Letter

Tightly Compacted Perovskite Laminates on Flexible Substrates via Hot-Pressing

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Abstract: Pressure and temperature are powerful tools applied to perovskites to achieve recrystallization. Lamination, based on recrystallization of perovskites, avoids the limitations and improves the compatibility of materials and solvents in perovskite device architectures. In this work, we demonstrate tightly compacted perovskite laminates on flexible substrates via hot-pressing and investigate the effect of hot-pressing conditions on the lamination qualities and optical properties of perovskite laminates. The optimized laminates achieved at a temperature of 90 °C and a pressure of 10 MPa could sustain a horizontal pulling pressure of 636 kPa and a vertical pulling pressure of 71 kPa. Perovskite laminates exhibit increased crystallinity and a crystallization orientation preference to the (100) direction. The optical properties of laminated perovskites are almost identical to those of pristine perovskites, and the photoluminescence quantum yield (PLQY) survives the negative impact of thermal degradation. This work demonstrates a promising approach to physically laminating perovskite films, which may accelerate the development of roll-to-roll printed perovskite devices and perovskite tandem architectures in the future.

Keywords: perovskite lamination; hot-pressing; recrystallization; flexible substrates

1. Introduction

Halide perovskites have exhibited intriguing properties including long carrier lifetimes, strong band-edge absorption, high photoluminescence quantum yield (PLQY), tunable emission of high color purity, low cost, and easy processing, emerging as a type of promising material for optoelectronic devices such as solar cells, light-emitting diodes, photodetectors, field effect transistors, memristors, and lasers [1–7]. Moreover, with the demands for portable, stretchable, and wearable devices enormously increasing, halide perovskites, which have exhibited mechanical flexibility [8], are a promising candidate. A number of methods have been applied for spreading halide perovskites on flexible substrates, such as doctor blading [9], spin-coating [10], slot-die coating [11], spray coating [12], vapor deposition [13], and inkjet printing [14]. Song et al. synthesized ultrathin two-dimensional (2D) CsPbBr$_3$ nanosheets on flexible substrates by ink-injecting [15], and Chen et al. reported a vapor-assisted solution process to manufacture methylammonium lead iodide (MAPbI$_3$) thin film. Kumar et al. demonstrated 2D FAPbBr$_3$ thin films by spin-coating, leading to ultra-flexible LEDs with a large area (3 cm$^2$) [10].

Recently, GPa-scale high pressure (1 GPa $\approx$ 10,000 atm), achieved through a diamond anvil cell, has been reported to induce phase transition and bandgap engineering of perovskites [16–19]. For instance, the high pressure can tilt the PbBr$_6$ octahedra of methylammonium lead bromide (MAPbBr$_3$) and destroy the long-range ordering of organic cations, leading to two phase transformations below 2 GPa and a reversible amorphization arising at approximately 2 GPa [16]. Similar phenomena were also...
observed for α-formamidinium lead iodide (α-FAPbI$_3$) at 0.3 and 1.7 GPa [17]. Apart from this, the pressure-induced optical response was investigated for a two-dimensional perovskite crystal, the photoluminescence of which was red-shifted continuously at pressures within 3.5 GPa [19]. As the pressure is increased to 60 GPa, the electronic landscapes of methylammonium lead iodide (MAPbI$_3$) can be largely altered and may make new electronic phenomena possible, such as superconductivity which is not accessible through conventional syntheses [18].

In addition to GPa-scale pressure, pressure in the range of MPa (1 MPa ≈ 10 atm), which can be easily attained in a typical mechanical testing environment, could also induce morphological and optical changes of perovskites. Pressure-induced crystallization of perovskites was observed during soft-stamp nanoimprinting, which was then used to prepare highly efficient perovskite solar cells [20]. Meanwhile, the emission spectral profile of layered perovskites was reported to be sensitive to cyclic mechanical loading in the range of tens of MPa due to the alignment of layered perovskite flakes [21]. More importantly, lamination can be achieved based on the recrystallization of perovskites, which is a promising strategy for industrial fabrication of perovskite devices since it can avoid the limitations of material choices, the issue of solvent compatibility, and device instability by forming a self-encapsulating structure [22–24]. Dunfield et al. demonstrated a lamination process at the perovskite/perovskite interface, where two half-device stacks were independently fabricated and subsequently laminated by balancing the chemical reaction MAPbI$_3$(s) + heat ⇌ MA(g) + HI(g) + PbI$_2$(s) [22]. Schmager et al. reported laminated perovskite solar cells using two separately processed half-stacks at the interface of the charge transport layer instead of the perovskite layer [23]. However, these two cases require either chemical reaction of specific perovskite components or functional materials. To realize a general approach to fabricating laminated perovskite devices, it is ideal to achieve a high-quality lamination at the perovskite/perovskite interfaces physically, regardless of the components of laminated perovskites.

