

# Can the Spacer Cation Affect the Preferential Growth and Phase Segregation in 2D Ruddelsden-Popper Perovskites?

Saeed Bayat<sup>a</sup>, Hossein Abdizadeh<sup>a,b,\*</sup>, Mohammad Reza Golobostanfard<sup>a,\*</sup>

<sup>a</sup> School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, Tehran, Iran

<sup>b</sup> Center of Excellence in Materials for Low-Energy Consumption Technologies, University of Tehran, Tehran, Iran

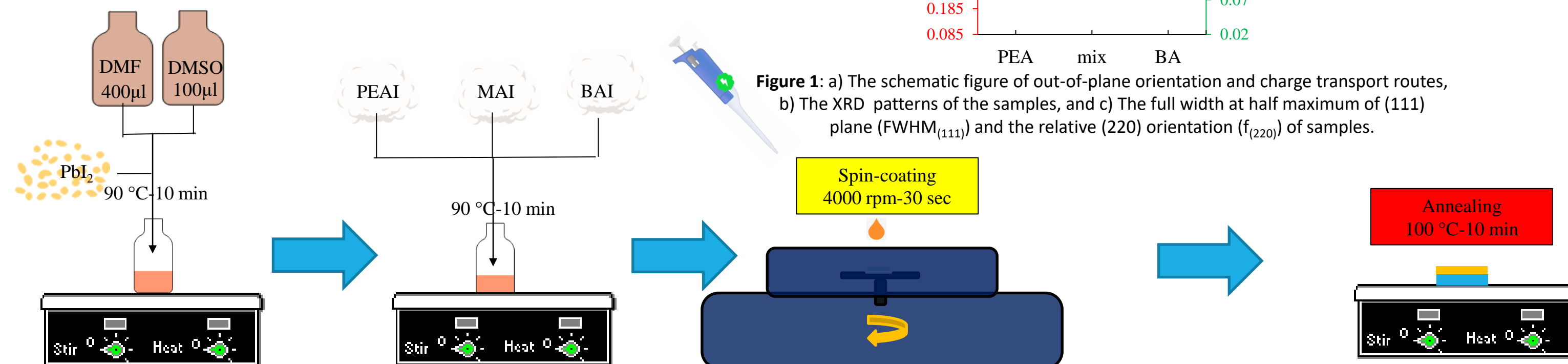
## ABSTRACT

Organic-inorganic halide perovskites (OIHP) are an emerging family of semiconductor materials widely used in the fabrication of optoelectric devices, including solar cells, due to their superior optical and electrical properties. Poor long-term stability of OIHPs is the main hindrance to the commercialization of perovskite solar cells. Using 2D Ruddelsden-Popper (RP) perovskites with multi-quantum wells (MQWs) structure is a common approach to improving perovskite solar cells' stability. However, the presence of MQWs structure restricts the transport of charges and thus reduces the photovoltaic performance of perovskite solar cells. Out-of-plane growth of 2D perovskite film can significantly improve carrier transport and consequently reduces the rate of non-radiative recombination. One of the main factors that affects the preferential growth of 2D perovskites is the type of spacer cation that exists in the 2D perovskites structure. Herein, butylammonium (BA) and phenetylammonium (PEA) spacer cations, as well as their combination, are employed in 2D perovskite thin film, and their effects on preferential growth and phase segregation have been investigated. X-ray diffraction (XRD) data shows that the BA-based 2D perovskite has more desirable (220) preferential direction but the preferred peaks of PEA-based 2D perovskite have higher intensity and narrower full width at half maximum (FWHM) than the BA-based counterparts, which is due to the rigid nature of the PEA molecule compared to the BA molecule. It is also observed that the replacement of BA instead of PEA significantly reduces phase segregation. This phenomenon is probably related to the phenyl ring of the PEA molecule, which is entirely solvophobic and slows down the formation of DMF:PEAI complex during the crystallization step, which in turn leads to the formation of small n 2D perovskite nucleus causing phase segregation. SEM images also represent that the BA,PEA-based film has a smoother surface and lower pinholes than the PEA and BA-based 2D perovskite.

