Excitons and biexcitons bound to a positive ion in a bismuth-doped inorganic-organic layered lead iodide semiconductor

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We have studied optical properties of an inorganic-organic layered lead iodide semiconductor doped with bismuth ions (Bi^{3+}). A new absorption band was observed at 2.15 eV that is by 0.21 eV lower than two-dimensional 1*s* excitons (2.36 eV) and is assigned to excitons bound to the bismuth ions. In the photoluminescence spectra with high excitation density ($\sim$0.4 MW/cm^2), a novel emission band was observed at the energy of 2.51 eV that is by 0.15 eV higher than the exciton resonance, and is attributed to biexcitons bound to the bismuth ions. On the basis of the experimental results, the binding energies of the bismuth-bound exciton and biexciton were estimated approximately as 210 and 10 meV, respectively. It is found that the binding energy of the positive-ion (Bi^{3+}) bound biexciton is by far smaller than that of the corresponding bound exciton. The much lower stability of the positive-ion bound biexciton is discussed.

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I. INTRODUCTION

Binding of excitons with a charged impurity such as ionized donors and acceptors in bulk semiconductors and insulators has been studied extensively since Lampert has predicted the existence of charged-ion exciton complexes.[1] Recently, there are great interests in those complexes in two dimensions, in which strong correlations of excitons with a charged impurity are expected due to the low-dimensional carrier confinements.[2–4] However, there are only a few experimental investigations on a charged-ion exciton complex in GaAs-$Al_xGa_{1-x}As$ quantum wells.[4] For a biexciton that is a bound state of two excitons, no observation of the complex with a charged impurity has been reported so far.

Here, we have paid our attention to inorganic-organic hybrid layered lead iodide semiconductors, in which the binding energy of excitons in the inorganic quantum wells is enormously large (around 300 meV) in comparison to artificially grown inorganic quantum-well semiconductors. As shown in Fig. 1, the inorganic layers comprised of corner-sharing lead iodide octahedra are sandwiched with organic ammonium layers. The inorganic layers with a single-atom-scale thickness ($\approx$6 Å) serve as a quantum well that has a large quantum size confinement of electrons and holes. The organic barrier layers, which have a remarkably smaller dielectric constant ($\varepsilon_\infty \sim 2-3$) than that ($\varepsilon_\infty \sim 6$) of the inorganic layers, provide a great dielectric confinement effect on excitons in the wells. The optical properties and electronic structures of a series of layered inorganic-organic lead iodide compounds have been studied in detail.[5–16] It is reported that both effects of those confinements on excitons lead to a very large binding energy of around 300 meV. In addition, biexcitons also have a large binding energy of $\sim$40 meV. For these reasons, we consider such an inorganic-organic layered compound with two-dimensionality and strong electron-hole correlations to be an interesting system for studies of exciton- and biexciton-charged ion complexes in two dimensions.

In this work, we have studied optical properties of an inorganic-organic layered lead iodide semiconductor doped with bismuth ions (Bi^{3+}). Bismuth doping of the layered compound, $(C_6H_5C_2H_4NH_3)PbI_4$, was carried out with a chemical solution method, which will be described below. In the doped crystal, the lead ions in the inorganic sheets are considered to be replaced by bismuth ions. Because of the larger valence number (3+) than that (2+) of the lead ions, the bismuth ions are regarded as a positive ion in the wells. Absorption, photoluminescence, and photoluminescence excitation spectra of the doped sample are compared with those of the undoped one for assignments. We estimate the binding energies of excitons and biexcitons bound to a positive ion, which are abbreviated as (+, exciton) and (+, biexciton) hereafter, respectively.[18] It is found that the binding energy of the positive-ion bound biexciton is much smaller than that of the corresponding exciton complex. The quite low stability of the (+, biexciton) state is discussed.

