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Optical properties of $(C_6H_5C_2H_4NH_3)_2PbI_{4-x}Br_x$ ($x = 0$–4) mixed-crystal doped PMMA films

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In recent years, considerable attention has been focused on nano-structured materials formed via self-assembly process. Self-assembly is generally defined as the spontaneous organization of molecules through noncovalent interactions without external intervention, such as hydrogen bonding, Van der Waals force and π-π interaction [1]. Lead-halide based organic-inorganic layered perovskite compounds, with the general formula $(RNH_3)_2PbX_4$ (R: C_nH_{2n+1}-, $C_6H_5C_nH_{2n}$-, X: halogen), are one of the typical self-assembled compounds consisting of lead halide sheets which are sandwiched by organic sheets [2, 3]. In these compounds, lead halide layers act as well layers and organic ones act as barrier layers. Since the lead halide well layers have higher dielectric constant and smaller band-gap than the organic barrier layers, these compounds show pronounced excitons with substantially large binding energy as large as a few hundreds meV [4–6]. As a result, these compounds exhibit interesting optical properties such as photoluminescence (PL) [5, 6], electroluminescence (EL) [7–9] and large optical nonlinearlity [10]. As far as optical properties are concerned, these compounds have considerable potentials for optoelectronic applications. However one difficulty in practical applications is poor stability against photo-irradiation, thermal-annealing and moisture [11]. In the previous study, marked improvement of thermal- and photo-stability was achieved for $(C_6H_5C_2H_4NH_3)_2PbI_4$ doped PMMA films [12]. From the view point of optical properties of exciton, mixed-halide crystals doped PMMA films are important, because the halogen ion replacement made it possible to control the exciton bands continuously towards visible (2.4 eV) to ultraviolet (3.6 eV) regions [13]. In this study, thin films of $(C_6H_5C_2H_4NH_3)_2PbI_{4-x}Br_x$ ($x = 0$–4) doped PMMA were fabricated and their optical properties were investigated.

Thin films of $(C_6H_5C_2H_4NH_3)_2PbI_{4-x}Br_x$ ($x = 0$–4, denoted as PhE-$PbI_{4-x}Br_x$ hereafter) doped PMMA were deposited on a SiO_2 glass substrate by a conventional spin-coating method as reported previously [12]. Poly(methyl methacrylate) (PMMA), stoichiometric amount of $C_6H_5C_2H_4NH_3X$ and PbX_2 (X = I and Br) were dissolved into N,N-dimethyl formamide [DMF, $HCON(CH_3)_3$]. The concentration of PMMA in DMF was 10 wt% and the weight ratio of PhE-$PbI_{4-x}Br_x$ to PMMA was fixed at 0.05. Using these precursor solutions, spin-coating was carried out at 2000 rpm for 60 s. After spin-coating, these films were subsequently dried at 60 °C for 1 day and then annealed at 125 °C for 10 min. Optical absorption spectra of films on glass substrate were recorded using a conventional Vis-UV spectrophotometer (JASCO V-570) at room temperature. The incident light beam was kept perpendicular to the sample surface. Temperature dependence of PL and photoluminescence excitation (PLE) spectra were measured from 90 to 373 K using a spectrophotometer equipped with cryostat (Perkin Elmer, LS-50B). A monochromated Xe lamp was used as an excitation source. The PL from samples was introduced into the monochromator and detected by a photomultiplier.

Fig. 1 shows the (a) Vis-UV optical absorption and (b) PL spectra of PhE-$PbI_{4-x}Br_x$ doped PMMA films measured at room temperature. As shown in Fig. 1a, these films exhibited narrow and intense absorption bands between 2.43 and 3.10 eV. These absorption bands have been attributed to excitons formed in the inorganic layers by the transition from $Pb^{2+}(6s)$ to $Pb^{2+}(6p)$ orbital [5]. Strong PL from the exciton band was also observed at 2.40 eV ($x = 0$) and at 3.07 eV ($x = 4$). As seen in this figure, it is apparent that both the exciton absorption and PL bands shift towards higher photon energy region with increasing the x value in the films. These results led us to strongly support the fact that PhE-$PbI_{4-x}Br_x$ mixed-halide crystals were successfully precipitated into the PMMA matrix by using spin-coating and subsequent annealing technique.

