Observation of Negative Photoconductivity (NPC) in $(CH_3NH_3)_3Bi_2(Br_xCl_{1-x})_9$ and optimising Br doping for efficient solar cell devices with NPC

P12

HyPe 2023

Paramesh Chandra§, Swapan Kumar Mandal*
Department of Physics, Visva-Bharati (Central University), Santiniketan, 731235, India
§parameshchandra28@gmail.com
*sk_mandal@hotmail.com

Introduction

- Perovskite materials, whether inorganic or hybrid, have exciting electronic and photoelectronic properties, making them promising for optoelectronic and photovoltaic devices. The development of a hybrid perovskite ($CH_3NH_3PbI_3$) based solar cell with an efficiency of over 25% is considered a breakthrough in perovskite materials research worldwide.
- The commercialization of perovskite photovoltaic solar cells (PSC) has been hindered by issues such as stability and the toxicity of lead (Pb).
- Strategies such as compositional tuning of perovskite and the replacement of Pb with Bi have been explored to address stability and toxicity concerns.
- High-defect density and ion migration in the active perovskite layer under external stimuli are believed to contribute to the instability and low device performance of PSC.
- The report focuses on the phenomenon of ion migration and photo segregation in Bi-based perovskite with mixed halide ratio, specifically $(CH_3NH_3)_3Bi_2(Br_xCl_{1-x})_9$, to understand its impact on electron transport and current flow. Controlled experiments were conducted to record current-voltage (I-V) and current-time (I-t) profiles of the perovskite layer under dark and light irradiation at temperatures ranging from 100-283 K.

References
- Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. J. Am. Chem. Soc. 2009, 131 (17), 6050−6051.
- Multi Stage Phase Segregation of Mixed Halide Perovskites under Illumination: A Quantitative Comparison of Experimental Observations and Thermodynamic Models. Adv. Funct. Mater. 2023, 33, 2206047.

Methods

Synthesis Process

MABiCl, $MABiBr_{0.33}Cl_{0.66}$, $MABiBr_{0.44}Cl_{0.55}$, $MABiBr_{0.55}Cl_{0.44}$, $MABiBr_{0.66}Cl_{0.33}$ were prepared by mixing in different ratios of MACl, MABr, and $BiCl_3$. The molar ratio of MACl, MABr, $BiCl_3$ was kept 3:0:2, 0:3:2, 0:12:5, 0:15:4, 0:6:1 for MABiCl, $MABiBr_{0.33}Cl_{0.66}$, $MABiBr_{0.44}Cl_{0.55}$, $MABiBr_{0.55}Cl_{0.44}$, $MABiBr_{0.66}Cl_{0.33}$ respectively.

