
Zhenghong Dai, Srinivas K. Yadavalli, Mingyu Hu, Min Chen, Yuanyuan Zhou, Nitin P. Padture*

School of Engineering, Brown University, Providence, RI 02912, USA

A R T I C L E   I N F O

Article history:
Received 4 March 2020
Revised 22 March 2020
Accepted 23 March 2020

Keywords:
Halide perovskites
Thin films
Mechanical behavior
Grain boundaries
Solar cells

A B S T R A C T

Organic-inorganic halide perovskite (OIH) thin films at the heart of the new perovskite solar cells (PSCs) are very brittle, limiting the mechanical reliability of PSCs. Here we show that fine-grained MAPbI₃ (prototypical OIH) films with grain size (~290 nm) smaller than the typical film thickness (~500 nm) tend to fracture intergranularly, resulting in low toughness (0.41 J m⁻²). In contrast, MAPbI₃/substrate interfacial fracture occurs in films with grains larger (~730 nm) than the film thickness, resulting in much higher toughness (1.14 J m⁻²). Thus, coarse-grained OIH films are deemed desirable for not only improved PSCs performance and stability but also mechanical reliability.

© 2020 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

The record efficiency of perovskite solar cells (PSCs), incorporating thin films of organic-inorganic halide perovskite (OIH) as light absorbers [1–3], has rocketed from 3.8% in 2009 [4] to 25.2% in 2019 [5], rivalling that of silicon solar cells. The promise of low-cost, solution-processed PSCs with high efficiencies [6], and their potential impact on the global renewable-energy landscape, is driving this effort worldwide. Also, the light-weight, thin-film nature of PSCS makes them uniquely suitable as flexible PVs for portable-power applications such as chargers, tents, backpacks, deployable rollups, drones, etc. [7–9]. Furthermore, OIHs are also useful in other potential applications such as light-emitting diodes, lasers, and detectors [10].

The low formation energies of OIHs makes it possible to solution-process them, at or near room temperature [6], but it also makes them unstable [11,12]. While significant progress has been made in improving the stability of OIHs [11,12], any devices incorporating OIHs will also need to be mechanically reliable if they are to operate satisfactorily for decades [12–16]. The mechanical stresses that the OIHs within PSCs will need to endure include internal residual stresses, stresses arising from thermal excursions, and externally-applied stresses during manufacturing and service. Unfortunately, the low formation energies of OIHs also makes them compliant (low Young’s modulus, $E$), soft (low hardness, $H$), and brittle (low fracture toughness, $K_{IC}$) [13–15,17–21]. For example, the prototypical OIH – methylammonium lead triiodide (CH₃NH₃PbI₃ or MAPbI₃) – has $E$ = 17.8 GPa, $H$ = 0.58 GPa, and $K_{IC}$ = 0.22 MPa.m¹/² (toughness, $G_C = K_{IC}^2/E \sim 2.7$ J m⁻²) as measured using nanoindentation of single-crystals [14].

In this context, the mechanical behavior of OIH grain boundaries is also important, because OIH thin films used in PSCs are invariably polycrystalline due to the way they are solution-processed. While there has been reference to the effect of grain size on the $G_C$ of OIH thin films by Rolston, et al. [15] there have been no systematic studies on this important topic. Furthermore, the mechanical behavior of the interfaces between OIH thin film and the adjacent functional layers needed in PSCs, such as electron-transport layer (ETL) or hole-transport layer (HTL), is equally important. Here we have characterized the fracture behavior, and measured the $G_C$ values, of MAPbI₃ thin films with two different average grain sizes. We find that fracture in thin films with an average grain size (~290 nm) smaller than the typical film thickness (~500 nm) occurs within the MAPbI₃ thin film intergranularly, with a low $G_C$ of 0.41±0.17 J m⁻². In contrast, when the average grain size (~730 nm) is larger than the film thickness, fracture is forced to occur along the interface between MAPbI₃ and the ETL, resulting in a much higher $G_C$ of 1.14±0.24 J m⁻². However, these values are still much lower than that of single-crystal MAPbI₃ $G_C$ of ~2.7 J.m⁻² [14].

The glass substrates (microscope slides, 37.5 x 12.5 x 1 mm³) used in this study were coated with a thin layer (~25 nm) of SnO₂, a commonly used ETL in PSCs, using a process described elsewhere [22]. The MAPbI₃ thin films (~500 nm thickness) were

* Corresponding author.