This work demonstrates perovskite laminates on flexible substrates via hot-pressing and investigates the effect of hot-pressing conditions on lamination qualities and optical properties of perovskite laminates. Instead of the chemical reaction of MAPbI$_3$, we utilize the hybrid nature and soft lattice properties of halide perovskites to obtain perovskite laminates, which is practicable for all halide perovskites. The lamination is based on recrystallization of perovskites when the heating and pressure are simultaneously applied, providing a facile, low-cost approach without complicated processes and facilities. This lamination approach is compatible with printing techniques for mass production, such as roll-to-roll and offset printing, as well as future tandem applications.

2. Experimental Methods

The CsPbBr$_3$-based precursor solution was prepared by mixing CsPbBr$_3$ (200 g/L in dimethyl sulfoxide (DMSO, Aladdin, Shanghai, China), molar ratio CsBr (99.999%, Sigma-Aldrich, Shanghai, China)/PbBr$_2$ (99.999%, Sigma-Aldrich, Shanghai, China) = 1.1:1) and polyethylene oxide (PEO, Aladdin) (20 g/L in DMSO) with the volume ratio 2:1. By adding PEO, the diffusion of CsPbBr$_3$ precursors could be limited. Thus, the grain size is significantly reduced, producing high-surface-coverage, pinhole-free thin films with lower surface roughness [25,26]. The polyethylene terephthalate (PET) substrates, prior to deposition, were sonicated in deionized water, then isopropanol alcohol, for 15 min each, and then UV–ozone treated for 15 min. The thin films were fabricated by spin-coating solutions onto flexible substrates inside an argon-filled glovebox, followed by 70 °C thermal annealing for 5 min. The fabrication method of pristine CsPbBr$_3$ thin films was the same as that of the thin films prepared for lamination. To make laminates, the two as-cast precursor films were stacked face to face and subsequently loaded into a custom-made hydraulic press machine with controlled temperature (room temperature, 70 °C, 90 °C, 150 °C) and pressure (5 MPa, 8 MPa, 10 MPa, 12 MPa).

The morphology of the perovskite films was characterized using a metallurgical microscope (Axio Scope.A1, ZEISS, Germany) and a field emission scanning electron microscope (FESEM, Nova NanoSem 450, FEI, USA). The crystal structures of perovskites were determined by X-ray diffraction
spectroscopy (XRD, D8A Advance, Bruker, Germany). The substrates with perovskite films after lamination were physically separated for metallurgical microscope, SEM, and XRD characterization. The absorption spectra were characterized by UV–visible spectroscopy (TU-1900, Purkinje, China). The photoluminescence (PL) spectra and PLQY were measured using a fiber-coupled spectrometer (QE Pro, Ocean Optics, USA), with an integrating sphere system, excited by a 365 nm laser. The PLQY values were calculated using Suzuki's method [27]. The time-resolved PL lifetimes were measured using a fluorescence lifetime spectrometer (FLS1000, Edinburgh Instruments, UK) excited by a 360 nm laser, and an optical filter was mounted in front of the detector to remove the excitation signal.

3. Results and Discussion

The lamination of perovskites is a powerful tool in device architectures and material bonding, and it cannot be achieved by conventional processing methods. In order to demonstrate the degree of mechanical bonding force of CsPbBr$_3$ perovskites after lamination, mechanical characterization was conducted. The laminated perovskite films were prepared by face-to-face hot-pressing two independently fabricated half-stacks of perovskite film on a flexible polyethylene terephthalate (PET) foil, as displayed in Figure 1a.