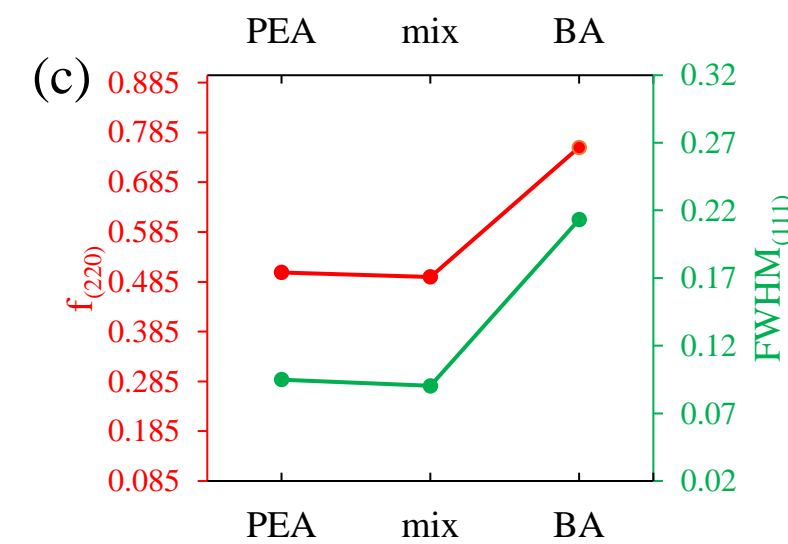
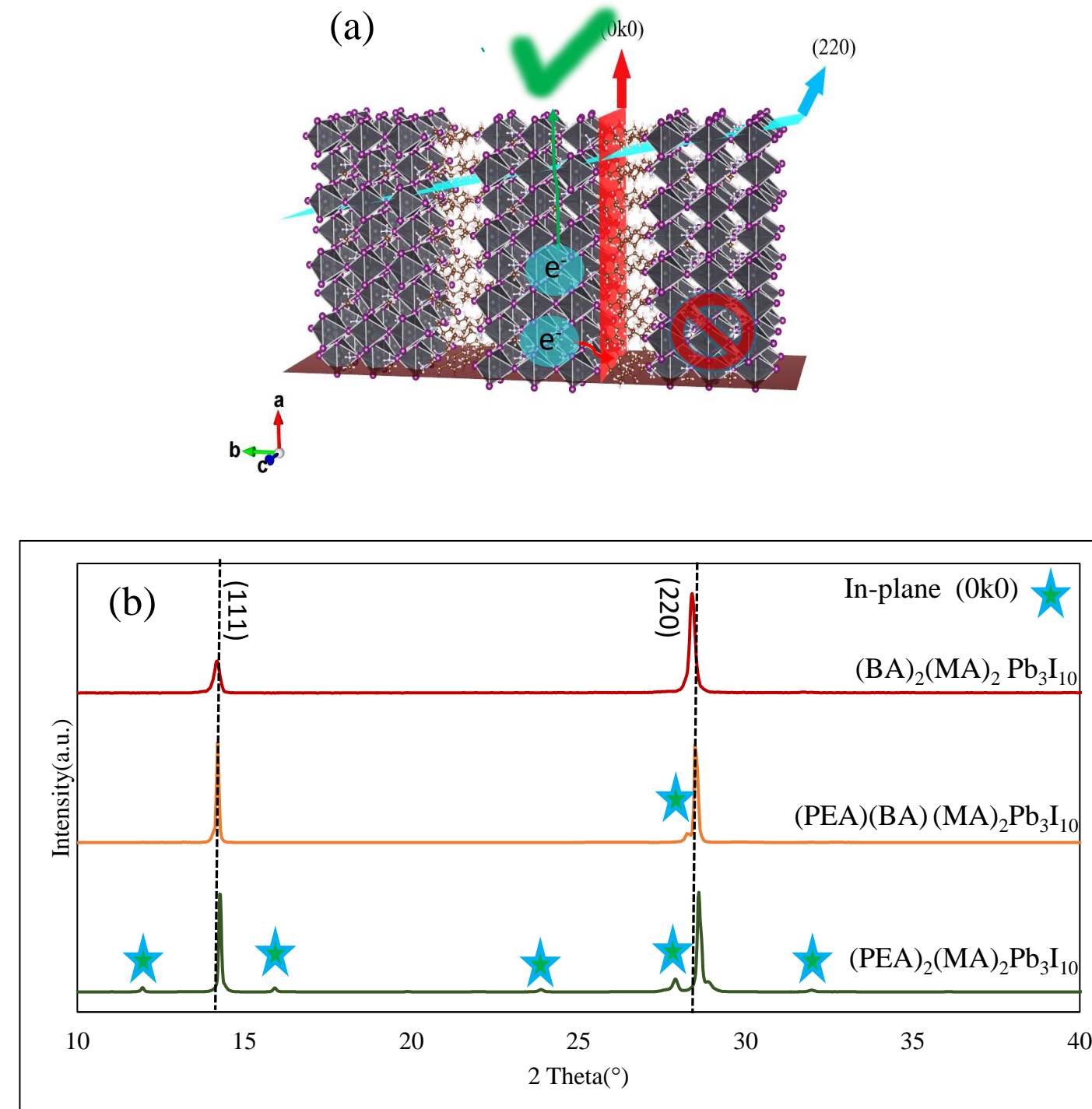
## OBJECTIVES

