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Communication

Efficient planar perovskite solar cells using halide Sr-substituted Pb perovskite

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ABSTRACT

Stability and lead toxicity issues of inorganic organic halide lead perovskite solar cells have significantly limited their commercial applications. The nontoxic strontium (Sr) can be a good candidate to reduce lead utilization due to their similar ionic radiuses. Here we uncovered the dramatic influence of Sr element substitution on the optoelectronic properties of perovskite films, including up-shifting conduction band edge energy level, increasing exciton binding energy and trap density states due to the isoelectronic impurity of electric neutral substitution. The incorporation of a small content of Sr (a≤0.05) into the $CH_3NH_3Sr_aPb_{1-a}I_{3-x}Cl_x$ crystal lattice can act positively impact on material thermal stability and solar cell device output voltage (~1.11 V). An overall highly photovoltaic efficiency of ~16.3% was achieved with a planar n-i-p structure of ITO/compact TiO_2/$CH_3NH_3Sr_aPb_{1-a}I_{3-x}Cl_x$/spiroMeOTAD/Au. Impedance characterization reveals an increased trap states induced by substitution Pb with Sr in the hybrid halide perovskites, and thus provide a deep understanding of the role of external elements on device physics.

1. Introduction

The power conversion efficiency of perovskite solar cells has increased from their debut of 3.8% in 2009 to the currently certified 22.1% in a short time [1]. It is indisputable that the organic-inorganic hybrid perovskite has emerged as a new family of photovoltaic materials for future application. These materials, with the formula of AMX_3 (A: $CH_3NH_3^+(MA^+)$ or $NH(CH_3)_2^+(FA^+)$; M: Pb^{2+}; X: Cl^-, Br^- or I^-), possess several appealing features such as high light absorption coefficient (~5.7×10^4 cm^{-1} at 600 nm) [2], ambipolar charge mobility (μ_h~0.6 $cm^2\ V^{-1}\ s^{-1}$) [3], as well as long electron and hole diffusion length (> 1000 nm) [4], whose band-gap can also be easily tailored through the choice of metal, inorganic anion and organic ligands [5–7]. However, it should be noted that the vulnerability of organic-inorganic perovskites to moisture, air, heat, or prolonged exposure to sunlight, together with toxicity issues, has slowed down the development process [8]. To date, the most reported organic-inorganic lead halide perovskite is $MAPbI_3$. The fast and irreversible degradation of $MAPbI_3$ confines virtually all measurements in a delicate environment. For example, significant decomposition effects have been observed during annealing of a $MAPbI_3$ at 85 °C even in inert atmosphere [9]. An unfavorable reversible structural phase transition from tetragonal to cubic for $MAPbI_3$ at 55 °C might cause photo- and thermal-instability of perovskite solar cells [10]. To date, efforts devoted to resolve instability have been shown to compromise performance. The toxicity of lead-based compounds further necessitates the pursuit of alternatives beyond $MAPbI_3$. Therefore, it is highly desirable to identify the right ingredients for perovskite to achieve ideal photo-electronic properties and strengthen stability at no cost to the environment.

Theoretical calculations have demonstrated that the ionic radius ratio $(r_A + r_X)/\sqrt{2}\,(r_M + r_X)$ should be close to 1 for a stable AMX_3perovskite [11]. So far most of candidates are selected in the group-14 elements. For instance, the perovskite compounds based on Sn have been widely investigated [12,13]. The Sn-based perovskite materials such as $MASnI_3$ benefit from an ideal band-gap (~1.3 eV) [14] with a correspondingly high theoretical photocurrent of 34 mA cm^{-2}. However, the $MASn_{1-x}Pb_xI_3$ perovskites suffer from lower stability and metallic conductivity due to an ease oxidation of Sn^{2+} to Sn^{4+} undesirably. In this case, Sn^{4+} acts as a p-type dopant within the material via a process referred to as 'self-doping' [10]. This causes low photo-voltage and poor stability of Sn-based

