Extremely photo-luminescent microcrystalline CsPbX3 (X=Cl, Br) films obtained by amorphous-to-crystalline transformation

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Extremely photo-luminescent microcrystalline $CsPbX_3$ ($X = Cl$, Br) films obtained by amorphous-to-crystalline transformation

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Abstract

The compounds $CsPbCl_3$ and $CsPbBr_3$, which are known to be one of the most luminescent semiconductors, show enhanced photoluminescence for thin films prepared by crystallization from the amorphous phase into microcrystalline/polycrystalline states. The microcrystalline state shows more than an order of magnitude stronger free-exciton emission than the polycrystalline state, as well as than bulk single crystal. A possible explanation for this phenomenon is given in terms of excitonic superradiance. The extreme radiance of the thin-film samples is fascinating when considering application in opto-electronic micro-devices.

Keywords: Film; Luminescence; Exciton; Mesoscopic; $CsPbCl_3$; $CsPbBr_3$

1. Introduction

Semiconductor microcrystals have attracted much attention over the last two decades owing to mesoscopic enhancement of linear and nonlinear optical properties. In the last several years many interesting studies have been carried out on a new type of microcrystals, i.e., $CsPbX_3$ ($X = Cl$, Br) microcrystals dispersed in crystal matrices, with the expectation of their possible application in fast scintillators and opto-electronic devices taking advantage of a very fast and strong free-exciton luminescence of the source compounds. The studies are based on the measurements of photoluminescence of the microcrystals thermally grown in Pb^{2+}-doped CsX [1–13] or $CsSrX_3$ [14] crystals and Cs^+-doped PbX_2 [12,15,16] crystals, and deal with quantum size effects on excitons, such as confinement-induced blue shifts of exciton energy and confinement-induced changes in the decay kinetics of excitons, or aim at elucidation of growth kinetics of the microcrystals. The decay-kinetics studies reveal that the radiative decay time of the free excitons in the microcrystals is further shortened by the effect of confinement on the excitons, suggesting that the inherently strong free-exciton luminescence for $CsPbX_3$ can be further enhanced in intensity by the confinement effect. Concerning direct comparison of the luminescence intensity between micro- and larger crystals, however, no studies have been reported so far, presumably due to difficulties in the sample preparation method.

Previously we showed that $CsPbCl_3$ and $CsPbBr_3$ can be rendered amorphous by quench deposition yielding film samples [17,18]. The amorphous films exhibit excellent transmittance below the absorption edge and have a well-defined, characteristic crystallization temperature, 302 K for $CsPbCl_3$ and 296 K for $CsPbBr_3$, at which their absorption spectra drastically change in outline, as shown in the insets in Fig. 1. The films, when crystallized at temperatures just above the crystallization temperature, are in a microcrystalline state, and change into polycrystalline state when they are subsequently annealed at higher temperatures; well identified various crystalline states, from microcrystalline to polycrystalline, can be achieved by suitable heat treatment of the films. Thus-prepared films, whether they are

