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Original research article

Enhancement of perovskite solar cells characteristics by incorporating mixed sodium/cesium cations

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ABSTRACT

In this work, combination of halides and MA, FA, Cesium (Cs) and Sodium (Na) cations were considered. The main structure of the cell absorbing layers was NaCsMAFAPb (IBr)₃. The formulation of CsMAFAPb(IBr)₃ without Na was used as a reference (control). Compositional cell cation by the mixture of MA_{0.2}FA_{0.7}Na_{0.05}Cs_{0.05}Pb (I_{5/6}Br_{1/6})₃ was used for comparison. Different characterization scheme such as IV measurements, Scanning Electron Microscopy, and X-ray Diffraction (XRD) were prepared to compare the performance of these two types of perovskite cell structures. SEM patterns showed the samples containing combined Na-Cs cations have a more compact surface with fewer pinholes. Also they exhibited higher efficiency compared to the reference sample. This was mainly due to the less defects of the interface surface. Moreover, better crystallinity was observed for the perovskite samples having Na-Cs combined cations from XRD pattern, which resulted in increase in charge transfer and also cell efficiency.

1. Introduction

Solar cells are optoelectronic devices that directly convert the sun light to electric energy. The first generation of solar cells are silicon solar cells [1]. These solar cells present high stability and efficiency but they have some drawbacks such as complex processing procedure, and high construction cost. These limitations encouraged the researchers to seek alternative cells with more affordable and less complexity Perovskite solar cells are new generation of nano structure-based solar cells. These types of solar cells can be competitive with the other commercialized sells and their absorbent layer have remarkable superiority such as the fantastic optoelectronic properties of inorganic metallic halides, long distribution, diffusion depth, adjustable band gap and low recombination [2–4]. Nowadays, by modification of perovskite solar cells the efficiency of about 22.1% has been reported by the researchers [5,6]. The general formulation of the adsorbent layer of perovskite solar cells is ABX₃, where A is a monovalent cation such as MA (methylammonium) (CH₃NH₃), formamidinium FA (CH₃(NH₂)₂), Cesium (Cs), Sodium (Na) or Rubidium (Rb); B is a bivalent metal such as germanium (Ge²⁺), tin (Sn²⁺) or lead (Pb²⁺), and X is an anion of the halogens group such as chlorine (Cl⁻), bromine (Br⁻) or iodine (I⁻) [7,8]. The highest efficiency was reported for Perovskite solar cells belongs to a lead-based and combined MA / FA cations, where their anions are Br / I compound halides [9–11]. Recently, Cesium cations have been added to these combined cations [12–16], known as triple cation solar cells. These solar cells, whose cation structure is FA / MA / Cs (FMCs), have higher thermal

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stability than the cells with combined MA / FA cations. Usually, the addition of inorganic elements to the perovskite compounds increases the entropy of the compound and also increases the stability of unstable materials. Also, the injection of various materials into the perovskite solution can change the nucleation rate, morphology, nucleus size and crystallinity of the perovskite, and ultimately alter the cell performance. The exchange of cation materials, or halides also enhances material characteristics such as increase in light absorption in the visible region [17], reduced induced exciting energy [18,19], increase in diffusion lengths of the charge carrier to micrometers [20,21], and creating the tunable band gap of 1.1–2.3 eV [22,23]. It has been also reported that could improve the efficiency and also phase stability for X = 5% by combining the cations of FA, MA, Cs and Br and I anion. The structure of $\text{FA}_{0.7}\text{MA}_{0.2}\text{Cs}_{0.1}\text{Pb}(\text{I}_{5/6}\text{Br}_{1/6})_3$, called FMC was made [24,25]. Some researchers have been carried out the effect of combining cesium with other Perovskite cations [26–28]. The results of others confirm that adding cesium cation to MA and FA cations caused cell recovery. Therefore, in this work we have investigated the effect of adding Cs/Na combined cations to MA and FA cations and examined the results.

