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# Optical Absorption of $BiI_3$ Clusters Embedded in $CdI_2$ Films

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$CdI_2$ and $BiI_3$ can be made solid solution by quench deposition over the full range of concentration ratio. On annealing of the solution, two-dimensional small clusters of $BiI_3$ are produced which are coupled to the lattice of $CdI_2$ host matrix and show confined-exciton absorption. There is too large a barrier for $Bi^{3+}$ ions to aggregate to form larger $BiI_3$ clusters because the aggregation requires two $Bi^{3+}$ ions to migrate in a pair in two dimensions. The present experiment opens up the possibility of a method for achieving designed small $BiI_3$ clusters embedded in the $CdI_2$ crystal matrix at high densities, with the clusters directly coupled to the lattice of the host matrix.

## 1. Introduction

It is of long standing that many workers have been interested in mesoscopic properties of nanodimensional particles. Various efforts have been made to obtain nanodimensional particles according to the object of investigation. In the study of quantum size effect on excitons, which is one of the best investigated mesoscopic properties exhibited by nanodimensional particles, the particles are usually embedded in a glass or crystal matrix. Such a specimen has mostly been prepared by means of quenching of thermal equilibrium for phase separation of an eutectic mixture. The resulting nanoparticles necessarily have a size and shape distribution, reflecting the phase equilibrium. Furthermore, the mole fraction of the particles is generally very small, typically of the order of 0.1 mol% or less. Preparation of a specimen containing nanoparticles of a definite size and shape with a high concentration is not merely desirable for the basic research of their mesoscopic properties, but for their application studies. One of the possible ways to obtain such a specimen is to incorporate nanocrystals into the crystal lattice of a favorable crystal. In the present work we attempted to incorporate $BiI_3$ clusters into $CdI_2$ crystal lattice at high densities.

Both $CdI_2$ and $BiI_3$ have ionic layered structures with a metal-ions sheet sandwiched between two hexagonally close-packed sheets of $I^-$ ions. The metal-ions sheet takes a close-packed structure for $Cd^{2+}$ ions and a honeycomb structure for $Bi^{3+}$ ions (the extra charge on $Bi^{3+}$ ions requires that a third of the close-packed sites remain unoccupied). The thickness of the unit layer is 6.84 Å in $CdI_2$ and 6.89 Å in $BiI_3$, and the interionic distances in the $I^-$-ions sheet are 4.24 and 4.33 Å, respectively [1]. The fairly similar values of these crystal-structure parameters of the two compounds are favorable for substituting $Bi^{3+}$ ions for $Cd^{2+}$ ions despite the difference in their valency; $BiI_3$ can be incorporated into the $CdI_2$ crystal lattice with three adjacent $Cd^{2+}$ ions substituted by two $Bi^{3+}$ ions on the cation sublattice, thus forming two-molecule $BiI_3$ clusters.

Such a stoichiometrical substitution is expected to take place up to a considerable concentration, owing to a fair lattice fit expected.

Study of $BiI_3$ clusters in $CdI_2$ was first reported by Kim et al. in 1996 [2]. They observed exciton absorption and luminescence of $BiI_3$ clusters embedded in a single-crystal $CdI_2$ matrix with the $BiI_3$ concentration of the order of 0.1 to 0.01 mol%. Recently, we doped $CdI_2$ films with $Bi^{3+}$ ions up to 10 mol% of cation concentration [3]. The heavy doping was achieved in the amorphous form of the films by quench deposition of the mixture of $CdI_2$ and $BiI_3$. Crystallization of the films resulted in well defined two-molecule $BiI_3$ clusters densely monodispersed in the $CdI_2$ polycrystalline matrix. In the present work we have obtained films of quench-deposited solid solutions of the two compounds over the full mixing range. It was shown by exciton spectroscopy that annealing of the films yielded various $BiI_3$ clusters coupled to the lattice of $CdI_2$ crystal matrix.

## 2. Experimental

Film samples of the mixture of $CdI_2$ and $BiI_3$ were obtained by the method of quench deposition. To prepare the source materials for the deposition, nominal amounts of $CdI_2$ and $BiI_3$ in powder form were mixed together and put in a silica-tube container. The container was evacuated to $5 \times 10^{-4}$ Pa at 200 °C for 24 h and tipped to get a vacuum-sealed ampoule of the mixture. The ampoule was heated to 500 °C, held at that temperature for 1 h, and then quenched in ice water to achieve homogeneity in the concentration of the mixture. The resulting mixture was informly colored to the eyes (yellow to dark brown with increasing $BiI_3$ concentration). Quench deposition of the mixture was carried out in the same way as described in [4]. In brief, the mixture was deposited onto a fused-silica substrate (the EDH grade from Nippon Sekiei Garasu Co.) cooled to 77 K in a vacuum of about $9 \times 10^{-6}$ Pa using a tungsten basket heating element placed 8 cm in front of the substrate; the deposition rate was about 20 nm/min. Such a high deposition rate was considered to be favorable for achieving the nominal composition ratio of $CdI_2$ and $BiI_3$ in the films, though the resulting composition ratio was not analyzed (a rough estimate of the composition ratio is given in Section 4).