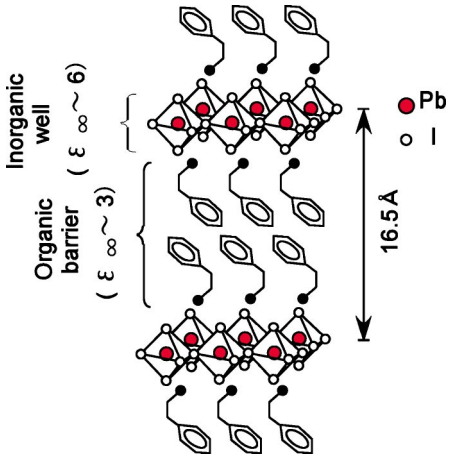

FIG. 1. A schematic picture of the crystal structure of the layered inorganic-organic lead iodide compound, $(C_6H_5C_2H_4NH_3)PbI_4$. The hexagonal rings denote a phenyl group (C_6H_5–).

II. EXPERIMENT

The undoped crystal was prepared according to the literature.[11] The doped crystal was synthesized by mixing the tetrahydrofuran solutions of lead iodide (PbI_2), bismuth iodide (BiI_3), and phenethylammonium iodide ($C_6H_5C_2H_4NH_3I$) at the molar ratio of 0.9:0.1:2 under argon atmosphere. The mixed solution was heated at 333 K for 30 min under the inert-gas atmosphere, and nitromethane was added as a poor solvent for crystallization after cooling down to room temperature. By slow evaporation of the solvents, dark red platelike crystals were obtained. From elemental analysis, it was shown that the crystals include bismuth ions at the Bi/Pb molar ratio of ~0.3%. The bismuth content is much smaller than that (10%) in the synthesis, which is owing to the different valence number from that of lead ions in the wells, as will be mentioned below. The dark red color is much different from that (yellowish orange) of the undoped crystal, which indicates the appearance of optical reflection and absorption in the visible region by the bismuth doping. The crystal structure was analyzed at 203 K by x-ray diffractions and found to be almost the same as that[17] of the undoped crystal.

From an electric conductivity measurement, the crystal is indicated to be an insulator with a resistivity larger than ~1 MΩ cm at room temperature. The magnetization was measured within a range from 2 to 300 K. The magnetization obtained by subtraction from the observed data by a diamagnetic part is negligibly small and hardly depends on temperature, which indicates that there are no localized spins and the material is diamagnetic. From these results, it is shown that the valence number of the bismuth ions is 3+, that is larger than that (2+) of the lead ions. It is considered that bismuth ions substitute lead ions in the inorganic layers, since bismuth ions (Bi^{3+}) have almost the same ion radius and form an octahedral complex with iodide ions similar to lead ions. Furthermore, in the optical study of the PbI_2 crystal doped with BiI_3, it is reported that Pb^{2+} is replaced by Bi^{3+}.[19] The difference in valence number between Pb^{2+} and Bi^{3+} may be the reason of the quite small bismuth content. The additional positive charge brought by the bismuth ions is compensated by the constituent ions. The charge compensation possibly occurs with the lack of the organic cations near the Bi^{3+} ions in the inorganic layers.

A charge-coupled device (CCD) camera cooled by liquid nitrogen and equipped with a polychromator was used as a detector. For optical absorption measurements, a halogen lamp was used as a probe light. In photoluminescence measurements, continuous-wave Xe-lamp light monochromated by a subtractive double monochromator and the third harmonic (355 nm) of a pulsed Nd:YAG laser with the repetition rate of 10 Hz and pulse width of ~5 ns were used as an excitation light. In all the experiments, the single crystal was set in a temperature controlled helium cryostat, and the lights were shed on the crystal surface parallel to the organic and inorganic layers. The optical absorption and photoluminescence excitation spectra are not corrected by optical reflection.

