Exploring Isovalent Substitution of Lead with Nickel in Methylammonium Lead Iodide Perovskites

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ABSTRACT

We replaced lead ions with nickel ions in methylammonium lead triiodide (MAPbI$_3$) perovskites and studied their electronic and photophysical properties. We synthesized thin films using solutions containing methylammonium iodide (MAI), PbI$_2$, and NiI$_2$ with varying Pb/Ni precursor ratios. We show that MAPbI$_3$ retains its three-dimensional perovskite structure in the presence of Ni$^{2+}$. We were able to incorporate up to 30\% Ni$^{2+}$ before we note the appearance of unconverted NiI$_2$ via X-ray diffraction. Although the structures of NiI$_2$ and PbI$_2$ are isostructural and the metal ions have the same oxidation states, the bulk material did not behave as a solid solution. Furthermore, the addition of Ni$^{2+}$ thoroughly quenched the emission of MAPbI$_3$, suggesting that Ni$^{2+}$ may act as a recombination center for excited charge carriers. Additionally, the materials displayed significant instability towards water. Thus, we conclude that there is a limited application for nickel and perhaps other transition metal ions as a replacement ion for lead in thin-film perovskite photovoltaic devices fabricated in these conditions.
INTRODUCTION

The environmental and toxicity concerns of lead in hybrid organic-inorganic perovskite (HOIP) solar may become a limiting factor in the large-scale and widespread deployment of these devices.\textsuperscript{1} Thus, there are continuing efforts to replace Pb\textsuperscript{2+} with other ions in the crystalline structure while maintaining the optical and electronic properties. The most obvious choices to replace Pb\textsuperscript{2+} are the group 14 ions such as Sn\textsuperscript{2+} and Ge\textsuperscript{2+}, which have been extensively studied.\textsuperscript{2,3} However, thus far, these ions have been met with limited success in part due to their instability to oxidation. Therefore, we need to explore other alternatives.\textsuperscript{1,4} A number of transition metal ions are of particular interest in the replacement of Pb\textsuperscript{2+} due to their rich oxidation chemistry, low toxicity, and relative abundance.\textsuperscript{3,5} In fact, computational screening studies predict that HOIPs containing metal ions such as Mg\textsuperscript{2+}, V\textsuperscript{2+}, Mn\textsuperscript{2+}, and Ni\textsuperscript{2+} are likely to function as direct bandgap semiconductors and are good candidates for replacing Pb\textsuperscript{2+} ions.\textsuperscript{6} However, these predictions have not been experimentally verified. Herein, we study the optical and structural properties of methylammonium lead triiodide (MAPbI\textsubscript{3}) films with varying degrees of Ni\textsuperscript{2+} substitution. We show that the three-dimensional (3D) perovskite structure is maintained with increasing ratios of NiI\textsubscript{2} of up to 30% Ni\textsuperscript{2+}. Interestingly, we observed that the mixing of NiI\textsubscript{2} and PbI\textsubscript{2} precursors did not produce uniformly mixed films in the solid-state, as analyzed by X-ray diffraction and visible absorption studies. We report optical bandgaps for the Ni\textsuperscript{2+} substituted films between 1.3 and 1.6 eV, which appear to be independent of the Ni\textsuperscript{2+} concentration. Furthermore, we observe quenching of emission from MAPbI\textsubscript{3} upon Ni\textsuperscript{2+} substitution, indicating the Ni\textsuperscript{2+} may act as a recombination center for charge carriers. Lastly, the Ni\textsuperscript{2+} substituted films displayed high sensitivity to water, as observed by rapid color changes of the films on exposure to ambient conditions. Thus, despite the optimal bandgap and structure of the materials, we
conclude that Ni\(^{2+}\) is not a promising candidate for Pb\(^{2+}\) replacement in these conditions (e.g. polycrystalline thin-films deposited from NiI\(_2\) precursors) for HOIP solar cells.

