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Band-gap tuning of lead halide perovskite using a single step spin-coating deposition process

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ABSTRACT

In this paper, we present a study of the structural and optical properties of organic–inorganic halide-based perovskite semiconductors with band gaps varying from NIR to visible at room temperature. Thin films of nanocrystalline $CH_3NH_3PbI_3$ with different concentrations of methylammonium iodide (MAI) have been successfully deposited onto glass substrates using single step spin-coating technique. The prepared films have been characterized by X-ray diffraction, optical absorption spectroscopy and photoluminescence measurements. X-ray diffraction scans revealed that even for stoichiometric atomic concentrations of MA:Pb:I of 1:1:3, the PbI_2 phase was also present. The PbI_2 phase showed a highly textured along the (001) direction in all the prepared films, with a crystallite size in the range of approximately 30–40 nm. The optical absorbance edge of $CH_3NH_3PbI_3$ thin films is described in terms of direct transition model proposed by Tauc in the strong absorption region. The band gap of the pure PbI_2 film was calculated to be 2.40 eV, whereas the band gap of the pervoskite film with stoichiometric ionic ratio of 1:1 PbI_2 and CH_3NH_3I was calculated to be 1.46 eV, while absorption coefficient is $\sim 10^5$ cm^{-1}. Photoluminescence measurements showed a red shift in the perovskite emission with increasing the MAI concentration, confirming the correct placement of the MA ions in the perovskite crystalline structure showing the PbI_2 octahedra. Our results confirm the existence of PbI_2 phase in the highly efficient perovskite solar cells, as demonstrated in the recent publication.

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1. Introduction

In the recent years, photovoltaics have become an active field for basic research and technology. The development of new materials has opened new perspectives for the production of cost effective and highly efficient photovoltaic devices. Hybrid organic–inorganic perovskite materials, such as $CH_3NH_3PbI_3$ have attracted the attention of the photovoltaic research community due to their promising performance as light harvesting material. The advantages of these compounds have already been demonstrated as a noteworthy example of potentially useful physical properties such as nonlinear optical properties, electroluminescence, organic-like mobility, magnetic properties, conductivity, and so forth [1]. Recent studies report that solar cells based on $CH_3NH_3PbI_3$ perovskite have promising photovoltaic efficiencies reaching over 20% [2]. Within the past 5 years, hybrid organic–inorganic perovskite solar cells have been reported to achieve remarkably a high power conversion efficiency jumping from 3.8% [2] in 2009 to 20.1% [3]. The stunning high efficiencies are due to $CH_3NH_3PbI_3$ perovskite ideal direct band gap, large absorption coefficient, high carrier mobility and simple fabrication techniques [4]. One of the important properties of the organic–inorganic perovskite for their use in photovolatic cells is the possibility to tune their optical properties (e.g., band gap).

2. Experimental details

A variety of techniques have been applied to deposit $CH_3NH_3PbI_3$ perovskite thin films, for instance, single-step solution deposition, vacuum deposition, sequential deposition, vapor assisted solution process, and vacuum thermal co-evaporation.

Among these methods, the sequential deposition of spin-casting first PbI_2 followed by equimolar CH_3NH_3I resulted in highest power conversion efficiency. This procedure resulted in perovskite thin films of most homogeneous morphology and the highest thin-film coverage, leading to a high performance of (PCE). In the present work, we successfully deposited $CH_3NH_3PbI_3$ perovskite films onto glass substrates by spin-casting technique; and the microstructure of films along with optical characteristics has been discussed.

3. Results and discussion

3.1. Microstructure studies

X-ray diffraction (XRD) study was used to identify the phases and estimation of sizes of the prepared nanocrystallites. Methylammonium lead iodide ($CH_3NH_3PbI_3$) films were formed via spin coating of an equimolar mixture of CH_3NH_3I and PbI_2 precursor solutions. The appearance of strong diffraction peaks located at $2\theta = 14.38°$ and $28.59°$ (Fig. 1(a)) was observed corresponding to the planes of (110) and (220), which is good in agreement with the previous reports [5], indicating that the tetragonal perovskite structure is formed [6]. Moreover, we also find that the impurity peaks around $12.76°$, $38.81°$ and $52.53°$ can be attributed to PbI_2 crystals in these samples [7]. No impurity peaks appeared in both steps, suggesting a complete formation of PbI_2 and its controlled transformation to $CH_3NH_3PbI_3$. Based on a calculation using the Scherrer equation, the average crystallite size of $CH_3NH_3PbI_3$

Table 1
Properties of $CH_3NH_3PbI_3$ thin films with different (MAI) concentrations.