To check the bonding degree between the two perovskite films, forces were exerted to separate the laminated films in either a horizontal or vertical direction, as shown in Figure 1b,c. The force was divided by the laminated area to calculate the pressure as the degree of bonding and the horizontal and vertical pulling pressures at different temperatures and pressures were summarized. It was found that the perovskite films can only be successfully laminated within the temperature range from 70 °C to 150 °C and pressure range from 5 MPa to 10 MPa. For samples laminated at 70 °C, the horizontal pulling pressures were 83 kPa, 125 kPa, and 241 kPa at imposed pressures of 5 MPa, 8 MPa, and 10 MPa, respectively. When the temperature increased to 90 °C, the horizontal pulling pressures increased to 114 kPa, 444 kPa, and 636 kPa, respectively. When the temperature reached 150 °C, the horizontal pulling pressures were 236 kPa, 219 kPa, and 295 kPa at imposed pressures of 5 MPa, 8 MPa, and 10 MPa, respectively. For samples laminated at 90 °C, the vertical pulling pressures were 13 kPa and 71 kPa at imposed pressures of 8 MPa and 10 MPa, respectively. When the temperature increased to 150 °C, the vertical pulling pressures were 14 kPa and 36 kPa, respectively. At a fixed temperature, the pulling pressure to separate two films increases as the imposed pressure increases, which means that the degree of bonding increases. The horizontal and vertical pulling pressure reach the optimal point simultaneously at 90 °C and 10 MPa. It is apparent that the perovskite films can only be laminated when both heat and pressure are applied. Pressure and heat have a synergistic effect on perovskite lamination and cause recrystallization of the perovskite. Room temperature or pressure without heat cannot lead to a successful lamination. However, when the imposed pressure was further increased to 12 MPa, the lamination failed regardless of the heating temperature, probably because the relatively high pressure damaged the recrystallization of the perovskite films.

To further prove the successful lamination of perovskites, we characterized the separated perovskite films after lamination (90 °C, 10 MPA) using a metallurgical microscope and SEM, as well as pristine perovskite films without lamination. As shown in Figure 1d, the result of metallurgical microscopy reveals distinct differences. The metallurgical microscope images are true color luminescence images excited by a mercury short arc lamp (OSRAM HBO 103 W/2). The emission area of films without lamination is complete and uniform, whereas that of separated laminated films becomes incomplete, meaning that the perovskite materials were transferred to the other stack after lamination. This phenomenon was confirmed in the SEM results shown in Figure 1e. The surface of the separated perovskite film became incomplete after lamination, proving that the perovskite on one stack was successfully bonded to the perovskite on the other stack. The laminating method is well reproducible, and laminates fabricated over half a year prior were still tightly compacted, demonstrating that the laminating method is effective long term as well.
Figure 1. (a) Schematic illustration of the lamination process of perovskite thin films on flexible substrates. (b) Horizontal and (c) vertical pulling pressure of perovskite laminates as a function of temperature and imposed pressure. (d) Metallurgical microscope and (e) SEM images of the pristine CsPbBr$_3$ thin film and the laminated CsPbBr$_3$ thin film at 90 °C and 10 MPa. (f) Normalized absorbance spectra of the laminate prepared at 90 °C and 10 MPa and the corresponding delaminated CsPbBr$_3$ film.

To demonstrate that the properties of the delaminated samples—which were obtained by physically separating the laminates—do not change when compared with their laminates, we characterized the absorbance spectra of the laminated samples before and after the delamination process, as shown in Figure 1f. The absorbance curves of the laminated and delaminated samples are almost identical,
which demonstrates that delaminated samples could act as a rational qualitative metric for lamination effects. The same method was also followed in the previous report [22].