Thus-prepared films were investigated by an improved optical absorption spectroscopy described in [5]. The method is based on simultaneous measurements of transmittance and reflectance of films from which their accurate optical densities can be determined. The measurements were made in the region of photon energies below 3.5 eV, in which $CdI_2$ is transparent and $BiI_3$ exhibits main low-energy spectral structures including the band-gap exciton peak.

We note that quench-deposited (at 77 K) $CdI_2$ films, which were in the amorphous state, were characterized by an excellent transmittance below 3.5 eV [6]. Furthermore, films crystallized thermally from the amorphous phase exhibited a very high transmittance compared to that of (crystalline) films deposited onto hot substrates, though the crystallization brought about devitrification with increasing thickness of the films, particularly above 100 nm thickness. The high transmittance is favorable for the measurement of the absorption of $BiI_3$ clusters embedded in the $CdI_2$ matrix. Therefore, in the present work we used the films quench deposited to thicknesses less than 100 nm (the thicknesses of the films were determined by an interference method [7]) and measurements of their absorption spectra were performed both on the as-deposited and on the annealed films. As a result, it was possible to observe detailed absorption features of the clusters and to analyze the line shape of the measured spectra with high accuracy.

## 3. Results

Figure 1 shows the absorption spectra at 77 K of the binary $(CdI_2)_{1-x}(BiI_3)_x$ system. For each value of $x$, the spectrum was first measured at 77 K on the as-deposited film (Fig. 1a). Then the film was heated at a rate of 1 K/min up to 333 K, annealed for 10 min at that temperature, and cooled again to 77 K at a rate of 10 K/min to measure the spectrum shown in Fig. 1b. To visualize the change of structures with $x$ of the spectrum, the individual spectra in the figure are normalized in such a way that the absorption intensities of the annealed films are unity at 3.3 eV. The true absorption intensities of the spectra together with the thicknesses of the films were used to estimate the concentration of $BiI_3$ in the films, as described in the next section.

As seen from Fig. 1a, the as-deposited films exhibit almost the same spectral structure for the values of $x$ up to 0.2, that is, the spectra are composed of two broad bands peaking at around 2.6 and 3.3 eV. For $x > 0.2$, there occurs a gradual and continuous change in the spectra, with the energy locations of the bands monotonically shifted to the lower energy side and also with the bands being less pronounced in feature with increasing values of $x$.

When the films are annealed, characteristic changes in the spectral structure occur depending on the values of $x$ as seen in Fig. 1b. For $x \leq 0.1$, there arises a sharp peak

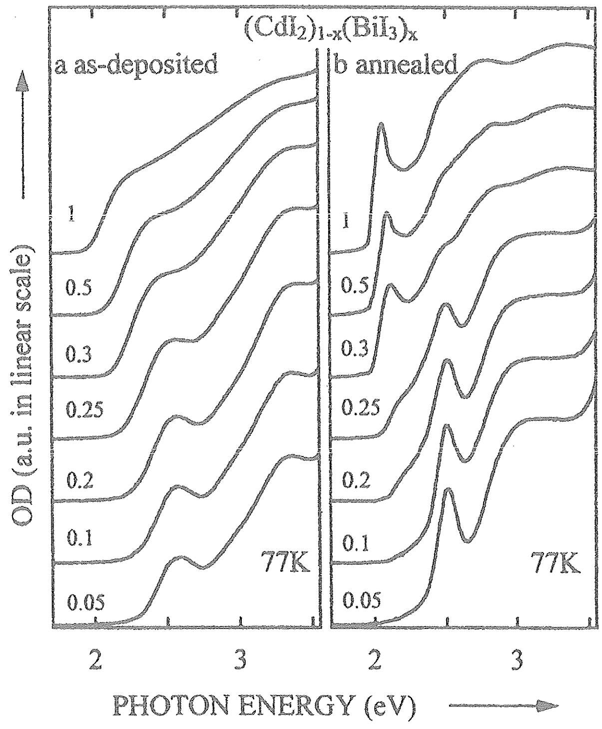

Fig. 1. Absorption spectra of quench-deposited films of the binary $(CdI_2)_{1-x}(BiI_3)_x$ system measured at 77 K for various values of $x$ indicated before (a) and after (b) annealing the films at 333 K for 10 min

