Bandgap and exciton binding energies in lead-iodide-based natural quantum-well crystals

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Abstract

We have performed optical absorption and electroabsorption studies on the lead-iodide-based natural quantum-well perovskite-type crystals with different well width \((\text{C}_6\text{H}_{13}\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_m\text{Pb}_m\text{I}_3(m \geq 2)\). With decreasing well thickness, \(m\); the resonance energies of the lowest-energy excitons shift to higher energy due to the increase of the bandgap. The binding energies and oscillator strengths of the excitons drastically increase due to the spatial confinement and image charge effect with decreasing \(m\): The bandgap of \((\text{C}_6\text{H}_{13}\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_m\text{Pb}_m\text{I}_3(m = 1)\) can be reproduced by the effective-mass approximations, while the effective-mass approach is not valid for \((\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4(m = 1)\).

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1. Introduction

In recent years, excitons confined in semiconductor nanostructures have been of great interests because of their enhanced binding energies due to the quantum confinement effect and corresponding huge optical non-linearities. The large family of the lead-halide-based perovskite-type crystals has been attracting much attention, since they exhibit distinctive optical properties due to their unique crystal structures. They are self-organized low-dimensional crystals, where \([\text{PbI}_6]\) octahedra form zero-, one-, two-, or three-dimensional networks [1–5]. Among them, the two-dimensional (2D) crystal group \((\text{C}_6\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4\) has been most intensely investigated, because they exhibit a number of fascinating characteristics, such as huge optical non-linearity with ultrafast response [6–8], bright electroluminescence [9], and outstanding scintillation characteristics [10]. \((\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4\) is one of the 2D crystals, where excitons are tightly confined in monomolecular layers of \([\text{PbI}_6]\) octahedra sandwiched between organic barrier layers consisting of alkyl ammonium chains \([\text{C}_6\text{H}_{13}\text{NH}_3]_2\) [11]. The bandgap of the barrier layer is much larger than that of the well layer by at least 3 eV, and the interfaces between the well and the barrier layer are intrinsically flat, because this crystal is made by self-organization; therefore, it has been considered that the excitons in this crystal might behave as an ideal 2D system. In fact, we have shown recently that the excitons in \((\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4\) are Wannier-type ones with comparatively strong 2D character [12]. Another unique feature of this crystal is that the dielectric constant of the barrier layer is much smaller than that of the well layers (the dielectric constants of the well and the barrier are about 6.1 and 2.1 [3], respectively), in which the effective Coulomb interaction between electrons and holes in the well layers is expected to be enhanced (so called image charge effect [13, 14]). We have shown recently that the image charge effect definitely play important roles in the excitonic properties in this crystal [15].

In addition, it had been shown that there exists a family of ‘2D–3D’ crystals \((\text{C}_6\text{H}_{2n+1}\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_m\text{Pb}_m\text{I}_3(m \geq 2)\), in which \(m\) and inorganic \([\text{PbI}_6]\) layers and organic \([\text{Cs}_2\text{NH}_3]\) barrier layers are stacking alternatively, forming multiple quantum well structure [16]. The three-dimensional (3D) analogue \(\text{CH}_3\text{NH}_3\text{PbI}_3\) [17] corresponds to the case \(m = \infty\). Since the thickness of the inorganic layers can be controlled by

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changing \( m \), systematic studies of the excitonic and electronic properties between the 2D and 3D crystals can be performed. In this study, we have made an optical absorption and electroabsorption (EA) study on this 2D–3D crystal group, and will present the results of the comparative study on these 2D–3D crystals.

