

Trend of Perovskite Solar Cells: Dig Deeper to Build Higher

Using solar energy efficiently to produce electricity has been the subject of intensive research because of the rapid increase of global energy demand and the need to reduce the emission of greenhouse gases from electricity generation by fossil fuels. Breakthroughs are needed to produce low-cost, high-efficiency solar cells with good durability. Organic–inorganic hybrid halide perovskites (e.g., $\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) have rapidly become a focal point of the photovoltaic (PV) community as a promising next-generation PV technology. The certified efficiency of a single-junction perovskite solar cell (PSC) has reached 20.1% after only a few years of active research. Despite this remarkable progress, many fundamental questions still remain that need to be addressed at both the material and device levels. During the 2015 Material Research Society (MRS) Spring Meeting (April 6–10, 2015, San Francisco, CA), hundreds of scientists and engineers gathered at Symposium C—Perovskite Solar Cells—to discuss recent progress, challenges, and future directions for PSCs.¹ This symposium, which lasted for 4 days (April 7–10), hosted about 75 talks and 75 posters. Four posters were selected for the Symposium's Best Poster Awards (Ahn C3.04, Kaltenbrumer C3.25, Yu C10.10, and Bokdam C10.33). The enormous success of this symposium is reflecting the growing number of research groups interested in PSCs, clearly highlighting the consolidation of this new technology. In this Guest Commentary, we summarize—based on the presentations and discussions at the symposium—our views on the recent trend and various issues that researchers have been studying to continue the successful development of PSCs.

Materials Preparation and Characterization. The majority of the talks and posters focused on the standard perovskite MAPbI_3 . The superior PV properties of MAPbI_3 , summarized in a theory-based talk (Yan C5.06), are mainly attributed to the combination of direct-band-gap p–p transitions enabled by the Pb lone pair s orbitals and perovskite symmetry, high ionicity, large lattice constant, and strong antibonding coupling between Pb lone pair s and I p orbitals. Significant effort was devoted to improving synthetic controls (for both solution and vapor-phase deposition) for growing high-quality perovskite films, leading to >17% efficiencies from many groups. Despite the rapid progress in making high-quality perovskite films, the perovskite growth mechanisms, especially using solution deposition, are still not fully understood. Cheng (C7.01), Zhou (C7.05), and others have suggested that controlling the nucleation and grain-growth processes is critical for preparing a uniform, compact perovskite thin film. Specifically, accelerating the nucleation rate with respect to the growth rate via adjusting processing conditions (e.g., second-solvent dripping or bathing) represents a good approach for making continuous pinhole-free perovskite thin films. Talks by Hillhouse (C11.04) and Xiao (C11.07) demonstrated that proper selection of postgrowth atmospheres could lead to much improved perovskite film quality (e.g., grain size and carrier lifetime). In particular, the vapor-equilibrated regrowth treatment (Hillhouse C11.04) is shown to dramatically improve the photoluminescence (PL)

lifetime of the MAPbI_3 film, so that it is substantially longer than that of the mixed halide $\text{MAPbI}_{3-x}\text{Cl}_x$. This result further confirms the importance of controlling the perovskite morphology. Cl has been extensively used to make high-quality MAPbI_3 films, although where and how much (x) Cl exists still lacks sufficient evidence. Snaith (C4.05) showed that Cl not only improves the quality of MAPbI_3 , by an increase of grain size, but also exists in the lattice of the perovskite by demonstrating the blue-shifted luminescence and band gap assigned to $\text{MAPbI}_{3-x}\text{Cl}_x$. AR-XPS analysis demonstrated that Cl is preferentially located near the $\text{TiO}_2/\text{MAPbI}_3$ interface (Pellegrino, C7.03).

