The effect of strontium and barium doping on perovskite-structured energy materials for photovoltaic applications

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ABSTRACT

Perovskite solar cell is a novel photovoltaic technology with the superior progress in efficiency and the simple solution processes. Develop lead-free or lead-reduced perovskite materials is a significant concern for high-performance perovskite solar cell. Among the alkaline earth metals, the Sr^{2+} and Ba^{2+} are suitable for Pb^{2+} replacement in perovskite film due to fitting Goldschmidt's tolerance factor. In this study, we adopted Ba-doped and Sr-doped perovskite structured materials with different doping levels, including 1.0, 5.0, and 10.0 mol%, to prepare perovskite solar cells. Both Ba-doped and Sr-doped perovskite structured materials have a related tendency in absorption behavior and surface morphology. At 10.0 mol% doping level, the power conversion efficiency (PCE) of Sr-doped perovskite solar cells is only ∼0.5%, but the PCE of Ba-doped perovskite solar cells can be achieved to ∼9.7%. Ba-doped perovskite solar cells showed the acceptable photovoltaic characteristics than Sr-doped perovskite solar cells. Ba dopant can partially replace the amount of lead in the perovskite solar cells, and it could be a potential candidate in the field of lead-free or lead-reduced perovskite energy materials.

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1. Introduction

Recently, perovskite solar cell has attracted a lot of attention that make it become one of the promising solar power technology, because of its high power conversion efficiency (PCE), low production cost, and easy fabrication process. Miyasaka *et al.* first published the study about developing perovskite solar cell with a PCE of 3.8% [1]. Moreover, Miyasaka and Snaith *et al.* further used the mixed halide perovskite (i.e. $CH_3NH_3PbI_2Cl$) to obtain an increased PCE to 10.9% [2]. After that, many research groups devoted to studying perovskite solar cells and enhanced the PCE to 22.1% at present [3–5]. Perovskite structured materials could be the potential material in the emerging photovoltaic field due to its rapid PCE improvement. The common chemical formula for perovskite compounds is ABX_3, where "A" and "B" are two cations. Moreover, ABX_3 needs to be a six coordination number element to form octahedron as BX_6. The ratio of ionic radius between A and B is

the major factor in forming perovskite structure. The octahedrons connect with each other by element X. Every eight octahedrons form a space where A cation is located. The ratio of ionic radius between A and B is calculated by tolerance factor. Tolerance factor between 0.9 and 1.0 leads to form cubic perovskite structure. Tolerance factor between 0.7 and 0.9 leads to form orthorhombic, rhombohedral or tetragonal perovskite structure [6]. Although perovskite-structured materials show the high PCE characteristics, it still has some challenges need to overcome, such as surface morphology roughness [7–9], difficult fabricating in air environment [10], electron–hole transportation [11–13], crystal status [14–16], and charge carrier life time [17,18]. High lead concentration is harmful to human and environment. The lead built up in the body causes serious health problems such as headache, reduced sensations, aggressive behavior, difficulty sleeping, abdominal pain, and anemia [19–21]. To overcome this problem, one of the solutions is to develop the lead-free or lead-reduced perovskite structured materials.

Many types of metal ions were used to replace the Pb^{2+} to synthesize various metal-doped perovskite compounds, including Bi^{3+}, Sn^{2+}, Ca^{2+}, Cu^{2+}, Na^+, and K^+. Miyasaka *et al.* reported the research of lead-free Bi perovskite solar cell. They successfully synthesized lead-free perovskite solar cell by replacing Pb^{2+} with Bi^{3+}. Because

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of the charge difference between Pb^{2+} and Bi^{3+}, the chemical formula of perovskite changed from ABX_3 to $A_3B_2X_9$ [22,23]. The highest PCE of lead-free Bi-based perovskite solar cell only showed 1.09% [24]. Navas *et al.* reported that Ca doping may cause perovskite structure changed from tetragonal crystal system to cubic crystal system [25]. In addition, many researchers focused on Sn-doped perovskite solar cells due to no lead existence. In 2014, Hao *et al.* studied Sn-based perovskite solar cell, and the results showed that the UV–vis spectra significant shifted from 800 to 1000 nm and its narrow band is ~1.1 eV. However, the PCE of Sn-based perovskite solar cell is still not higher than the Pb-based perovskite solar cell [26]. Hao *et al.* reported the other research at the same year. They set the lead-free Sn-based perovskite solar cell as the base and replaced iodine with bromine. The results displayed the significant enhancements of V_{OC} and FF, but J_{SC} decreased rapidly with the increasing the concentration of bromine [27]. Chang *et al.* reported a research about doping alkali metal (K and Na) into $MAPbI_3$, and both perovskite solar cells showed the high photovoltaic performance than the non-doped perovskite solar cell. The PCE of K-doped and Na-doped perovskite solar cells were improved from 12.8% to 15.3% and from 12.8% to 14.5%, respectively [28]. Jahandar *et al.* doped $CuBr_2$ into $MAPbI_3$ to enhance the photovoltaic performance, and their results showed increased short circuit current and PCE improved from 13.18% to 17.09% [29]. Pazoki *et al.* demonstrated the some alkaline-earth metals (Ca, Sr, and Ba) are the potential candidates to replace the toxic lead in perovskite structured materials due to the same charge and the similar ionic radius [30].