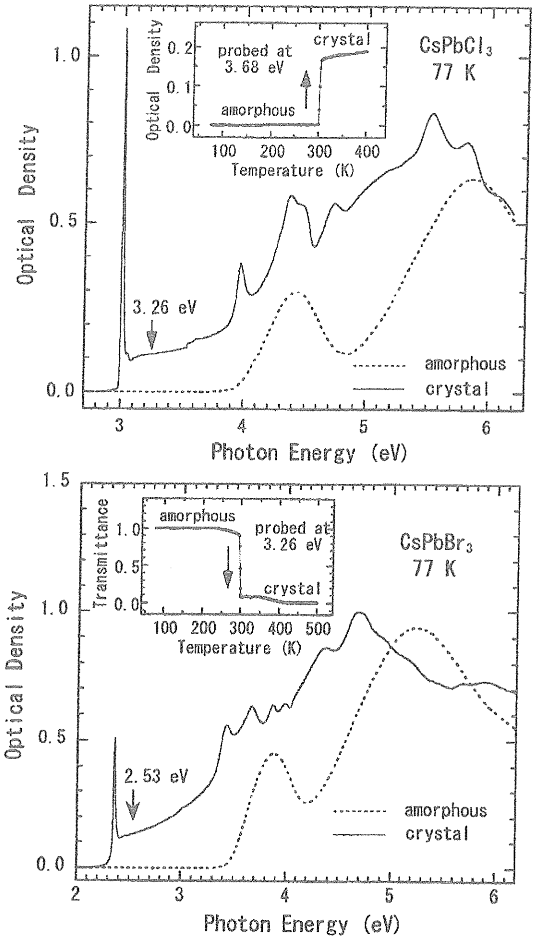

Fig. 1. The absorption spectra of $CsPbCl_3$ (upper half) and $CsPbBr_3$ (lower half) films at 77 K for the amorphous (dashed curve) and crystalline (solid curve) states. The downward arrows indicate the energy positions of the luminescence-exciting lights used. The insets illustrate the change in optical density ($CsPbCl_3$) or transmittance ($CsPbBr_3$) during crystallization.

in the microcrystalline or polycrystalline states, show excellent transmittance compared with polycrystalline films deposited onto hot substrates. The microcrystalline state is characterized by blue-shifted exciton absorption due to quantum size effect on the exciton, while the polycrystalline state shows a very sharp exciton resonance (Fig. 1); such a sharp exciton resonance is not achieved for films directly prepared on hot substrates.

It is well known that exciton spectroscopy provides powerful means for investigating crystallinity of materials on a nm-scale when the materials show sharp exciton resonance [19]. In particular, spectral line-shape and peak energy and quantum yield for free-exciton luminescence are very sensitive to the state, or quality, such as lattice imperfections and size of microcrystals [20]. Therefore, free-exciton spectroscopy is frequently conveniently used for characterizing microcrystals or quantum dots [21]. In fact, in all the existing works which deal with the $CsPbX_3$ ($X = Cl$, Br) microcrystals dispersed in crystals [1–16] or constituting films [17,18], the authors are successful in assessing the microcrystals solely by means of free-exciton spectroscopy. For example, the blue shift of free-exciton energy can be used to estimate the mean size of the microcrystals. Concerning the mean size of the microcrystals determined by free-exciton spectroscopy on a nm-scale, there has been no independent evidence from structural studies, such as by X-ray diffraction spectroscopy or by electron microscopy, both for the microcrystals dispersed in crystals [1–16] and for the microcrystals constituting films [17,18].

In the present work, we measured luminescence spectrum of $CsPbCl_3$ and $CsPbBr_3$ films for both microcrystalline and polycrystalline states using the same starting amorphous films, to directly compare the luminescence efficiencies between the two states. Free-exciton spectroscopy was conveniently applied to in situ monitoring of the transformation of the films from amorphous to microcrystalline/polycrystalline states. It was found that the microcrystalline state shows more than an order of magnitude stronger free-exciton luminescence than the polycrystalline state. To our knowledge, such a direct comparison which is performed by using the same starting specimens and which distinctly reveals mesoscopic enhancement of free-exciton luminescence for the microcrystalline state has not been reported for any semiconductor so far.

2. Experimental

The amorphous films of $CsPbCl_3$ and $CsPbBr_3$ were obtained by quench deposition onto silica-glass substrates kept at 77 K. The deposition was carried out in a vacuum of about 9×10^{-6} Pa using a tungsten basket heating element placed 8 cm in front of the substrate. The crystallization into the microcrystalline state and subsequent crystal growth into the polycrystalline state were achieved through repeated heating/cooling cycles using a resistive heater, with the heating rate of 10 K/min and the cooling rate of 50 K/min. The highest temperature experienced by the films was increased with the run number of the heating/cooling cycles. For each run of the cycles, photoluminescence and absorption spectra of the films at 77 K were measured in situ by a liquid nitrogen-cooled CCD spectrometer equipped with a 0.47 m grating monochromator. A 500 W xenon lamp, in combination with a 0.5 m grating monochromator, and a 30 W deuterium lamp were used as the light sources for the photoluminescence and absorption measurements, respectively.