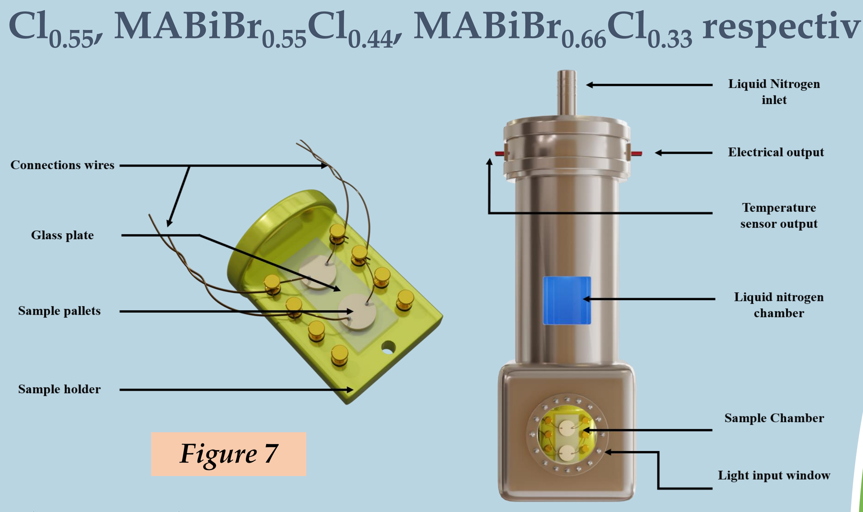

Figure 7

Electrical transport measurement Setup

The samples are placed inside a cryogenic-chamber (JANIS, USA) under vacuum conditions. Electrical measurement is done using *Keithley 6514 electrometer and an Arduino-based lab-made variable voltage source.* The *I-V* characteristics are measured for each sample (voltage step of 0.5 V) in the range of 0 V to 5 V and reversed. *I-t* measurement is also done in this system, keeping the temperature constant at 100K and 283 K, respectively. The samples are illuminated through the optical window of the cryostat using an LED light source of Intensity of 10 mW/cm² and an external relay control for the switch on/off timing.