2. Experimental procedures

In this work, two types of cells have been made, one type containing a Cs/Na Perovskite and the other type, as reference cell, and only contains Cesium cation. All layer materials in the other parts of the both types of cells were the same. To prepare the Fluorine-doped Tin Oxide (FTO) films, FTO glasses with dimensions of 1.4×1.4 cm were firstly etched and then rinsed with water and soap, distilled water, acetone and ethanol, respectively then were placed in an ultrasonic machine for ten minutes and at the last stage, the glasses were heated to 120°C for 20 min in an oven. Then using the required solutions, the layers coating was performed at room temperature and humidity of 13%. The solution layers were made as follows:

2.1. Blocking layer

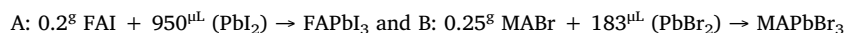
The precursor of this layer is titanium Titanium Isopropoxide (TTIP), 70 μl chloride acid 2 M was mixed with 5 ml pure ethanol. Also 700 μl TTIP was mixed with 5 ml pure ethanol then the first solution was dropped onto the second solution, while it was spinning on a stirrer. For the blocking layer 200 μl of this solution was poured on the samples which were rotated using a spin coating device. The coating of the layers performed at speed of 2000 rpm for 30 s then the samples were heated for one hour at 500°C .

2.2. Compact layer

One gram of dyed titanium dioxide was mixed with 5 ml of pure ethanol and was stirred for 12 h with a magnetic stirrer and with no heating. Amount of 50 μl of this solution was poured on the sample while rotating by a spin coating device at speed of 4000 rpm for 30 s. Finally, the samples were heated at 500°C for half an hour.

2.3. Absorber layer

Firstly, 3.5 ml Perovskite solution with structure of $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ was prepared as follows: The amount of three milliliter solution of 1.5 M of PbI_2 was prepared. Also the amount one milliliter solution of 1.5 M of PbBr_2 with density of 550.5 mg/1 ml. The solvent used for PbI_2 and PbBr_2 was with the volumetric ratio of 4 Dimethylformamide (DMF) in one-unit volume of Dimethyl sulfoxide (DMSO). During dissolving PbI_2 and PbBr_2 , they were heated on a hot plate for 10 min at 180°C , while were shaken with hand. The Perovskite solution was then prepared with the following procedure:



The “C” solution is a Perovskite solution that includes two combined cations of FA and MA as well as two combined anions of the Br and I. After combining the A and B solutions, for 950 μl of the Perovskite solution ($\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$) 50 μl of the combined cation of (CsNaI_2) was added to provide the final solution of the Perovskite. To provide the control sample, 950 μl of the Perovskite solution, was added to 50 μl of combined cation of (CsI_2).

The solution of CsI cation with molar weight of 389.715 g/1 and the solution of NaI cation with molar weight of 224.835 g/1 were prepared using DMSO solvent and then these two solutions were combined in equal proportions, to obtain the new combined cation of NaCsI_2 . Finally, the amount of 5% of the total solution of the main Perovskite from NaCsI_2 solution was added to the main perovskite solution. the amount of 40 μl Perovskite solution was used per sample for the absorber layer. The ambient temperature and the humidity were 30°C and 13%, respectively. The deposition of Perovskite solution layer was performed in two stages using the so-called spin coating method:

Step 1: 1000 rpm/min for 15 s and Step 2: 4000 rpm/min for 30 s

At the last 15 s of the step 2 of layer deposition, an amount of 200 μl of Ethyl acetate was slowly poured for less than a second on the sample. After the layer deposition of Perovskite, the samples were sintered at 100°C for one hour.

2.4. Spiro-OMeTAD layer

In solar cells this layer acts as hole-transporting layer. To prepare one milliliter of the required solution the following procedures were fulfilled:

- 1 72.3 mg of Spiro was added to one milliliter of Chlorobenzene
- 2 520 mg of LiTFSI was added to one milliliter of Acetonitrile

Firstly, 28.8 μl (equal to 26.6 mg) of 4-tert-butylpyridine (TBP) was added to the solution provided in the stage 1. Then 17.5 μl of the solution provided in the stage 2 was added to the aforementioned solution. Subsequently, this solution was spun for 30 min at 60 °C. After sintering the Perovskite layer, the samples are left until their temperature reach to room temperature and then the Spiro-OMeTOD solution is deposited by spin coating method. For this coating the amount of 30 μl of Spiro was poured on each sample. This was carried out at 4000 rpm for 30 s. The samples were then placed inside a desiccator for 16 h to prevent moisture absorption.