III. RESULTS

Optical absorption (OA), photoluminescence (PL), and PL excitation (PLE) spectra of the undoped and Bi^{3+}-doped crystals are shown in Fig. 2. The PL spectra were measured with the excitation by Xe-lamp light at 2.48 eV. The PLE spectra of the undoped and doped samples were obtained with detecting PLs at 2.35 and 1.4 eV, respectively. First, we describe the results reported for the undoped crystal previously. The optical absorption and photoluminescence spectra have already been reported in Refs. 7, 8, 11, and 16. The absorption of two-dimensional 1*s* excitons in the inorganic wells, being the lowest excitation, takes place at 2.36 eV with a peak absorption coefficient on the order of $\alpha \approx 10^6$ cm^{-1} at low temperature. The band-to-band transitions exhibit a step structure with an edge at 2.58 eV. The exciton binding energy was estimated as 0.22 eV. The PL spectrum at low temperature (≈2 K) is dominated by emission bands between 2.328 and 2.343 eV that were tentatively attributed to excitons bound to some impurities and/or defects, together with a very weak PL band of free excitons at around 2.35 eV. In our experiment, the absorption of the undoped crystal grows from 2.33 eV and is saturated above 2.35 eV because of the large exciton absorption coefficient. In the PL spectrum, as shown with dotted vertical bars in the right

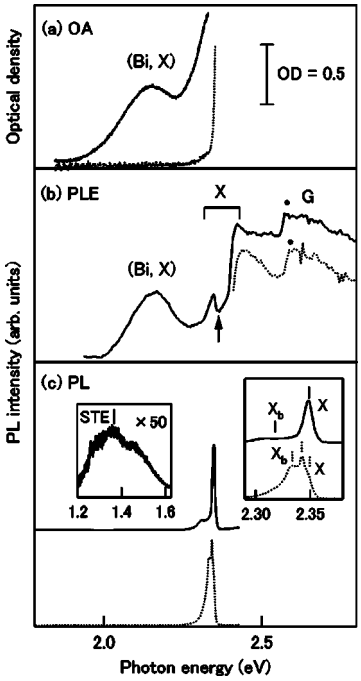

FIG. 2. (a) Optical absorption (OA), (b) photoluminescence excitation (PLE), and (c) photoluminescence (PL) spectra of the Bi^{3+}-doped (solid curves) and undoped (dotted curves) crystals measured at 4 K. The excitation photon energy for the PL spectra is 2.48 eV. The PLE spectra were measured by detecting PL at 1.4 eV for the doped sample and 2.35 eV for the undoped one. Right inset: horizontally expanded PL spectra of the doped (upper) and undoped (lower) samples at around 2.34 eV. Left inset: a PL spectrum of the doped sample between 1.20 and 1.63 eV. *X*, X_b, (Bi, *X*), STE, and *G* stand for free excitons, bound excitons, bismuth-bound excitons, self-trapped excitons, and band-to-band transitions, respectively. In (b), the horizontal square bracket denotes the energy region of the free-exciton absorption. The arrow designates the energy of the free-exciton reflection peak and the two solid circles the onset energies of the band-to-band transitions (*G*). See text.

inset, there are a few features with a main peak at 2.342 eV and a shoulder between 2.280 and 2.339 eV, which are assigned to bound excitons, as reported previously. At the higher-energy tail, a faint shoulder is observed at 2.349 eV, which corresponds to the PL due to radiative recombination of free excitons. The excitation spectrum of the PL at 2.35 eV is shown above 2.410 eV, since the excitation light influences the spectrum below the energy. In the spectrum, two structures are observed at 2.439 and 2.586 eV. For the former, the PL decreases below 2.439 eV. The decrease is due to strong optical reflection of the free excitons at 2.36 eV (marked with an arrow). It is reported that the maximum reflectance by excitons exceeds 0.75.[7] For the latter structure, the step with an edge of 2.586 eV (marked with a solid circle) is assigned to the band-to-band transitions, which is consistent with the reported result.

