

Multimodal Characterization of Perovskite Materials Using the HORIBA SMS-320 System: Integrating Raman, PL, and TRPL Spectroscopies



Application Note

Perovskites
OSD-2024-5-24

Yu-Pei Tseng and Francis Ndi, HORIBA Instruments, Piscataway, NJ

Introduction

Perovskite materials have generated strong interest in the research and industrial communities for Photovoltaic (PV) applications. This is primarily due to their excellent solar conversion efficiency, low cost of fabrication, and ease of deposition on different substrates. However, the many advantages of Perovskite materials for PV applications are countered by their equally strong vulnerabilities to degradation from prolonged exposure to light, high temperatures, moisture, and air pollution. This is in addition to other challenges inherent in fabricating uniform and high-quality Perovskite films for commercial applications. The challenges of developing stable perovskite material and fabrication processes for commercial use require the use of several spectroscopic

techniques such as Raman, Photoluminescence (PL), and Time-resolved photoluminescence (TRPL), etc. to characterize and optimize the material design and fabrication processes. Frequently, the spectroscopic metrology techniques mentioned above come on separate instruments which can be costly with the added difficulty of locating sub-micron-sized regions of interest across different instruments. In this paper, we discuss the use of the SMS-320 from HORIBA for Perovskite material characterization, see Figure 1, highlighting its multimodal capabilities. The SMS-320 is multimodal – enabling several spectroscopies such as Raman, PL and TRPL, etc. on one platform. With the added benefit of sample co-location across different techniques, enabling micron-scale correlative spectroscopy.

