

Effects of domain size in polycrystalline perovskite organic-inorganic hybrids investigated by spatially resolved optical spectroscopy

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Abstract – We apply spatially resolved optical spectroscopy techniques, micro-Raman and micro-PL, to investigate individual perovskite single crystalline domains whose sizes are much larger than that of the diffraction limit laser spot, and compare the results to those of small polycrystalline domains with size below the laser spot size. The large and small domains show drastically different Raman and PL spectra, in terms of spectral features, intensity, and excitation density dependence. The excitation density dependence reveals possible local structural changes due to laser heating at relatively high illumination density. In addition, we also examine the changes in optical properties associated with the structural degradation of the perovskite - converting back to PbI_2 after exposing the sample to air with humidity.

Index terms – Perovskite, domain size, μ -Raman, μ -PL

I. INTRODUCTION

As a solar cell absorber material, organic-inorganic hybrid structure $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ or MAPbI_3 is perhaps the material that has showed the fastest efficiency growth among all the currently known absorber materials.[1-3] More significantly, the newer devices have adopted all solid-state device structures that closely resemble the thin-film solar cell technologies based on CdTe and CIGS. However, this material system is facing a critical issue, i.e., poor chemical stability. Most perovskite PV devices were made out of polycrystalline perovskite materials with relatively small domain size, typically a few hundred nm or smaller. Although there is no clearly established dependence of the device performance on the crystalline domain size, there is some indication that devices with larger crystalline domains seem to perform better than those with smaller domains.[4] Furthermore, there is also a hint of the dependence of the device performance on the preferential crystalline orientation of the domains.[5] There are already a large explosive number of publications in the perovskite PV research. Much of the rapid progress has been in the material engineering, with some efforts in the characterization of the basic material properties, such as absorption,[6] carrier decay and diffusion.[7, 8] However, most of the material studies were performed using

macroscopic techniques averaging over many small domains (e.g., smaller than the extracted diffusion length) of polycrystalline thin-films. Given the complexity of the material and the fact there are so many variables in the material synthesis and device processing, these types of measurements prevent the possibility to definitely study many physical properties that are sensitive to crystalline symmetry thus crystalline orientation and optical polarization. Therefore, it is highly desirable to be able to study individual large domains in order to derive intrinsic properties of the material, and evaluate the potential effects of varying domain size on device performance.

In this work, we apply spatially resolved optical spectroscopy techniques, primarily micro-Raman and micro-PL, to investigate individual single crystalline domains whose sizes are much larger than that of the diffraction limit laser spot, and compare the results to those of small polycrystalline domains with size below the laser spot size. The large and small domains show drastically different Raman and PL spectra, in terms of spectral features, intensity, and excitation density dependence. The excitation density dependence reveals possible local structural changes due to laser heating at relatively high illumination density. In addition, we also examine the changes in optical properties associated with the structural degradation of the perovskite converting back to PbI_2 after exposing the sample to air with humidity.

II. EXPERIMENT DETAILS

Poly-crystalline thin-film materials and devices were fabricated by a two-step process.[4] The films had relatively large crystalline domains, typical of 500 nm to 1 μm , but $\sim 5 \mu\text{m}$ domains were not so difficult to find (the largest found was about $12\mu\text{m}\times 20\mu\text{m}$).

μ -Raman/PL spectroscopy was performed with a Horiba Jobin Yvon HR800 confocal Raman system with a CCD detector using a 532 nm laser as excitation source. With a

100x (NA = 0.9) objective lens, the laser spot size is $\sim 0.72 \mu\text{m}$, and the spatial resolution is about half of the laser spot size.

Raman peaks in the large domain. Even for the area of small domains, Raman peaks that match some of those observed in