Results

UV-Vis data

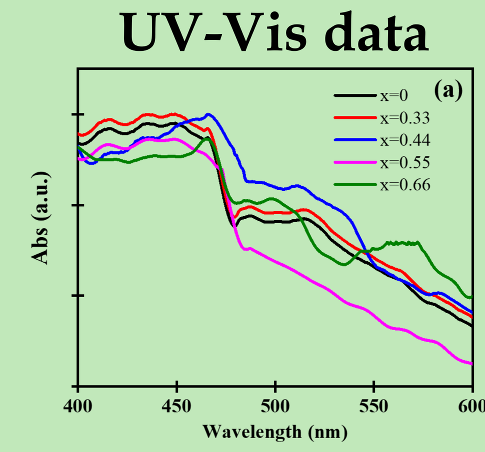

Figure 1

Time dependent photoluminescence data

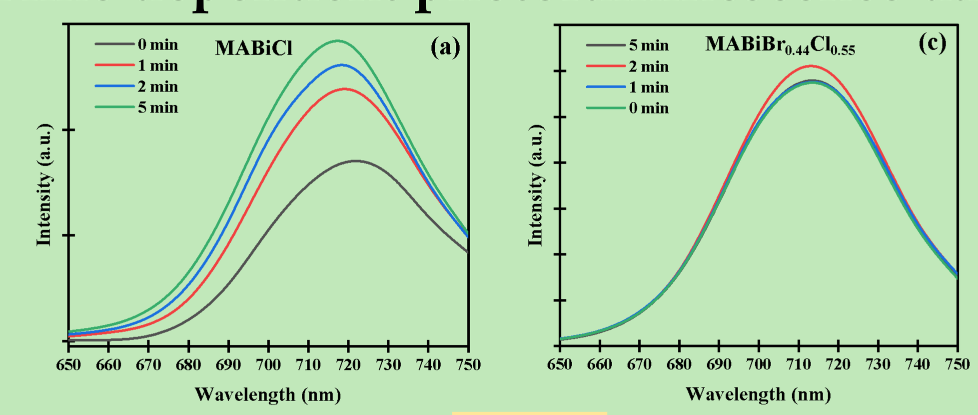

Figure 2

SEM images

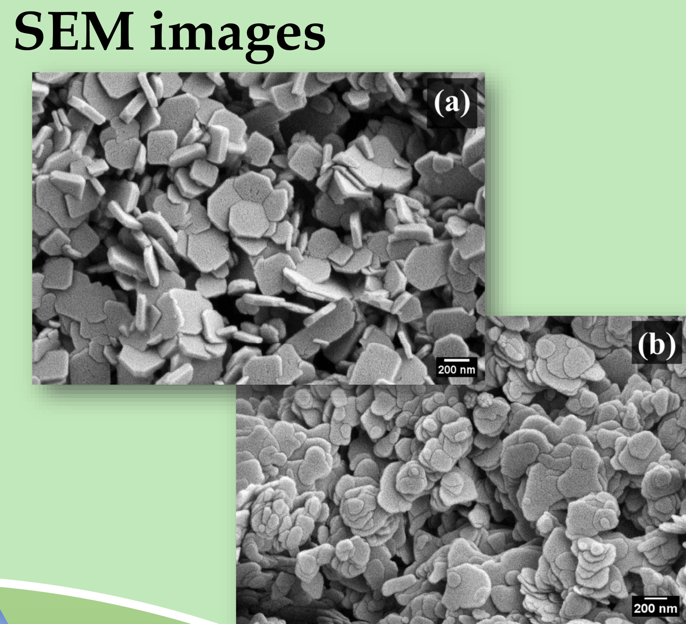
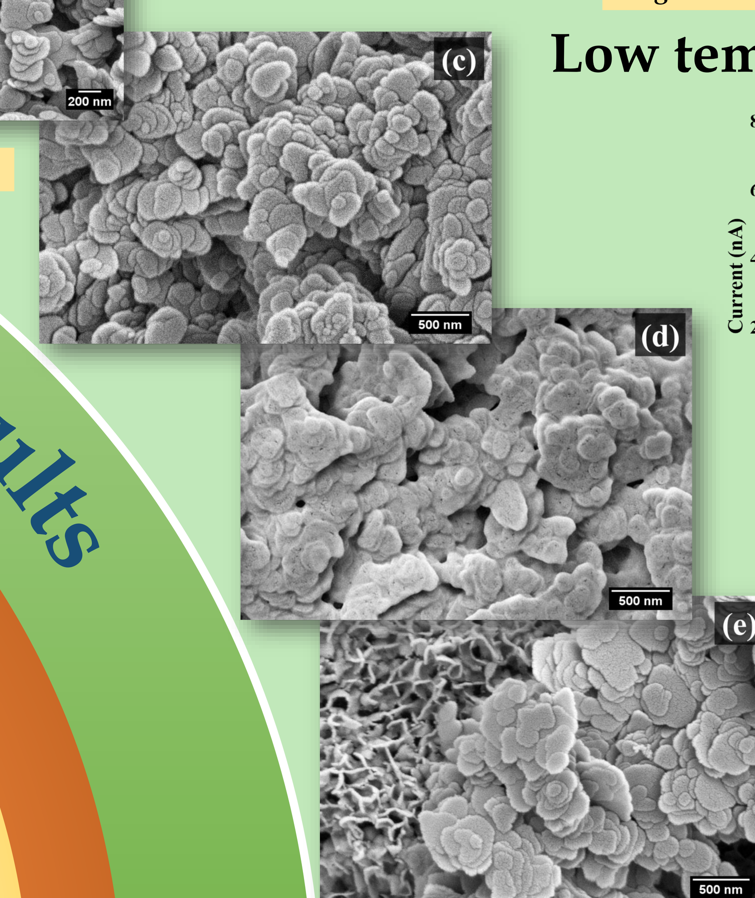