- ❖ Effect of spacer cations on the preferential orientation of 2D RP perovskites.
- ❖ Effect of spacer cations on the phase segregation of annealed 2D RP perovskites.
- ❖ Utilizing mixed spacer cation as a new strategy for improving 2D perovskite film quality.

## MATERIALS & METHODS

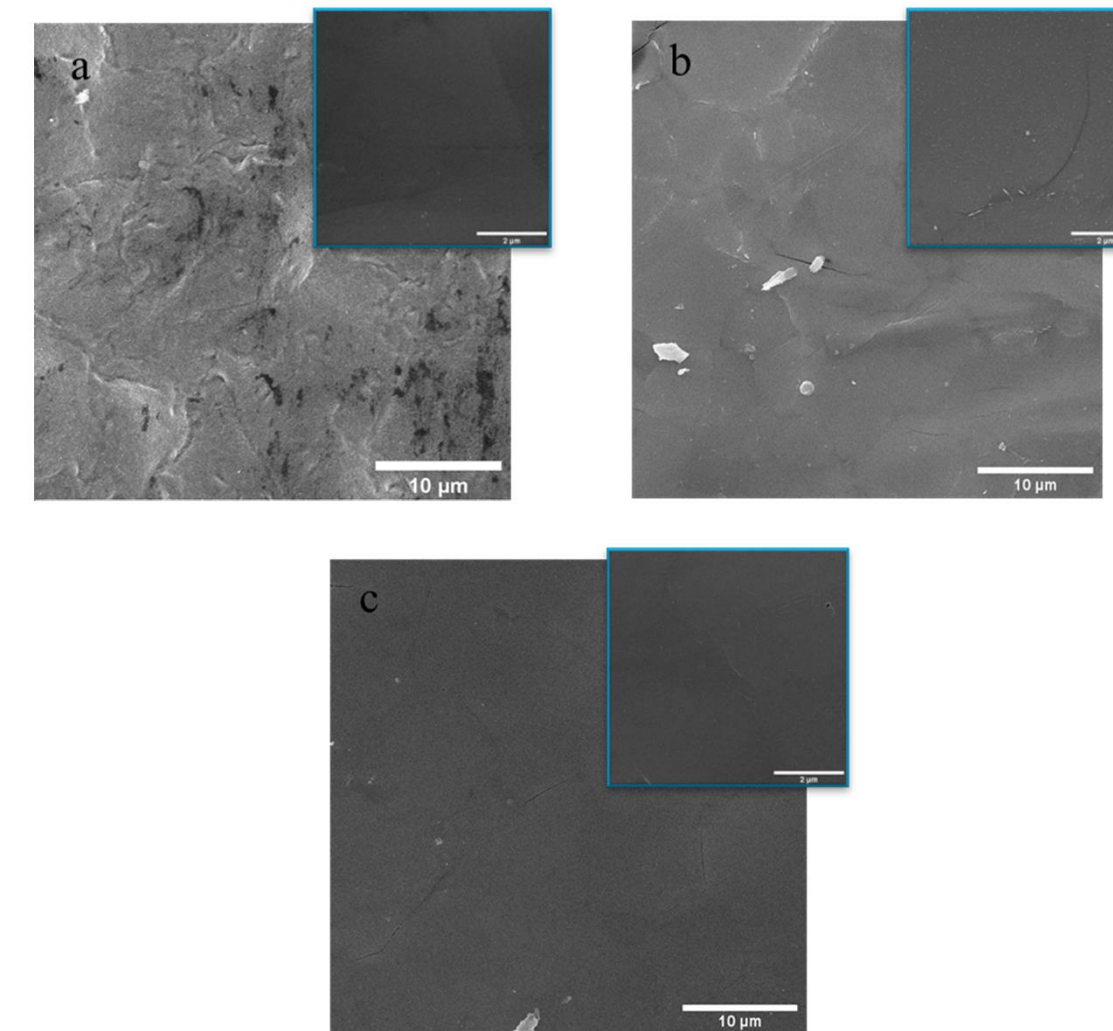


## RESULTS



**Figure 1:** a) The schematic figure of out-of-plane orientation and charge transport routes, b) The XRD patterns of the samples, and c) The full width at half maximum of (111) plane (FWHM<sub>(111)</sub>) and the relative (220) orientation (f<sub>(220)</sub>) of samples.

- Fig.1-a shows the structure of 2D RP perovskite and desirable charge transport path.
- In XRD pattern of samples, the peak position of 14.2° and 28.5° that are related to the (111) and (220) planes, are the prominent peaks in all samples thus the out-of-plane growth is dominant in all of them (Fig.1-b).
- the low-intensity peaks belonging to (0k0) planes can be seen in the (PEA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> pattern, which represented the undesirable in-plane growth of 2D RP perovskite (Fig.1-b).
- In (PEA)(BA)(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> sample, the peak position of (111) plane is shifted about -0.04° compared to PEA-based and +0.08 compared to BA-based sample. It represents the simultaneous presence of PEA<sup>+</sup> and BA<sup>+</sup> in the structure of (PEA)(BA)(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> sample (Fig.1-c).
- The full width at half maximum of (111) plane (FWHM<sub>(111)</sub>) of (PEA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> is lower than BA-based counterpart, which represents high crystal quality and coarser crystallite size of PEA-based sample (Fig.1-c).
- The f(220) diagram indicates that the BA-based sample has more intense (220) oriented preferential growth than PEA-based sample which shows the preferential orientation highly depends on type of spacer cation molecules (Fig.1-c).



