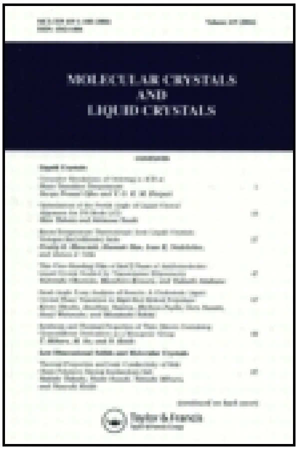

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Effect of Cation-Mixing on Photo Luminescence of PbI_2-based Organic/Inorganic Perovskite Thin Films

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The influence of cation-mixing on photo luminescence(PL) of PbI_2-based organic/inorganic perovskite thin films expressed by chemical formula $(C_6H_9C_2H_4NH_3)_2PbI_4$ was investigated. Cation-mixing to inorganic layer by addition of ZnI_2 or CdI_2 did not affect the character of exciton in the films because all optical spectra of the $(CHE)_2(Pb,M)I_4$ films were the same profile. Dependence of PL intensity at 2.4eV of photon energy($PL_{2.4}$) on inorganic layer compositions was changed by kind of additive cation. In the case of Zn addition, $PL_{2.4}$ was uniformly decreased with an increase of additive amounts of Zn. On the other hand, $PL_{2.4}$ of the $(C_6H_9C_2H_4NH_3)_2(Pb, Cd)I_4$ films remarkably increased with increasing of Cd concentration up to 20mol%Cd. It was obvious that cation-mixing with Cd is effective to advance the optical properties of the $(C_6H_9C_2H_4NH_3)_2PbI_4$ films. Relationships between $PL_{2.4}$ and layer structure of the films were discussed according to structural analysis using XRD.

Keywords cation-mixing; optical properties; organic/inorganic perovskite films; crystalline structure

INTRODUCTUION

PbI_2-based organic/inorganic perovskite compounds expressed by the chemical formula $(RNH_3)_2PbI_4$ self-organize a super lattice structure naturally. Using the compounds, it is easy to fabricate semiconductor thin films with quantum-well structure where an inorganic semiconductor layer of PbI_4 is sandwiched by organic barrier layers of RNH_3. These films show strong exciton absorption even at room temperature because of quantum-confinement effects due to their low-dimensional structure. Moreover, it is possible to design the semiconductor films by chemical modification on the composites of metal halide and organic ammonium. From these attractive properties, the organic/inorganic perovskite compounds are expected to use as light-emitting devices. The interesting materials, however, are not put any practical use currently caused by so low luminous efficiency of them at room temperature. To improve the optical propereties, effect of anion-mixing[1] or introduction of organic chromophores[2] were investigated. But there is not enough knowledge about chemical design of the inorganic layers now.

In this paper, effects of cation-mixing on photo luminescence of PbI_2-based organic/inorganic perovskite thin films were studied.

EXPERIMENTAL PROCEDURE

$C_6H_9C_2H_4NH_2$(CHE) was used as an organic ammonium layer in this study. After reacting CHE with HI and recrystallizing, $C_6H_9C_2H_4NH_3I$(CHEI) was gained. PbI_2(97%) was used as a matrix metal halide of an inorganic layer. ZnI_2(99.9%) and CdI_2(99.9%) were adopted to perform cation-mixing. DMF solutions with organic/inorganic materials and different additive amounts of M(M= Zn, Cd) were prepared. $(CHE)_2(Pb, M)I_4$ (M= Zn, Cd) thin films were fabricated from these solutions by spin-coating method (8000rpm) on quartz glass substrates. Absorption and PL spectra of the thin films were measured. Structures of them were analyzed using XRD.

RESULTS

All absorption spectra of the $(CHE)_2(Pb,M)I_4$ films were the same profile with a strong exciton absorption at 2.4eV. It came to clear that the cation-mixing should have no influence on the characteristics of exciton in the films. The absorbance determined at 2.4eV decreased uniformly with increasing MI_2 concentration of the films. And, all PL spectra of the films were also the same profile as shown in Fig.1. Relationships between $PL_{2.4}$, where $PL_{2.4}$ is PL intensity at 2.4eV, and MI_2 concentration of the $(CHE)_2(Pb,M)I_4$ films were shown in Fig.1. In the case of ZnI_2 addition, no cation-mixing effect was gained because $PL_{2.4}$ decreased uniformly with an increase of ZnI_2 concentration. On the other hand, $PL_{2.4}$ of the $(CHE)_2(Pb,Cd)I_4$ films increased with increasing the amount of CdI_2 up to 20 mol%Cd. Then after passing through the maximum, it decreased contrarily. From the result, remarkable cation-mixing effect was obtained by addition of Cd ion. It is therefore evident that cation-mixing is effective to improve the optical properties of the $(CHE)_2PbI_4$ film.