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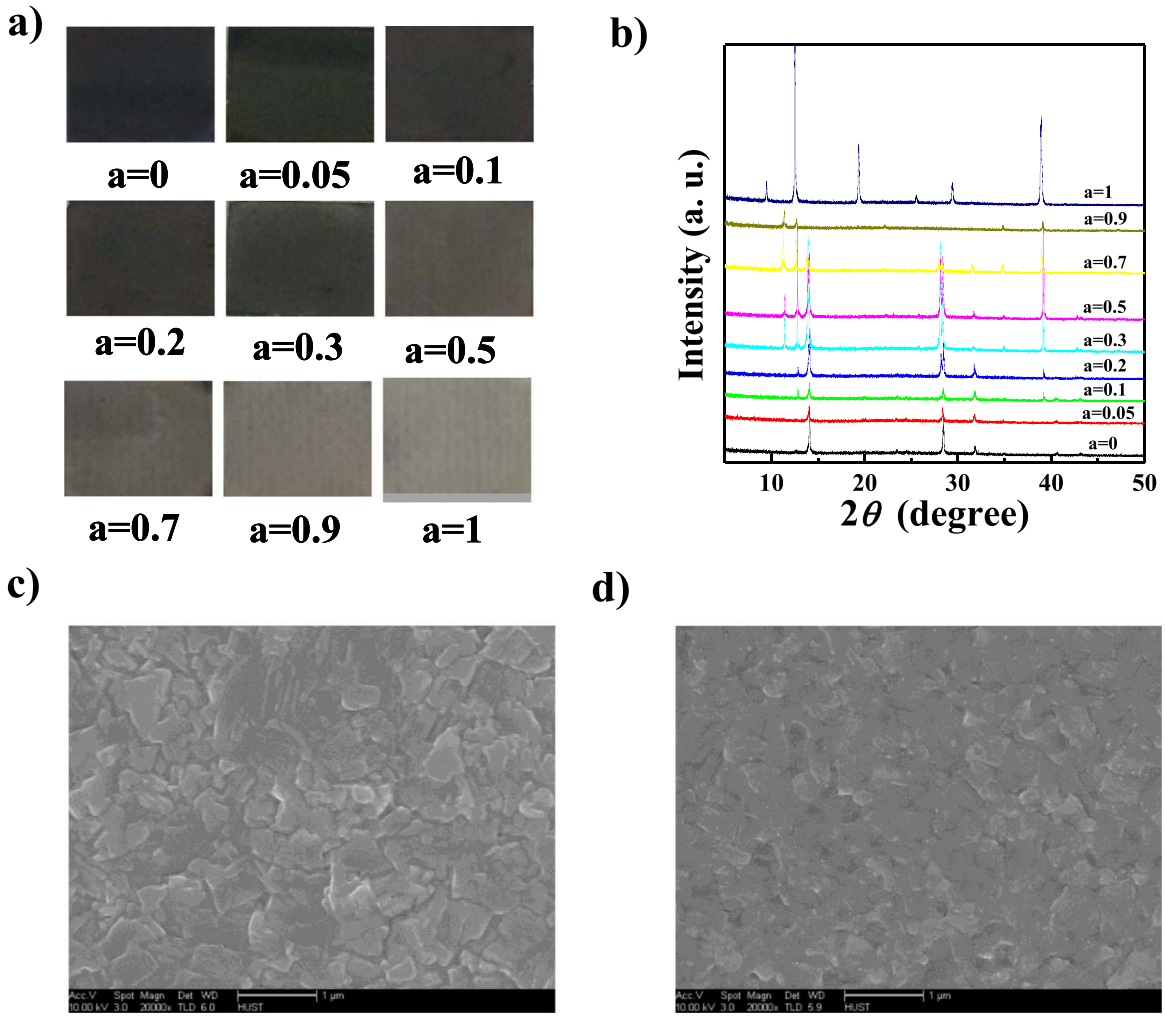