Peak positions of the exciton absorption and PL bands of PhE-$PbI_{4-x}Br_x$ doped PMMA films as a function of Br contents, x are plotted in Fig. 2a. The peak position of the exciton absorption bands shifted linearly towards high photon energy with increasing the Br content, x in the films. It is generally accepted that the fundamental optical transition in $(RNH_3)_2PbX_4$ (X: halogen) is similar to that of PbX_2 [5, 14, 15]. In PbX_2, the top of the valence bands is composed of Pb(6s) orbital hybridized with X(np) orbital and the bottom of the conduction bands has Pb(6p) character. Therefore, the mixing effect of Br(4p) orbital into Pb(6s) + I(5p) strongly correlated to the band gap of PhE-$PbI_{4-x}Br_x$ mixed-halide crystals. Consequently, the linearity change in the exciton absorption band observed here suggested that the band structure of PhE-$PbI_{4-x}Br_x$ mixed-halide crystals was successfully achieved by replacing I with Br. As to the PL bands, continuous shift towards high photon energy was also observed, but PL bands located lower photon

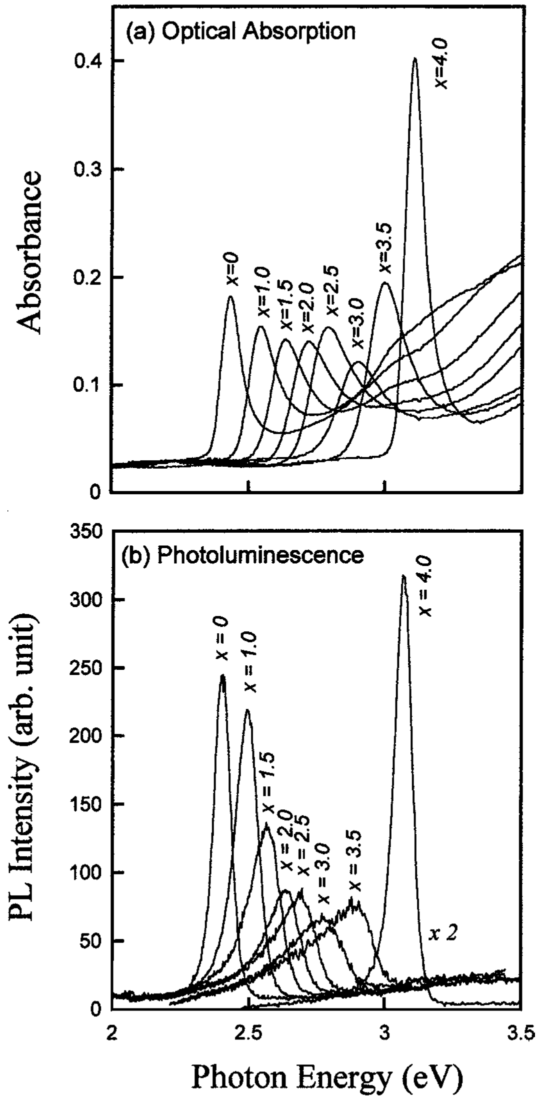

Figure 1 Room temperature (a) optical absorption and (b) photoluminescence spectra of $(C_6H_5C_2H_4NH_3)_2PbI_{4-x}Br_x$ doped PMMA films.