Figure 4

Variable temperature *I-V* data

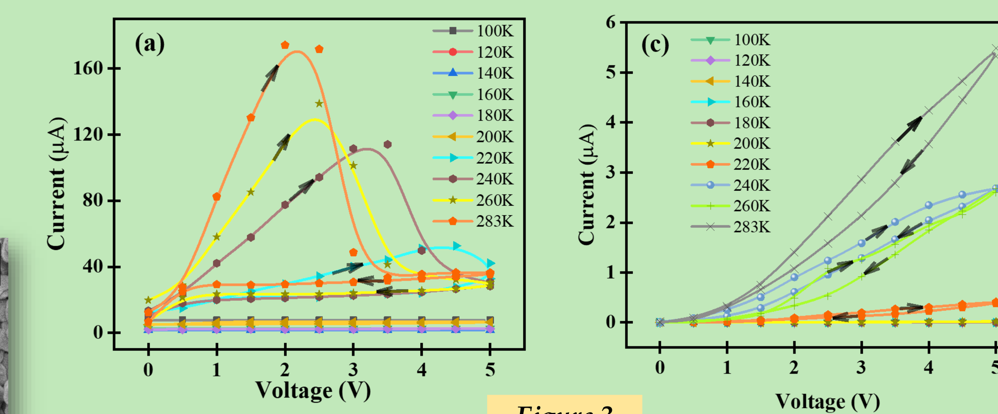

Figure 3

Low temperature *I-t* data

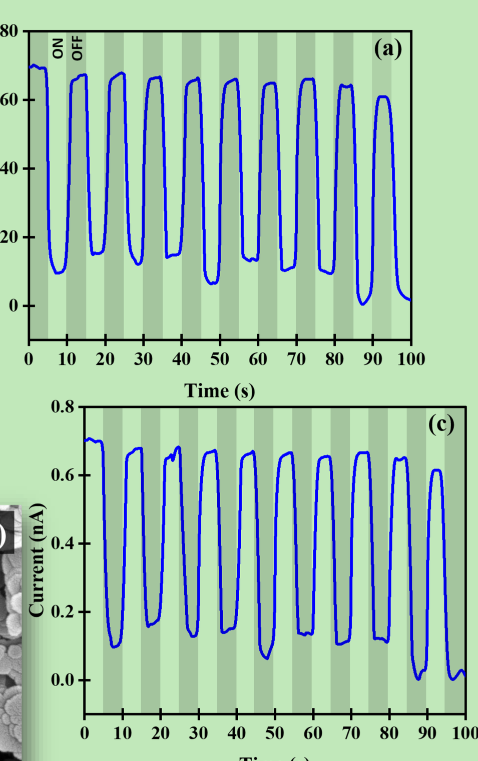

Figure 5

Device Characteristic

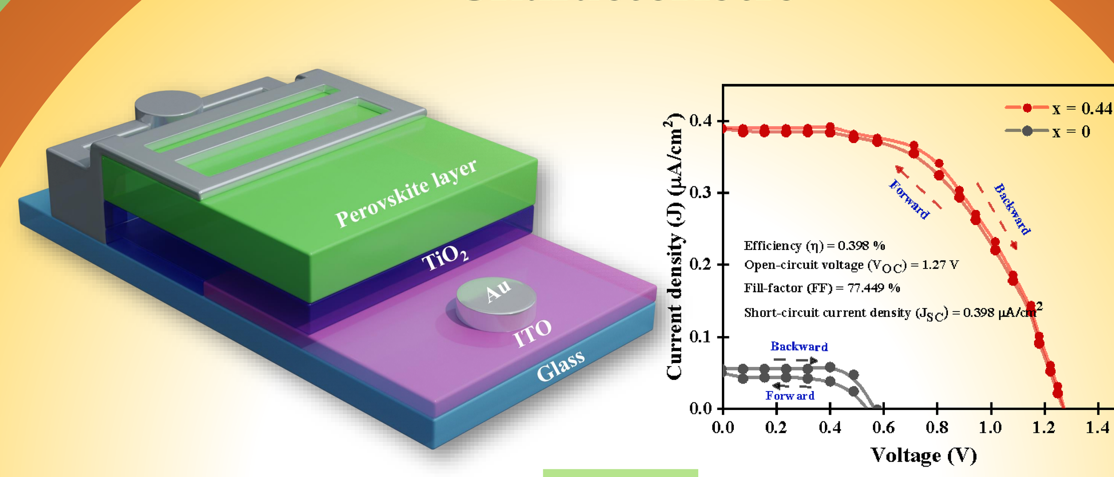

Figure 6

J-V characteristic curve for both forward and reverse scanning direction of the device using $MABiBr_{0.44}Cl_{0.66}$ (red line) and MABiCl (black line) as the absorber layer is depicted. From (a), the calculated results of the solar cell parameters are efficiency = 0.398 %, V_{OC} = 1.27 V, FF = 77.449%, and J_{SC} = 0.398 μA/cm² for $MABiBr_{0.44}Cl_{0.66}$ and the efficiency corresponding to MABiCl is lower than 0.1%.