Sample no.	Required concentration of CH_3NH_3I	Crystallize size (nm)	Band gap (eV) PbI_2	Band gap (eV) $CH_3NH_3PbI_3$
1	0.0	34.85	2.40	–
2	10	35.79	2.37	–
3	20	35.79	2.34	–
4	30	35.78	2.30	–
5	40	35.77	2.22	1.70
6	50	34.85	2.14	1.65
7	60	34.84	2.04	1.62
8	70	33.96	1.91	1.59
9	80	33.23	1.85	1.55
10	90	34.91	1.81	1.53
11	100	35.78	1.72	1.46

nanocrystals is tabulated in Table 1.

3.2. Optical studies

To check the variation of optical properties in the alloyed hybrid halide perovskite, we measured the UV–visible absorption spectra of $CH_3NH_3PbI_3$ perovskites which is shown in Fig. 1(b). The absorption onset is red-shifted after substituting CH_3NH_3I, which is associated with band gap narrowing upon methylammonium ion concentrations doping. Its absorption covers a wide range of light from the visible to the near-IR region, indicating the formation of $CH_3NH_3PbI_3$ perovskite on the substrate [8]. The onset
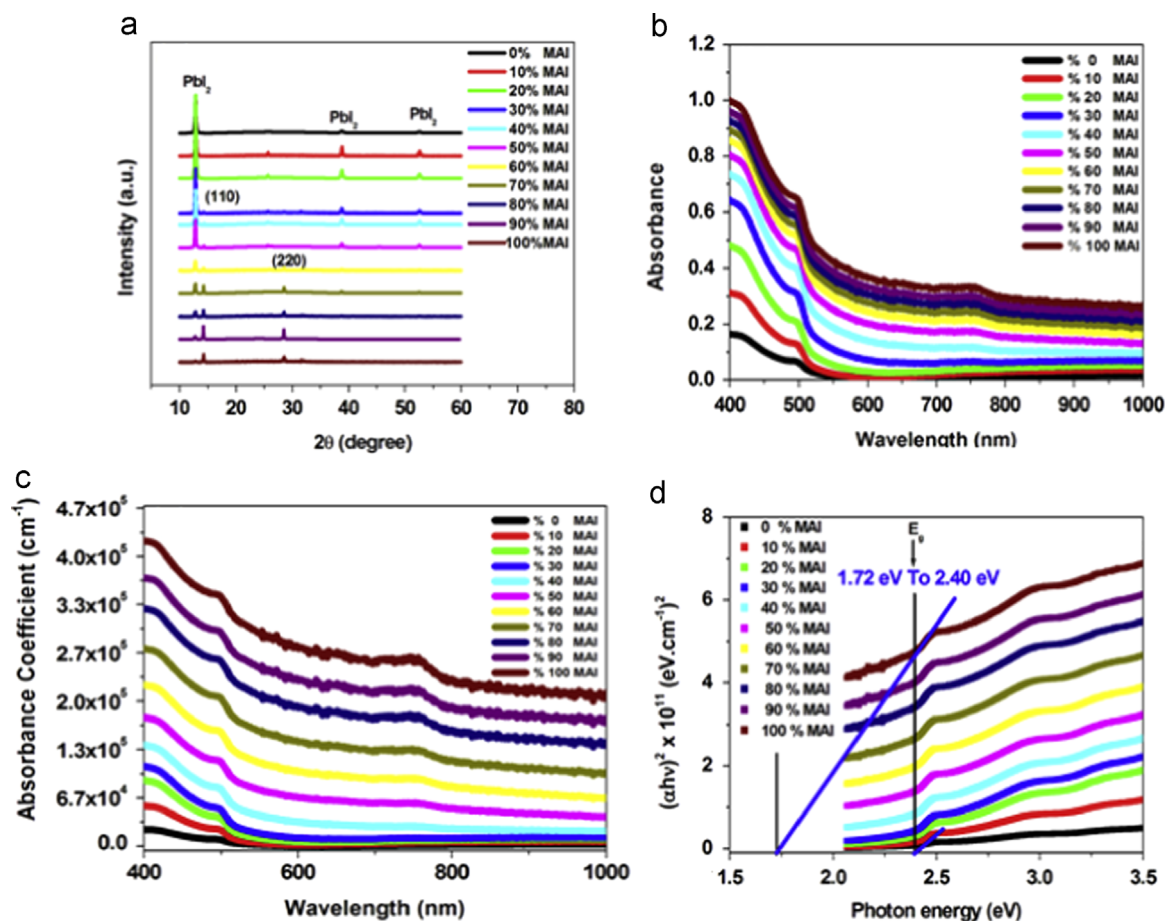
Fig. 1. (a) X-ray diffraction patterns of $CH_3NH_3PbI_3$ films with (MAI) concentrations; (b) absorption spectra of $CH_3NH_3PbI_3$ films as a function of unconverted PbI_2 phase fraction; (c) α vs $h\nu$ for $CH_3NH_3PbI_3$ films as a function of unconverted PbI_2 phase fraction; (d) plot of $(\alpha h\nu)^2$ vs $h\nu$ for $CH_3NH_3PbI_3$ thin films changes with increasing (MAI) concentrations at 500 nm.