To further understand the morphological change during the lamination process, we characterized the crystallinity of perovskite films before and after lamination using XRD. According to the powder diffraction file (PDF) card shown in Figure 2a, the peaks locating at 15.2°, 21.5°, 30.7°, and 37.8° were assigned to the (100), (110), (200), and (211) planes of a typical CsPbBr₃ cubic structure, respectively. All CsPbBr₃ films with and without lamination exhibited three main diffraction peaks corresponding to the (100), (110), and (200) planes. No noticeable peak shift was observed after the heat-only process or the lamination process, indicating the absence of lattice macrostrain or homogenous changes in the crystal structure [28]. Although it is hard to rule out the possibility that the strain induced by hot-pressing might be released once the laminates were separated, such a possibility is quite small according to prior work [22]. In striking contrast, the heated or laminated CsPbBr₃ films gained sharper diffraction peaks compared to the pristine one, and the full widths at half-maximum (FWHMs) of the peaks were clearly narrowed, as summarized in Figure 2b. The peak of tetragonal two-dimensional phase CsPb₂Br₅ at 11.67° reported in prior work [29–31] was not observed in our samples, which is attributed to a shorter period of heating time and the existence of PEO in our case. It is interesting to notice that heating perovskite film without applying pressure can also evidently decrease the FWHM values. Compared to the pristine film before lamination, the FWHMs of diffraction peaks at 15.2°, 21.5°, and 30.7° were reduced to 95%, 81%, and 65% of their initial values, respectively, at a heating temperature of 90 °C. When the heating temperature was 150 °C, the FWHMs of diffraction peaks at 15.2°, 21.5°, and 30.7° were reduced to 75%, 73%, and 49%, respectively. When heat and pressure were simultaneously applied, the FWHMs of the three peaks maintained the same decreasing trend. Since both increased crystallinity with fewer defects and a larger grain size with fewer grain boundaries can result in a sharper XRD peak [32], these results indicate that the grains in perovskite films were larger in size and crystallinity increased.

![Figure 2](image-url)

**Figure 2.** (a) XRD patterns of the pristine CsPbBr₃ film and the separated laminates prepared under different conditions, and the corresponding histograms of XRD (b) FWHMs and (c) relative peak intensities of the (100), (110), and (200) planes.
To judge the recrystallization and crystallization orientation change of the perovskite laminates, we compared the relative intensity of each peak in the same sample, as shown in Figure 2c. The relative intensity was taken as the ratio of the intensity of one peak to the total intensities of the three main peaks at 15.2°, 21.5°, and 30.7°. The relative intensities of the dominant diffraction peaks corresponding to the (100), (110), and (200) lattice planes also varied significantly, proving recrystallization of the laminated perovskites [20,33]. It was found that the relative intensities of the (100) and (200) diffraction planes increased monotonically with increasing imposed pressure, while the intensity of the (110) plane decreased after lamination. The lamination induces a change in crystallinity from a (110)-dominant scenario to a (100)- and (200)-dominant scenario. When compared with the heated samples without applying pressure, the pressure-induced recrystallization was much more significant and preferred crystallization orientation along the (100) and (200) planes. It was reported that the (100) peaks in perovskites have a high relationship with heavy atoms Pb and Br with long-range ordered packing [16] and are able to provide efficient charge transport [34,35].

XRD provided evidence of substantial recrystallization and an overall improved crystal quality upon lamination. These results reveal explicitly that changes in FWHM are mainly derived from heat and changes in crystal orientation originating from pressure. When heated at a high temperature, the perovskite softens and the external pressure applied to the soft perovskite layer leads to recrystallization. Under the synergistical effect of temperature and pressure, the interatomic distances of perovskite can be adjusted, and thus, the crystallographic symmetry can be affected.

As to the optical properties of perovskite laminates, the CsPbBr$_3$ films show an absorption edge at 516 nm and a bright green PL emission centered at 528 nm under ambient conditions, as shown in Figure 3a,b. The absorption and PL spectral profiles remained almost unchanged before and after lamination. This behavior under MPa-scale pressure is consistent with prior work [21], which means that a comparatively low compressive pressure is not able to lead to strong lattice distortions in the lead halide perovskite crystallographic structure.

![Figure 3](image)

**Figure 3.** (a) Absorption and (b) photoluminescence (PL) spectra of the pristine CsPbBr$_3$ film and the laminates prepared under different conditions. (c) Time-resolved photoluminescence of the pristine CsPbBr$_3$ thin film and the laminates prepared at 90 °C and 10 MPa.