EXPERIMENTAL METHODS

**Precursor Solutions.** In a nitrogen-filled glove box, methylammonium iodide (158 mg, 1 mmol) and PbI\(_2\) (461 mg, 1 mmol) were added to a vial followed by 1 mL of a co-solvent containing anhydrous dimethylformamide (DMF) and dimethylsulfoxide (DMSO) (v:v 8:2). For mixtures of ions, up to 0.5 mmol NiI\(_2\) (50% Ni\(^{2+}\)) was added to the PbI\(_2\) solution in various ratios while maintaining the total metal halide salt content at 1 mmol. For example, the 30% Ni\(^{2+}\) mixture was prepared by adding 0.7 mmol of PbI\(_2\) and 0.3 mmol of NiI\(_2\) to total 1 mmol. We also experimented with 2-fold decrease in precursor concentrations (0.5 mmol MAI and 0.5 mmol NiI\(_2\)/PbI\(_2\)), and we observed similar structure and optical properties in these films. The solutions were prepared based on the procedure reported by Siegler et.al.\(^7,8\) The solutions were stirred on a hot plate at 110 °C for 2 h. DMSO solutions containing NiI\(_2\) appeared light green in color, consistent with solvated Ni\(^{2+}\) ions. The solutions were kept hot until just before film preparation, since removing them from the heat-induced precipitation of the NiI\(_2\) salt. Solutions were prepared directly before spin coating, as old solutions appeared to degrade over time resulting in X-ray diffraction patterns with impurity phases.

**Hybrid Organic Inorganic Perovskite Films.** Glass substrates (1 mm × 1 mm) were washed by sonicating in a soap and water bath, then with water, acetone, and isopropyl alcohol for 20 min each. The substrates were dried in an oven and 140 °C for at least 1 h. Hot precursor solutions were spin cast onto the substrates in non-ambient conditions (50 μL at 3000 rpm for 30 s). The films were then annealed at 110 °C for 5-25 min. Longer annealing times led to increase in the
intensity of the peaks associated with PbI$_2$ as observed by powder X-ray diffraction. For X-ray diffraction, the films were encapsulated in a mylar plastic sample holder. For optical studies, the films were encapsulated in between 2 pieces of transparent packing tape to protect the samples from exposure to ambient water. The films appeared to rapidly degrade upon exposure to ambient conditions (within a matter of minutes) as noted by a color change from black to light brown/clear. No immediate color change was noted for encapsulated films upon exposure of ambient conditions. However, to prevent water exposure, the films were only removed from non-ambient conditions for testing and were returned to the dry environment upon completion.

**Physical Characterization.** Absorption studies were carried out on an Agilent Cary 50 Bio spectrophotometer. Films were measured in transmission mode from 300 – 900 nm. The optical bandgap was estimated from Tauc plots analysis and assumed a direct, allowed transition. Emission studies were carried out on an Agilent Cary Eclipse Fluorescence spectrophotometer. Films were excited at $\lambda_{ex} = 450$ nm and measured from 700 – 850 nm. Powder X-Ray diffraction (XRD) was taken in a Bragg-Brentano configuration using a Rigaku SmartLab SE X-ray diffractometer with a D/tex 250 Ultra ID Si strip detector. Measurements were taken from $2\theta = 10^\circ$ to $50^\circ$ with a Cu K$\alpha$ (1.542 Å) X-ray source.