absorption band of $CH_3NH_3PbI_3$ perovskite can be tuned from (1.46 eV) to (2.40 eV), resulting in color tunability for colorful solar cells. The first absorption peak at 760 nm corresponds to the direct band gap transition from the first valence band (VB_1) to CB while the other at 500 nm to the transition from the second valence band (VB_2) to CB [9]. The dependence of the optical absorption coefficient with the photon energy has been known to help to study the type of transition of electrons and semiconductors' bandgap energy as well. The optical absorption coefficient (α) is evaluated from the absorption spectra using the relation [10]

$$\alpha = \frac{OD}{d} \qquad (1)$$

where α is the absorption coefficient and d is the sample thickness. The calculated α for the $CH_3NH_3PbI_3$ perovskite film is 10^5 cm^{-1} at 501 nm (Fig. 1(c)), which is approximately an order of magnitude higher than that previously reported [5]. They estimated α of $CH_3NH_3PbI_3$ to be 1.5×10^4 cm^{-1} at 550 nm, while our calculation yields between 4.4×10^4 and 5.1×10^5 at 501 nm. As compared to inorganic semiconductors [11], $CH_3NH_3PbI_3$ has a very similar range of absorption coefficient. Due to the reasonably high α of $CH_3NH_3PbI_3$ in the visible region, it is possible to form a sufficiently thin yet strongly absorbing film, which is crucial to a bilayer device. According to Tauc's law, the absorption coefficient is related to band gap (E_g) as follows [12]:

$$\alpha(h\nu) = A^* \left(h\nu - E_g\right)^m \qquad (2)$$

where A^* is a constant, which does not depend on photon energy and E_g is the optical band-gap energy. Figs. 1(d) and 2(a) show the plots of $(\alpha h\nu)^2$ vs $h\nu$ for the studied thin films deposited on glass substrate at room temperature. The value of E_g for films is determined by extrapolation of the linear part of this relationship and the interception from the abscissa (at $\alpha = 0$, $E_g = h\nu$). The values of E_g for all films deposited at room temperatures are given in Table 1. We wanted to further investigate how the optical absorption of the film changes with increasing (MAI) concentrations. The pure PbI_2 film shows a band gap of 2.40 eV, consistent with the yellow color of PbI_2. As the PbI_2 film is gradually converted to the perovskite, the band gap is progressively shifted toward 1.72 eV. The deviation of MAPbI$_3$'s band gap (1.72 eV) from that of the bulk MAPbI$_3$ material (1.55 eV) could be explained by the effects of crystallite sizes and interfacial interaction of MAPbI$_3$ [13]. We can also notice the presence of a second absorption in the light absorber layer, in which the gap gradually red shifts from 1.70 eV to 1.46 eV as the CH_3NH_3I concentration is decreased from 100% to 40%. Fig. 2(b) indicates that direct band gap decreases with increase of molar concentration of the precursor material. It could be due to the increase of density of localized state in the conduction band.