**Figure 2:** FESEM image of 2D RP thin film with different spacer cation: a) (BA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub>, b) (PEA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub>, and c) (PEA)(BA)(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> (the inset is a high magnification image (×30k)).

- FESEM images of samples show that the BA-based sample has rough surface with high pinhole density.
- The PEA-based sample possesses dense and packed grains with a very coarse average grain size (about 4 μm), but the presence of PbI<sub>2</sub> particles indicates severe phase segregation which is proved in its XRD pattern.
- The (PEA)(BA)(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> sample has uniform and pinhole free surface without PbI<sub>2</sub> particles.

## CONCLUSION

In conclusion, the effect of bulky spacer cation on the phase segregation, preferential growth, and morphology of 2D RP perovskite is studied. The PEA-based sample has an excellent smooth morphology, but the BA-based sample has a non-uniform and rough surface. Instead, the phase segregation and partially in-plane orientation are observed in the PEA-based sample, which is probably related to the phenyl ring of PEA molecules which acts as a solvophobic agent. On the other hand, it is observed that the (PEA)(BA)(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> sample has good uniform morphology with a segregation-free surface and a large grain size compared to other samples. The low FWHM<sub>(111)</sub> and the negligible amount of in-plane oriented phase in this sample indicates that the synergistic effect of two types of cation improves the crystallinity and surface quality of (PEA)(BA)(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> thin film. Finally, it was observed that the type of spacer cation not only changes the total amount of the preferred planes but also plays a decisive role in determining the phase orientation and phase segregation of the 2D RP perovskites.

## CONTACT



Ssaeed.bayat@ut.ac.ir

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