E-mail address: nitin_padture@brown.edu (N.P. Padture).

https://doi.org/10.1016/j.scriptamat.2020.03.044
1359-6462/© 2020 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
solution–deposited on the ETL-coated glass substrates using the ‘solvent-engineering’ method [23]. Briefly, the precursor solution was prepared by dissolving 159 mg of MAL (Greatcell, Australia) and 461 mg of PbI₂ (Sigma-Aldrich, USA) in 620 mg of N,N-dimethylformamide (DMF; Acros Organics, USA) to obtain a 50 wt% solution. The solution was then spin-coated at 4000 rpm for 20 s total. At the 7th second of spinning, 250 µL of the anti-solvent chlorobenzene (Sigma-Aldrich, USA) was dripped at the center. The as-coated wet film was then annealed at 120 °C for 10 min on a hot-plate (uncovered) to obtain fine-grained MAPbI₃ thin films. To obtain coarse-grained MAPbI₃ thin films, the ‘solvent-annelling’ method was used [24,25]. Here, the as-coated wet film was covered by an inverted Petri dish and annealed at 120 °C for 20 min on the hot-plate, where a 10 µL drop of dimethyl sulfoxide (DMSO; Acros Organics, USA) was placed near the substrate under the Petri dish. Subsequently, the as-processed surfaces of both types of MAPbI₃ thin films were coated with thin layer (~160 nm) of polymethylmethacrylate (PMMA) for protection. This was accomplished by spin-coating 80 µL of a 10 wt% PMMA (Sigma-Aldrich, USA) solution in chlorobenzene at 4000 rpm for 20 s while not damaging the MAPbI₃ thin film. This was allowed to dry at room temperature for 30 min. All the aforementioned steps were performed in a N₂-filled glovebox. A thin layer of epoxy (Hysol, USA) was then applied onto the PMMA layer to ‘glue’ another cleaned glass substrate on top. The ‘sandwich’ double cantilever beam (DCB) specimens were then cured in a drybox for 12 h, and the excess epoxy at the edges was cleaned off with a razor blade before mechanical testing.

The DCB specimens were tested using a method described elsewhere [15]. Briefly, a planar crack was introduced along the width (B = 12.5 mm) dimension of the specimen by inserting a razor blade into the ‘sandwich.’ Aluminum tabs were glued to the glass substrates on either side of the ‘sandwich’ specimen at the cracked end of the long dimension (37.5 mm). The cracked DCB specimens were loaded in tension to ‘peel’ the specimen apart using a Delaminator apparatus (DTS, USA). A constant displacement rate of 0.4 µm.s⁻¹ was used, and the load (P) - displacement (Δ) response was recorded during loading. The crack length (a) of the DCB sample was estimated using the compliance method in conjunction with the following relation: [15]

$$a = \left( \frac{d\Delta}{dP} \times \frac{BEh^3}{B} \right)^{\frac{1}{2}} - 0.64h,$$

where B (= 12.5 mm) and E (= 70 GPa) are the width and the Young’s modulus of the glass substrate, respectively, and h (= 1 mm) is the half-thickness of the DCB specimen (all the layers in the ‘sandwich’ are much too thin and are neglected). The toughness Gc is then given by the relation: [15]

$$G_c = \frac{12P_c^2a^2}{B^2Eh^3} \left( 1 + 0.64 \frac{h}{a} \right)^2,$$

where Pc is the peak load at failure. Five DCB specimens were tested for each grain size, and the average Gc and the standard deviation values are reported for each set.

Scanning electron microscopes (SEMs; LEO 1530 VP, Zeiss, Germany or Quattro ESEM, ThermoFisher Scientific, USA) were used to observe top surfaces of the as-processed fine-grained and coarse-grained MAPbI₃ thin films. The grain sizes were determined using the linear-intercept method on the SEM images, in conjuction with the ImageJ image-analysis software, where ~100 grains were used for each set of materials. Note that the naturally formed grooves were assumed to represent the grain boundaries, which can lead to some overestimation of the grain size in OIHP thin films [26,27]. The mating fracture surfaces of the failed DCB specimens after mechanical testing were also observed in the SEM. X-ray diffraction (Discovery D8, Bruker, Germany) was performed on the top surfaces of the as-processed MAPbI₃ thin films, and the mating fracture surfaces.

Figs. 1A and 2A show SEM images of the top surfaces of as-processed fine-grained and coarse-grained MAPbI₃ thin films with estimated average grain sizes of ~290 nm and ~730 nm, respectively. The indexed XRD patterns in Figs. S1A and S1B in Supplementary Material (SM) confirm single-phase MAPbI₃ in both the fine-grained and coarse-grained thin films, respectively.

