

Thesis title - Understanding the Optoelectronic Properties of Different Perovskite Semiconductors for Development of Cost-efficient, Eco-friendly and Recyclable Perovskite Technology

Abstract

The advent of organic-inorganic halide perovskites has been a major breakthrough in the field of photovoltaic research. The prominent interest of the photovoltaic community in this technology is accounted for its low cost and easy solution processable fabrication technique along with its excellent optoelectronic properties. However, its mass commercialization has not seen the light of day due to some inherent issues such as structural and ambient instability in operating environment conditions and the presence of toxic lead. In this thesis work, we have worked towards devising solutions for these hurdles in the path of the commercialization of perovskite solar cells. Initially, we worked on the MAPbI₃-based perovskite, which is known to be highly unstable under operating environmental conditions such as humidity, temperature, oxygen presence, and illumination. On exposure to the ambient, the MAPbI₃ perovskite is decomposed and left with a remnant lead iodide (PbI₂) layer as a by-product. Owing to the toxicity of lead which has health implications and the high expenses involved in the disposal of hazardous waste, the disposal of this lead waste is a major concern, especially in developing countries. Therefore, we realized that either we need to substitute the lead or we need to make sure to reuse it, therefore the idea of recycling perovskite solar cells comes as a great relief. In this thesis, we have shown that the final decomposed product of perovskite, the PbI₂ film, can successfully be recycled to perovskite extending the life span of the perovskite-based material to multiple folds and hence reducing the payback period even further. This work furnishes a comparative study among the three fabrication routes to prove the viability of efficient recycling, which paves the path for selecting a better precursor composition. We have carried out an extensive study on the recycling of degraded perovskite films which are fabricated via three different routes (i.e. Sequential deposition, 3CH₃NH₃I:Pb(Ac)₂ and 3CH₃NH₃I:PbCl₂) and encountered that not all the films can be recycled efficiently. The film deposited with precursor composition 3CH₃NH₃I:Pb(Ac)₂ shows efficient recycling pertaining to the optoelectronic properties comparable to the original perovskite but it is not the case with the other two methods. We have also stated the reasons behind ineffective recycling using the other

two methods. We also underline the fact that if this highly crystalline degraded PbI_2 film can be utilized back into MAPbI_3 it may result in altogether supreme optoelectronic properties.

The presence of volatile MA^+ in MAPbI_3 , which is highly unstable under thermal stress and humidity, prevents its mass commercialization. So, over the course of time, FAPbI_3 and CsPbI_3 perovskites have emerged as potential alternatives with better thermal stability and suitable band gap. However, both of these suffer from notable phase instability, rendering their application into photovoltaic devices quite challenging. In this thesis, we have devised a method to stabilize the γ - CsPbI_3 photoactive phase by incorporation of Mg^{2+} in the lattice. Successful replacement of around 15% toxic Pb with Mg has been achieved in the CsPbI_3 lattice. Two photoactive phases were obtained in Mg containing $\text{CsPb}_{1-x}\text{Mg}_x\text{I}_3$ films, one at a low temperature ranging from 80-140°C and the other above 320°C, whereas in the pristine CsPbI_3 film, the photoactive phase is obtained only above 320°C. Polymorph reversal mechanisms have been studied for the pristine CsPbI_3 films and $\text{CsPb}_{1-x}\text{Mg}_x\text{I}_3$ films. The work reported herein illustrates a comprehensive understanding of the structural and optoelectronic properties of the various phases obtained in fresh $\text{CsPb}_{1-x}\text{Mg}_x\text{I}_3$ films at various temperatures and after the recuperation of the photoactive phase post exposure to ambient. In addition, the role of Mg incorporation on the film morphology has been extensively studied. These findings suggest that the Mg incorporation not only drastically reduces the formation temperature for the photoactive phase but also enhances the phase stability and thermal stability of the photoactive phase of CsPbI_3 . Interestingly, Mg incorporation has led to an enhancement in the optoelectronic properties of the CsPbI_3 film and resulted in better film morphology.

Although the incorporation of Mg led to enhanced phase stability and optoelectronic properties it still lacked behind in terms of long term ambient stability. Therefore in the subsequent study, we have devised a method for long term stabilization of the γ - CsPbI_3 photoactive phase by incorporation of Mg^{2+} and Tris(2-aminoethyl)amine (TAEA) in the lattice. Interestingly, our finding suggests that the presence of both Mg and TAEA is crucial for the long-term ambient stability of the photoactive phase. The $\text{CsPb}_{1-x}\text{Mg}_x\text{I}_3$ film containing TAEA crystallizes to the γ -phase at two temperatures, one at a low temperature ranging from 120-150°C and the other above 320°C, whereas the TAEA containing CsPbI_3 film crystallizes to a black phase only above 320°C. The $\text{CsPb}_{1-x}\text{Mg}_x\text{I}_3$ films containing TAEA formed at low temperatures are found to be the most

stable among all the films. The optimized $\text{CsPb}_{0.85}\text{Mg}_{0.15}\text{I}_3$ containing TAEA is found to showcase drastically enhanced thermal stability of more than 7 months when continuously exposed to 85°C in an N_2 atmosphere and ambient phase stability of more than 20 days when stored in an ambient environment with $\text{RH}\sim 60\text{-}70\%$. Along with the enhanced stability $\text{CsPb}_{0.85}\text{Mg}_{0.15}\text{I}_3$ containing TAEA has also shown superior optoelectronic properties than the CsPbI_3 and $\text{CsPb}_{0.85}\text{Mg}_{0.15}\text{I}_3$ films.

Owing to the notable phase instability of FA-based perovskites, $\text{FA}_{1-x}\text{Cs}_x$ perovskite composition is a widely accepted alternative for better phase and thermal stability. In this thesis, we have presented a detailed comparative study of the TAEA containing films with the pristine $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.90}\text{Br}_{0.10})_3$ films. Interestingly, our findings demonstrate that the presence of TAEA leads to a drastic enhancement in optoelectronic properties of the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.90}\text{Br}_{0.10})_3$ films also. This improvement in optoelectronic properties is accounted for by the improved structural and morphological properties and defect passivation in TAEA containing film. TAEA addition leads to a reduction in the metallic Pb^0 content in the target films. The $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.90}\text{Br}_{0.10})_3$ films containing TAEA also exhibit drastically enhanced thermal stability of more than 7 days under continuous exposure to extreme conditions of high humidity, illumination, and thermal stress at 85°C . Additionally, these TAEA containing films also showcase extremely high ambient stability of more than 180 days in illumination and highly humid conditions with $\text{RH}\sim 60\text{-}70\%$.

In the subsequent study, we analyzed the effect of the incorporation of In^{3+} on the phase stability of $\gamma\text{-CsPbI}_3$ using the addition of InI_3 and InCl_3 in different quantities in the CsPbI_3 precursor. Based on the results, we found that the incorporation of both salts resulted in enhanced phase stability and absorption properties. It is noticed that the addition of InCl_3 to an optimum concentration leads to enhanced optoelectronic properties and improved surface morphologies. However, the InI_3 containing films show diminished photoluminescence properties.

All the above results pave the path toward the realization of the devised perovskite compositions for a cost-efficient, recyclable, comparatively less toxic, and long-term stable perovskite technology with enhanced optoelectronic properties.