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Reversible Band Gap Narrowing of Sn-based Hybrid Perovskite Single Crystal with Excellent Phase Stability

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Abstract: An intriguing reversible band gap narrowing behavior of the lead-free hybrid perovskite single crystal DMASnI₃ (DMA = CH₃NH₂CH₃⁺) from yellow to black is observed without phase transformation. We discuss the transformation mechanism in detail. More interestingly, the transformed samples in black can rapidly self-heal into yellow ones when exposed to deionized water (DI water). Contrary to other hybrid perovskites, DMASnI₃ crystals exhibit excellent water phase stability. For example, DMASnI₃ was immersed in DI water for 16 h and no decomposition was observed. Inspired by its excellent water phase stability, we demonstrate a potential eco-friendly application of DMASnI₃ in photo-catalysis for H₂ evolution in DI water. We present the first H₂ evolution rate of 0.64 μmol h⁻¹ with good recycling properties for pure DMASnI₃ crystals. After the narrowing process, the optical band gap of DMASnI₃ can be lowered from 2.48 eV to 1.32 eV. Systematical characterizations are applied to investigate their structures and optoelectronic properties. The reversible band gap narrowing behavior and outstanding electrical properties, such as higher carrier mobility and long carrier lifetime show that DMASnI₃ has a great potential for optoelectronic applications.

Since hybrid perovskites were first used as light absorbers in solar cells, organic-inorganic hybrid perovskites have rapidly attracted the world's attention.^[1-5] Great efforts have been made from materials growth to device fabrications and the record cell efficiency jumped from 3.8% to 23.3%,^[6,7] surpassing many conventional semiconductor absorbers. The outstanding performance of these materials has endowed lead-containing perovskites with great potential in optoelectronics industry. Despite this achievement, the toxicity of lead (Pb) and the lack of stability, hinder their further optoelectronic applications.^[8]

Sn has been proposed to replace lead to form the less toxic

perovskites like MASnI₃, FASnI₃, and got an efficiency of over 6% to 9%.^[9-13] However, the quick oxidation of them leads to poor photovoltaic performance, and all materials and devices fabrication processes have to be performed in nitrogen gas atmosphere to avoid quick degradation.^[14-17] Unlike the MASnI₃, FASnI₃,^[9] or MAPbI₃,^[18] most hybrid perovskites are not very useful for photovoltaic applications, due to their large band gap (> 2 eV), even though they have high air stability.^[19, 20]

Herein, we show an intriguing reversible band gap narrowing behavior of DMASnI₃ single crystals with excellent water phase stability without phase transformation. Unlike the transformation from MAPbI₃·H₂O to MAPbI₃ with the crystal structure changing from tetragonal to monoclinic (Figure S1),^[21] the DMASnI₃ kept its structure before and after the transformation. The detailed narrowing process is shown in situ in Figure 1a. The original DMASnI₃ crystal exhibits a rod-like yellow morphology. Once the crystals are exposed to the air, the yellow DMASnI₃ gradually turns to black while keeping their morphology unchanged. If the temperature is increased to 50 °C, the transformation process will be shortened (Figure S2). This can also be observed obviously from the bulk single crystals (Figure S3). More interestingly, this process is reversible (Figure 1c). After the treatment of the DI water, the DMASnI₃ self-heal from black to yellow and can further transform into black again, as their XRD patterns match well with the initial calculated (see Figure 1(b-e) and Figure S4).

Figure 1. (a) In situ observation of the DMASnI₃ transformation from yellow to black at room temperature in air. (b) The powder XRD patterns of the samples. (c) In situ observation of the reversible DMASnI₃ transformation process at 80 °C in air. (d, e) The corresponding powder XRD patterns of the samples before and after the treatment of DI water.

The crystal structures were determined by the single-crystal X-ray diffractions at different temperature. Figure 2 (a-f) displays the ball-and-stick diagrams of the crystal structures before and after the transformation. Both of them belong to the orthorhombic crystal system and *Pnna* space group at room

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temperature. Even at 350 K, the crystal structures keep the space group of *Pnna*, which are in agreement with the XRD patterns of above. The related single-crystal parameters of DMASnI_3 before and after the transformations are presented in Tables S1 (see the Supporting Information). Different from DMASnI_3 , DMAGel_3 and DMAPbI_3 crystals do not present the similar self-deepening phenomena. Their crystal structures are shown in Figure S5, which exhibit the orthorhombic and hexagonal crystal system with the *Pna2*₁ and *P6*₃/*mmc* space group, respectively.^[19] The related single-crystal parameters are presented in Table S2.

