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Time-resolved photoluminescence studies on localization effects in orthorhombic phase of $CH_3NH_3PbI_3$ perovskite thin film

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ABSTRACT

We present the localization effects in orthorhombic phase of $CH_3NH_3PbI_3$ perovskite materials by temperature-dependent photoluminescence and time-resolved photoluminescence. Our investigations indicate that the tetragonal inclusions in the orthorhombic phase of $MAPbI_3$ at low temperature are the main reason for the formation of localization states with a depth of about 22.3 meV. The coexistence of the tetragonal and orthorhombic phases also results in an abnormal behavior of luminescence intensity from 12 to 80 K. The detailed understanding of luminescence characteristics upon the orthorhombic phase in $MAPbI_3$ at low temperature can expand ideally the application fields of perovskite materials.

1. Introduction

Recently, methylammonium lead iodide perovskite material $CH_3NH_3PbI_3$ (named $MAPbI_3$) have attached much attention due to its novel optical and electronic properties, such as a direct bandgap with high absorption coefficients over the visible to near-infrared range, small exciton binding energies and long-range balanced charge carrier diffusion lengths [1–3]. It is complicated that the $MAPbI_3$ exhibits an orthorhombic phase (space group: *Pnma*) at low temperature, and the orthorhombic phase transforms into a tetragonal phase (space group: *I*4/*m*) above about 160 K, and the cubic phase (space group: *Pm*3*m*) can be observed when the temperature is higher than about 330 K [4,5]. Furthermore, the bandgap structure of $MAPbI_3$ depended on the crystal phase at different temperatures could make $MAPbI_3$ being a potential candidate for optoelectronic device applications [6,7].

Compared to the intensive reports on the charge carrier dynamics of $MAPbI_3$ with tetragonal or cubic phase for enhancing the efficiencies of perovskite solar cells [8,9], the photophysical properties of $MAPbI_3$ belonging to orthorhombic phase at low temperature have been less investigated. Recent studies have indicated that the free carriers are photoexcited at room temperature whereas the Wannier–Mott excitons are dominant at low temperature [8–10], which induce the different natures of recombination channels between the different crystal phases. So far, several reports present that a broad PL signal composited by multiple peaks of $MAPbI_3$ at low temperature could be arose from tetragonal inclusions in the orthorhombic phase of $MAPbI_3$ [11,12], and means the existence of localized states including bound excitons [6,13,14]. Although the localization characteristics of photoexcited electrons and holes in tetragonal or cubic phase of $MAPbI_3$ have been well understood [15–17], that in the orthorhombic phase of $MAPbI_3$ has not interpreted clearly yet. In this work, we investigate the temperature-dependent relations between the peak positions, integrated intensity and carrier lifetime by photoluminescence (PL) and time-resolved PL (TRPL) measurements to clarify the localization effects in orthorhombic phase of $MAPbI_3$ materials.

2. Experimental procedures

The preparation of methylammonium lead triiodide ($MAPbI_3$) perovskite layer is similar to the work published by Ko et al. [18]. The process was described as the following steps: first, 1.25 M lead iodide (PbI_2) in DMF was spin-coated onto TiO_2 nanoparticles layer at a speed of 4000 rpm for 30 s and heated at 100 °C for 30 min. In the next step, the transformation from PbI_2 to $MAPbI_3$ perovskite was completed by spin-coating onto the PbI_2 film at a speed of 4000 rpm for 30 s using an isopropanol solution with methylammonium iodide (MAI) in 30 mg/mL. Then the film was heated at 100 °C for 30 min. The SEM image displayed in the inset of Fig. 1 confirms that a uniform and dense

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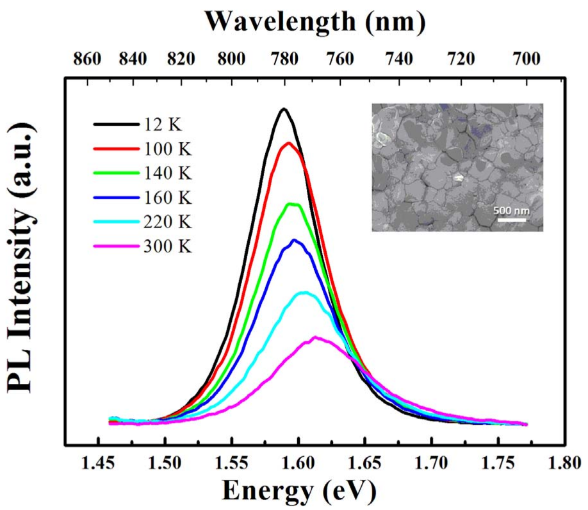

Fig. 1. PL spectra of $MAPbI_3$ thin film at selected temperatures.

$MAPbI_3$ thin film has been prepared, which is in good agreement with the presented SEM results [18,19].

The PL and TRPL were measured by using a diode laser with an excitation wavelength of 686 nm (PicoQuant). The diode laser produces light pulses with 50 ps duration and a repetition rate of 1 MHz. PL measurement was setup using a spectrometer (Zolix omni − λ 500) with a grating of 1200 grooves/mm, and detected using a photomultiplier tube (PMT). TRPL was performed using the technique of time-correlated single-photon counting (TCSPC). The luminescence decay was detected with a high-speed PMT, followed by a computer plug-in TimeHarp counting card, which was triggered with a signal from the diode laser. Janis Research Model CCS-150 and LakeShore Model 321 temperature controller were used to carry out the temperature-dependent PL spectrum.