One interesting area related to material preparation is to understand the role of perovskite grain size (or grain boundaries). Many groups are able to produce >17% PSCs using polycrystalline perovskite films based on micrometer- or submicrometer-sized grains; however, a clear trend by various groups is to increase grain size, as mentioned above. The general assumption is that grain boundaries in polycrystalline perovskite films could host deep-level defects, leading to non-radiative recombination (NRR) loss in a solar cell. Along this direction, Nie (C1.07) presented an interesting solution approach (hot casting) to make millimeter-sized crystal grains, which is further shown to be necessary for achieving >17% efficiency in their study. However, more characterizations were requested by the audience to verify the single-crystalline nature of the apparent grains, as well as to understand the relatively low photovoltage, lower than what is reported by others using smaller perovskite grains. Regarding the role of grain boundaries, Snaith (C4.05) presented the use of confocal fluorescence microscopy coupled with scanning electron microscopy to spatially resolve the PL decay dynamics in the mixed halide perovskite $\text{MAPbI}_{3-x}\text{Cl}_x$. The results show that grain boundaries display faster NRR. Similarly, Xiao (C11.07) pointed out NRR at grain boundaries in MAPbI_3 films. In addition, electron-beam-induced current and electron energy loss spectroscopy mapping were also shown to be useful to examine grain boundaries. Clearly, more studies with high spatial resolution are necessary to understand the role of grain boundaries (Xiao C11.07). In this regard, the focused ion beam can be a viable method for preparing specimens for high-resolution transmission electron microscopy studies, as demonstrated by several groups (e.g., Padture C5.03, Park C6.01, Cheng C7.01, Xiao C11.07).

Perovskite Composition Control with Band Gap Tuning. In addition to the standard MAPbI_3 perovskite composition, researchers are showing increased interest in perovskites based on $\text{HC}(\text{NH}_2)_2$ (or FA) or the mixture of FA and MA (e.g., Grätzel C1.01, Seok C1.05, Etgar C1.06, Dalal C2.01, Snaith C4.05, Park C6.01, Zhao C11.03, Bein C11.08, Ruiz C11.05, Wozny C12.05). The advantages of using the FA-based perovskite include higher photocurrent density (due mainly to the smaller optical band gap of FA-based perovskites) and

Published: June 18, 2015

the demonstrated higher thermal stability (Snaith C4.05) than MA-based perovskites. Some of the best-performing devices (>20%) reported at this meeting are based on a cocktail of FA- and MA-based perovskites (Grätzel C1.01 and Seok C1.05).

Another area of interest related to perovskite composition control is the development of wide-band-gap perovskites (using mixed iodide and bromide) (e.g., McGehee C1.02, Zhao C7.02, Zhou C7.05, Hillhouse C11.04). One primary motivation for pursuing wide-band-gap perovskites is to build high-performance tandem devices. To this end, perovskites have been used as the top cell with many existing PV technologies (e.g., Si, CIGS, CZTS, dye-sensitized solar cells [DSSCs], organic PVs) to construct tandem devices with various configurations. For example, using a beam splitter, Park reported a 28% PSC/Si tandem device (C6.01), and Segawa showed a 21.5% PSC/DSSC tandem device (C4.02). McGehee demonstrated an 18.6% PSC/CIGS tandem using a four-terminal stacking device and 13.7% for a monolithic two-terminal PSC/Si tandem cell (C1.02). A 10.9% two-terminal PSC/CZTSSe tandem device was also demonstrated by Teodorov (C12.03). Of note is that a remarkable open-circuit voltage (V_{oc}) of 1.61 V at one sun is achieved for a single-junction device using MAPbBr₃ and ICBA electron transport material (Wu C6.03). In contrast, the I–Br mixed perovskites, which have more appropriate band gaps for the top cell in a tandem, generally show V_{oc} values similar to the MAPbI₃-based device despite their larger band gaps. This is presumably caused by the light-induced phase separation (I-rich and Br-rich phases) pinning the maximum V_{oc} (Hoke, C5.04). However, meeting participants also mentioned that different synthetic approaches and conditions might affect (enhance or eliminate) this phase stability issue. More studies are expected to further examine this specific (potential) issue for I–Br mixed perovskites.