2.5. Cathode layer

After 16 h of the Spiro layer coating, the cathode layer was coated with a golden conductor by vacuum evaporation method, using Physical vapor deposition (PVD) apparatus. The least amount of required gold for this purpose was 75 mg and gold was coated at the rate of 4 A_0/s .

2.6. Materials and apparatus

All chemical solvents were provided from Merck Company, Germany. MA and FA were purchased from Dyson Company, UK. Spiro was obtained from Boron Company, USA. TBP was purchased from Aldrich Company. Other materials were purchased from Sharif Solar Company, IRAN. The characterization of cells was performed using a Sunlight Simulator under standard conditions (1.5 A M and humidity of 13%). The device was calibrated using a standard silicon cell, and light intensity of 100 mW/cm^2 in the range of 380–9000 nm spectrum.

3. Results and discussion

In this work, the combined cation of CsNaI_2 was added to $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ compound and hence a new combined four-cation as $\text{NaCsMAFAPb}(\text{IBr})_3$ was obtained, which is shown in Fig. 1.

In this compound the proportion of cesium is equal to sodium and the proportion of sodium-cesium iodide is five percent of the main solution of the Perovskite. The non-sodium compound which has been previously worked by others (e.g. Saliba et al. 2016) is considered as control sample. To fabricate this compound, only a CsI cation was added to the main Perovskite of $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ and hence the composition of this compound is $\text{CsMAFAPb}(\text{IBr})_3$. The proportion of CsI to the main Perovskite solution is also five percent. Subsequent to cells fabrication, their voltage-current characterization, Efficiency, SEM and X-ray diffraction (XRD) were compared and discussed. The graph of voltage-current (Fig. 2) and other cells characteristics (Table 1) show that the cell efficiency of the containing NaCsI_2 cations compare to the control cell (containing only CsI_2 cation) is improved. The efficiency of a cell containing Sodium/Cesium cations is 1.52 times higher than the cell with only Cesium cation, showing a better performance.

The X-ray diffraction (XRD) also shows that the Perovskite containing Sodium/Cesium cations (Fig. 3a) has a higher secondary peaks than the Perovskite containing only Cesium cation (Fig. 3b). This implies a better crystallization and a higher purity of the Perovskite containing Sodium/Cesium compared to the Perovskite with only Cesium. The Perovskite peak containing NaCs was formed at $2\theta = 14.7^\circ$ and the PbI_2 peak was formed at $2\theta = 12.7^\circ$. Moreover, there is no indication of yellow hexagonal phase peak of FAPbI_3 . This is an advantage for the Perovskite containing NaCs cations.

The presence of an additional PbI_2 peak in the Perovskite reduces the conductivity and consequently, reduces the transfer of charge and current, while the lack of this peak in the cell containing Sodium/Cesium cations would improve this weakness. These

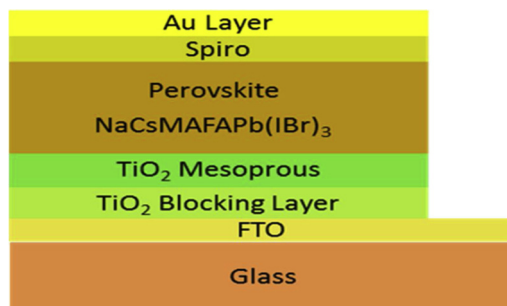


Fig. 1. The layers of the solar cell under study in this research.