2. Experimental

We have prepared the 2D–3D crystals \((\text{C}_6\text{H}_{13}\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{m-1}\text{Pb}_m\text{I}_{3m+1} (m = 1, 2, 3)\) with Tabuchi’s procedure [18]. We first prepared \( n \)-alkylamine \( \text{C}_n\text{H}_{2n+1}\text{NH}_3\text{I} (n = 1, 6) \) by reacting \( \text{C}_n\text{H}_{2n+1}\text{NH}_2 \) with a stoichiometric amount of HI aqueous solution in a flask cooled with water. The obtained solutions were evaporated to remove water followed by washing with diethyl ether to obtain white powder of \( \text{C}_n\text{H}_{2n+1}\text{NH}_3\text{I} \). To obtain ‘monolayer’ (i.e. \((\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4 \) to \( m = 1 \)), \((\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{NH}_3\) were reacted with a stoichiometric amount of \( \text{PbI}_2 \) in acetone. Single crystalline sample of monolayer were obtained by slowly evaporating the obtained solution. Thin films of monolayer were made by spin-coating the obtained solutions on glass substrate. To obtain ‘bilayer’ (\( m = 2 \)), \((\text{C}_6\text{H}_{13}\text{NH}_3)_2(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{I}_7 \), stoichiometric amount of \( \text{C}_6\text{H}_{13}\text{NH}_3\text{I}, \text{CH}_3\text{NH}_3\text{I} \) and \( \text{PbI}_2 \) were reacted in dimethyl-formamide (DMF). On the other hand, pure ‘trilayer’ (\( m = 3 \)), \((\text{C}_6\text{H}_{13}\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{PbI}_{10} \), were not be obtained by reacting stoichiometric amount of \( \text{C}_6\text{H}_{13}\text{NH}_3\text{I}, \text{CH}_3\text{NH}_3\text{I} \) and \( \text{PbI}_2 \). It was found that, however, trilayer were most efficiently prepared when these materials were reacted in the following non-stoichiometric condition: \( \text{C}_6\text{H}_{13}\text{NH}_3\text{I} : \text{CH}_3\text{NH}_3\text{I} : \text{PbI}_2 = 2 : 3 : 3 \) in molar ratio [18]. While thin films of bilayer and trilayer were also easily prepared by spin-coating the obtained solutions onto glass substrates, single crystals of bilayer and trilayer were not obtained. However, the optical properties of these thin films are considered to be almost identical with those of single crystalline samples as measured with normal incidence, because our X-ray diffraction study showed that the spin-coated polycrystalline films are highly orientated with the \( c \)-axis perpendicular to the substrate surfaces (i.e. with the well layers parallel to the surfaces).

EA measurements have been carried out at 5 K on these thin films in the transverse and longitudinal configurations, where the electric fields are applied parallel to the quantum-well layers in the transverse configuration, and perpendicular to the quantum-well layers in the longitudinal configuration. In both configurations, ac electric fields with no dc bias were applied with a frequency of 1 kHz. The samples used in the transverse configuration were polycrystalline films spin-coated on the glass substrate on which gold electrode was deposited. The modulated electric fields were applied across the gap between the gold electrodes. On the other hand, the sample used in the longitudinal configuration was a polycrystalline film spin-coated on an ITO-deposited glass substrate, onto the top of which gold electrode was deposited. The modulated electric fields were applied between the ITO and gold electrode. The sample was mounted on the sample holder in a cryostat evacuated to \( 10^{-5} \) Torr and maintained at 5 K. A light from a xenon lamp made monochromatic by a monochromator was focused onto the sample and the transmitted light was detected by a photomultiplier tube. The transmitted light being detected by a photomultiplier tube has dc and ac components, which are proportional to the transmission \( T \) the modulated \( \Delta T/T \), respectively. The dc components were measured with a digital multimeter, while the ac components were recovered by a lock-in amplifier synchronized at twice the field frequency. We have confirmed that there was no electroluminescence in the modulated signals by checking the modulated signals when the light was blocked off. The EA spectra were obtained by calculating \( -\Delta T/T \) each wavelength.

