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A study on mixed halide perovskites

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Abstract- In recent years, the emergence of organic/inorganic lead halide perovskite based absorbers has led to unprecedented growth in the efficiencies of solar cells. Methyl ammonium lead iodide (MAPI) is a widely explored perovskite in the recent years. This work proposes the use of $CH_3NH_3PbBrCl_2$, a mixed-halide perovskite to construct a Perovskite Solar Cell (PSC) prototype to explore cost-effectiveness. A preliminary comparative investigation is carried out on the working of the PSC prototype sensitized with MAPI and the newly proposed mixed halide. The output voltage obtained from the proposed material is comparable to the one obtained from the well-established MAPI used to sensitize a PSC prototype under similar conditions. These results pave way for further development of mixed halide perovskites.

Keywords — Perovksite, Mixed-halide perovskite, methyl ammonium lead halide (MAPI), TiO_2, solar cell prototype

I. Introduction

We rely heavily on non renewable fossil fuels for our sustenance, but in recent years the excessive use of these resources and their impact on the environment has been a growing concern . This has led to a quest to find clean and green energy in order to find a permanent solution for this situation which gets worse with every day that passes by. Recent progress in the field of solar energy concentrates on solar cells that are cost effective and this is where dye sensitized solar cells (DSSC) come in. They are cheaper and have better power conversion efficiencies compared to a conventional silicon based solar cell[1].A breakthrough in photovoltaic technology was the invention of perovskite based solar cells. Perovskites are absorber materials that have the ABX_3 crystal structure.

Perovskite solar cells are now considered an effective alternative for traditional solar cells. The conventional metal-halide perovskites used in solar cells are based on the (MAPI) crystal structure. The most commonly studied perovskite absorber is methylammonium lead trihalide ($CH_3NH_3PbX_3$, where X is a halogen atom such as iodine, bromine or chlorine), with an optical bandgap between 1.5 and 2.3 eV. Another promising perovskite is Formamidinum lead trihalide ($H_2NCHNH_2PbX_3$) with bandgaps between 1.5 and 2.2 eV [2]. Metal halide perovskites have some features that make them the best choice for solar cell application. Their high coefficient enables the creation of ultrathin films to absorb the complete visible solar spectrum [3]. They are preferred over traditional silicon solar cells due to their simplicity. Silicon cells require expensive setups and equipment, multistep processes and high temperature and vacuum conditions to manufacture. Meanwhile, the perovskite solar cells can be made with simpler techniques and minimal equipment. In most of these PSCs, TiO_2 acts as photo anode for the solar energy conversion. Among the three polymorphs of TiO_2 namely, anatase, rutile and brookite, the anatase phase shows better photo catalytic activity [4]. ZnO also possesses similar band gaps to TiO_2 and can be used as an alternative photoanode[5].

This paper aims at exploring the lesser known mixed halide perovskites of bromine and chlorine and comparing the results obtained with most widely explored MAPI type perovskite. Such a mixed halide is proposed in order to minimize the sensitizer cost in comparison to MAPI based ones. The entire process of building the prototype was done in a cost effective way with minimal lab equipment and by using low cost substitutes, for example carbon soot was used instead of carbon powder, which is expensive.

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II. EXPERIMENTAL

A. Materials and methods

The precursor powders of CH_3NH_3Cl (AR grade) and $PbBr_2$ (AR grade) were purchased from Loba Chemie, India. The mixed halide perovskite ($CH_3NH_3PbBrCl_2$) was prepared by mixing the CH_3NH_3Cl and $PbBr_2$ in the 2:1 ratio to obtain a golden yellow powder[6] indicating the formation of mixed halide perovskite. The powder thus obtained is downsized using the mortar and pestle. The TiO2 photoanode was prepared by adding 7- 8 drops of vinegar to TiO_2 powder (AR grade) obtained from SD Fine Chemicals, India. The TiO2 paste thus obtained was also ground in a mortar and pestle until suspension with a smooth consistency was obtained. This TiO_2 suspension was added on the conductive side of the ITO glass substrate to obtain the photoanode using Doctor's blade method. The counter electrode was made by the careful deposition of carbon soot from candle on ITO coated glass.
The mixed halide sample was investigated for crystalline peaks by X-ray diffraction technique using Bruker device with Cu Kα radiation. The thickness, refractive index and optical constants were determined using spectroscopic ellipsometry using a Jobin Yvon Ellipsometer (UVISEL). The optical studies were carried out on UV-Vis spectrophotometer from Perkin and Elmer Lamba35 between 200-800 nm wavelength range.

III. RESULT AND DISCUSSION

A. X-Ray diffraction analysis:

The XRD spectra of the mixed halide perovskite is shown in Fig. 1. The spectra reveals the crystalline nature of the powders. The peaks obtained from the sample are similar to those attained using other halide perovskites reported in the literatures [7]. Prominent diffraction peaks occur at 2θ (degree). = 15.52, 21.9, 31.08, 34.78, 38.2, 41.26, 44.34, 47.18 These peaks are attributed to (100), (310), (420), (500), (520), (530), (620), (622) indices respectively of mixed halide perovskite.
The most prominent peak for $CH_3NH_3PbBr_2Cl$ occurred at 2θ= 15.52 which is similar to the reported 2θ range of 14 – 16◦ for other combinations such as $CH_3NH_3PbI_3$, $CH_3NH_3PbI_2Br$, $CH_3NH_3PbIBr_2$ and $CH_3NH_3PbBr_3$ [8,9] It is noted that replacement of iodine halide by bromine in the perovskite leads to an increase in the diffraction angle. The average crystallite size for the mixed halide perovskite is 46 nm which is calculated using the Scherer formula (Eqn 1),

$$d= k\lambda/(\beta\cos\theta) \qquad \text{Eqn (1)}$$

where k – shape factor (0.9), λ - wavelength of X-Ray (1.54 Å), θ - angle of incidence, β - full width at half maximum of peak of XRD pattern.