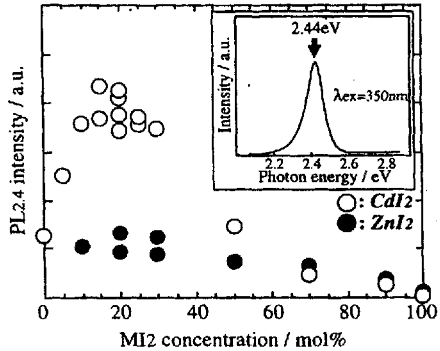

FIGURE 1 Dependence of $PL_{2.4}$ of $(CHE)_2(Pb, M)I_4$ thin films on MI_2 concentration at room temperature.

XRD profiles of the $(CHE)_2(Pb,M)I_4$ films were shown in Fig.2. It was apparent that the structures of the films were changed by kind of additive cation. In the case of Zn addition, phase separation should come about in the $(CHE)_2(Pb,Zn)I_4$ films because of some characteristic peaks observed in the films. In contrast the same diffraction pattern, which

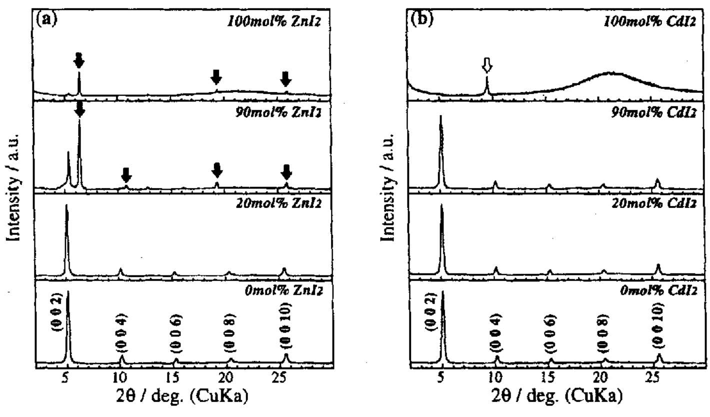

FIGURE 2 X-ray diffraction patterns of (a) $(CHE)_2(Pb, Zn)I_4$ and (b) $(CHE)_2(Pb, Cd)I_4$ thin films. The allows point out peaks of secondary phase in the films.

possessed only peaks assigned to (0 0 2*l*) was obtained in all of the $(CHE)_2(Pb,Cd)I_4$ films. It was suggested that the films were highly oriented the c-axis perpendicular to the substrate surface and the PbI_2 made solid solution layers with CdI_2 in the films.

DISCUSSIONS

It was thought that the difference of dependence of PL2.4 on inorganic layer composition was attributed to structures of the films. Although Zn and Cd are congener and dissociate into same valence ion, the crystalline structure of the metal halides made up of Zn is distinct from that composed of Cd. ZnI_2 is the HgI_2 type structure, which Zn^{2+} ions exist interlayer of the FCC close-packing of I^- ions. Coordination number of Zn^{2+} is 8. PbI_2 and CdI_2 have CdI_2 type structure. M'^{2+}(M'= Pb, Cd) ions locate voids of octahedra formed by the HCP close-packing of I^- ions. M'^{2+} coordinates 6 anions. On the basis of that difference, Zn^{2+} would not be introduced into the octahedra consist of Pb^{2+} and I^-, and ZnI_2 and CHEI make another compound. As the result, phase separation might be come about. On the other hand, the solubility limit of CdI_2 into PbI_2 is very large since both of them have the same structure. But, from XRD measurements the effect of CdI_2 introduction on the structure of the films was not so large, that is, the perovskite layer structure is determined by PbI_2 and CHEI. It was inferred that the effect of cation-mixing with Cd ion was to relieve the structural strain by substituting the smaller size cation, Cd^{2+} (r_{Cd2+}=0.97Å), for Pb^{2+} (r_{Pb2+}=1.20Å), and to form more coherent structures with the organic layers and the inorganic layers in the films, consequently.

CONCLUSIONS

Effect of cation-mixing on optical properties of PbI_2-based organic/inorganic perovskite thin films was investigated. As results, it was become clear that cation-mixing using a cation which formed solid solution with PbI_2 was effective to increase PL intensity of the films.

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