3. Results and discussion

3.1. Optical absorption

Fig. 1(a) shows the optical absorption spectrum of monolayer single crystal, which were obtained by transforming its reflection spectrum using Kramers–Kronig relation. Fig. 1(b) and (c) show, respectively, the optical
absorption spectra of bilayer and trilayer spin-coated films at 5 K. In these optical absorption spectra, any abrupt leaps of the optical absorption spectra with decreasing temperature like those of \((\text{C}_{10}\text{H}_{21}\text{NH}_{3})_{2}\text{PbI}_{4}\) [3] are not observed. The optical absorption spectrum of the 3D thin film [17] is shown in Fig. 1(d), for comparison. The arrows in Fig. 1(a)–(d) indicate the lowest-energy excitons of monolayer, bilayer, trilayer, and 3D crystal, respectively. The peak located at 1.92 eV in Fig. 1(c) may be attributable to the lowest-energy excitons in ‘tetralayer’ \((m = 4)\), \((\text{C}_{6}\text{H}_{13}\text{NH}_{3})_{2}(\text{CH}_{3}\text{NH}_{3})_{3}\text{Pb}_{4}\text{I}_{13}\) [4].

The oscillator strengths of the lowest-energy excitons become larger as \(m\) decreases, which is quite reasonable because the decrease of \(m\) reduces the Bohr radius due to the spatial quantum confinement effect. The resonance energies of the lowest-energy excitons in monolayer, bilayer, trilayer, tetralayer, and 3D crystals are summarized in Table 1. The resonance energies of the lowest-energy excitons exhibit blueshift with decreasing numbers of the inorganic \([\text{PbI}_{6}]\) layers, \(m\); which is mainly due to the increase of the bandgap, because the narrower the width of the inorganic layers, the smaller the dispersion of the bands, resulting in wider bandgap [19].

### Table 1

| Crystals    | \(m\) | \(E^{\text{res}}\) (eV) | \(E^{\text{b}}\) (meV) | \(E_{\text{g}}\) (eV) |
|-------------|-------|----------------------|---------------------|------------------|
| Monolayer   | 1     | 2.34                 | 361\(^a\)           | 2.70             |
| Bilayer     | 2     | 2.14                 | 260                 | 2.40             |
| Trilayer    | 3     | 2.02                 | 150                 | 2.17             |
| Tetralayer  | 4     | 1.92                 | 100\(^b\)           | 2.02             |
| 3D          | \(\infty\) | 1.65                 | 50\(^c\)           | 1.70             |

\(a\) Tanaka et al. [15].
\(b\) Koutselas et al. [4].
\(c\) Tanaka et al. [17].

### 3.2. Electroabsorption

Fig. 2(a) shows the optical absorption spectrum of monolayer spin-coated film at 5 K. We have shown that the excitons in monolayer are Wannier-type ones [12]; the 1s, 2s excitons, and the bandgap are located at 2.339, 2.595, and 2.700 eV, respectively [15]. The EA spectra under several values of electric fields in the transverse and the longitudinal configurations are shown in Fig. 2(b) and (c), respectively. We have previously shown the following: (1) the EA spectra around 2.34 and 2.60 eV in the transverse configuration had been attributed to the Stark shift of the 1s excitons and the life-time broadening of the 2s excitons, respectively. This is justified because the shapes of the EA spectra around the 1s and 2s excitons are identical with the first derivative, and second derivative of the optical absorption spectrum, respectively [12]. These behavior are reasonable, because (a) the exciton Stark shift is typical of excitons with large binding energy (i.e. the 1s excitons) whose ionization fields are much larger than the applied electric field, and (b) the exciton broadening is a characteristic of a weakly coupled exciton (i.e. the 2s excitons) ionized under the applied electric field [20]. (2) the EA spectra around 2.34 and 2.60 eV in the longitudinal configuration are due to the blueshift of the 1s excitons and the redshift of the 2s excitons under the applied electric fields, respectively. This is justified because the shapes of the EA spectra around the 1s and 2s excitons are identical with the sign-reversal shape of the first derivative, and first derivative of the optical absorption spectrum, respectively. The suppression of the broadening of the 2s excitons is reasonable because the barrier layer impede their
ionization. The seemingly unusual blueshift of the 1s exciton is due to the large reduction of excitons binding energy under the applied electric filed exceeding that of bandgap [15]. Apparent difference between the EA spectra in the transverse configuration and those in the longitudinal configuration indicates that the excitons have very strong 2D anisotropic characters. In addition, the EA spectra above the bandgap (2.700 eV) in the longitudinal configuration is completely suppressed indicating that the carriers in monolayer are tightly confined two-dimensionally.

