  $a_{\rm H} = 0.53 \text{ Å}$ , and  $R_{\rm y} = 13.6 \text{ eV}$ are the diamagnetic shift, Bohr radius, and Rydberg constant of the hydrogen atom, respectively, and  $m_0$  is the free electron mass. From these equations, we determined the Bohr radii  $a_{\rm B}$ , binding energies  $E_{\rm b}$ , and reduced masses  $\mu$  of the excitons of the 3D crystals, which are summarized in Table 1. Here, the dielectric constant of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is assumed to be 6.5 [20], while that of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> (4.8) is obtained from the absolute reflectivity in the transparent region. Oscillator strengths of the excitons deduced from the longitudinal-transverse splitting and effective g factors are also included in Table 1. Relatively large Bohr radii justify the assumption of Wannier excitons. For comparison, the previously reported data are included in the parentheses in Table 1. It is found that the obtained exciton binding energy in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> agrees well with the reported value obtained from the temperature dependence of its luminescence intensity [15]. We also notice that the obtained exciton binding energy in CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> is much smaller than the value Koutselas et al. reported, because we have used a larger  $\varepsilon$  than they had in their calculations [16]. We believe that our data is more reliable because our  $\varepsilon$  has been determined experimentally. Smaller Bohr radius and larger binding energies of the excitons in CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> compared

to those in  $CH_3NH_3PbI_3$  are quite natural results of the lower dielectric constant which reduces dielectric screening of the Coulomb interaction between the electrons and holes. Undoubtedly, the lower dielectric constant in  $CH_3NH_3$ -PbBr<sub>3</sub> comes from the larger bandgap energy. Smaller extent of the exciton wave function is, in turn, reflected in larger oscillator strength and larger effective *g* factor.

In summary, we have measured the optical absorption spectrum of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and MA spectra of CH<sub>3</sub>NH<sub>3</sub>-PbBr<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> in order to compare the electronic structures and excitonic properties of the two 3D crystals. The electronic structure of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> is qualitatively the same as that of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> except that the former possesses a larger bandgap than the latter as a result of the halogen substitution. The  $\Gamma_4^-$  lowest-energy excitons are of normal 3D Wannier-type characters. The smaller dielectric constant associated with the larger bandgap in CH<sub>3</sub>NH<sub>3</sub>-PbBr<sub>3</sub> results in larger binding energy, smaller Bohr radius, larger effective *g* factor, and larger oscillator strength of the lowest-energy excitons in CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> compared to those in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>.

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