Hysteresis, Ferroelectricity, and Working Principles. This topic was one of the most discussed at this symposium. As Kamat (C2.06) commented, the hysteresis during the current density–voltage (J – V) measurement can be misused to represent false performance results for evaluating a PSC. Thus, many presenters were questioned at the meeting about the J – V measurement conditions (e.g., voltage scan direction and rate). To make the situation more complicated, it was also shown (e.g., Tress C4.03) that one could reach a hysteresis-free J – V curve at either very slow or very fast scan rates. Thus, simply reporting hysteresis-free J – V curves with both forward and backward scans is not sufficient to validate the actual device performance. Consequently, as initially suggested by Snaith (C4.05), a stabilized output at the maximum power point should be checked. This approach has been adopted by many groups, as shown in their talks at the meeting.

The degree of hysteresis can be influenced by the device configuration, selecting contacts, and growth method (e.g., Grätzel C1.01, Huang C1.03, Snaith C4.05, Park C6.01, Miyasaka C6.04). A number of possible causes have been proposed to account for the hysteresis, including ferroelectric polarization, ion movement, capacitive charge, interfacial charge extraction, and charge trapping/detrapping. However, no consensus seems to have been reached at this point. Huang (C1.03) attributes the huge switchable PV effect to ion migration. The idea of ion migration is also supported by other talks (e.g., Tress C4.03, De Bastiani C4.04, Hoke C5.04). It was proposed that the interaction of PCBM with I can inhibit the movement of I ions, which might be a reason for the low hysteresis observed for the inverted perovskite device using

PCBM instead of TiO₂ as the electron-selecting contact. The interfacial charge separation, especially at the electron contact, seems to be critical for reducing hysteresis, as shown by Snaith (C4.05) and Miyasaka (C6.04). This also seems to be consistent with the low hysteresis found for PSCs based on mesoporous TiO₂ electrodes. Evidence of the ferroelectric property was also presented at the meeting and could also account for the hysteresis and switchability. Results of piezoresponse force microscopy were presented by Bisquert (C2.05), Padture (C5.03), and Park (C6.01). The retention of field-induced polarization depends on the perovskite morphology, and it can last >60 min with large perovskite crystals (Park C6.01). Local amplitude/phase contrast and loops were observed at frequencies as high as 1 MHz, and domain-switching was demonstrated. However, polarization-electric field loop measurements on MAPbI₃ films over large areas showed strong frequency dependence but no obvious ferroelectric behavior (Padture C5.03). More experiments considering spatial, temporal, and temperature effects are necessary to better understand the ferroelectric properties of perovskites.

It is important to highlight that the working principles of PSC are far away from being completely understood. Bisquert (C2.05) points out the observation of different characteristic times in PSC from nanoseconds to seconds, and at this moment, the physical processes behind these times are not clear.

Stability. For PSCs to become a viable PV technology, they must demonstrate good reliability or stability for high-efficiency devices. Moisture has generally been considered detrimental to perovskites. It was initially thought, based simply on the apparent color change, that moisture would decompose MAPbI₃ perovskite to form PbI₂. Kamat (C2.06) indicated that when exposed to moisture in the dark, MAPbI₃ would actually form a hydrate similar to MA₄PbI₆·2H₂O, which is likely caused by the weak hydrogen bonding between MA and PbI₆. In addition to the moisture-induced stability issue, the organic cation (MA) is often found unstable when heated at elevated temperature (Zhao C7.02). In this regard, the larger cation FA is shown to have much improved thermal stability (Snaith C4.05). Ito (C11.01) presented studies of the atmosphere and environmental effect on perovskites and found a better stability of FAPbI₃ than MAPbI₃. However, Seok (C1.05) presented evidence of perovskite and non-perovskite phases both coexisting in FAPbI₃ at room temperature, which was attributed as a source to the stability problem of FAPbI₃. This issue could be addressed by doping (or alloying) with a small amount of cubic MAPbBr₃.