For the doped crystal, we can see new features. In the absorption spectrum, a new absorption band is observed at 2.15 eV. In addition, it is seen that the low-energy tail of the exciton absorption is expanded. Since this absorption band is not observed in the undoped crystal, it is indicated that the absorption is associated with the bismuth ions. The broadening of the exciton absorption was also observed in bismuth-doped bulk PbI_2 (Ref. 19) and considered to be due to scattering with the bismuth impurities. In the PL spectrum, three emission bands are observed, as marked by solid vertical bars in the left and right insets. The main emission band is a sharp PL centered at 2.35 eV, which is assigned to free excitons. The second is a weak shoulder between 2.29 and 2.33 eV. The last one is a much weaker broad PL band at around 1.4 eV. The second PL is also observed in the same energy region in the undoped sample and considered to be due to excitons bound to some impurities and/or defects (not Bi^{3+}). At present, the bound excitons have not been clarified yet. However, we shall not consider it any more here, since it is not important for our purpose in this work. In the doped sample, the free-exciton PL is much more predominant than the bound-exciton PL in comparison to the undoped one. The difference between the two samples is attributed to suppression of the bound-exciton PL via reabsorption in the doped crystal. As shown in Fig. 2(a), in the energy region between 2.29 and 2.33 eV, where the bound-exciton PL is observed, the absorption coefficient of the doped sample is rather enhanced due to bismuth doping. The third PL band at 1.4 eV is not observed in the undoped crystal, revealing to be associated with the bismuth ions. In the excitation spectrum of the PL at 1.4 eV, three structures are observed. One is the exciton absorption band between 2.34 and 2.43 eV (shown by a horizontal square bracket), the second is due to band-to-band transitions with a band edge at 2.58 eV (displayed with a solid circle), and the last one is at 2.15 eV. The exciton absorption band has a dip structure at 2.36 eV marked with an arrow, which is made by the strong reflection of the free excitons, as observed partly in the PLE spectrum of the undoped crystal. Similar dip structures were observed in the photoconductivity excitation spectra of the undoped crystal, as reported in Ref. 8. The observations of the discernible dips due to the exciton reflection guarantee high quality of the crystal. Assuming the band edge at 2.58 eV to correspond to the onset of the band-to-band transitions, the exciton binding energy ($E_{b(\text{exciton})}$) is estimated as 220 meV, which is in good agreement with the reported value.[7] The third absorption band at 2.15 eV has the same transition energy as the new band in the absorption spectrum. From those results, we attribute the absorption at 2.15 eV observed in the absorption and PLE spectra to excitons bound to the bismuth ions. The binding energy of the Bi^{3+}-exciton complex, which is defined with respect to the exciton energy (2.36 eV), is estimated as 210 meV. The large binding energy indicates that excitons are bound strongly to Bi^{3+}. The Stokes shift of the PL at 1.4 eV is obtained to be ~0.8 eV, which indicates remarkable lattice relaxation of the exciton bound to a bismuth ion. The broad PL band at around 1.4 eV is probably due to a self-trapped exciton (STE) around a bismuth ion.

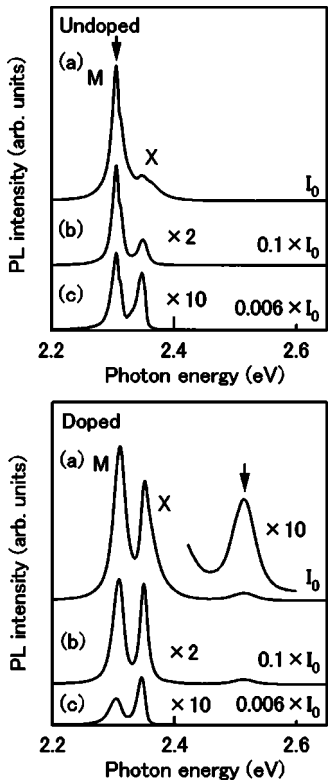

FIG. 3. PL spectra of the undoped (upper) and doped (lower) crystals measured at 4 K under intense excitations by using the third harmonic (λ=355 nm) of the YAG laser. The excitation power is increased from (c) to (a). The maximum laser power (I_0) is ~0.4 MW/cm^2, and each laser power is displayed on the right-hand side. *X* and *M* denote free excitons and free biexcitons, respectively.

