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Optical properties of $CH_3NH_3PbX_3$ (X = halogen) and their mixed-halide crystals

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Thin films of microcrystalline $CH_3NH_3PbX_3$ (X = halogen) as well as their mixed-halide crystals were fabricated by the spin-coating technique, and their optical properties were investigated. X-ray diffraction investigation revealed that $CH_3NH_3PbBr_{3-x}Cl_x$ ($x = 0$–3) were successfully formed on glass substrate self-assembly and oriented with the a-axis. Owing to due to their large exciton binding energy, these materials showed clear exciton absorption and free-exciton emission in the visible region at room temperature. Replacing Br with Cl made it possible to control the band structure of these materials. As a result, the peak position of the exciton band shifted continuously towards blue region with increasing the Cl content in the films. © *2002 Kluwer Academic Publishers*

1. Introduction

Recently, crystals of $(RNH_3)_2PbX_4$($R = C_nH_{2n+1}$- or $C_6H_5C_2H_4$-) and $CH_3NH_3PbX_3$ (X = halogen) families have been growing interest because of their unique optical and electrical properties, such as photoluminescence, electroluminescence, large third-order optical nonlinearity and so on [1–4]. The former compounds correspond to two-dimensional layered perovskite structures. They consist of lead halide semiconductor layers sandwiched between organic insulator layers [5, 6]. The inorganic well layer has higher dielectric constant and smaller bandgap than the organic barrier layer in these compounds. The exciton binding energy, therefore, is significantly enhanced due to the dielectric and quantum confinement effects [7]. The latter family, on the contrary, corresponds to three-dimensional cubic perovskite structures which lack organic barrier layers [6]. As a result, the exciton binding energy of $CH_3NH_3PbX_3$ is much smaller than that of $(RNH_3)_2PbX_4$. For example, the exciton binding energy of $(RNH_3)_2PbI_4$ is 170 to 330 meV, while it is only 45 meV for $CH_3NH_3PbI_3$ [8, 9]. At this point, however, there are only few investigations about optical properties of cubic perovskite compounds and their mixed-halide crystals: $CH_3NH_3PbX_{3-y}$ X'_y (X and X' = halogen) [10]. In this paper, thin films of microcrystalline $CH_3NH_3PbX_3$ and their mixed-halide crystals were synthesized, and its optical properties were investigated.

2. Experimental procedure

Thin films (*ca.* a few ten nanometers in thickness) of microcrystalline $CH_3NH_3PbBr_{3-x}Cl_x$ ($x = 0$–3) were prepared on SiO_2 glass substrate by the spin-coating technique as reported previously [11]. The 0.5 wt% of N, N-dimethylformamide [DMF, $HCON(CH_3)_2$] solutions were used in this study. These films were characterized by X-ray diffraction spectra (Rigaku, RINT2500 X-ray diffractometer) using monochromated Cu K_α radiation (40 kV, 60 mA). Optical absorption (OA) spectra (JASCO, V-570 spectrophotometer) and photoluminescence (PL) spectra (Perkin Elmer LS-50B spectrophotometer) were recorded at room temperature. Note that the incident light beam was kept perpendicular to the substrate surface for the OA measurement. For the PL measurement, a monochromated Xe lamp was used as an excitaton source. The sample was irradiated by a monochromated light beam at an angle of 60°.

3. Results

Fig. 1 shows the typical X-ray diffraction pattern of the $CH_3NH_3PbCl_3$ film on glass substrate. As seen in this figure, sharp (h 0 0) ($h = 1$–3) diffraction peaks were observed at angles of 15.51°, 31.36° and 47.89°. Similar XRD patterns were also obtained for the $CH_3NH_3PbBr_{3-x}Cl_x$ films. This evidence led us to suggest that the films fabricated on glass substrate were single phase and were highly oriented with the a-axis self-assembly. The inset of Fig. 1 shows the lattice parameter of the a-axis of the $CH_3NH_3PbBr_{3-x}Cl_x$ films as a function of Cl content. The lattice parameter decreased monotonously with increasing Cl content, which gave us strong support that the mixed crystals were successfully formed on glass substrate by the present technique.

OA spectra of the $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_{3-x}Cl_x$ films recorded at room temperature are shown in Fig. 2. In the OA spectrum of $CH_3NH_3PbI_3$ film, plotted as dotted line, there are no obvious excition absorption bands. This is due to the comparable exciton binding energy of $CH_3NH_3PbI_3$ (45 meV) than that of k_bT at room temperature (25 meV, k_b = Boltzmann constant, $T = 298$ K) [8].