Fig. 3(a) shows the optical absorption spectrum of bilayer spin-coated film at 5 K. The prominent peak at 2.14 eV (A) is attributed to the lowest-energy excitons. The EA spectra of bilayer under several values of electric fields in the transverse configuration is shown in Fig. 3(b). Fig. 4 shows the electric field dependence of the EA signal amplitudes of negative peaks at 2.14 eV (A), 2.32 eV (B1), and 2.40 eV (B2). The EA signal amplitude at 2.14 eV (A) is proportional to the square of the applied electric field, $F^2$. Fig. 5 shows the EA spectrum in the transverse configuration under the field strength of 25.4 kV/cm and the second derivative of the absorption spectrum with respect to the photon energy. The shape of the EA spectrum around 2.14 eV (A) is identical with the second derivative of the optical absorption spectrum. Based on these results, the structure of the EA spectra at 2.14 eV (A) is attributed to the exciton broadening [20], which indicates that the lowest-energy excitons in bilayer have smaller binding energy than those in monolayer. On the other hand, the EA signal amplitude at 2.32 eV (B1) is also proportional to $F^2$, while that at 2.40 eV (B2) is proportional to $F^{1.7}$. From these electric field dependence, we suppose that the bandgap is located around 2.40 eV (B2) and Frantz–Keldysh signals, whose EA signal amplitudes are proportional to $F^{3/2}$ in the low-field limit [21], are superimposed on the observed EA signal.

Fig. 3(c) shows the EA spectra of bilayer under the several values of electric fields in the longitudinal configuration. First, in order to obtain the EA signal magnitude around the lowest-energy excitons in the longitudinal configuration as large as in the transverse one, we should apply electric fields about four times larger than that for the transverse one; which indicates that the excitons have still strong 2D characters. Second, the EA spectra from 2.40 eV (B) to 2.60 eV in the longitudinal configuration are completely suppressed. Since this behavior is essentially the same with $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$, the bandgap of bilayer is determined to be at 2.40 eV, from
which the binding energy of the lowest-energy exciton are obtained to be 260 meV. Although the obtained binding energy of the lowest-energy excitons are smaller than that in monolayer (361 meV [15]), it is at least five times as large as that of the lowest-energy excitons in the 3D crystal, CH$_3$NH$_3$PbI$_3$ (50 meV [17]). Since the spatial quantum confinement only quadruples the exciton binding energy in the 2D limit, this strong enhancement factor (>5) indicates that the image charge effect plays an additional role in the drastic enhancement of the excitons binding energy.

Fig. 6(a) shows the optical absorption spectrum of trilayer spin-coated film at 5 K. The EA spectra under several values of electric fields in the transverse and the longitudinal configurations are shown in Fig. 6(b) and (c), respectively. The EA spectra in the longitudinal configuration are the same in shape with those in the transverse one, in contrast with the case of monolayer or bilayer. It is thus supposed that the excitonic and electronic properties of the trilayer crystal are not so 2D as those of the monolayer or bilayer. However, in order to obtain the EA signal magnitude around the lowest-energy excitons in the longitudinal configuration as large as in the transverse one, larger electric fields by a factor of ~3 are needed. This indicates that the lowest-energy excitons in trilayer still exhibit large anisotropy. Fig. 7 shows the EA spectrum in the transverse configuration under the field strength of 18.5 kV/cm and the second derivative of the absorption spectrum with respect to the photon energy. The shape of the EA spectrum around 2.02 eV (A) is identical with the second derivative of the optical absorption spectrum, indicating that the EA spectra around 2.02 eV (A) is attributed to the exciton broadening [20]. Unfortunately, the bandgap energy of trilayer had not been determined from the EA spectra. However, since the optical absorption spectrum around 2.17 eV (C) has step-like shape, we may attribute this structure to the bandgap. From the bandgap determined in this way, the binding energy of the lowest-energy exciton in trilayer is estimated to be 150 meV.