Fig. 1B and C are SEM image and photograph, respectively, of the fracture surface of the top half of the fine-grained DCB specimen after failure. The presence of MAPbI₃ is clearly seen (appears dark visually), which is confirmed by the XRD pattern in Fig. S1A in SM. Similarly, Fig. 1D, E, and S1A confirm the presence of MAPbI₃ on the mating fracture surface on the bottom side of the failed fine-grained DCB specimen. This indicates that fracture in the fine-grained DCB specimen occurs within the MAPbI₃ thin film, and the grain-size scale roughness observed in the SEM images in Fig. 1B and D indicates intergranular fracture. This is depicted schemati-
of the three-calystically (cross-section) in Fig. 1F. The corresponding $G_\text{C}$ is measured to be 0.41±0.17 J.m$^{-2}$ (Fig. 3), and it represents the grain-boundary toughness (cohesion) of the fine-grained MAPbI$_3$ thin film.

Fig. 2B and C are SEM image and photograph, respectively, of the fracture surface of the top half after failure of the coarse-grained DCB specimen, showing a relatively smoother fracture surface. The presence of MAPbI$_3$ is clearly seen, which is confirmed by the XRD pattern in Fig. S1B in SM. In contrast, Fig. 2D, E, and S1B indicate little presence of MAPbI$_3$ on the smooth mating fracture surfaces on the bottom side of the failed coarse-grained DCB specimen. These results indicate that the failure has occurred at the MAPbI$_3$/ETL interface in this case, as depicted schematically (cross-section) in Fig. 2F. The corresponding $G_\text{C}$ is almost three times higher at 1.14±0.24 J.m$^{-2}$ (Fig. 3), and it represents the toughness (adhesion) of the MAPbI$_3$/ETL interface. This failure mode is attributed to the fact that, unlike the fine-grained thin films, ‘horizontal’ lower-toughness grain boundaries do not exist in the coarse-grained thin films, thereby forcing the fracture to occur along the next weakest path, i.e. the MAPbI$_3$/ETL interface.

The results from this study clearly highlight, for the first time, the benefit of larger grains in improving the overall fracture resistance of OIHFP thin films for PSCs, and thereby the reliability. This is consistent with the other general improvements observed in both the performance and stability of PSCs by increasing the grain size (decreasing the grain-boundary density) in OIHFP thin films [6,26,28–31], which is largely due to the reduction in photocarriers scattering, recombination sites, and ingestion of environmental species.
Bending experiments were also performed, where the fine-grained and coarse-grained MAPbI$_3$ thin films were also deposited using the same procedure as above, but on flexible polyethylene terephthalate (PET) polymer substrates (15 × 10 mm$^2$, ~178 μm thickness) coated with indium-doped tin oxide (ITO; ~100 nm thickness) transparent-conducting oxide (obtained commercially; Sigma Aldrich, USA). These specimens were bent around a glass mandrel of radius 7.4 mm with the MAPbI$_3$ film on the outside (tension), using a procedure described elsewhere [16]. The specimens, while being bent (Fig. 4C), were observed inside the SEM. Fig. 4A and B are top-surface SEM images of fine-grained and coarse-grained MAPbI$_3$ thin films, respectively, showing intergranular ‘channeling’ cracks, which is depicted schematically in Fig. 4C for the coarse-grain case. The intergranular nature of fracture in the fine-grained thin film is not surprising as the grain-boundary toughness is significantly lower than the single-crystal toughness (Fig. 3). But importantly, these results show that grain boundaries in both fine-grained and coarse-grained thin films are equally weak. This supports the above argument that the interfacial fracture in the coarse-grained DCB specimen (Fig. 2) occurs because of the paucity of ‘horizontal’ grain boundaries.

Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement
The financial support for this research from the Office of Naval Research (grant# N00014-17-1-2232) and the National Science Foundation (grant# OIA-1538893 and OIA-1929019). The authors thank N. Rolston for helpful discussions.

Supplementary materials
Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.scriptamat.2020.03.044.

References


SUPPLEMENTARY MATERIAL


Zhenghong Dai, Srinivas K. Yadavalli, Mingyu Hu, Min Chen, Yuanyuan Zhou, and Nitin P. Padture*

School of Engineering, Brown University, Providence, RI 02912, USA

* Corresponding author. Email address: nitin_padture@brown.edu (N.P. Padture)

Figure S1. Indexed XRD patterns of top surface of as-processed MAPbI\textsubscript{3} thin film, top fracture surface, and bottom fracture surface: (A) fine-grained and (B) coarse-grained.