In the above experiment, free-exciton photoluminescence spectroscopy was exploited for in situ monitoring of the change of the crystalline phase during the repeated heating/cooling cycles of the films. We used the term "microcrystalline" or "polycrystalline" state, according as the free-exciton emission band of the films showed or did not show a detectable red shift with the rise of the annealing temperature. Once the films were annealed at 500 K for 10 min, they no longer showed such a red shift and exhibited the same free-exciton peak energy as that for the films directly deposited onto 500-K substrates. Therefore, we defined the resulting films as the polycrystalline films, although the crystallite-sizes in the films were not determined. On the other hand, crystallite-sizes for the microcrystalline state were determined from the blue shift of the free-exciton energy relative to that for the polycrystalline state, in the same way as that employed, for example, in [2,13], under the assumption of effective-mass approximation using the exciton parameters reported in [22]. The largest mean crystallite-size detectable by the exciton spectroscopy was about 24 nm for $CsPbCl_3$ and about 27 nm for $CsPbBr_3$, as determined from the smallest detectable blue shift, about 1 meV. The films whose mean crystallite-sizes determined by the exciton spectroscopy are smaller than these "critical" sizes were defined as the microcrystalline films; necessarily the polycrystalline films have larger mean crystallite-sizes than the "critical" sizes.

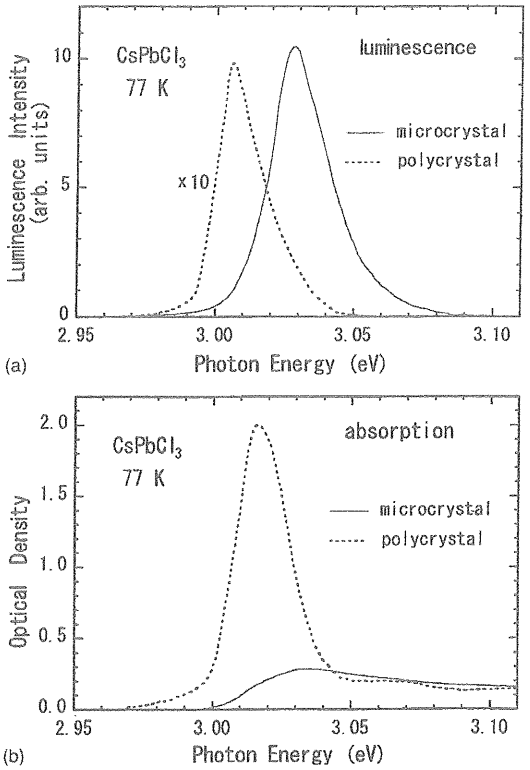

Fig. 2. The luminescence (upper half) and absorption (lower half) spectra of a $CsPbCl_3$ film measured at 77 K for the microcrystalline (solid curves) and polycrystalline (dashed curves) states using the 3.26 eV exciting light.

3. Results

Figs. 2 and 3 show examples of the exciton luminescence (upper half) and absorption (lower half) spectra of $CsPbCl_3$ and $CsPbBr_3$ films, respectively, measured at 77 K for the microcrystalline (solid curves) and polycrystalline (dashed curves) states. The highest annealing temperature and annealing time duration experienced by the films to reach the microcrystalline state were, respectively, 306 K and 10 min for $CsPbCl_3$ and 300 K and 10 min for $CsPbBr_3$, and those for the polycrystalline state were, respectively, 500 K and 10 min for both $CsPbCl_3$ and $CsPbBr_3$. The luminescence was excited at 3.26 eV for $CsPbCl_3$ and 2.53 eV for $CsPbBr_3$, shown by the downward arrows in Fig. 1, and recorded in the configuration of backward scattering normal to the film surfaces to minimize reabsorption, with the incident angle of the exciting light set at 45°.