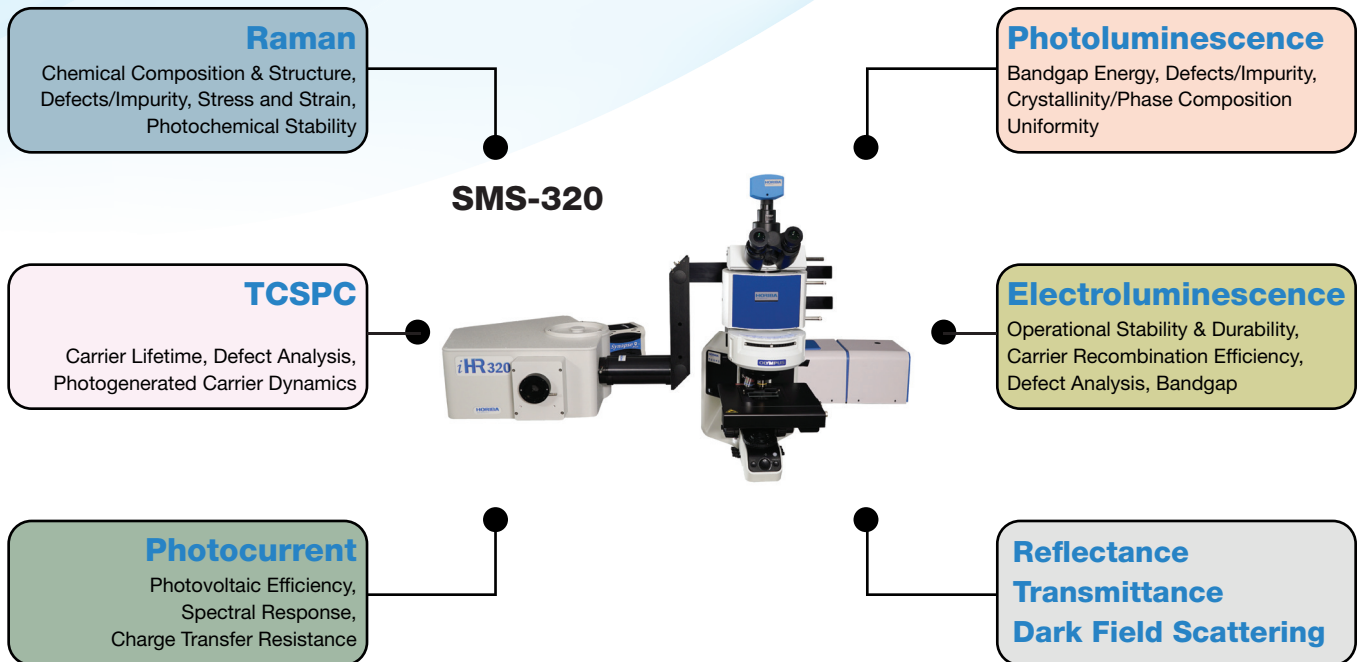


Figure 1: Picture of the Standard Microscope System (SMS-320), highlighting its multimodal capabilities for Perovskite research, including Raman spectroscopy, Photoluminescence, Time-Correlated Single Photon Counting (TCSPC), Electroluminescence, Photocurrent, Reflectance/Transmittance analysis, and Dark-field scattering.

Method

The perovskite structure, ABX_3 , contains cations like MA^+ (A), Pb^{2+} (B), and halide ions I^- (X). In solar cells, it is positioned between the hole and electron transport layers, with front and back electrodes, see Figure 2(a-b).

The SMS-320 system, shown in Figure 1, was used in this study. It features three lasers with wavelengths of 375 nm (continuous), 485 nm (pulsed), and 532 nm (continuous). This setup allows for Raman spectroscopy, photoluminescence (PL) analysis, and TCSPC measurements to study, monitor, and improve perovskite materials.

Measurement

Raman

Using a 532 nm laser in the SMS-320 system, Raman spectra of a $MAPbI_3$ film were captured. The spectra showed a degradation-indicative band around 110 cm^{-1} (Figure 3(a-b)), suggesting the presence of a degradation-related compound [1]. Serial measurements were taken at 10, 18, and 21 minutes (Figure 3(a)). Notably, after 18 minutes, a new band appeared at around 137 cm^{-1} (Figure 3(b)), with the intensity of the 110 cm^{-1} peak decreasing, suggesting chemical changes in the film.

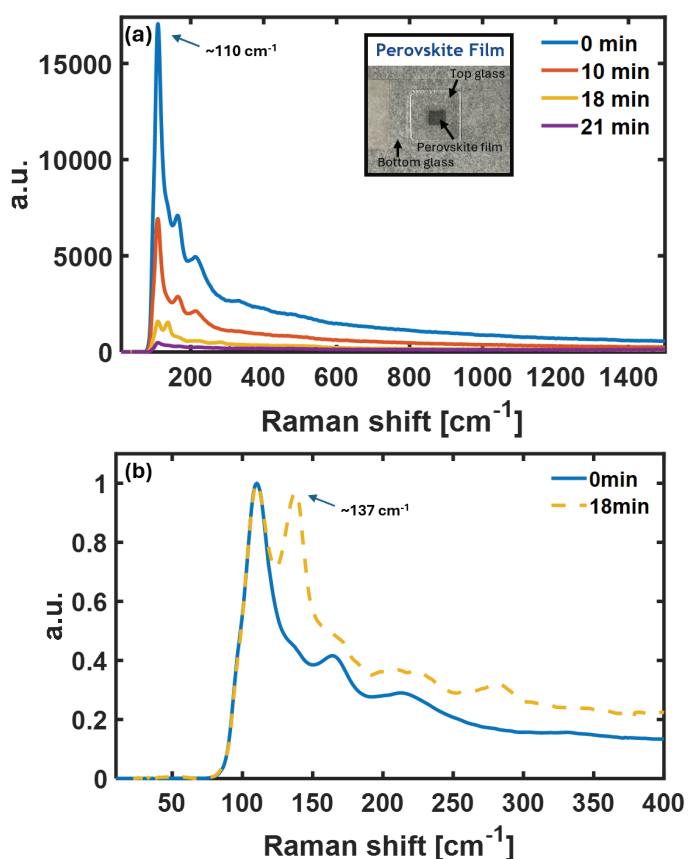


Figure 3: (a) Raman spectrum of a $MAPbI_3$ sandwich sample obtained using the SMS-320 system, with a photographic depiction of the $MAPbI_3$ film encapsulated between two glass plates (inset). (b) Normalized Raman spectrum of the $MAPbI_3$ sandwich sample, captured at intervals of 0 and 18 minutes.