RESULTS AND DISCUSSION

We prepared films with varying degrees of nominal Ni$^{2+}$ mol fraction ranging from 0-50% Ni$^{2+}$. All films with Ni$^{2+}$ content between 0% and 50% showed evidence of 3D perovskite in the
tetragonal phase,\textsuperscript{9} as seen in the powder X-ray diffraction patterns (Figure 1). We observed a broad, amorphous peak in all samples between $21^\circ - 27^\circ 2\theta$ resulting from the air-free mylar sample holder. Upon addition of $\geq 40\% \text{Ni}^{2+}$, we observe a new peak at $13.5^\circ 2\theta$, which corresponds to the (330) plane of NiI\textsubscript{2} present as a secondary phase (Figure 1d). This peak shifts to lower $2\theta$ values upon the incorporation of $50\% \text{Ni}^{2+}$ may arise due to the poor signal-to-noise of this peak. Films containing $\geq 40\% \text{Ni}^{2+}$ displays an additional peak at $\sim 11^\circ 2\theta$, which is typically attributed to lower dimensional perovskite (1D) phases.\textsuperscript{10,11} Thus, we conclude that the upper limit of $\text{Ni}^{2+}$
incorporation into the 3D perovskite structure under these conditions is 30%. We note that NiI$_2$ solubility in the precursor solution was relatively low, even at high temperatures. We hypothesize that the 40% and 50% Ni$^{2+}$ concentrations likely exceed the solid solubility limit of Ni$^{2+}$ substitution in the MAPbI$_3$ films, thus resulting in the formation of NiI$_2$.

In pristine MAPbI$_3$ film (0% Ni$^{2+}$), we observed a small peak at 12.5° 2θ corresponding to PbI$_2$. We attribute sample degradation to the high annealing temperature. As expected, annealing at this temperature for a longer time (25 min) results in an increased relative intensity of PbI$_2$-related peaks. Additionally, pristine MAPbI$_3$ films display preferred orientation along the (110) plane (Figure 1a). This orientation is preserved with nominal Ni$^{2+}$ concentrations up to 7% (Figure 1b). Interestingly, upon addition of 10% Ni$^{2+}$, there is a reorientation of the films along the (112) plane (Figure 1c). However, despite the orientational change, the patterns clearly show that the 3D perovskite structure is maintained in these films. We initially hypothesized that this result could be due to the insolubility of the precursor NiI$_2$ at these concentrations, causing it to precipitate more quickly onto the substrate resulting in new orientation of the films. However, when we increase the concentration of Ni$^{2+}$ further (13–15% Ni$^{2+}$), we note that the orientation of the films reverts back to (110) as observed in the lower concentrated samples (Figure 1c). Therefore, we rule out the possibility that this response is due entirely to the solubility of NiI$_2$ under these conditions. This behavior likely indicates that there is a secondary factor playing a role during the crystallization of these materials. The cause and nature of this response remains unknown.
To determine if these films behave as a solid solution, i.e., Ni$^{2+}$ and Pb$^{2+}$ mix uniformly and randomly, we evaluated the d-spacing of the (110) peak as a function of Ni$^{2+}$ concentration (Figure 2). Since Ni$^{2+}$ (70 ppm) is a smaller ion than Pb$^{2+}$ (119 ppm), we expect the d-spacing to decrease with increasing incorporation of Ni$^{2+}$ corresponding to a shrinking lattice size. Furthermore, we expect a strong linear correlation between the unit cell parameters and Ni$^{2+}$ ion concentration for a material with uniform mixing of the two metal ions. Interestingly, we did not observe any linear correlation between these two factors, nor did we observe a reduction in the d-spacing.

From this result we conclude that Ni$^{2+}$ and Pb$^{2+}$ mixtures do not mix uniformly at the nominal concentrations that we prepared. This may indicate that Ni$^{2+}$ is not incorporated into the 3D structure. However, lack of diffraction peaks corresponding to unconverted NiI$_2$ and low dimensional perovskite, as well as the orientational influence of Ni$^{2+}$ in these compositions, suggests that it does influence the overall structure of the bulk material. Another possibility is that Ni$^{2+}$ is not incorporated into the B site of the ABX$_3$ perovskite structure when high nominal doping
concentrations are used. For example, is possible that Ni\(^{2+}\) could be excluded to grain boundaries, form secondary phases, or could create halide anti-site defects.