In both $CsPbCl_3$ and $CsPbBr_3$, and for both microcrystalline and polycrystalline states, the luminescence was concentrated at or around the exciton-resonance photon energy region, and no other luminescence was observed although the measurements were carried out in the region down to 1.4 eV. The blue shift of the exciton energy for the microcrystalline state, with respect to that for the polycrystalline state, is more clearly observed in the luminescence spectra than in the absorption spectra; the exciton confinement energy is 22 meV for $CsPbCl_3$ (Fig. 2b) and 19 meV for $CsPbBr_3$ (Fig. 3b), which lead to the mean crystallite-sizes 5.1 and 6.2 nm, respectively, under the assumption of effective-mass approximation. Notably, in both $CsPbCl_3$ and $CsPbBr_3$, the exciton luminescence is strongly enhanced in intensity by the effect of confinement on the excitons—note that the luminescence spectra for the polycrystalline state are plotted on a magnified scale in intensity. The ratio of the integrated luminescence intensities for the microcrystalline and polycrystalline states was shown to amount to 13 for $CsPbCl_3$ and 15 for $CsPbBr_3$. We note that, in both $CsPbCl_3$ and $CsPbBr_3$, the luminescence for the polycrystalline state, though very weak in intensity compared to that for the microcrystalline state, was clearly observed at elevated temperatures, for example, at 340 K for $CsPbCl_3$, whose luminescence for single crystals is completely quenched at that temperature [23]. It is considered that even the polycrystalline films, prepared via the amorphous phase, exhibit higher luminescence efficiency than the single crystals.

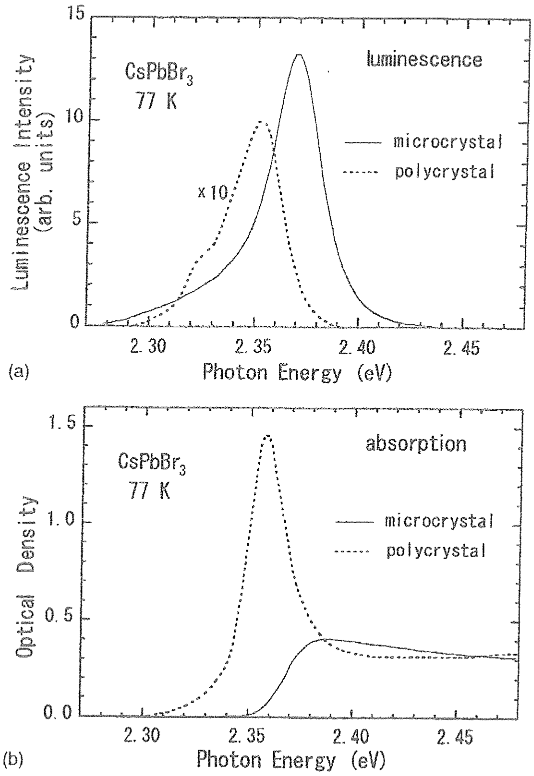

Fig. 3. The luminescence (upper half) and absorption (lower half) spectra of a CsPbBr$_3$ film measured at 77 K for the microcrystalline (solid curves) and polycrystalline (dashed curves) states using the 2.53 eV exciting light.

Similar measurements were carried out for several films of CsPbCl$_3$ and CsPbBr$_3$ and also for every cycle of the heating/cooling operation of the individual films. The measured luminescence spectra were always enhanced in intensity when the luminescence peak energies were blue-shifted with respect to that for the polycrystalline state. It was confirmed that the strongest luminescence intensity is observed for the blue shifts in the range 20–24 meV for CsPbCl$_3$ and 18–21 meV for CsPbBr$_3$, which correspond to the microcrystallite-sizes of the respective compounds in the ranges 5.3–4.9 and 6.4–5.9 nm, respectively; for both compounds, larger blue shifts up to about 35 meV, but weaker luminescence intensities, were observed in earlier heating/cooling cycles.