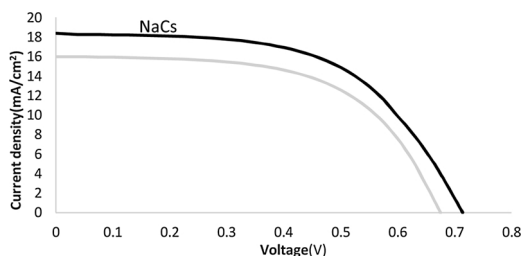


Fig. 2. Current-voltage curve for the cells with NaCs cations (Black line) and Cs cation (grey line).

Table 1

Characteristics of the solar cells with NaCs and Cs cations.

Eff(Max) (%)	Stdv ± Eff(Ave) (%)	FF(%)	V _{oc} (V)	J _{sc} (mA/cm ²)	Cation
Max = 9.52	9.08 ± 0.32	72.87	0.71	18.40	NaCsI ₂
Max = 8	7.62 ± 0.34	72.14	0.69	16.07	CsI

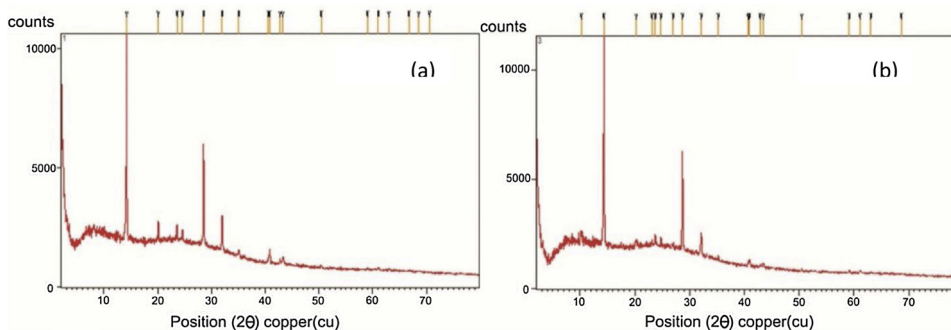


Fig. 3. XRD curves of the cell samples with different cations, (a) the cell containing NaCsI₂ cations and (b) containing only CsI cation.

results are consistent with the other works carried out on Perovskite [16].

According to the SEM images (Fig. 4), the Perovskite containing Sodium/Cesium cations (Fig. 4a) has fewer pinholes than the Perovskite containing Cesium cation (Fig. 4b). The fewer pinholes can cause better transfer charge within the cell. It also reduces the charge carriers trapping, consequently will facilitate the current inside the cell and thereby improve its efficiency. The occurrence of more pinholes implies more resistance pathways inside the cell which causes to decrease cell Shunt resistance.

4. Conclusions

In this regard combined cations of NaCsI₂ were added to Perovskite solar cell and its characteristics and performance were compared with the control cell having only CsI₂ cation. The cell characterization results of I–V, XRD and SEM Tests confirm that the Perovskite solar cell containing combined halide and cations (FAMANaCsPb(IBr)₃) with four cations has better performance than the perovskite solar cell containing triple-cation (FAMACsPb(IBr)₃).

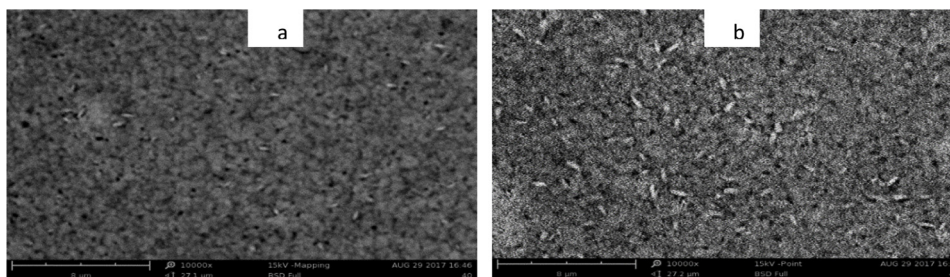


Fig. 4. Scanning electron microscope (SEM) image of the cells, (a) the Perovskite solar cell containing Sodium/Cesium combined cations (NaCsI₂) and (b) the Perovskite solar cell containing only Cesium cation (CsI₂).

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