Figure 2. Photos of DMASnI_3 used to determine crystal structure before and after the transformation, (a) yellow DMASnI_3 , (d) black DMASnI_3 , (g) black DMASnI_3 at 350 K. Ball-and-stick diagrams of crystal structures for the DMASnI_3 single crystals. (b) Yellow DMASnI_3 , (e) black DMASnI_3 , (h) black DMASnI_3 at 350 K. In the $\{\text{SnI}_6\}$ octahedral structure unit of (c) yellow DMASnI_3 , (f) black DMASnI_3 , (i) black DMASnI_3 at 350 K. The N and C elements represent the disordered organic groups; hydrogen atoms bonded to the C or N atoms were omitted for clarity.

To understand the consequent oxidation process, we employed X-ray photoelectron spectra (XPS) for the black DMASnI_3 single crystal to study the valence states of Sn^{2+} , as shown in Figure S6 (a, b). As we know, the peaks of 486.3 eV and 487.3 eV are associated with Sn^{2+} and Sn^{4+} , respectively. Here, the Sn 3d_{5/2} peak at 486.3 eV demonstrates the oxidation state of Sn^{2+} (Figure S6b).^[22] The FTIR results also suggest the stable phase of DMASnI_3 before and after the transformation from yellow to black, as shown in Figure S6(c, d). The reason for this transformation was also investigated in detail (Figure 3). After the treatment of DMASnI_3 crystals in pure O_2 , the peak of SnI_4 emerge obviously, demonstrating the degradation of the crystals (Figure 3a). However, when the sample was exposed to vacuum, the crystal color and their XRD patterns kept stable

(Figure 3b). Once the crystals were exposed to the air, the yellow DMASnI_3 turned to black and their surface exhibited a phenomenon of roughness and abundant of the iodine element in comparison to the yellow DMASnI_3 , evidenced by the EDS (Energy Dispersive X-Ray Spectroscopy) and XRF (X Ray Fluorescence) measurements of Figure S7 and Table S3. More experiments were carried out and the results of which are shown in Figure 3(c, d). After 10 days, the I_3^- ions were identified from the XPS and Raman spectrum,^[23, 24] indicating the formation of iodide vacancies. As reported by H. I. Karunadasa, et al, the high density of defects may lead to band-edge reconstruction and the decrease of band gap.^[25] Thus, the possible underlying mechanism is that the iodide defects induce the band-edge reconstruction and decrease the band gap while keeping the crystal structure stable. First-principles calculations were also conducted to verify this mechanism. The trend of band gap variation matches well with that of experiments after the introduction of iodide vacancies, as shown in Figure S8. Moreover, due to the increase of the trap-state density, the single crystal transformed into the poly-crystal, demonstrated by the single crystal X-Ray diffraction (Figure S9), with crystal structure keeping the same. Intriguingly, after the further treatment of DI water, the DMASnI_3 crystals recovered into their original states (Figure S10-S11), indicating that the color-changing transformation is a reversible process. Unusually, the DMASnI_3 crystal kept its structure integrity when they were immersed in different solvents for a long period of time, indicating its excellent phase stability. Exceptionally, DMASnI_3 remained stable after it was immersed in the DI water for 16 h (Figure S12). With excellent water stability, DMASnI_3 shows great potential for eco-friendly applications. For example, DMASnI_3 can be used as photo-catalyst for H_2 evolution in DI water rather than in the saturated HI solution of lead perovskite as reported.^[26] The first H_2 evolution rate of $0.64 \mu\text{mol} \cdot \text{h}^{-1}$ with good recycling properties are shown in Figure S13. Note that, due to the formation of O_2 after the evolution of H_2 , the peaks of SnI_4 is formed (Figure S13 b).

Figure 3. (a, b) The XRD patterns of DMASnI_3 single crystals before and after the exposure to O_2 and vacuum. (c) XPS of I 3d spectrum. (d) Raman spectrum of the DMASnI_3 before and after the transformation.