Conclusions

- Controlled current-voltage (I-V) and current-time (I-t) profiles of the perovskite layer under dark and light irradiation at temperatures ranging from 100-283 K.
- The detection of ion migration phenomena using the low-temperature electrical method is the highlight of our work.
- The effect of compositional tuning of halides (Br and Cl) on ion migration and electron transport was highlighted.
- NPC magnitude depended on the halide composition ratio and temperature.

Discussions

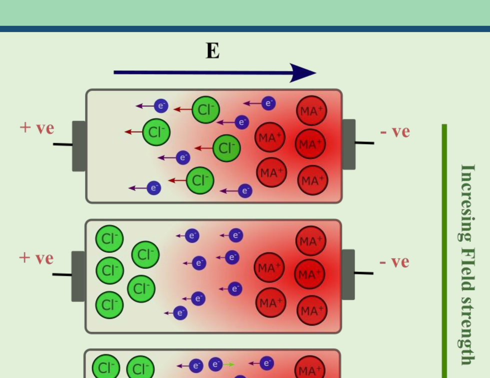

Figure 8

Schematic diagram showing the effect of ion migration to explain the experimentally obtained *I-V* characteristics. The application of an external electric field initiates the movement of electrons and Cl^- ions, giving rise to the increase in current with increasing voltage. When the Cl^- ions start to accumulate on the opposite side, it results in an opposite electric field, which corresponds to the peak value of the current. After completion of the ion migration process, the opposite electric field reaches its maximum, and the current decreases with increasing voltage.

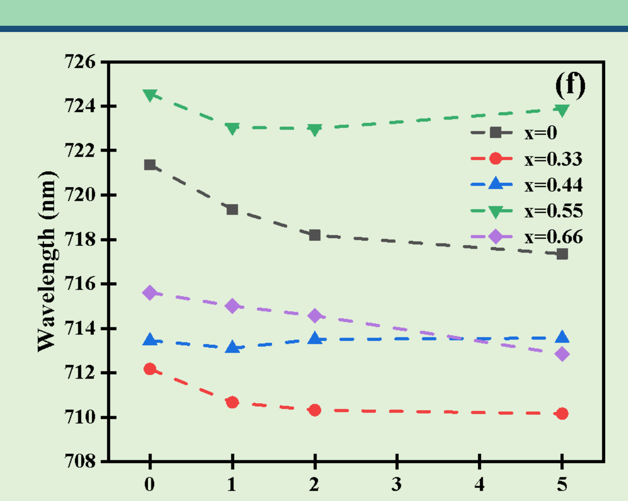

Figure 9

PL peak energy values are plotted in with time and different Br doping concentrations. The plots show that the PL energy peak tends to blue shift. The maximum blueshift is observed for the undoped x = 0 sample and decreases with Br doping concentration.

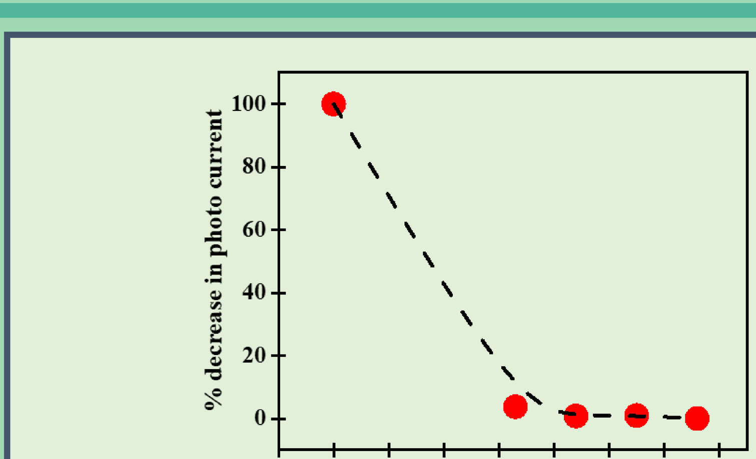

Figure 10

Plot of % decrease in (negative) photocurrent (nA) with increase in Br content in the mixed halide perovskite. The charge screening effect arising out of two separate charge centres (Cl^- and Br^- ions) plausibly leads to the observed result.