Although the band gap was not affected after lamination, the thin film morphology and perovskite crystallinity changed, which consequently affected the PLQY. The PLQY values of the perovskite laminates slightly decreased, whereas those of the perovskite films heated without applying pressure decreased severely. Specifically, the absolute PLQY value was reduced from 40% for the pristine CsPbBr$_3$ thin film to 35% for the sample laminated at 90 °C and 10 MPa. On the contrary, the value dropped down to 12% for the sample only heated at 90 °C. Table 1 summarizes the PLQY values of pristine CsPbBr$_3$ film and the laminates prepared under different conditions. To investigate the photophysical properties of the perovskite films after lamination, time-resolved photoluminescence (TRPL) decay profiles were measured, and the results are shown in Figure 3c. The PL lifetimes were obtained by
fitting the decay curves with a biexponential decay function including a fast decay component \( \tau_1 \) and a slow decay component \( \tau_2 \). The laminated perovskite film exhibits biexponential decays with a \( \tau_1 \) value of 0.52 ns and a \( \tau_2 \) value of 4.90 ns, while the pristine film has slightly larger \( \tau_1 \) and \( \tau_2 \) values \( \tau_1 = 0.57 \text{ ns}, \tau_2 = 5.33 \text{ ns} \). The biexponential decay curve indicates that the photoluminescence decay behavior is attributed to more than one photodynamic process, such as trap-assisted recombination and bimolecular recombination. Since the recombination kinetics in perovskites strongly depends on the carrier dynamics, the difference in generated carrier density in pristine and laminated samples may induce a slight difference in the recombination decay rate. Table 2 summarizes the photodynamic parameters of the pristine \( \text{CsPbBr}_3 \) thin film and the film laminated at 90 °C and 10 MPa, including the coefficients \( A_1 \) and \( A_2 \) of the biexponential decay function, the fast decay component \( \tau_1 \), and the slow decay component \( \tau_2 \).

### Table 1. Summary of photoluminescence quantum yield (PLQY) values of pristine \( \text{CsPbBr}_3 \) film and the laminates prepared under different conditions.

| \( \text{CsPbBr}_3 \) Thin Film | Pristine | Heated (90 °C) | Laminated (90 °C, 8 MPa) | Laminated (90 °C, 10 MPa) | Heated (150 °C) | Laminated (150 °C, 8 MPa) | Laminated (150 °C, 10 MPa) |
|-------------------------|----------|----------------|-------------------------|--------------------------|----------------|-------------------------|--------------------------|
| PLQY                    | 40%      | 12%            | 26%                     | 35%                      | 12%            | 15%                     | 33%                      |

### Table 2. Summary of the photodynamic parameters of pristine \( \text{CsPbBr}_3 \) thin film and the film laminated at 90 °C and 10 MPa.

| \( \text{CsPbBr}_3 \) Thin Film | \( A_1 \)  | \( A_2 \)  | \( \tau_1 \) (ns) | \( \tau_2 \) (ns) |
|-------------------------|-------------|-------------|-------------------|-------------------|
| Pristine                | 0.73        | 0.27        | 0.57              | 5.33              |
| Laminated at 90 °C and 10 MPa | 0.79       | 0.21        | 0.52              | 4.90              |

For the heated \( \text{CsPbBr}_3 \) thin films without pressure applied, the significant PLQY loss is attributed to the sky-rocketing nonradiative decay rate, and the significant PLQY recovery observed with the addition of pressure indicates efficient passivation of the nonradiative recombination. According to previous reports, heating at 90 °C without applying pressure accelerates agglomeration on the perovskite thin film and causes thermal degradation of the photoluminescence of \( \text{CsPbBr}_3 \) crystals [36–38], but the addition of external pressure to laminated perovskite films induces pin-hole area reduction and gap compression, which could reduce trap-assisted nonradiative recombination to a large extent [37]. Therefore, the lamination process has a very limited negative contribution to the PLQY of perovskites.

### 4. Conclusions

In conclusion, we demonstrated tightly compacted perovskite laminates on flexible substrates via hot-pressing. The optimal perovskite laminates were achieved at 90 °C and 10 MPa; these could sustain a horizontal pulling pressure of 636 kPa and a vertical pulling pressure of 71 kPa. The perovskite laminates exhibited increased crystallinity and a change in crystallization orientation, which was affected by temperature and pressure synergistically. The absorption edge and PL emission peak of the perovskite laminates were identical to those of the pristine perovskites, and the PLQY value also survived the negative impact of thermal degradation. This work demonstrates a promising approach to physically laminating perovskite films, which may accelerate the development of roll-to-roll printed perovskite devices and perovskite tandem architectures in the future.

**Author Contributions:** B.Y. and S.Z. developed the idea and designed the experiments. B.Y. carried out the fabrication and characterizations. Y.X. performed the XRD measurements. P.Z. and Y.D. participated in the characterizations. B.Y., Y.X., P.Z., Y.D., Q.O. and S.Z. analyzed the data and discussed the results. B.Y. wrote the initial draft of the paper and the remaining authors contributed to finalizing this paper. All authors have read and agreed to the published version of the manuscript.
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