Figure 3 shows PL spectra of the undoped and doped crystals with intense excitations by using the pulsed laser. The excitation density is increased from (c) to (a). For the undoped crystal, two PL bands are observed at 2.31 and 2.35 eV. The PL at 2.35 eV is ascribed to excitons. The PL at 2.31 eV increases with the laser power more strikingly than the exciton PL and is dominant with the higher excitation densities. The spectral shape of the PL at 2.31 eV has a longer tail at the lower-energy side, which represents a typical inverse Boltzman distribution function of PL spectra due to radiative recombination of biexcitons, leaving an exciton

behind. The lower-energy tail is explained by thermal distributions on the biexciton ω-k dispersion curve. Biexcitons in the lead iodide quantum wells have been studied by PL[11,13,14] and pump-probe[16] spectroscopies in detail. It is reported that the biexciton PL is at 2.31 eV and the binding energy is ~50 meV. From these results, the PL at 2.31 eV is attributed to biexcitons. In the spectra, a sharp peak is observed at 2.306 eV on the biexciton PL band, as displayed with an arrow. Similar PL spectra were observed in Refs. 13 and 14, in which it was explained by the stimulated emission of biexcitons. For the doped crystal, the exciton PL at 2.35 eV is dominant under the weak excitation condition in the spectrum (c), while with increasing the excitation density two PL bands at 2.31 and 2.51 eV increase superlinearly. Since the energy of the PL at 2.31 eV is the same as that of biexcitons in the undoped sample and the spectrum has a tail at the lower-energy side, it is attributed to radiative recombination of biexcitons.[20] As compared to the PL spectra of the undoped sample, the biexciton PL is relatively weak to the exciton PL. That results from suppression of the biexciton PL by reabsorption. As shown in Fig. 2(a), remarkable absorption exists in the energy region with bismuth doping in contrast to the undoped sample. Also, the lack of the stimulated emission in the doped sample can be explained by the reabsorption. On the other hand, the newly observed PL band at 2.51 eV is not observed in the undoped crystal. Thus it is indicated to be concerned with the bismuth ions. The transition energy is by 0.15 eV higher than the exciton resonance (2.36 eV). The PL spectrum is almost symmetrical, which is indicative of emissions from a bound state.

The laser power dependences of the integrated PL intensities in the undoped and doped crystals are shown in Fig. 4. The laser power dependences of exciton and biexciton PL intensities have been investigated extensively.[13,14] For the undoped sample with intense laser excitation, in which the biexciton PL is comparable to the exciton one, it is reported that when the excitation photon energy is above the exciton resonance the exciton and biexciton PLs grow with about 0.7th power and almost linear laser power dependences, respectively, showing striking saturation behaviors. The derivations of the exciton and biexciton PL intensities from linear and square dependences, respectively, were considered to be probably due to nonradiative relaxations by exciton-exciton, exciton-biexciton, and biexciton-biexciton inelastic scatterings induced by rises of exciton and biexciton effective temperatures, which increase with laser power. In our experiment, the excitation energy of 3.49 eV is much higher than the exciton resonance (2.36 eV) and such laser power dependences are anticipated. From the plots for the undoped sample, the exciton and biexciton PLs exhibit 0.77th power and linear dependences on the laser power, respectively, which is in accordance with the reported results. For the doped crystal, the exciton and biexciton PLs show 0.9th and 1.1th power dependences, respectively, and the intensity of the PL at 2.51 eV is proportional to the 1.35th power of the excitation density. The exciton and biexciton dependences are close to those of the undoped crystal. It is obvious that the PL at 2.51 eV increases superlinearly with the laser power. Furthermore, it is seen that the PL intensity at 2.51 eV is saturated at the laser power of ~400 kW/cm^2,