4. Discussion

The luminescence spectra for CsPbCl$_3$ (Fig. 2, upper half) are different in feature from any exciton luminescence of CsPbCl$_3$ reported so far, i.e., bulk CsPbCl$_3$ crystals, CsPbCl$_3$ aggregates dispersed in crystal matrices and polycrystalline CsPbCl$_3$ films. For example, the luminescence spectrum of the bulk crystal measured at liquid nitrogen temperature [24] is composed of three bands, peaking at 2.987, 2.950 and 2.914 eV with the integrated intensity ratio of about 1:2:0.4, which are deduced in [24] from the measured spectrum by a line-shape analysis using Gaussian fits. The highest-energy band is attributed to free excitons and the lower-energy bands to trapped excitons. At lower temperatures below 40 K, the free-exciton luminescence becomes strongest in intensity. The FWHM of the free-exciton luminescence band is almost the same in the temperature range at and below liquid nitrogen temperature, giving the values in the range 70–80 meV. In polycrystalline films [25], a free-exciton emission band with the peak energy 2.960 eV and the FWHM about 30 meV is observed at 5 K together with weaker lower-energy emission due to trapped excitons. For CsPbCl$_3$ aggregates dispersed in crystal matrices, complicated emission spectra are observed depending on the specimens heat-treated in different ways, and sometimes plate-like growth [1–3] of CsPbCl$_3$ microcrystals occurs in a suitably heat-treated CsCl crystal matrix, exhibiting several emission bands due to recombination of free excitons confined in various CsPbCl$_3$ plates with different thicknesses. On the other hand, the present luminescence spectra for CsPbCl$_3$ are consistently composed of a single, free-exciton emission band with the smaller FWHMs, 23 meV for the microcrystalline state and 18 meV for the polycrystalline state, without exhibiting any trace of trapped-exciton emission. The smaller FWHMs, at 77 K, even than that observed at 5 K for the polycrystalline film, mean small inhomogeneous line-broadening and/or well-averaged crystallites size for the microcrystalline state. In particular, reflecting the high-quality nature of the present film, there is no trace of trapped-exciton emission. The absence of trap states for the free excitons means that lattice imperfections such as impurities and lattice distortions are drove away from the interior of the individual crystallites. It is notable that excitons even in the microcrystalline film are free from being trapped, despite the expectation [26] of a high density of surface states due to a large surface to volume ratio for individual microcrystals in the film. To conclude, both microcrystalline and polycrystalline states of high quality can be achieved by heat treatment of the same starting amorphous CsPbCl$_3$ film.

Luminescence studies of CsPbBr$_3$ have been reported for bulk crystals and for microcrystals dispersed in crystal matrices. Three resolvable emission bands are known for bulk crystals, namely that due to free excitons and those due to two kinds of trapped excitons [6]. The emission properties are strongly influenced by defects in the crystals. On the other hand, in the case for microcrystals, although a general tendency such as found for the bulk crystals, i.e., free excitons plus two kinds of trapped excitons, also holds, different luminescence spectra have been observed, depending on the difference in the heat-treatment parameters such as annealing temperature and/or its duration and on the difference in the Pb^{2+}-ion concentration in the dispersed systems [2,7–9].

The luminescence spectrum for the microcrystalline state in the present $CsPbBr_3$ film (Fig. 3, upper half) is very similar in structure to that observed for "nanocrystals" embedded in "best" samples reported in [9], apart from the smaller FWHM and the higher peak energy of the free-exciton emission band for the former, i.e., respectively 28 and 2.369 eV, than for the latter, i.e., respectively about 44 meV and about 2.351 eV at 80 K as read from Fig. 2 in [9], by about 16 and 18 meV, respectively. The smaller FWHM means a higher quality and the larger peak energy suggests a smaller mean size, of the crystallites in the film. Following [9], we attribute the lower energy tail, observed for the microcrystalline state at energies below 2.35 eV, to trapped excitons. The trapped-exciton emission is, relative to the free-exciton emission, enhanced in the polycrystalline state. We note here that the same luminescence spectra (Fig. 3, upper half) are consistently observed for films prepared via the amorphous state by the same heat treatments as above, i.e., annealing at 300 and 500 K for the microcrystalline and polycrystalline states, respectively, both for 10 min, in contrast to the cases for heat-treated CsBr:Pb crystals, where "best" samples such as those reported in [9] are not always achieved.

The present $CsPbX_3$ ($X = Cl$, Br) films provide suitable specimens for directly comparing the efficiencies of exciton luminescence between the microcrystalline and polycrystalline states, since the luminescence measurements can be performed using the same starting films for both states. Such a direct comparison has not been made for any of heat-treated CsX:Pb [1–13], $CsSrX_3$:Pb [14] and PbX_2:Cs [12,15,16] ($X = Cl$, Br) crystals studied so far, probably because of difficulties in the sample preparation technique—indeed, there occurs aggregation and/or dissociation of Pb^{2+} ions during the heat treatment, as reported, for example, in [13]. The present films, prepared by crystallization from the amorphous phase, clearly show that the microcrystalline state exhibits much stronger exciton luminescence than the polycrystalline state.