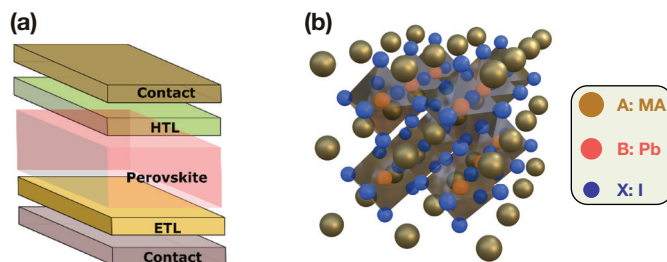


Figure 2: (a) Schematic representation of a perovskite solar cell architecture, with the perovskite layer ($MAPbI_3$) sandwiched between the hole transport layer (HTL) and electron transport layer (ETL). The structure includes contact layers on both the top and bottom. (b) Atomic model of $MAPbI_3$, showing the methylammonium (MA) cations, lead (Pb) ions, and iodine (I) ions in the perovskite crystal lattice.

Assessing the homogeneity of perovskite films is crucial for the quality of photovoltaic devices. Raman 2D mapping can identify local inhomogeneities and potential signs of degradation. Figure 4(a) shows a white light image of crystallized perovskite captured using a 50x objective on the SMS-320. Figure 4(b) presents a Raman 2D map, indicating potential degradation areas and correlating the features observed in Figure 4(a) with degradation signals.

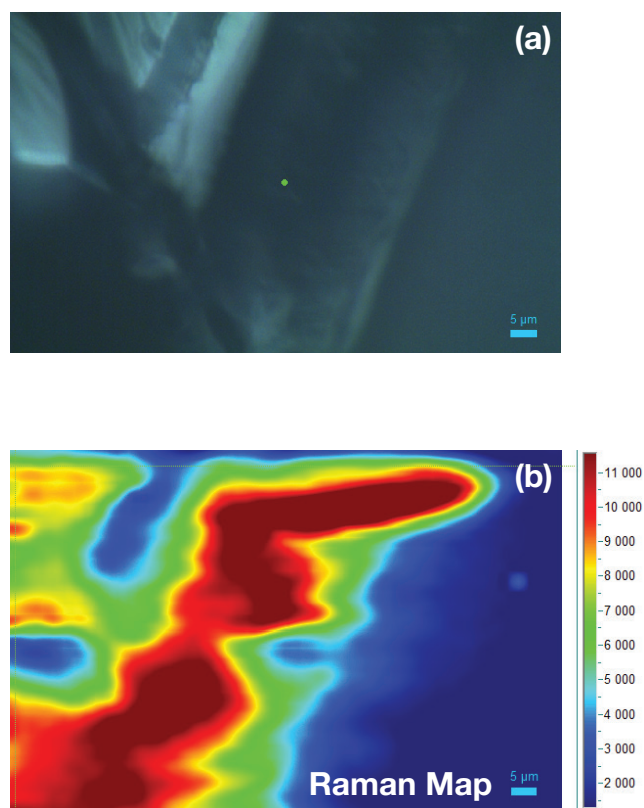


Figure 4: (a) White light image of the crystallized $MAPbI_3$ structure in the sandwich sample. (b) Two-dimensional Raman mapping of the perovskite structure, corresponding to the region shown in (a) and featuring a wavelength region that could potentially indicate degradation.

Photoluminescence & TCSPC

Using the SMS-320 system, the photoluminescence (PL) spectra of the MAPbI₃ film were captured, as shown in Figure 5. The sample, excited by a 485 nm pulsed laser, exhibited a PL peak around 766 nm, indicating a bandgap of approximately 1.61 eV, consistent with literature findings [2]. This peak, central to the MAPbI₃ PL spectrum, indicates electron-hole recombination and luminescence. This method also assesses bandgap tuning effectiveness and detects impurities and defects through changes in PL emission intensity and wavelength.