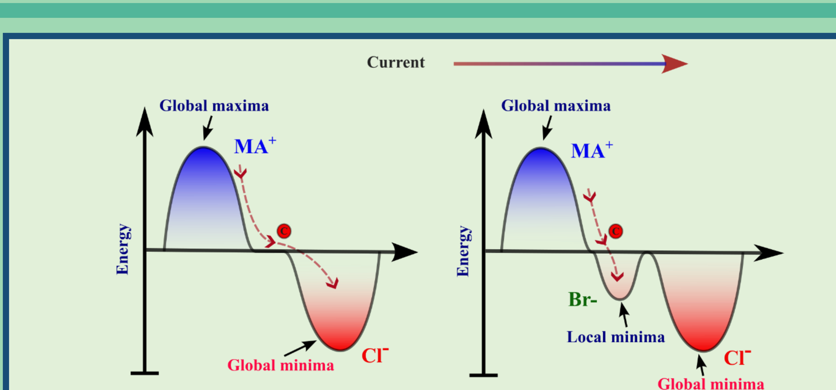

Figure 11

For x = 0, the light illumination creates an energy valley and peak for the motion of charge carriers, which in turn causes the negative photocurrent. In the case of mixed halides, the motion of carriers is restricted between a local minimum and global maxima.

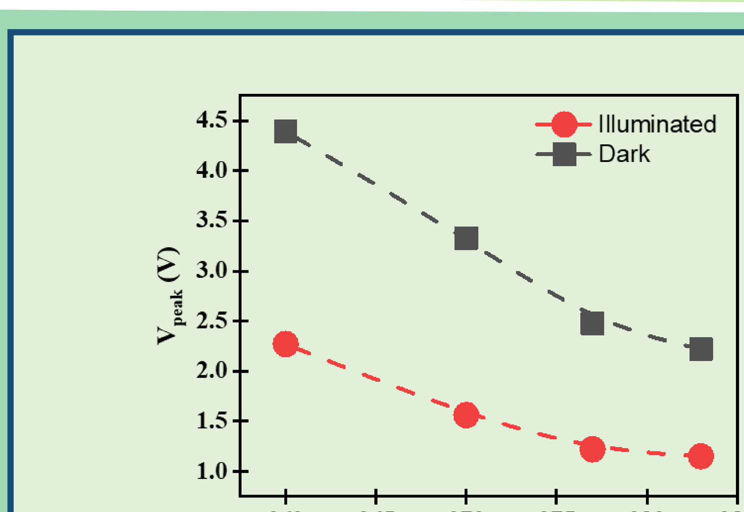

Figure 12

Plot of V_{peak} at peak current with temperature. The peak voltage tends to decrease with the increase in temperature and illumination of light. We treat the external electric field, temperature, and illumination of light to be external biases that contribute to the ion migration process. The data reflects the influence of external biases on the ion migration phenomenon.

Reference
- *Observation of Negative Photoconductivity in $(CH_3NH_3)_3Bi_2(Br_xCl_{1-x})_9$: Correlating Ion Migration, Stability, and Efficiency in Mixed Halide Perovskite Solar Cell.* Paramesh Chandra and Swapan Kumar Mandal *The Journal of Physical Chemistry C* 2023 127 (47), 23109-23121. DOI: 10.1021/acs.jpcc.3c06427