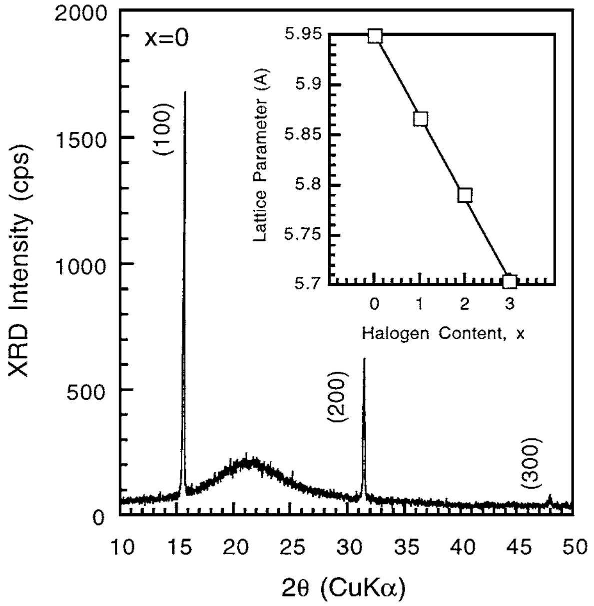

Figure 1 X-ray diffraction pattern of the $CH_3NH_3PbCl_3$ film fabricated on glass substrate. The inset shows the lattice parameter of the *a*-axis of the $CH_3NH_3PbBr_{3-x}Cl_x$ films ($x = 0$–3) as a function of Cl content.

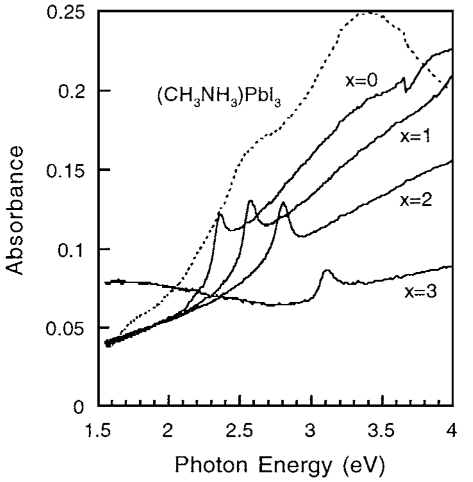

Figure 2 Room temperature Visible-UV optical absorption spectra of the $CH_3NH_3PbI_3$ (dotted line) and the $CH_3NH_3PbBr_{3-x}Cl_x$ films (solid line).

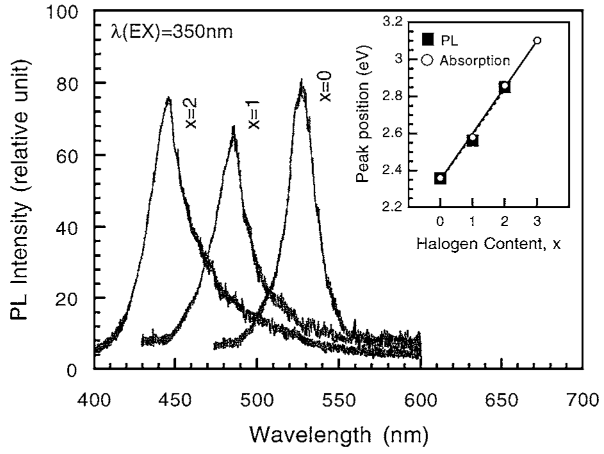

Figure 3 Photoluminescense (PL) spectra of the $CH_3NH_3PbBr_{3-x}Cl_x$ films measured at room temperature. Note that the excitation wavelength is 350 nm. The inset shows the change in the peak position of exciton absorption (open circles) and PL band (closed squares) of the $CH_3NH_3PbBr_{3-x}Cl_x$ films as a function of Cl content.

In contrast, the $CH_3NH_3PbBr_{3-x}Cl_x$ films showed clear absorption peaks. These spectra resemble that of $CH_3NH_3PbI_3$ measured at low temperature below 77 K [9]. The typical optical absorption band observed for $CH_3NH_3PbI_3$ at 77 K has already been attributed to the excition formed by the transition from Pb^{2+}(6s) to Pb^{2+}(6p) [12]. Therefore, the absorption bands observed here can also be attributed to the exciton. Regarding the peak position of the excition absorption of the films, these bands shifted continuously towards high photon energy with increasing Cl content and located at visible region.