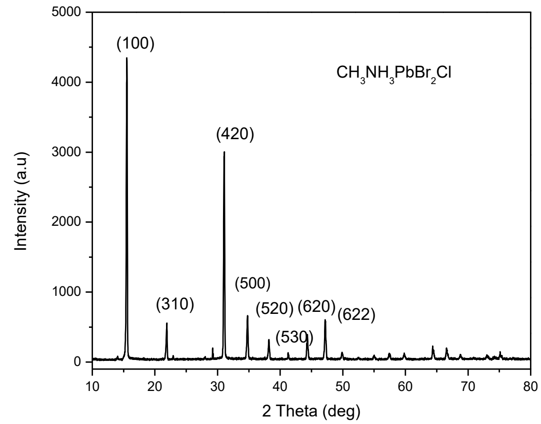

Fig.1 XRD spectra of the mixed halide perovskite, $CH_3NH_3PbBr_2Cl$

B. Spectroscopic Ellipsometry:

Spectroscopic ellipsometry characterization of TiO_2 film was done using Jobin Yvon HORIBA UVISEL ellipsometer to understand the thickness and uniformity of the photoanode film. A refractive index of 2.6 and a thickness of 470 nm within an error of 10nm at different spots were obtained, thus indicating uniformity. The model used for ellipsometry simulation is given in Fig.2.

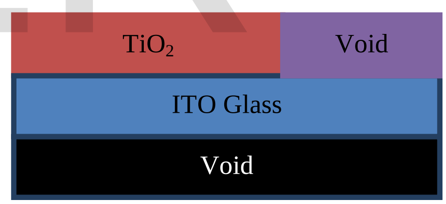

Fig.2 Model for ellipsometry simulation

C. Device Assembly:

PSC was done by clamping two ITO glass slides together as shown in Fig. 7, one coated with TiO_2 and other one with carbon soot from candle flame. TiO2 coated slide acts as working electrode and other slide works as counter electrode. After clamping two glass slides together, an electrolyte was introduced in a gap between two slides for current conduction. Initial attempts were made with configuration similar to that of Dye Sensitized Solar Cell but by replacing the dye sensitizer with MAPI one. With device configuration of ITO/TiO_2/MAPI Perovskite/carbon soot coated ITO with electrolyte, about 250mV was obtained which degraded upon illumination. Without the usage of electrolyte such as in typical PSC configuration and removing the Hole transport layer (Fig.3), MAPI perovskite under ambient room conditions yielded about 33mV in dark, which increased to 58 mV under illumination.

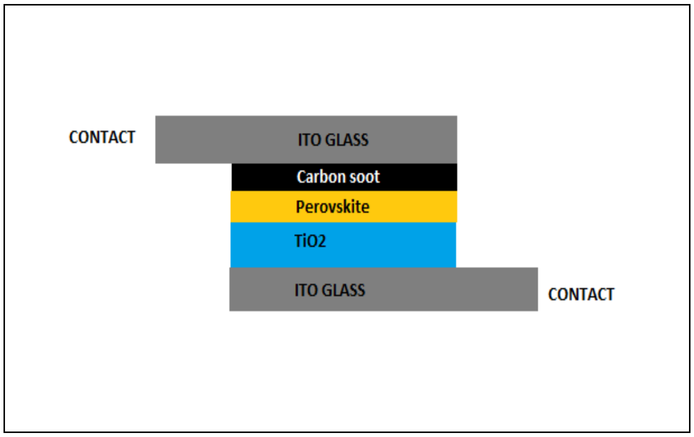

Fig. 3. Schematic diagram of PSC architecture

Our mixed halide perovskite based device with configuration ITO/TiO_2/perovskite/Caron soot coated ITO obtained upto 370mV. The measurement of the device prototype was carried out using a simple multimeter by establishing contact on the front and back electrode using binder clips as shown in Fig. 4, and tested for repeatability and consistency. The voltage obtained from mixed halide perovskite also degraded upon illumination.

Fig. 4. Measurement on the device prototype

IV. Conclusion

High-quality perovskite film could greatly promote the photoelectric conversion efficiency and stability. Prototype device of perovskite solar cells with structure: ITO/TiO_2/perovskite/Carbon soot /ITO were fabricated and assembled. TiO_2 paste was obtained by mixing with vinegar which served as a low cost substitute for acetic acid. The refractive index of TiO_2 obtained (2.6) was similar to those obtained in various established experiments (2.4). The proposed mixed halide perovskite was prepared using manual mixing leading to the transformation of white powder precursors to golden yellow. The XRD analysis showed a good structural quality of the mixed halide perovskite. The average crystalline size obtained through the analysis was 46nm. The perovskite powder is hygroscopic and absorbs moisture from air quickly and therefore a rapid degradation was observed. However under ambient conditions, the device was assembled to have a relative analysis of the well explored MAPI with the mixed halide perovskite assembled under similar conditions. A significant increase is noted in the mixed halide perovskite as compared to MAPI PSC thus offering promising potential of the proposed material for device explorations. The future scope lies in understanding the mechanism of degradation post illumination. Utmost care must be taken to ensure that there is minimum exposure to ambient conditions as it can contaminate the compound and lead to irregularities in test results.

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