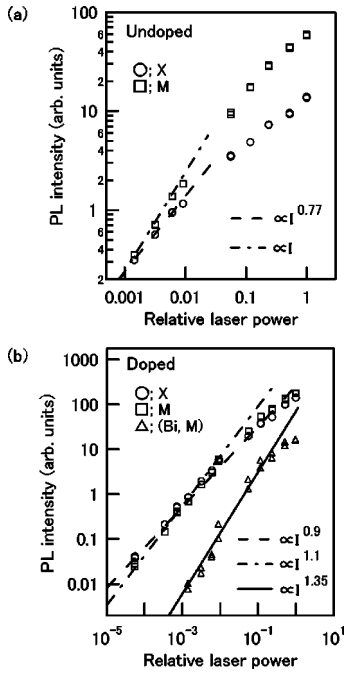

FIG. 4. Integrated intensities of the PL bands observed for the undoped (a) and bismuth-doped (b) crystals as a function of laser power (I). The PL intensities of free excitons and free biexcitons are plotted as open circles and squares, respectively, and the PL at 2.51 eV as open triangles. The broken, dash-dotted, solid lines stand for the laser power dependences displayed on the lower right-hand sides. The maximum laser powers are ~0.4 MW/cm^2 for both the experiments. X, M, and (Bi, M) stand for free excitons, free biexcitons, and bismuth-bound biexcitons, respectively. See text.

while the exciton and biexciton PLs still increase. From the results obtained for the PL at 2.51 eV, it is attributed to biexcitons bound to the bismuth ions. We will discuss other possibilities later.

The temperature dependence of the PL spectra in the doped crystal observed with intense excitation was investigated, as shown in Fig. 5. In the spectra, the exciton and biexciton PL bands blueshift and are broadened as temperature increases. However, the energy of the PL at 2.51 eV is hardly changed with temperature. The integrated intensity of the PL at 2.51 eV as a function of inverse temperature is plotted in Fig. 6. From the figure, the PL efficiency remains almost constant up to $T=20$ K. Above 40 K the intensity decreases and almost disappears below 100 K, whereas the exciton and biexciton PLs are still observed at the temperature. Those results reveal that the initial state of the PL at 2.51 eV is neither free excitons nor free biexcitons. Assuming that the decrease of the PL is due to a thermally activated nonradiative relaxation process, we analyzed the temperature dependence by the equation, $A_0/[1+A_1\exp(-E_a/k_BT)]$, where A_0 and A_1 are coefficients and E_a is an activation energy. The parameters were obtained as $A_0=1.06$, $A_1=50$, and $E_a=13$ meV from the fitting shown by the solid curve in the figure. A most probable nonradiative relaxation process of bismuth-bound biexcitons is ionization to free biexcitons. According to the interpretation, the binding energy, which is defined with respect to the energy of free biexcitons, is esti-

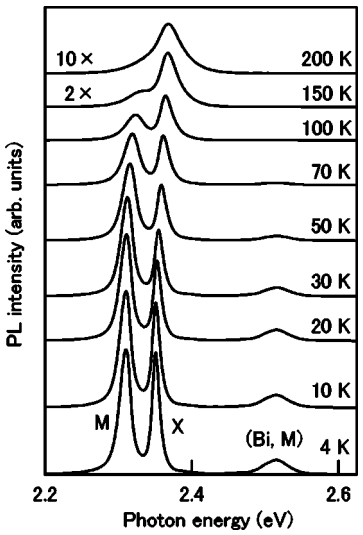

FIG. 5. Temperature dependence of the PL spectra of the doped sample observed under intense excitation by using a nanosecond pulse laser. The temperatures are listed on the right-hand side. *X*, *M*, and (Bi, *M*) stand for free excitons, free biexcitons, and bismuth-bound biexcitons, respectively.

mated to be about 13 meV from the temperature dependence.

