Supporting Information

Designation of A Novel and Highly Stable Lead-Free Cs_2NaBiI_6 Double Perovskite for Photovoltaic Application

Chu Zhang, Siowhwa Teo, Shuai Zhao, Zhanglin Guo, Zhenhua Xu, Liguo Gao, Tingli Ma

1. Calculation of tolerance factor (t) and octahedral factor (μ)

Tolerance factor (t) and octahedral factor (μ) were both determined to predict the structure of our synthesized double perovskite to determine whether the crystal structure can be octahedral.

$$t = (r_A + r_X)/\sqrt{2}(r_B + r_X)$$

$$\mu = r_B/r_X$$

where r_A, r_B, and r_X are the ionic radii of elements A, B, and X, respectively. In the case of the double perovskite halides, the ionic radii of B and B′ are averaged to obtain the r_B value. The calculated tolerance factor and octahedral factor of our synthesized CNBI double perovskite relative to typical $MAPbI_3$ are tabulated in Table S1. It shows that CNBI has similar tolerance factor as the MAPbI3, hypothesizing that our synthesized CNBI is in octahedral structure. While the smaller μ of CNBI indicates crystal lattice instability. However, it should be notified that the calculated t and μ factors are just predictions, while the actual crystal shape and stability were to be assured through practical experiments.

Table S1. Calculated tolerance and octahedral factors of CNBI as compared to $MAPbI_3$.

Photo-Active Material	Tolerance factor (t)	Octahedral factor (μ)
CNBI	0.849	0.466
$MAPbI_3$	0.83	0.54

2. The XRD reference of the sample

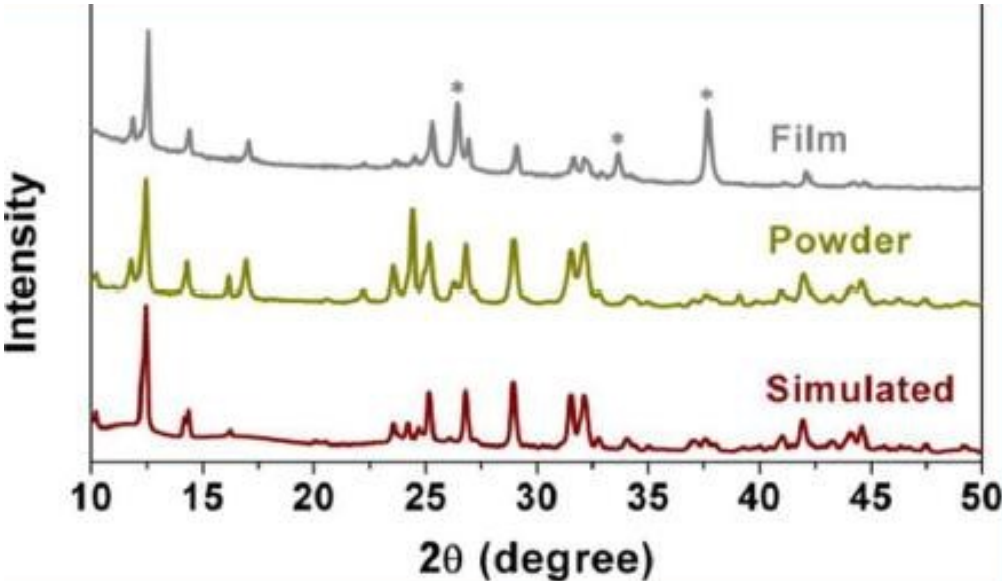

Fig. S1 Reference XRD pattern (MA2AgBiI6) [1]

3. The SEM images showing the asymmetric growth of the sample crystals

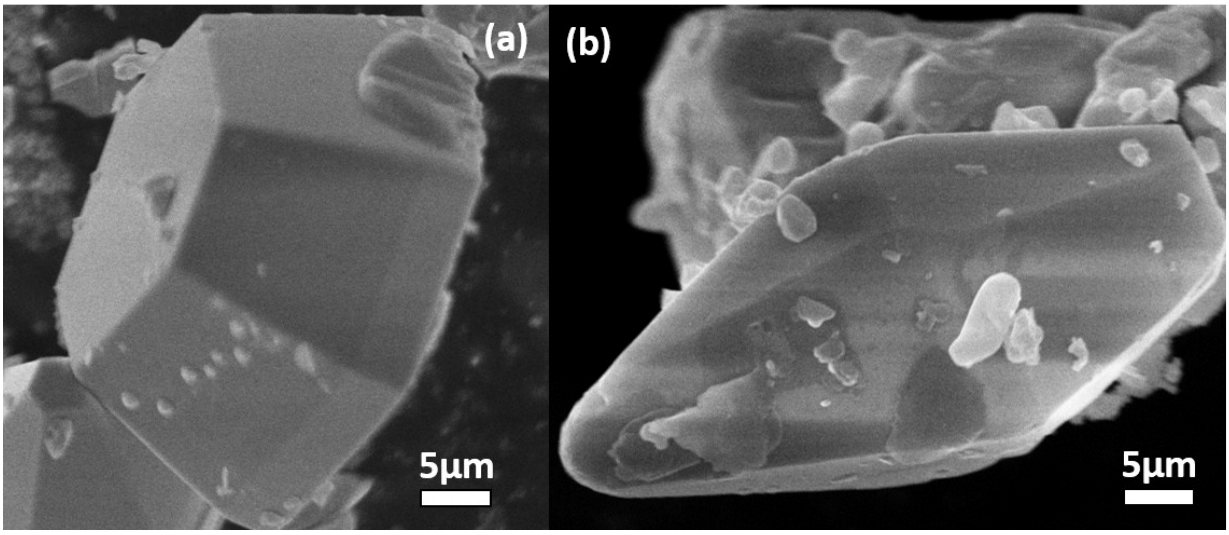

Fig. S2 SEM images of the crystals grown in (a) asymmetric double frustum and (b) asymmetric shuttle morphology.