The variations of UV-vis diffuse reflectance spectra demonstrate the band gap narrowing of yellow DMASnI₃, as shown in Figure 4. Notably, the black DMASnI₃ displays significantly 438 nm red-shifted light absorption peak with the band gap value of 1.32 eV (Figure. 4b), compared with the yellow DMASnI₃. The corresponding UPS spectrum was also provided to determine their HOMO and LUMO values, as shown in Figure S14. The corresponding thin film also exhibits the band gap of 1.86 eV with the PL peak position located at ~650 nm (Figure 4c, d). The XRD patterns and SEM images are shown in Figure S15. As we know, > 30% PCE can be achieved for the

tandem solar cells, if top-cell with bandgap of 1.70-1.85 eV is combined with Si bottom-cell.^[27, 28] The DMASnI₃ thin film has great potential in tandem solar cell applications. To investigate the transport properties of perovskite thin film and single crystals, we also estimated their carrier lifetime by using TRPL measurements. All the TRPL spectra of perovskite were fitted by bi-exponential decays, including the fast and slow components (Figure 4e, f).^[27, 29] Obviously, both of them exhibit long carrier lifetimes, which is desired for the high efficiency hybrid perovskite solar cell.^[29-31]

Figure 4. UV-vis diffuses reflectance spectroscopy for DMASnI₃. (a) Yellow DMASnI₃, (b) black DMASnI₃, (c) black DMASnI₃ thin film. (d) Typical PL spectra for the black DMASnI₃ thin film, Time-resolved photoluminescence spectra for black DMASnI₃ thin film (e) and black DMASnI₃ single crystal (f).

Figure 5. (a) Dark current-voltage curve of DMASnI₃ single crystals for space charge limited current analysis. (b) The variation of trap-state density and dielectric constant with a change of test frequency. (c) The variation of carrier mobility and dielectric constant with a change of test frequency. (d) Carrier

mobility and (e) Resistivity of black DMASnI₃ single crystals measurements by Hall Effect measurements (RT). (f) Dark current-voltage curve of DMASnI₃ thin film for space charge limited current analysis.

The trap-state density and the carrier mobility μ of DMASnI₃ single crystals were also estimated according to the space charge-limited current (SCLC) method, as shown in Figure 5.^[27, 32, 33] As the increase of test frequency, the dielectric constant and the defect density exhibit a downturn in the order of 10^{11} cm^{-3} , while the carrier mobility exhibits an uptrend, which was estimated according to the Mott-Gurney's power law:^[27, 32] The mobility values match well with the result of Hall Effect measurements (Figure 5 c, d). The resistivity of black DMASnI₃ single crystals was also measured by Hall Effect measurements in the order of $10^7 \Omega\text{-cm}$, as shown in Figure 5(e). Moreover, the trap-state density of the DMASnI₃ was also estimated with the thickness of 200 nm in the order of 10^{16} cm^{-3} (Figure 5f), which is comparable with that in previous reports of MAPbI₃ ($\sim 10^{15}$ to 10^{16} cm^{-3}).^[34] All the related parameters of the above are presented in Table S4. We also calculated the carrier diffusion length by combining carrier lifetime with carrier mobility. The best-case diffusion length of 3.89 μm and the worst-case diffusion lengths of 0.82 μm were estimated (Table S5).^[35, 36]

The thermos-stability of black DMASnI_3 crystal was determined by the thermogravimetric analysis (in Figure S16a). The DSC curve ranging from 100 K to 375 K demonstrates the phase transition temperature of 230 K (Figure S16b), where the space group is changed from $Pnna$ to $Pna2_1$ (Figure S16(c-d)). The related single-crystal parameters are presented in Table S6.

In summary, we reported an intriguing and reversible band gap narrowing behavior of the lead-free single crystal DMASnI_3 and further revealed the mechanism of narrowing in detail. In addition to the reversible process, DMASnI_3 crystals exhibit excellent phase stability in different solvents, even immersed into DI water for 16 h without decomposition. Removing the toxicity of the lead, our results not only exhibit an abnormal and intriguing phenomenon, but also show many desirable photoelectric properties for solar-cell application, such as narrow band gap, high stability, high carrier mobility and long carrier recombination lifetime, which shed light on highly promising applications in photovoltaic and other optoelectronic devices.

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Keywords: reversible • band gap narrowing • lead-free • phase stability • optoelectronic properties

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Reversible band gap narrowing behaviour of Sn-based hybrid perovskite single crystal was first revealed with excellent phase stability, narrow band gap, higher carrier mobility and longer carrier lifetime, which is encouraging for the optoelectronic application.

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