One of likely explanations for the enhanced luminescence yield of the microcrystalline state may be given in terms of excitonic superradiance. Excitonic superradiance is a cooperative radiation process of a coherently delocalized exciton in a crystal, leading to a very short radiative decay time depending on the coherence length, i.e., the extent of the coherently delocalized exciton. Since the coherently delocalized exciton state is the coherent superposition of all the lowest electronic excited states at individual unit cells contained in the crystal, such an ideal state is generally not achieved in a bulk crystal due to lattice imperfection, as well as lattice vibration, even at very low temperatures. However, the situation is different in the case of a very small crystallite, nanocrystal or microcrystal, because the exciton coherence length is limited to the size of the crystallite and thus because the exciton can easily be coherently delocalized throughout the crystallite. Therefore, excitonic superradiance has only been observed for microcrystals and/or nanocrystals of high quality—review articles are available in [27,28].

Nikl et al. studied picosecond decay kinetics for the $CsPbCl_3$ microcrystals [3] dispersed in CsCl crystals and for the $CsPbBr_3$ microcrystals [7,8] in CsBr crystals. They found very short radiative decay times of free excitons in the range 20–40 and 90–300 ps for the $CsPbCl_3$ and $CsPbBr_3$ microcrystals, respectively, both at 10 K. They ascribed the short decay times to excitonic superradiance in the microcrystals. It is quite reasonable to assume that the superradiance-induced very rapid radiative decay causes a very high luminescence yield of the confined excitons. The extremely enhanced luminescence for the microcrystalline state of the present films is suggestive of excitonic superradiance observed in an alternative experiment, although direct measurements of decay kinetics and its microcrystal-size dependence are necessary to reach the definite conclusion. To say the least, the microcrystalline films of $CsPbCl_3$ and $CsPbBr_3$ provide alternative, extremely densely microcrystal-dispersed specimens for studying mesoscopic enhancement of optical properties of microcrystals.

Finally we note that the microcrystalline state of $CsPbX_3$ ($X = Cl$, Br) films prepared by the present method show intense stimulated emission under high-power excitation, in favor of the assumption of excitonic superradiance. For example, under 1 MW/cm^2 excitation using an N_2 laser (photon energy, 3.68 eV), the luminescence at 77 K for the microcrystalline state of a $CsPbCl_3$ film of 78 nm thickness was almost completely dominated by stimulated emission, due to free exciton–free exciton inelastic collisions, even for the perpendicular-to-film emission, not film-edge emission, in great contrast to the case for the polycrystalline state, where no stimulated emission was observed at 77 K under the same excitation, as well as to the case [29] of single crystals, where stimulated emission at 77 K has been evidenced only for near-crystal-edge emission; this latter case means that a long optical path within the irradiated crystals is required in order to evidence the occurrence of the stimulated emission. Details concerning the stimulated emission will be reported elsewhere [30], including the results of lasing experiments as well as gain measurements.

5. Conclusion

Highly photo-luminescent thin films of $CsPbCl_3$ and $CsPbBr_3$ were prepared by crystallization from the amorphous phase into several different crystalline states. In situ photoluminescence measurements were carried out for every state using the same starting amorphous films, to directly compare the luminescence efficiencies between the different crystalline states. The luminescence spectrum of the $CsPbCl_3$ films consistently exhibited a single, free-exciton emission band for every state without showing trapped-exciton bands, unlike the case for single $CsPbCl_3$ crystals. For the $CsPbBr_3$ films, the luminescence spectra were characterized by free-exciton emission appearing as a main band, and only a weak trace of emission due to trapped excitons was observed at the low-energy tail part of the main band, in contrast to the case of bulk $CsPbBr_3$ crystals. In both films, the microcrystalline state showed more than an order of magnitude stronger free-exciton emission than the polycrystalline state, as well as than bulk single crystals. The extreme radiance was suggestive of excitonic superradiance observed in an alternative experiment. The extremely densely microcrystal-dispersed thin films of $CsPbCl_3$ and $CsPbBr_3$, which are characterized by intense photoluminescence, are fascinating when considering application in opto-electronic micro-devices.

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