From the energies of free excitons and biexcitons and bismuth-bound excitons, the binding energy of the Bi^{3+}-bound biexciton is estimated to be ~10 meV, as illustrated in Fig. 7. Taking into account the large spectral width of the absorption band of the Bi^{3+}-bound exciton, the estimation of the binding energy of the Bi^{3+}-bound biexciton is not so accurate. However, the binding energy is in good agreement with the value (≈13 meV) estimated from the temperature dependence. The result strongly supports the assignment to bismuth-bound biexcitons. In comparison to the Bi^{3+}-bound exciton, it is clearly demonstrated that the binding energy of the Bi^{3+}-bound biexciton is by far smaller than that (210 meV) of the corresponding bound exciton.

IV. DISCUSSION

Here, we discuss the stabilities of the complexes of excitons and biexcitons with the bismuth ion, which is regarded as a positive ion. The binding energies of positive-ion bound excitons and biexcitons, $E_{b(+,\text{exciton})}$ and $E_{b(+,\text{biexciton})}$, which are defined with respect to the energies of excitons and biexcitons, respectively, are expressed as follows:

$$E_{b(+,\text{exciton})} = E_1 + E_2 - E_{b(\text{exciton})}, \tag{1}$$

$$E_{b(+,\text{biexciton})} = E_1 + E_1' + E_2 + E_2' - 2E_{b(\text{exciton})} - E_{b(\text{biexciton})}. \tag{2}$$

The E_1 and E_2 denote the ionization energy of the hole in the (+, exciton) complex and that of the electron in the $(+,e)$ complex, respectively. E_1' and E_2' stand for the energy required for the ionization of the hole in the (+, biexciton) complex and for that of the electron in the (+, exciton, *e*) complex. Since in the (+, exciton) and (+, biexciton) states

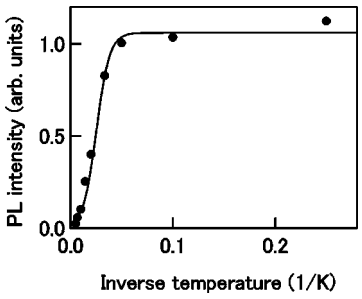

FIG. 6. Integrated intensity of the PL at 2.51 eV as a function of inverse temperature. The solid curve is obtained by fitting (see text) with an activation energy of 13 meV.

the hole is considered to move around the $(+,e)$ and (+, exciton, *e*) complexes that can be regarded to be neutral, respectively, E_1 and E_1' are expected to be much smaller than E_2 and E_2', respectively. In consequence, Eqs. (1) and (2) turn out to be $E_{b(+,\text{exciton})} \cong E_2 - E_{b(\text{exciton})}$ and $E_{b(+,\text{biexciton})} \cong E_2 + E_2' - 2E_{b(\text{exciton})} - E_{b(\text{biexciton})}$, respectively. With the values of $E_{b(+,\text{exciton})}$ (210 meV) and $E_{b(\text{exciton})}$ ~220 meV), E_2 is approximately estimated as ~430 meV. With $E_{b(+,\text{biexciton})}$ (~10 meV) and $E_{b(\text{biexciton})}$ (50 meV) estimated from the experiment above, the value of E_2' is obtained as ~70 meV. Although the values may not be so accurate since we ignore E_1 and E_1' entirely for the estimations, it is obvious that E_2' is remarkably smaller than E_2. Thus the quite low stability of the (+, biexciton) state is related to the small E_2' value. The E_2' value, which is the electron ionization energy of the (+, exciton, *e*) state, is determined by Coulomb interactions among the four charge carriers involving the positive charge of the bismuth ion. In order to discuss the E_2' value quantitatively, a numerical calculation of E_2' is needed. However, the small E_2' value is interpreted qualitatively in terms of strong electron-electron repulsion, as follows. In the $(+,2e,h)$ complex, the two electrons may be bound to the bismuth ion due to strong electron-positive ion interactions in order to take a stable configuration. However, as the two electrons are localized around the bismuth ion, an electron-electron Coulomb interaction increases significantly, which prevents strong bindings of the two electrons with the positive ion. As a result, the E_2' value turns out to be much smaller than the E_2 value. Thus the small binding energy of