4. The stability access of the cells.

Solar cells fabricated with the CNBI were stored in the ambient environment for 14 days to decide the stability of the devices. The I-V performance curves of the selected samples are shown in Fig. S3, and the values obtained were summarized in Table S2.

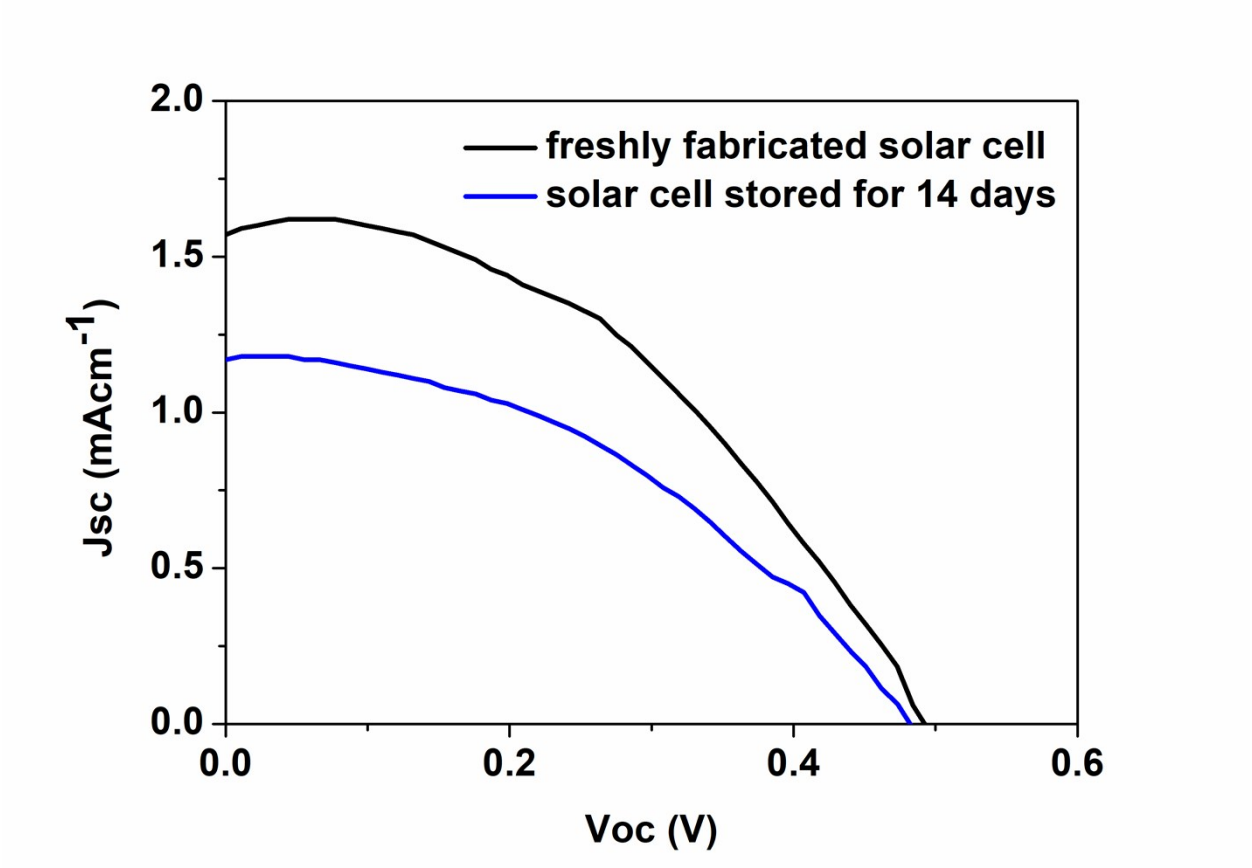

Fig. S3 The I-V curves of solar cell devices. Black line represents the fresh cell, while the blue line represents the cell after a storage period of 14 days.

Table. S2 Parameter comparison of the cells fresh and after storage

	PCE (%)	Voc (V)	Jsc (mA.cm^{-1})	FF
Freshly made	0.33 ± 0.07	0.45 ± 0.02	1.80 ± 0.20	0.40 ± 0.04
After storage	0.27 ± 0.06	0.45 ± 0.02	1.50 ± 0.20	0.39 ± 0.04

Reference:

[1]. P. Cheng, T. Wu, Y. Li, L. Jiang, W. Deng and K. Han, ***New J. Chem.***, 2017, **41**, 9598-9601.