3.3. Photoluminescence spectroscopy

Photoluminescence (PL) measurement is a perceptive helpful technique to explore the optical properties of semiconducting materials. Fig. 2(c) shows the PL emission spectra peaks of the MAPbI$_3$ perovskites thin films, the emission peaks of each sample
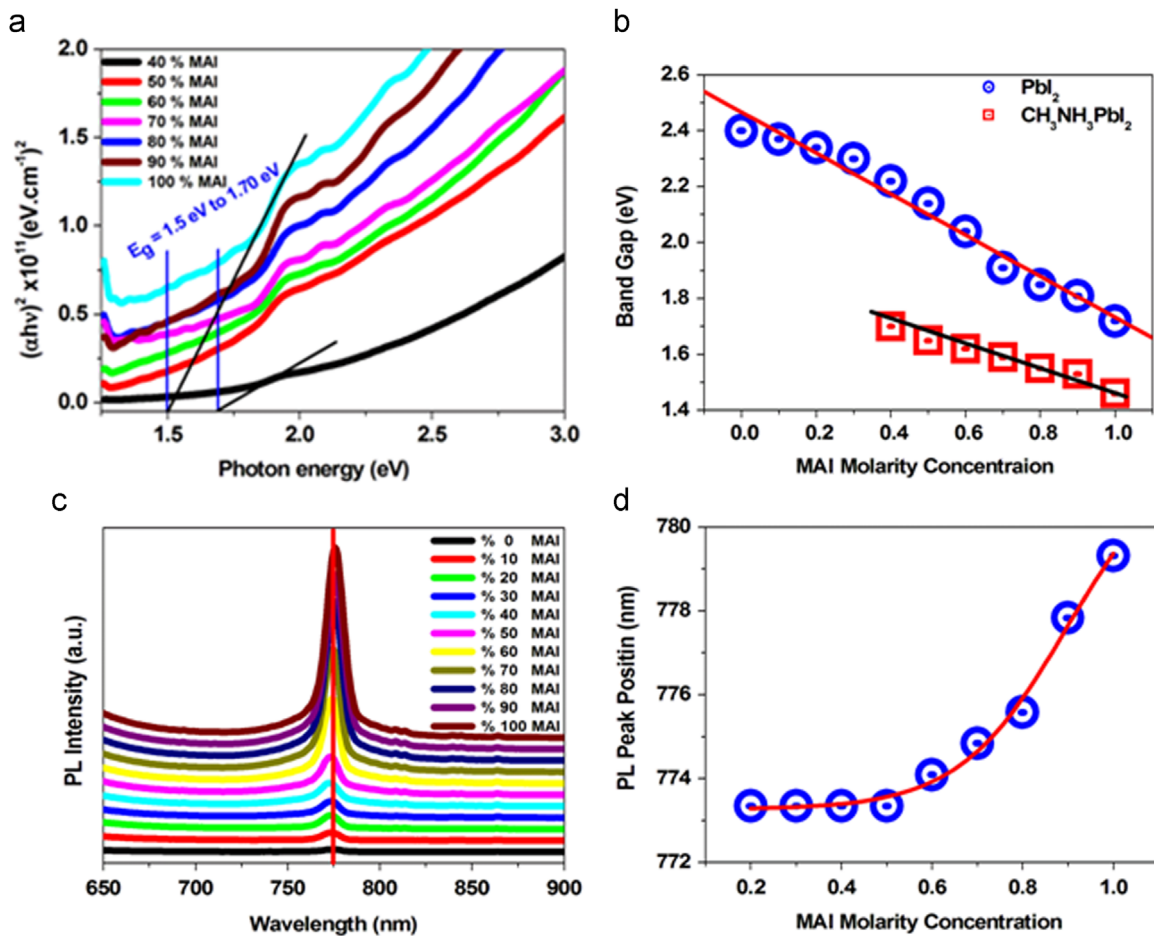

Fig. 2. (a) Plot of $(\alpha h\nu)^2$ vs $h\nu$ for $CH_3NH_3PbI_3$ thin films changes with increasing (MAI) concentrations at 770 nm; (b) variation of E_g with (MAI) concentrations for $CH_3NH_3PbI_3$ thin films; (c) emission spectra of $CH_3NH_3PbI_3$ with different (MAI) concentrations at room temperature; and (d) PL peak vs (MAI) concentrations for $CH_3NH_3PbI_3$ thin films.

exhibit a small shift to the longer wavelength side [14]. The variation of PL peak position vs (MAI) concentration is shown in Fig. 2 (d). Note that all perovskite samples were prepared and tested under the same conditions. It is surprising that such a slight variation in the composition can lead to such a remarkable difference in their PL emission intensities. The exact reason is still not clear, while we speculate that it might be associated with the orientation and vibration restraint of the PbI_2 in the perovskite lattice as the MA ions substitution rate varied, confirming the correct placement of the MA ions in the perovskite crystalline structure confirming the PbI_2 octahedra. Based on the above superior light emitting properties, $MAPbI_3$ is considered to be a promising candidate for photovoltaic applications.

4. Conclusion

In summary, the microstructure and optical properties of $CH_3NH_3PbI_3$ perovskite thin films prepared by the single step spin-coating technique have been investigated. A remarkable red shift of the absorption edge was achievable by increasing the methylammonium iodide (MAI) concentrations ($0 \leq x \leq 100$). The reported $CH_3NH_3PbI_3$ perovskite is promising for low-cost thin-film solar cells due to its tunable bandgap between 1.46 and 2.40 eV and a large absorption coefficient of over 10^5 cm^{-1}. The slightly red-shifted and homogenously broadened PL spectra exhibit features consistent with phonon coupling as the dominant spectral broadening mechanism of the emission from $CH_3NH_3PbI_3$. Our findings underline the potential of organometal halide perovskites for a wider range of optoelectronic applications beyond photovoltaic energy conversion.

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