at 2.50 eV followed by strong absorption at higher energies. (The sharp rise of the absorption intensity above 3.5 eV is due to the onset of the fundamental absorption of the host $CdI_2$; this is also the case for the as-deposited films in Fig. 1a.) By increasing the value of $x$ up to 0.25, a shoulder shows up at energy around 2.2 eV, with the sharp peak weakened in intensity but with the peak energy unchanged. For $x = 0.3$, the shoulder grows to a peak located somewhat lower in energy. This accompanies the simultaneous degradation of the 2.5 eV peak. By further increase of the value of $x$, the new peak slightly shifts to the lower energy side and finally reaches the $BiI_3$ exciton peak located at 2.06 eV ($x = 1$).

## 4. Discussion

It was possible in [3] that two-molecule $BiI_3$ clusters, which will be referred to as $BiI_3$ dimers below, were densely (up to 10 mol%) monodispersed in $CdI_2$ films by the method of quench deposition, as stated in Section 1. Their absorption spectrum was characterized by a broad band at 2.59 eV for the as-deposited (amorphous) films and an excitonic peak at 2.50 eV for the annealed (crystalline) films. These spectral behaviors (for $x \leq 0.1$) are reproduced in Fig. 1 (in [3], the spectrum was presented only for $x = 0.05$).

As seen from Fig. 1a, the broad band persists at higher $BiI_3$ concentrations and finally amalgamates into the first band of $BiI_3$. This behavior upon making mixture of the first band is very similar to a persistence type of spectral behavior frequently observed for exciton absorption in halogen-substituted binary metal-halide solid solutions [8]. Therefore, it is probable that the mixture of $CdI_2$ and $BiI_3$ is in the state of solid solution, that is, there occur stoichiometrical replacements of any three adjacent $Cd^{2+}$ ions by two $Bi^{3+}$ ions successively for increasing $BiI_3$ concentration in the mixture. As a result, $BiI_3$ dimers are considered to be uniformly distributred in the $CdI_2$ matrix. Concerning the annealed films, however, the situation may be somewhat different, in view of their spectral characteristics discussed below.

As is well known, the spectral lineshape for oscillator-like optical transitions is often fitted with a Gaussian or Lorentzian, or their modifications. The Gaussian function is used to fit the band whose broadening is dominated by the randomly distributed local variation of the associated electronic states in a sample. This type of broadening, called inhomogeneous broadening, is always observed for absorption related to localized states such as those of impurities or imperfections, since the transition energies for these states vary from one point to another in the sample. On the other hand, the Lorentzian function accounts for a homogeneous broadening related to the lifetime of the associated excited states. For example, for exciton absorption in a crystal, the lifetime of every individual exciton created by the light absorption is reduced by collisions with phonons or defects in the crystal, resulting in the lifetime broadening of the absorption band. In both cases, however, modifications of the functional form are often more practical for obtaining the best fit to experimental data.

In the previous study in [3], the first absorption band of the $BiI_3$ dimers in the as-deposited films was well fitted to a skewed Gaussian function [9], while for the annealed films, a nice fit was achieved by using the asymmetric Lorentzian function proposed by Toyozawa [10] to describe weak coupling of exciton with phonon (both functional forms are given in [3]). Therefore, we performed similar lineshape analysis for the spectra shown in Fig. 1.