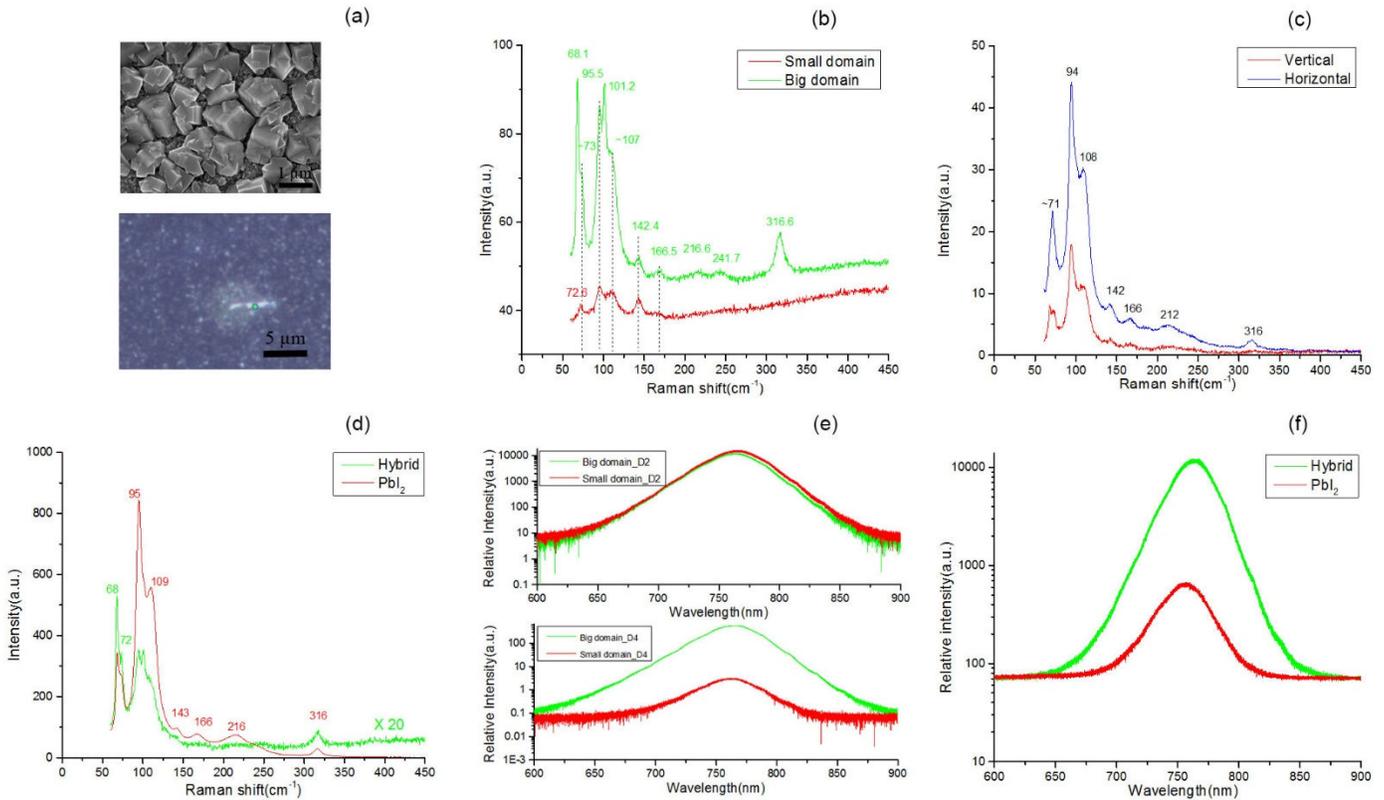


Fig. 1. μ -Raman and PL spectra of hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. (a) Typical SEM image and optical image showing a large elongated hybrid crystalline domain; (b) Raman spectra of the large domain shown in (a) and an average spot; (c) Polarized Raman spectra with polarization parallel and perpendicular to the longer edge of the large hybrid domain in (a); (d) Raman spectra of another large hybrid domain taken before and after converting back to PbI_2 ; (e) PL spectra of one large hybrid domain and an average spot measured at two excitation powers (D2 and D4, two orders of magnitude change); (f) PL spectra of the same large domain in (d) taken before and after converting back to PbI_2 .

The laser power was varied between 3-300 μW , above which a permanent structural change occurs. The measurements were performed at room temperature.

III. EXPERIMENTAL RESULT

Fig. 1 summarizes μ -Raman and μ -PL data comparing large and small domains, revealing optical anisotropy, and showing changes in optical properties before and after sample degradation. Fig. 1(a) is an optical image of a sample area containing one large crystalline domain ($\sim 5\mu\text{m} \times 1\mu\text{m}$) with a typical SEM image from a general area. Fig. 1(b) compares Raman spectra between the large domain of Fig. 1(a) and a typical spot with smaller domains, measured with power level D2 ($\sim 300\mu\text{W}$). In contrast to the previous reports where no well-resolved Raman peak was observed at room temperature,[9, 10] we have observed multiple well-resolved Raman features, in particular on the individual large domains like the one shown in Fig. 1(a). Even for the small domain,

the large domain were also resolved, although with much lower intensities. The large domain sample further allows us to perform polarization analyses. As revealed in Fig. 1(c), the elongated domain in Fig. 1(a) exhibits strong optical anisotropy between the directions parallel and perpendicular to the elongated edge. Although we do not know the exact orientation of this domain at this time, the anisotropy seems to suggest the c axis of the crystal is in the growth plane for this particular large domain. We note that a few Raman modes of the hybrid, for instance, ~ 73 , ~ 96 , and $\sim 107 \text{ cm}^{-1}$, are very close to those observed in 2H PbI_2 [11] which might be due to the fact that the first nearest neighbor coordination of Pb with 6 I's are the same between PbI_2 and the hybrid. The presence of additional Raman peaks (68.1 and 101.2 cm^{-1}) indicates the material structure is different from that of PbI_2 . Fig. 1(e) compares the PL spectra of large and small domains, measured with power level D4 ($\sim 3\mu\text{W}$). The PL spectra show a peak at $\sim 1.63 \text{ eV}$ near the expected bandgap of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$. Besides the intensity difference, they show

drastically different excitation power dependence: the contrast is reversed between the low and high excitation density with the small domain region being much weaker at low excitation but stronger at high excitation. This peculiar phenomenon, which is expected to be directly relevant to the solar cell performance with varying illumination density, is likely related to the interplay between the bulk and surface defects. The results seem to suggest that the small domains suffered more from the nonradiative recombination loss at low excitation density due to perhaps surface defects. Nevertheless, such defects were saturated or passivated at high excitation density. Since the thin-film materials are known to degrade in a few days if exposed to air (the sample turned yellow, the known color of PbI_2 , gradually). As shown in Fig. 1(d) and (f), the Raman and PL signal, respectively, increases by about a factor of 50 and decreases by about a factor of 15 after a sample was fully converted from the hybrid phase (dark) to PbI_2 (yellow), when measured from the same location on the sample where a large hybrid domain was identified initially. In the meantime, there is a shift in the PL peak energy.

In addition, we have found that when excited with 441.6nm laser, some large domains showed a very weak PL peak near 515 nm or the bandgap of PbI_2 , [12] indicating the existence of some traces of PbI_2 .

IV. CONCLUSION

By performing spatially resolved optical spectroscopy measurements, we have shown that large and small crystalline domains of perovskite hybrid exhibit significantly different optical properties: (1) the large domain shows much stronger Raman intensity and more features than the small domain; (2) the large and small domain have very different excitation power dependences for their PL intensities. In addition, large domain sample show strong optical anisotropy in Raman, and exposure to air leads to perovskite to PbI_2 conversion, leading to strongly enhanced Raman and weakened and shifted PL.

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