energy than the exciton absorption bands in each case. Fig. 2b shows full-width at half-maximum (FWHM) of the exciton absorption and PL bands of PhE-$PbI_{4-x}Br_x$ doped PMMA films. The FWHM value of the absorption band varied from 83 to 236 meV, and the maximum FWHM value was observed at $x = 2.0$. The FWHM value of the PL bands also increased with increasing the Br content, x. However, the maximum FWHM value was observed at $x = 3.5$. In Fig. 2c, Stokes shift of PhE-$PbI_{4-x}Br_x$ doped PMMA films is plotted as a function of Br content, x. The Stokes shift was estimated from the difference of the peak position at maximum intensity between the exciton absorption and PL bands. Stokes shift of PhE-PbX_4 doped PMMA films showed 30 meV for both cases of $X = \text{I}$ and Br. This value was relatively large compared with that of polycrystalline PhE-PbX_4 films on glass substrates, 8 meV ($X = \text{I}$) and 9 meV ($X = \text{Br}$) [13]. In PhE-$PbI_{4-x}Br_x$ doped PMMA films ($0 < x < 4$), Stokes shift increased with increasing the Br content, x and showed maximum value of 160 meV at $x = 3.5$. By comparison with Fig. 2b and c, the FWHM value of the PL band and Stokes shift showed similar behavior against the Br content, x. Generally there exist two different types of PL from excitons, called as free-exciton emission and as self-trapped exciton (STE) emission. The former is a sharp emission with small Stokes shift and the latter is broad PL with large Stokes shift. In PhE-$PbI_{4-x}Br_x$ doped PMMA films ($x < 4$), therefore, the types of PL turned to STE process from free-exciton emission by replacing I with Br. In our previous study, both the impurity induced STE and lattice strain induced STE are possible mechanism for the PL properties [13]. Relatively large Stokes shift observed for PhE-PbX_4 doped PMMA films can probably be attributed to defects or lattice strains formed in PhE-PbX_4 precipitates.

Fig. 3 shows the integrated PL intensity from the exciton as a function of the inverse temperature. In PhE-PbX_4 ($X = \text{Br}$ and I) doped PMMA films shown in Fig. 3a, the PL intensity gradually decreased as the temperature rises to 170 K. At higher temperature than 250 K, the PL intensity decreased exponentially as $\exp(-E_a/k_BT)$ (k_B: Boltzmann constant) with $E_a = 170 \pm 20$ meV for $X = \text{I}$ and 350 ± 50 meV for $X = \text{Br}$. The activation energy obtained here is comparable to the binding energy of exciton of polycrystalline PhE-PbI_4 (220 meV) and PhE-$PbBr_4$ (430 meV), respectively [6, 16].

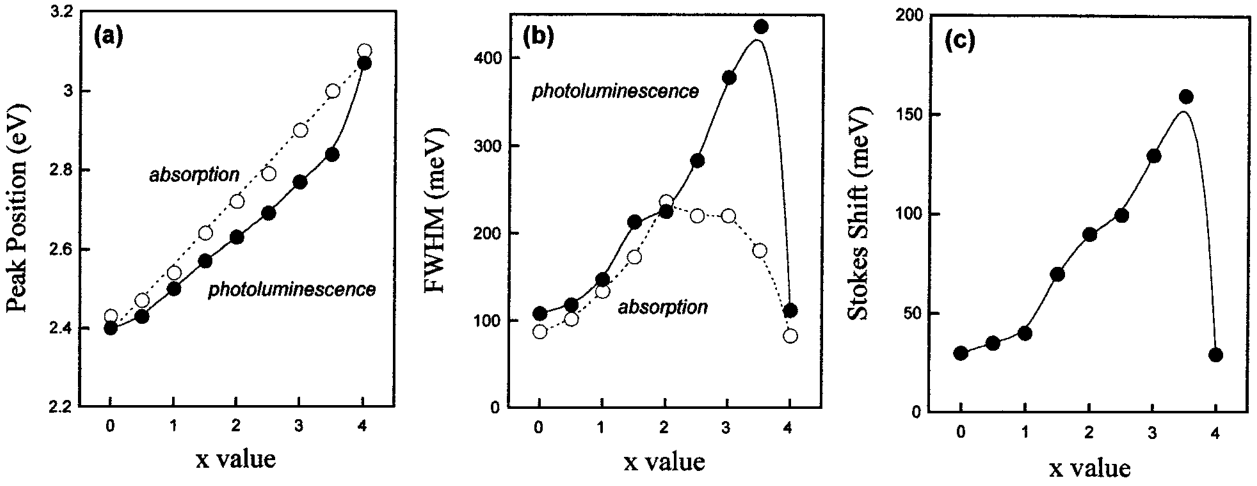

Figure 2 Changes in the (a) peak position, (b) full-width at half-maximum (FWHM) of the exciton absorption and PL bands and (c) Stokes shift of $(C_6H_5C_2H_4NH_3)_2PbI_{4-x}Br_x$ doped PMMA films as a function of Br content, x.