PL spectra of the $CH_3NH_3PbBr_{3-x}Cl_x$ films measured at room temperature are shown in Fig. 3. Note that the excitation wavelength of the incident light beam is 350 nm. Although the films were three-dimensional cubic perovskite structure, PL from the exciton was observed even at room temperature. However, the PL intensity of these films was very low compared with that of two-dimensional layered perovskite compounds, $(C_6H_5C_2H_4NH_3)_2PbBr_4$ for example [11]. The inset of Fig. 3 shows the peak position of the exciton absorption and PL band of the films as a function of Cl content. As seen in this figure, these bands shifted monotonously towards high photon energy with increasing Cl content. This indicates that the band structure of $CH_3NH_3PbBr_{3-x}Cl_x$ mixed-halide crystals can be controlled by the halogen ion replacement. Moreover, the peak position of the PL band located at the same position of the exciton absorption band. Therefore, it is concluded that the PL from the $CH_3NH_3PbBr_{3-x}Cl_x$ films is consistent with the free-exciton emission.

4. Discussion and summary

In this paper, thin films of microcrystalline $CH_3NH_3PbBr_{3-x}Cl_x$ mixed-halide crystals were fabricated by using the spin-coating technique and their optical properties were characterized. XRD study revealed that the mixed-halide crystals were successfully fabricated by the present technique. Optical measurements suggested that these compounds showed clear exciton absorption and luminescence at room temperature.

As to the exciton absorption and luminescence bands, these bands were influenced by halogen ion replacement. Excitonic peak position of the $CH_3NH_3PbBr_{3-x}Cl_x$ films obtained in this study is summarized in Table I. Data from ref. [13] are also given in parenthesis. With increasing Cl content in the

TABLE I Excitonic peak position of the $CH_3NH_3PbBr_{3-x}Cl_x$ films

Composition (x)	Optical absorption (OA) (eV)	Photoluminescence (PL) (eV)
0	2.35 (2.33)	2.35 (2.32)
1	2.57	2.55
2	2.81	2.77
3	3.11 (3.12)	– (3.04)

Data from ref. [13] are given in parenthesis.

films, as indicated in Table I, both the exciton absorption and luminescence bands shifted continuously towards high photon energy region. With regards to the optical transition in $[PbX_6]^{2-}$ octahedra based compounds, such as $(RNH_3)_2PbX_4$ ($R = C_nH_{2n+1}$- or $C_6H_5C_2H_4$-) and $CH_3NH_3PbX_3$ (X = I, Br and Cl), the top of the valence band is composed of the Pb(6s) orbital hybridized with the X(np) ($n = 3$–5) orbital, and bottom of the conduction band has mainly Pb(6p) character [12, 14]. For $CH_3NH_3PbBr_{3-x}Cl_x$ mixed-halide crystals, therefore, the degree of hybridization of the Cl(3p) orbital into the Pb(6s) + Br(4p) orbital influences the excition band since the energy level of Cl(3p) is relatively low compared with that of Br(4p).

The exciton binding energy of some lead halide-based organic-inorganic hybrid compounds has estimated by using optical absorption spectra. In the case of $(RNH)_3PbX_4$, the exciton binding energy is about 220 meV (X = I, $R = C_6H_5C_2H_4$), 430 meV (X = Br, $R = C_6H_5C_2H_4$) and 550 meV (X = Cl, $R = C_{10}H_{21}$), respectively [10, 15]. For $CH_3NH_3PbX_3$, the 45 meV (X = I) and the 150 meV (X = Br) exciton binding energy has been reported [8, 9, 15]. With decreasing atomic number of halogen, the exciton binging energy increased in both cases. The increase in the exciton binding energy by changing halogen can be consistent with ionic character of the Pb-X bond in $[PbX_6]^{2-}$ octahedra. From these references, therefore, the exciton binding energy of $CH_3NH_3PbBr_{3-x}Cl_x$ mixed-halide crystals should be substantially larger than that of K_bT at 298 K. Consequently, these mixed-halide crystals showed clear exciton absorption and luminescence at room temperature.

A more detail study for the mixed-halide crystals, low temperature absorption and luminescence for example, is currently underway and will be reported elsewhere.

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