MASrI$_3$ and MABaI$_3$ could be a stable perovskite structure calculated by the density functional theory. Because $MASrI_3$ and $MABaI_3$ are the wide bandgap materials [30], they show the poor absorption in visible and infrared wavelengths. However, the slight doping using Sr^{2+} and Ba^{2+} in the perovskite structured materials can decrease the bandgap [31]. In this study, we developed the lead-reduced perovskite structured materials to fabricate the perovskite solar cells in the glovebox (nitrogen atmosphere, H_2O and $O_2 < 0.1$ ppm). The well-known perovskite structured material for photovoltaic application is $CH_3NH_3PbI_3$. We used Ba^{2+} or Sr^{2+} doped into $CH_3NH_3PbI_3$, because both alkaline earth metal ions are perfectly fitting the tolerance factor. The photovoltaic performance of Ba-doped perovskite solar cells is usually higher than Sr-doped perovskite solar cells. Hence, Ba-doped perovskite structured materials can replace the lead without decreasing the photovoltaic performance, so it could be a potential candidate in the field of perovskite structured energy materials.

2. Experimental details

2.1. Perovskite solution preparation

The methylammonium iodide (CH_3NH_3I, MAI) was synthesized by following literature [32]. The preparation of perovskite precursor solution was mixing MAI and lead chloride ($PbCl_2$, 99%, Acros) with mole ratio 2.6:1 in 0.5 mL dimethylformamide ($HCON(CH_3)_2$, DMF, anhydrous, 99.8%, Acros) at 39.0 wt%. Doped perovskite precursor solution was prepared by mixing MAI, lead chloride, barium iodide (BaI_2, 99%, Acros), and strontium iodide (SrI_2, 99%, Acros) depended on atomic ratio in 0.5 mL dimethylformamide.

2.2. Electron transporting layer precursor solution preparation

A 2.5 mL of ethanol (C_2H_5OH, 99.5%, Acros) was mixed with 375 μL of titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$, TTIP, >97%, Acros) in a 7.0 mL sample bottle. Then, 35 μL of 2.0 M HCl was added to 2.5 mL of ethanol in another sample bottle. Subsequently, HCl solution was dropped into Ti precursor solution, and the mixed

solution was filtered by 0.2 μm PTFE filter. Finally, TiO_2 precursor solution was synthesized for preparing electron transporting layer.

2.3. Hole transporting layer precursor solution preparation

We prepared 2,2′,7,7′-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD, STAREK Scientific) solution by following steps. In the beginning, 104 mg lithium-bis-(trifluoromethanesulfonyl) imide ($C_2F_6LiNO_4S_2$, Li-TFSI, 99.95%, Aldrich) was added in 200.0 μL acetonitrile (CH_3CN, 99.5%, Acros) to prepare lithium salt solution. Then, 28.5 μL 4-tert-butylpyridine ($C_9H_{13}N$, tBP, 96%, Acros) and 17.5 μL lithium salt solution were dropped into 1.0 mL chlorobenzene (C_6H_5Cl, CB, 99.8%, Acros), and they were mixed together by heating magnetic stirrer. Finally, 80 mg spiro-OMeTAD powder was added in 1.0 mL of the mixed solution.

2.4. Fabrication of the perovskite solar cells

We cleaned the FTO glass by ultrasonicator using detergent for 5 min, methanol for 20 min, and isopropanol for 20 min. The TiO_2 precursor solution was spin-coated on FTO glass at 1000 rpm for 40 s followed by calcination process at 550 °C for 30 min. After that, the perovskite solution was spin-coated at 2000 rpm for 40 s in Mbraun glovebox system (nitrogen atmosphere, H_2O and $O_2 < 0.1$ ppm). Then, the spiro-OMeTAD solution was spin-coated at 4000 rpm for 30 s. Finally, the gold electrode was thermally deposited on the device surface with a shadow mask with 0.09 cm^2 active area by the thermal evaporation techniques.

2.5. Characterization

The photovoltaic characteristics of the device were analyzed under AM 1.5G sunlight (Newport-69920, 100 mW/cm^2) which was calibrated by a silicon reference solar cell with KG-5 filter and the current density-voltage (J–V) data was recorded by source meter (Keithley 2410). The delay time between each data plot is 10 ms. The morphology of metal-doped perovskite layers was observed by scanning electron microscope (SNE-4500M, SEC). UV–vis absorption spectra were measured by UV–vis spectrometer (V-630, Jasco). The curve was measured from 600 nm to 900 nm with 1000 nm/min scan rate. X-ray patterns were measured by X-ray diffractometer (XRD, Bruker, D2 phaser with Xflash 430, Germany). All of samples were measured from 10° to 50° with CuKα beam ($\lambda = 1.54$ Å). The photoluminescence (PL) spectra were measured by a continuous-wave diode laser ($\lambda_{exe} = 440$ nm, PDLH-440-25, DongWoo Optron Co. Ltd.), and the signals were analyzed by photomultiplier tube detector system (PDS-1, DongWoo Optron Co. Ltd.). The time-resolved photoluminescence (TRPL) spectra were measured with an average power 1.0 mW plus laser and operated at 312.5 MHz under 2 μs duration time, which was used for excitation. The signals were analyzed by time-correlated single photon counting spectrometer (WELLS-001 FX, DongWoo Optron Co. Ltd.).

3. Results and discussion

The XRD patterns of Sr and Ba doped perovskite materials with different doping concentrations are shown in Fig. 1(a). We can observe that the intensity at 2θ of 14.27° which is the diffraction peak of perovskite (1 1 0) facet. The magnified XRD patterns in the range between 13.5° and 15.5° are shown in Fig. 1((b) and (c)). When Ba or Sr is doped into the perovskite-structured material, the intensity of (1 1 0) facet is decreased with increasing the doping concentration. However, Sr-doped perovskite material presented the decreased (1 1 0) facet and formed the phase transition. This result exhibited that the original tetragonal crystal structure was