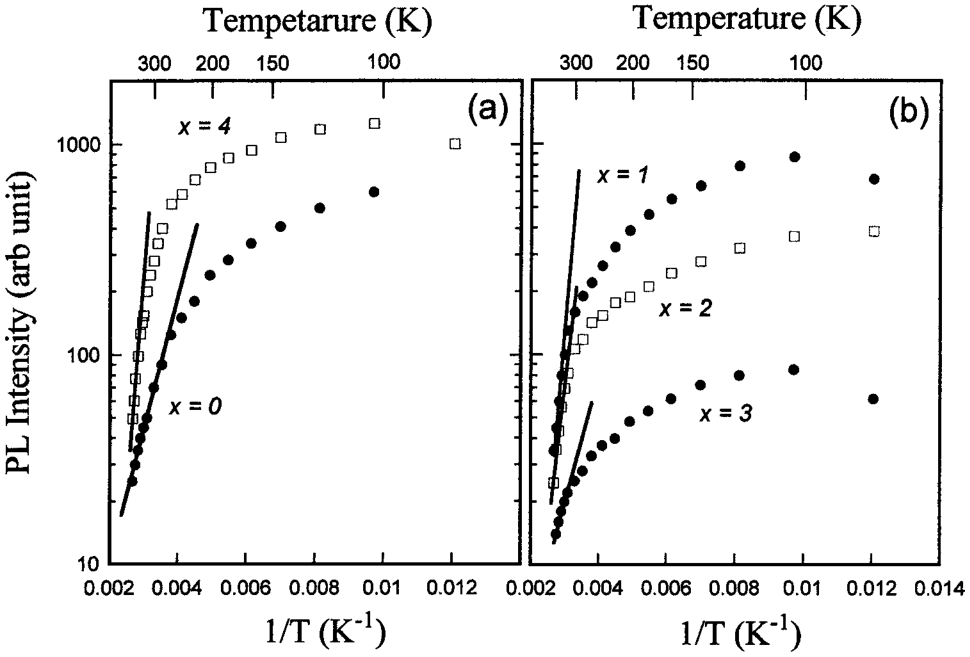

Figure 3 Integrated PL intensity of the exciton bands of $(C_6H_5C_2H_4NH_3)_2PbI_{4-x}Br_x$ doped PMMA films as a function of inverse temperature.

There is general consensus that the thermal quenching of PL from the exciton is attributed to the ionization, and therefore, these values can probably be regarded as the binding energy of exciton, E_b. In PhE-$PbI_{4-x}Br_x$ doped PMMA films shown in Fig. 3b, gradually decrease in the PL intensity was also observed with increasing temperature up to 250 K. The PL intensity decreased exponentially as $\exp(-E_a/k_BT)$ with $E_a = 265 \pm 20$ meV ($x = 1$), 250 ± 20 meV ($x = 2$) and 130 ± 20 meV ($x = 3$), respectively. At present, we are not able to find the relationship between the binding energy of exciton and Br content, because the types of PL changed from free-exciton emission to STE process by replacing I with Br, as mentioned before.

In this study, thin films of $(C_6H_5C_2H_4NH_3)_2$-$PbI_{4-x}Br_x$ ($x = 0$–4) doped PMMA were fabricated by using spin-coating and subsequent annealing technique, and their optical properties were investigated. PhE-$PbI_{4-x}Br_x$ ($x = 0$–4) precipitates were successfully formed into a PMMA matrix. These films showed clear exciton absorption and photoluminescence at room temperature. Although the types of emission changed from free-exciton emission to self-trapped exciton (STE) emission by replacing I with Br, these films showed large activation energy of photoluminescence. More detailed studies on the optical properties of PhE-$PbI_{4-x}Br_x$ mixed-halide crystals doped in electrically conductive polymers and UV light emissive polymers are being carried out.

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