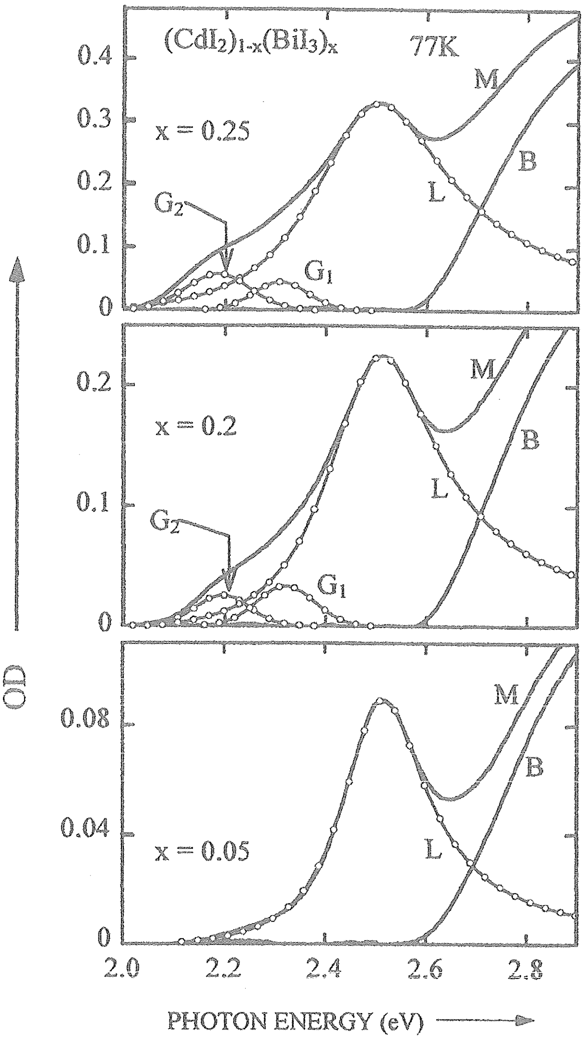

Fig. 2. Spectral decomposition of the annealed $(CdI_2)_{1-x}(BiI_2)_x$ films. Measured spectrum (M) is decomposed into the Lorentzian (L) and background absorption (B) for $x = 0.05$, and into the Lorentzian (L) and two Gaussians ($G_1$, $G_2$) with the remnant as the background absorption (B) for $x = 0.20$ and 0.25

Figure 2 shows the spectral decomposition of the annealed films for $x$ up to 0.25 in the exciton transition energy region. The measured spectra (M) were decomposed into a Lorentzian (L) and the background absorption (B) for $x = 0.05$, and into a Lorentzian (L) and two Gaussians ($G_1$, $G_2$) with the remnant as the background absorption (B) for $x = 0.20$ and 0.25. For all the cases B was almost exactly zero in intensity below 2.6 eV, indicating a nice decomposition of the measured spectra (any Lorentzians, instead of the Gaussians $G_1$ and $G_2$ in the figure, were by no means well fitted to the measured spectra). The integrated intensity ratio of L, $G_1$ and $G_2$ was 1:0.09:0.06 for $x = 0.2$ and 1:0.07:0.09 for $x = 0.25$. The Lorentzians were shown to have almost the same peak energy ($\approx$2.50 eV) for all $x$, but with an increase of the full width at half maximum (FWHM) for $x \geq 0.2$: FWHM = 0.21 eV for $x \leq 0.1$, while FWHM = 0.27 and 0.33 eV for $x = 0.20$ and 0.25, respectively. The Gaussians also had nearly the same peak energies for $x = 0.2$ and 0.25 ($\approx$2.32 eV for $G_1$ and $\approx$2.19 eV for $G_2$).

It was shown in [3] that the Lorentzian for $x \leq 0.1$ exhibited the same line shape independently of $x$ with excellent reproducibility and thus its FWHM was due to homogeneous broadening; the homogeneous broadening was strongly enhanced due to the effect on the exciton of confinement together with the peak energy of the exciton ($BiI_3$ has a very small exciton effective Bohr radius of 6 Å [11]; the exciton absorption of the bulk crystal is known to have a very large homogeneous broadening, 65 meV [12] at 77 K with the peak at 2.072 eV [13]). Since the $BiI_3$ dimers are coupled to the lattice of the $CdI_2$ crystal matrix, penetration of the exciton into the surrounding $CdI_2$ lattice should be taken into account. If any two $BiI_3$ dimers are situated close in positions, their penetrated exciton wave functions may overlap with each other. This may result in a broadening of the exciton absorption line. Such a broadening may be responsible for the increased FWHM for $x = 0.2$ and 0.25, although the main cause of the large FWHM is still attributed to the homogeneous broadening due to scattering or trapping of confined excitons by the surface states.

It is probable that there is too large a barrier for $Bi^{3+}$ ions to aggregate to form larger $BiI_3$ clusters, because the aggregation requires the two $Bi^{3+}$ ions to migrate in a pair in order to maintain electrical neutrality for every $Bi^{3+}$ dimer (if a single $Bi^{3+}$ ion, or both a single $Bi^{3+}$ ion and a single $Cd^{2+}$-ion vacancy, migrates, there occurs net charge transfer on the cation sublattice, which is not permissible). Furthermore, the clustering of $Bi^{3+}$ ions is considered to occur in two dimensions. This may account for why the $BiI_3$ dimers can densely be dispersed in the $CdI_2$ crystal matrix without forming larger clusters. For larger clusters to be formed in the matrix, a very high concentration of the $BiI_3$ dimers should be necessary. The weak Gaussian bands $G_1$ and $G_2$ observed for $x \geq 0.2$ in Fig. 2 may be attributed to larger two-dimensional clusters, presumably planar tetramers and hexagon clusters, respectively, although structural studies (such as those using Raman and infrared spectroscopies) are necessary for a direct support. Concerning these clusters, there are several possible sites of the charge compensating $Cd^{2+}$-ion vacancies in the $Cd^{2+}$-ion sublattice, and the vacancies are considered to be delocalized over these sites. This is favorable for explaining the Gaussian, instead of Lorentzian, line shape for the exciton absorption in these clusters.