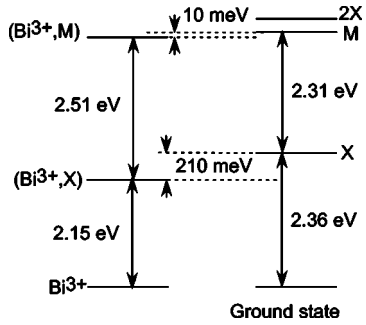

FIG. 7. Energy diagrams of excitons and biexcitons bound to the bismuth ions (left-hand side) and of free excitons (*X*) and biexcitons (*M*) (right-hand side).

the positive-ion bound biexciton results from the electron-electron Coulomb interaction. As this is the first observation of the charged-ion bound biexciton state and there exist no theoretical and no other experimental works to compare, further investigations are required to understand the stability in more detail.

We discuss other possibilities in assignment of the PL at 2.51 eV. First, we consider so-called P-line emissions. P-line emissions stem from exciton-exciton scatterings, in which one exciton is excited to a higher exciton state and the other recombines radiatively. As a result, the emission appears at the lower energy side than the exciton resonance, which is not the case. If the exciton is left in the bismuth-bound exciton state, PL should be observed at 2.57 eV, which is not the case. Furthermore, as mentioned above, from the temperature dependence it is found that the initial state of the PL at 2.51 eV is not free excitons. Therefore it cannot be attributed to P-lines. The second is the possibility of the transition from free biexcitons to the bismuth-bound excitons. Similarly, the temperature dependence clearly indicates that the initial state of the PL at 2.51 eV is not free biexcitons. For this reason, the second possibility is excluded.

As described earlier, we consider that the charge compensation that is necessary in the bismuth doping is likely followed with the lack of the phenethyl ammonium cations near the bismuth ions in the inorganic layers. The electrostatic interactions of excitons and biexcitons with the positively charged ammonium ions are considered to be relatively weak as compared to those with the bismuth ions that locate in the wells, because of the spatial separation between the organic and inorganic layers, although the contribution cannot be neglected entirely. Thus we consider that the stabilities of the positive-ion bound exciton and biexciton are mainly determined by the Coulomb interactions with the bismuth ions.

V. CONCLUSION

In conclusion, we have studied optical properties of the bismuth-doped inorganic-organic layered lead iodide compound. Features due to bismuth doping were observed in the absorption, photoluminescence, and photoluminescence excitation spectra. An absorption band at 2.15 eV is ascribed to excitons bound to a bismuth ion, and a photoluminescence band observed at 2.51 eV with high excitation density to biexcitons bound to a bismuth ion. Based on the experimental data, the binding energies of the bismuth-bound excitons and biexcitons were estimated approximately as 210 and 10 meV, respectively. It was demonstrated that the binding energy of the (+, biexciton) complex is much smaller than that of the (+, exciton) complex in the two-dimensional system. The much lower stability of the biexciton complex was discussed and interpreted in terms of a strong electron-electron Coulomb interaction.

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[18] In this paper, we use the abbreviations of positive-ion bound states such as (+, exciton) and (+, biexciton) for clarity. It should be noted, however, that the shapes of the wave functions of the bound excitons and biexcitons may be different from those of free excitons and biexcitons, respectively. An alternative to the abbreviations, therefore $(+,e,h)$ and $(+,2e,2h)$, may be more appropriate in that sense.
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