The bandgap energies of monolayer, bilayer, and trilayer are summarized in Table 1. The binding energies of the lowest-energy excitons in them are also summarized in Table 1. The data for tetralayer ($m=4$) obtained by Koutselas [4] are also included. Fig. 8 shows the well-width dependence of the bandgap energy. The solid line is the calculated line using the effective-mass approximation along the c-axis so that the lowest-energy excitons in the longitudinal configuration as large as in the transverse one, larger electric fields by a factor of ~3 are needed. This indicates that the lowest-energy excitons in trilayer still exhibit large anisotropy. Fig. 7 shows the EA spectrum in the transverse configuration under the field strength of 18.5 kV/cm and the second derivative of the absorption spectrum with respect to the photon energy. The shape of the EA spectrum around 2.02 eV (A) is identical with the second derivative of the optical absorption spectrum, indicating that the EA spectra around 2.02 eV (A) is attributed to the exciton broadening [20]. Unfortunately, the bandgap energy of trilayer had not been determined from the EA spectra. However, since the optical absorption spectrum around 2.17 eV (C) has step-like shape, we may attribute this structure to the bandgap. From the bandgap determined in this way, the binding energy of the lowest-energy exciton in trilayer is estimated to be 150 meV.

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the bandgap of bilayer, trilayer, and tetralayer were well reproduced. The parameters we have used in the calculation are summarized as follows: (1) the bandgap of the well and the barrier are 1.70 eV [17] and 5.50 eV [3], respectively. The band offset are set to be 0.9 and 2.8 eV. (2) \( m^w_{e,h} = m^w_{h} = 0.30 m^w_{0} \), which are assumed from the reduced mass of the lowest-energy excitons in the 3D crystal, \( \mu = (m_{e,h}^{-1} + m_{h,w}^{-1})^{-1} = 0.15 m^w_{0} \). Here, \( m^w_{0} \) is the free electron mass. Here \( m^w_{e,h} \) and \( m^h_{e,h} \) represent the effective masses of the electrons (e) or holes (h) in the well layers and barrier layers, respectively. (3) We have set, \( m^w_{e} / m^w_{h} = m^w_{h} / m^w_{0} = 0.4 \).

As we have calculated under many other conditions, when effective mass approximations can reproduce the bandgap of \((\text{C}_6\text{H}_{13}\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{m-1}\text{Pb}_n\text{I}_{2m+1} (m = 2)\), they cannot reproduce that of \((\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{Pb}_4\). This seems quite reasonable because there is only one [PbI_6] octahedron layer in the direction of \(c\)-axis, can be well reproduced by the effective mass approximation.

4. Conclusions

In summary, optical absorption and electroabsorption studies on the lead-halide-based quantum-well crystal \((\text{C}_6\text{H}_{13}\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{m-1}\text{Pb}_n\text{I}_{2m+1} (m = 1, 2, 3)\) have been investigated. With decreasing well thickness: (1) the excitons resonance energy exhibit blueshift due to the increase of the bandgap; (2) the binding energy and oscillator strength of the excitons drastically increase, which is due to the spatial confinement and image charge effect. The bandgaps of the crystals with \(m \geq 2\) are reproduced by the effective-mass approximation, while the effective-mass approach is not valid for the monolayer crystal, which is reasonable because there is only one [PbI_6] octahedron layer in the perpendicular direction to the well layers.

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