Oxford Photovoltaics has shown very promising efficiencies from encapsulated devices that are stable for 1000 h at 85 °C and 85% humidity under dark (Snaith C4.05). Even more encouragingly, Grätzel (C1.01) has shown that when a mesoporous TiO₂/ZrO₂/C is infiltrated with perovskite, the device is stable under continuous light soaking at one sun for 1000 h, but no humidity conditions were provided. Nevertheless, the same device architecture also displayed no evidence of device degradation when tested in the hot desert in Saudi Arabia for 7 days or placed in an oven at 80–85 °C for 3 months.² These results suggest that perovskite might be intrinsically stable. Of course, more tests are required to fully understand the stability of perovskite materials and devices under a variety of operating conditions, and this is a key issue for the definitive consolidation of this technology.

Pb-Free Perovskites. Although most talks are still based on Pb-containing perovskites, there is a clear effort from multiple groups to pursue Pb-free perovskites. The motivation of this research direction is to avoid the environmental concern of the toxicity of Pb, although this is still a subject of debate.³ However, Cahen (C5.01) shows that due to the low thickness of the perovskite layer in a typical PSC, even if the full Pb content was transferred to earth, the Pb levels would not become very different than the level already present in the urban soil. Sn has been studied as one potential candidate to replace Pb in the standard perovskite structure, for example, MASnI_3 . However, the main challenge is that Sn^{2+} can be easily oxidized to Sn^{4+} , rendering the material useless for solar conversion. It is shown that using a mixture of Pb and Sn (e.g., $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$) can relatively enhance the material stability in air compared to that for the pure Sn-based perovskite (Hayase C8.02). Instead of using CsSnI_3 , Chang (C8.01) suggested using Cs_2SnI_6 , which has a band gap of 1.26 eV. Cs_2SnI_6 has a high-symmetry cubic structure, and Sn is already in the +4 oxidation state, and thus, it is more stable in air and moisture. These results are promising, but there are also questions about the exact oxidation state of Sn in Cs_2SnI_6 (Xiao C8.03). In searching for Pb-free perovskites, Mhaisalkar (C6.02) presented much broader material possibilities using both experimental and theoretical approaches. Some interesting alternatives (e.g., using Cu and 2D configurations) have been explored but yielded relatively low efficiencies.

In addition, there are other topic areas that have also demonstrated significant progress. For example, several spectroscopic techniques (e.g., transient absorption, microwave conductivity, photoinduced absorption) have been used by several groups to obtain a basic understanding of the charge carrier formation, separation, transport, and recombination processes in various sample configurations (Savenije C2.02, Kamat C2.06, Diau C9.01, Yang C9.03). Toward future commercialization of PSCs, low-temperature processes applicable to plastic substrates have been proposed by Jung (C11.02), and Watson (C11.06) demonstrated that it is possible to process PSC in a roll-to-roll fashion and reduce the annealing from tens of minutes (hot plate) to seconds (infrared lamps) to several milliseconds (flashing). Finally, alternative devices to solar cells with outstanding performances have been also reported as photodetectors (Yang C4.01), LEDs (Tan C12.06), or lasing (Ha C12.07).

In summary, although no new record efficiencies were reported at the symposium, there was clear evidence that the perovskite community has made good progress toward better understanding the fundamental material properties and device operation principles. For example, significant advances have been made in the areas of crystal growth, composition control, J - V hysteresis, ionic movement, and material and device stabilities. These efforts definitely led to improved yield (reproducibility) of high-efficiency cells. However, for PSCs to become a relevant, deployable PV technology, much more effort is required to demonstrate that PSCs are efficient, stable, and scalable. With the growing interest from the scientific community and more contributions from people with various expertise, the future of PSCs looks very promising.

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ACKNOWLEDGMENTS

Symposium C of the 2015 MRS Spring Meeting was co-organized by Kai Zhu, Tsutomu Miyasaka, Jin Young Kim, Iván Mora-Seró. The work at the National Renewable Energy Laboratory was supported by the U.S. Department of Energy under Contract No. DE-AC36-08-GO28308. K.Z. acknowledges the support by the U.S. Department of Energy (DOE) SunShot Initiative under the Next Generation Photovoltaics 3 program (DE-FOA-0000990). J.Y.K. thanks the support by the KIST internal fund and by the Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2012M3A7B4049989).

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