Fig. 1. a) Optical images and **b)** the XRD patterns of the $MASr_aPb_{1-a}I_{3-x}Cl_x$ (a=0–1) films. SEM images of perovskites of **c)** a=0 and **d)** a=0.05 onto ITO/TiO_2 subtracts.

perovskite devices. It is noted that a minimum content of Pb is necessary aiming to stabilization Sn [14]. Partial substitution has been used to describe the alloyed perovskite solid solution of methylammonium lead iodide and its analogues (for example $MASn_{1-x}Pb_xI_3$) [15,16]. The potential of Ge-based halide perovskite compounds ($AGeI_3$, A=Cs, $HC(NH_2)_2$ or CH_3NH_3) for solar cells application has also been investigated [17,18]. Although some of these compounds ($AGeI_3$) can be stable up to 150 °C and the resulted devices exhibited encouraging photocurrent density, the solar cells suffered from very poor open circuit voltage due to Ge^{4+} formation. In addition to this, these compounds exhibit poor solubility in polar solvents [19], which limits the solution-processed device fabrication protocol.

Generally it can be highly possible to substitute lead by other cations rather than group-14 elements, which has been become one of important research directions for exploring new organic-inorganic halide perovskite materials [20–22]. For example, the $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ (x=0.9)-based perovskite has been proposed, offering an outstanding V_{OC} of 1.19 V with fill factor (FF) of 87.9% [23]. However, it is difficult to prepare smooth Mn-based binary perovskite films via solution processes. Very low PCEs in the range of 0.32–0.83% were found by varying the molar weight of Mn from 0.1 to 0.2. Recently, a breakthrough on binary metal perovskite has been observed with In^{3+} substitution for Pb, showing a remarked PCE of 17.55% with a $MAPb_{0.85}In_{0.15}I_3Cl_{0.15}$ absorbing layer due to a good crystal quality with multiple ordered crystal orientations [24]. We note that the different valence of In^{3+} and Pb^{2+} may induce a disordered valence in perovskite which easily changes the crystal structure. Furthermore, Moon et al. found that the conductivity of $MAI(PbI_2)_{1-x}(CuBr_2)_x$ (x≤0.1) can be enhanced significantly by Cu doping due to effective enhancing charge carriers [25]. So far replacement or substitution for Pb in organometal halide perovskites is far away from satisfactory. Therefore, it is highly desirable to explore other replacements or substitutes for achieving lead-less or even lead-free perovskites for solar cells application with considerable PCE and stability in addition to fundamental understanding their working principle.

The first principle calculation has indicated that the highly possibility of replacement of lead with alkaline-earth metals, among which the nontoxic and relatively inexpensive strontium (Sr) can act as good candidate [26,27]. The ionic radius of Sr^{2+} is almost identical to Pb^{2+}(Sr^{2+}=132 pm, Pb^{2+}=133 pm), suggesting a highly possible exchange between them without affecting the perovskite crystal structure. Likewise, the calculation based on coupled cluster method onto Sr^{2+} and Pb^{2+} ions has sufficiently indicated similar bonding patterns for their halogen salts [27]. Furthermore, density functional theory calculation has predicted the strontium perovskite ($MASrI_3$) to be a stable phase. Very recently, Sessolo et al. demonstrated the impact of Sr substitution on the optoelectronic properties of $MAPbI_3$:Sr^{2+}(Sr^{2+}/Pb^{2+}≤5%) perovskite, exhibiting a longer charge carrier lifetime. We noted a PCE of 15% with a high fill-factor (85%) was achieved with a planar p-i-n structure device and an optimum Sr^{2+} molar concentration of 2% [28]. In this study, we investigated on $MASr_aPb_{1-a}I_{3-x}Cl_x$ perovskites as light absorbers for high performance planar n-i-p heterojunction perovskite solar cells, in which spiroMeOTAD and compact TiO_2 are used as hole and electron transport layers, respec-