It is better to mention here that the substitution of three $Cd^{2+}$ ions by two $Bi^{3+}$ ions leaving one $Cd^{2+}$-ion site unoccupied (vacancy) on the cation sublattice in $CdI_2$ is reminiscent of the so-called Suzuki phase frequently observed in alkali halides doped with divalent cations [14]. In terms of such an ordered phase having a particular stoichiometry, however, it is difficult to give an account for the spectral variation with the $BiI_3$ concentration. In particular, the idea that the first peak at 2.50 eV is related to Suzuki phase is negated because the same peak is observed for two-molecule $BiI_3$ clusters confined in a zeolite cage [15] as mentioned in [3].

The densely dispersed $BiI_3$ dimers are in great contrast to the case of Bi-doped bulk $CdI_2$ crystals in [4]. The as-grown samples in [4] exhibited a weak, but clearly discernible, sub-band around 2.2 eV due to larger clusters of $BiI_3$ molecules in the absorption spectrum for a very small concentration of $BiI_3$, 0.1 mol%, although the sub-band did not greatly increase in intensity during the subsequent heat treatments of the samples for producing larger clusters. In our film samples, however, the $BiI_3$ dimers are monodispersed up to 10 mol% and larger clusters exhibiting the sub-band around 2.2 eV are produced only for the films with larger $BiI_3$ concentrations.

The spectra for $x \geq 0.3$ in the annealed films are all characterized by a prominent first band as seen in Fig. 1b. To determine the peak energy of the band, its line shape was fitted to a Gaussian or a Lorentzian. It was of Gaussian type for $x = 0.3$ and of Lorentzian for $x = 0.5$ and 1, giving the peak energies 2.13, 2.10 and 2.06 eV, respectively. The gradual red shift of the band with increasing value of $x$ is attributable to relaxation of the quantum confinement of excitons, with the implication that the higher the $BiI_3$ concentration, the larger clusters grow in the films.

Finally, mention is made of a rough estimate of the $BiI_3$ concentration in the films investigated. The first bands of the as-deposited films were of the Gaussian type for all the values of $x$ and it was shown that the integrated absorption intensity of the Gaussian per unit thickness was roughly proportional to $x$ (with the deviation less than a few percent). Therefore, the nominal value of $x$ is considered to give a rough estimate of the true $BiI_3$ concentration in the film, in view of the relatively close crystal-parameter values between $CdI_2$ and $BiI_3$ as mentioned in Section 1.

## 5. Conclusion

$CdI_2$ and $BiI_3$ can be made (amorphous) solid solution by quench deposition over the full range of concentration ratio, despite the different cation valencies of the two compounds. On annealing of the solid solution, two-dimensional clusters of $BiI_3$ exhibiting confined-exciton absorption showed up which were coupled to the lattice of the $CdI_2$ crystal matrix with the cluster size depending on the $BiI_3$ concentration. For $BiI_3$ concentrations less than 20 mol%, $BiI_3$ molecules appeared as the two-molecule clusters. In the range from 20 to 25 mol% of $BiI_3$ concentration, weak absorptions due to the four-molecule (planar tetramers) and six-molecule (hexagon) clusters were observed, although a large part of the exciton absorption was still due to the two-molecule clusters. From the existence of the $BiI_3$ molecules as the two-molecule clusters up to such high $BiI_3$ concentrations, it was suggested that there was too large a barrier for $Bi^{3+}$ ions to aggregate to form larger $BiI_3$ clusters. This is because the aggregation requires the two $Bi^{3+}$ ions to migrate in a pair in two dimensions. The present experiment opens up the possibility of a method for producing designed small $BiI_3$ clusters embedded in the $CdI_2$ crystal matrix at high densities, with the clusters directly coupled to the lattice of the host matrix. For example, the size of the clusters is expected to be controllable by developing annealing performance as well as by varying the $BiI_3$ mole fraction. We are in progress in achieving densely dispersed hexagon $BiI_3$ clusters (stable due to high symmetry) in a controlled manner. The results will be reported later.

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