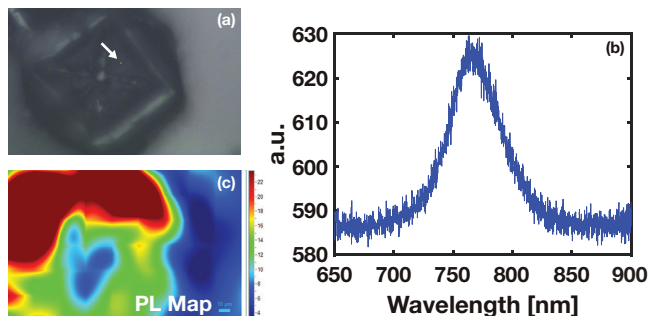


Figure 5: (a) White light image showing the MAPbI₃ structure within the sandwich sample. (b) Photoluminescence (PL) spectra obtained from the area indicated by the white arrow in (a), with 485 nm excitation. (c) Two-dimensional PL mapping of the perovskite structure, corresponding to the region in (a), showing a distinct peak at 766 nm.

The SMS-320 system, equipped with a TCSPC module, captured the PL decay and charge carrier lifetimes of the MAPbI₃ film, as shown in Figure 6(c). These data is crucial for understanding carrier transport efficiency in photovoltaic design. Additionally, the 2D PL-decay mapping, displayed in Figure 6(c), helps assess potential defect properties and perovskite uniformity, assisting in optimizing carrier lifetimes through defect minimization.

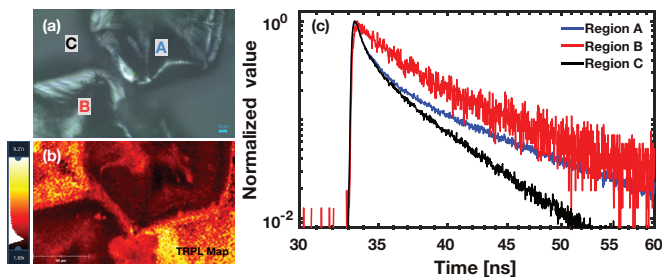


Figure 6: (a) White light image showing the MAPbI₃ structure within the sandwich sample. (b) Two-dimensional PL decay mapping of the perovskite structure, corresponding to the region shown in (a), with a PL peak around 766 nm. (c) PL decay time of the MAPbI₃ sandwich sample, acquired at the locations marked as regions A, B, and C in (a).

Conclusion

In this paper, we explored the use of the SMS-320 system for the characterization of perovskite materials, focusing on its multimodal capabilities. The SMS-320 integrates several spectroscopies, including Raman, PL, and TRPL, all on one platform. This integration enables micron-scale correlative spectroscopy, addressing the challenges posed by the need for multiple separate instruments. The system proved instrumental in conducting detailed analyses of MAPbI₃ samples, aiding in identifying degradation-related compounds and determining bandgap through PL peak identification. The PL decay time analyses shed light on charge transport efficiency, while 2D mapping identified local defects and impurities. The SMS-320's versatility and co-location benefit, allowing analysis without repositioning, address key challenges in the development of stable perovskite materials for photovoltaic (PV) applications. Moreover, the system's modular design facilitates future expansion, including capabilities such as electroluminescence (EL) and photocurrent analysis, enhancing its utility in assessing PV device efficiency. For more information, please visit our [website](#).

References

- [1] Zhou, Y., Garces, H. F., & Padture, N. P. (2016). Challenges in the ambient Raman spectroscopy characterization of methylammonium lead triiodide perovskite thin films. *Frontiers of Optoelectronics*, 9(1), 81–86.
- [2] Basumatary, Pilik, Juhi Kumari, and Pratima Agarwal. "Probing the defects states in MAPbI₃ perovskite thin films through photoluminescence and photoluminescence excitation spectroscopy studies." *Optik* 266 (2022): 169586.

HORIBA

info.sci@horiba.com

USA: +1 732 494 8660
UK: +44 (0)1604 542 500
China: +86 (0)21 6289 6060

France: +33 (0)1 69 74 72 00
Italy: +39 06 51 59 22 1
Brazil: + 55 (0)11 2923 5400

horiba.com/scientific

Germany: +49 (0) 6251 8475 20
Japan: +81 (0)3 6206 4721
Other: +1 732 494 8660