3. Results and discussion

Fig. 1 exhibits the PL spectra of $MAPbI_3$ thin film taken at selected temperatures of 12, 100, 140, 160, 220, and 300 K. It shows the 12 K PL spectrum with a broad linewidth locating at about 1.590 eV (~ 780 nm). Interestingly, the peak energy of PL spectrum would exhibit an anomalous behavior of blueshift with increasing the temperature, which is contrary to typical semiconductors. The PL peak positions as a function of temperature are replotted in Fig. 2, which are derived from the average PL data for three different films prepared by the same process. The blueshift of the PL peak positions could be separated into three distinct regions in the temperature range from 80 K to 160 K.

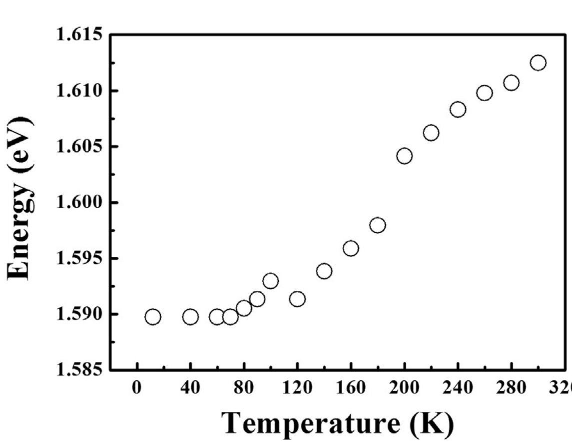

Fig. 2. Temperature dependence of PL peak position for the $MAPbI_3$ thin film.

Below 80 K, the PL peak position is temperature independent, but blueshifts with increasing temperature above 80 K. It is noticed that the PL peak position exhibits a *v*-like variation with temperature within the temperature range from 80 K to 160 K. It is noted that the exact location and depth of the v-like variation may vary with samples. For instance, Ref. 20 by Tahara et al. on $MAPbI_3$ thin film showed a shallow *v* occurring at ~ 80 K, but that of Ref. 13 by Wehrenfennig et al. on Cl-doped $MAPbI_3$ thin film depicted a more distinct v-like variation at a higher temperature. Reference 13 also showed that the occurrence of the *v*-like variation is also depending on whether the measurements were taken during heating (~ 140 K) or cooling (~ 105 K) process. The present study showed a shallow *v* more conform with that of Tahara el al. but occurring at a higher temperature of ~ 120 K. The overall consistency of our results comparing to the literature is reasonable. In addition, all studies point clearly to the existence of phase transition from orthorhombic to tetragonal with the latter being dominant at higher temperature within the 80–160 K temperature range [13,20,21]. Above 160 K, the PL signals originated from the tetragonal $MAPbI_3$ have been attributed to the near-band-edge (NBE) transition, exhibiting a continuous blueshift as temperature increased to 300 K.

So far, it can be known that the luminescence feature of $MAPbI_3$ is originated by the photoexcited electrons and holes, which behave as the free carriers at room temperature or intermediate temperature region (80–160 K), but as the excition at lower temperature [7]. Milot et al. further indicated that an increasing presence of excitons toward the lowest temperature exhibits an increasing localization response [7]. In Fig. 3(a), the 12 K PL spectrum with a broad emission band can be further decomposed into two peaks at 1.633 and 1.588 eV by fitting with Gaussian function. Referring to the recent interpretations [13,20,21], the higher and lower peaks can be assigned to the low-temperature orthorhombic and the high-temperature tetragonal phase, respectively. The coexistence of the two phases yields a complex performance of PL spectrum in the $MAPbI_3$ thin film at low temperature. The selected PL spectra at different temperatures are also decomposed into two peaks by fitting with Gaussian function, and shown in Fig. 3(b) ~(d). It is observed that the higher energy peak originated from the orthorhombic phase diminishes significantly up to 140 K and becomes negligible at 160 K. The performance can be explained by the structural phase transition from orthorhombic to tetragonal. The observation is consistent with the previous reports [13,20,21].

To observe the excitonic dynamics in the $MAPbI_3$ at low temperature, the emission energy depended PL lifetimes illustrated in Fig. 4 are carried out. As shown in the inset of Fig. 4, the PL lifetime can be obtained by fitting the luminescence decay profile monitored at the PL peak with single exponential decay function as the red solid curve. The

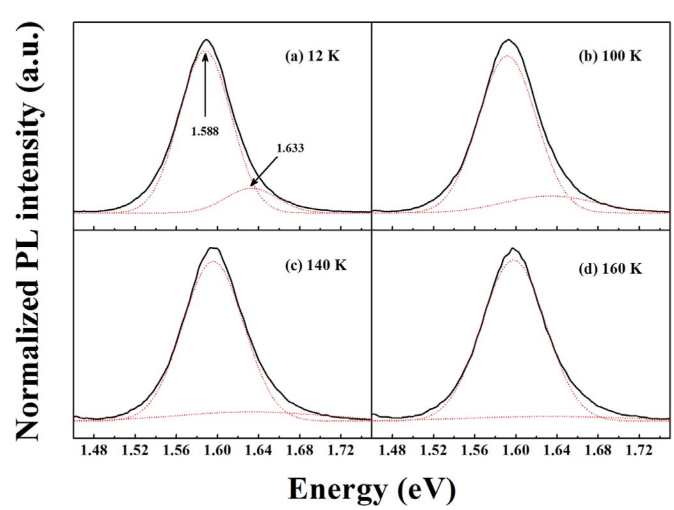

Fig. 3. PL spectra of $MAPbI_3$ thin film at (a) 12 K, (b) 100 K, (c) 140 K, and (d) 160 K. The spectra have been decomposed into two Gaussian peaks.