To evaluate the optical properties of the films, we conducted absorption and emission experiments at room temperature. The absorption and emission spectra of pristine MAPbI\(_3\) (0\% Ni\(^{2+}\)) are shown in Figure 3a. We observe an optical bandgap for MAPbI\(_3\) at approximately 1.4 eV (Figure 4) and emission at 1.6 eV (773 nm). The optical bandgaps of samples containing Ni\(^{2+}\) range from 1.3 – 1.6 eV (Figure 4b), extrapolated from a Tauc plot (Figure 4a).\(^{12}\) We note that the observed band gaps appear to be independent of Ni\(^{2+}\) concentration, which is another indicator that the Ni\(^{2+}\) may not be incorporating into the B site of the material, since the band edge is primarily derived from the metal and halide orbitals of the BX\(_6\) octahedra.\(^{13}\)

In the visible region, the incorporation of Ni\(^{2+}\) produces two broad absorption features between 3.0 – 3.75 eV, which are not observed in pristine MAPbI\(_3\) (Figure 3b). Interestingly, the increased absorption coefficients in the visible range would be favorable for a solar cell device. However,
we also report strong emission quenching in these samples with the addition of any amount of Ni$^{2+}$ (Figure 3c). We hypothesize that Ni$^{2+}$ may act as a recombination center in devices due to the presence of low-lying ligand field states that introduce non-radiative recombination pathways for the excitonic excited state. The lowest lying ligand field state in NiI$_2$ single crystals occurs in the near-IR region at ~0.9 eV, which supports the hypothesis that lower lying orbitals in Ni could provide sub gap states. This observation is additionally consistent with theoretical calculations for MA(Pb$_{1-x}$Ni$_x$Br$_3$) which show that partial Ni$^{2+}$ substitution leads to new mid-gap states. Reported MAPbI$_3$ solar cell devices doped with 10% Ni$^{2+}$ show a significant reduction in current density, which is consistent with trap states inducing non-radiative recombination of charge carriers. These results are not consistent with what has been observed for systems with 3% Ni$^{2+}$ substitution, which shows that emission is retained in these systems.

In the present work, our films were encapsulated in a layer of clear plastic tape for the emission measurements. This encapsulation most likely significantly reduces the light power input and emission from the films, as indicated by the relatively low emission intensity of the control sample (0% Ni$^{2+}$). Therefore, the complete quenching effect we observe in even the lowest concentration (1% Ni$^{2+}$) samples is most likely an overestimation of the actual quenching capability of Ni$^{2+}$ in this system. Additionally, these materials displayed significant moisture sensitivity, with color changes from black to light brown/clear in a matter of seconds on exposure to moisture. Given
this, we speculate that these materials are highly sensitive to changes in sample preparation and relative measurement conditions.

CONCLUSION

We show that partial substitution of up to 30% Ni$^{2+}$ into MAPbI$_3$ thin films is possible while retaining the 3D perovskite structure. Ni$^{2+}$ concentrations above 30% result in new low dimensional perovskite phases and unconverted NiI$_2$ precursor. We do not observe correlations between unit cell parameters and Ni$^{2+}$ concentration, which suggests that Ni$^{2+}$ does not mix uniformly and may not substitute into the B site of the ABX$_3$ perovskite as anticipated. The bandgap of the mixed materials ranges from 1.3 – 1.6 eV and is enhanced in the visible region with the incorporation of Ni$^{2+}$, which is optimal for a solar cell device. However, emission quenching suggests that Ni$^{2+}$ may introduce new low-lying states that act as charge carrier traps which would limit device performance. Additionally, the significant water sensitivity of the materials limits the potential application of these materials in solar cells. Thus, we conclude that given the conditions presented in this paper, Ni$^{2+}$ is not a good candidate for Pb$^{2+}$ replacement in thin-film MAPbI$_3$ solar cells prepared under these conditions.

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