



Thin Film Perovskite Active Layer Formation And Its Stability Analysis

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Abstract : The photovoltaic performance is mainly based on high spectrum absorption due to narrow band gap and balanced charge transport properties with long diffusion lengths. To improve the perovskite layer performance and to maintain long term stability. The following parameters are to be concentrated: (i) crystal lattice determination, (ii) formation of perovskite layer, (iii) pretending the structure of perovskite coated films, (iv) high efficient photon harvesting and (v) reduced recombination process. To obtain a pure perovskite structure (AMX_3) by hybrid materials is a challenging one due to the possibilities of crystal plane overlapping, determination of crystal plane and crystal structure for integrated materials. The proposed work will be describing the new perovskite material Phenylammonium Strontium Chloride ($PASrCl_3$) and Methyl ammonium chloride ($MASrCl_3$) formation with stable and reduced band gap. Structural determination was done by X-ray diffraction (XRD), and FESEM characterizations.

Keywords: Perovskite, Phenylammonium, Methylammonium, Recombination, Solar simulator

Introduction

The generation of electricity from photovoltaic cells is safe and effective because the photovoltaic cell systems are toxic free. Photovoltaic panels are solid state semiconductor devices. The electronic state of valence and the low energy conduction states determine the band gap and other important properties of photovoltaic materials. To a great extent, a new technique of thin-film photovoltaic cells based on hybrid halide perovskite absorbers emerged which rapidly increase power conversion efficiency than conventional silicon solar cells.¹ Perovskite photovoltaic cell is a potential candidate for upcoming high performance, energy efficient and next generation solar cell devices by the combination of organic and inorganic thin films.

Initially, ABO_3 perovskite structure is obtained as semiconductor material with direct or indirect band gap which as low cost and abundant materials. To boost the performance of solar cells, poly-silicon solar cells were fabricated.^{7,8} Also, inorganic perovskite nanostructures (ZnO , $ZnSnO_3$) are employed for more energy and sensing applications with different coating techniques like spray pyrolysis, spin coating and dip coating.^{9,10} The layered chalcopyride based solar cell with non-toxic material (Zinc sulfide - ZnS) used as window layer.¹¹

The perovskite is a naturally available mineral with AMX_3 with novel structure orientation that carries out the properties of high charge carrier mobility of inorganic material and increased photo sensitivity of organic material. The main advantage of perovskite material is their ability to be processed from solution to thin film at relatively low temperature. The AMX_3 crystal structure, A (organic cation, cuboctahedral), M (inorganic cation octahedral), X anion halides (iodide (I^-), chloride (Cl^-), bromide (Br^-), fluoride (F^-)). A and M are divalent and trivalent with O_h symmetry. When A is too small to fill cavity occurs between octahedral tilting results in lowering of system symmetry.²

Designs of perovskite layered photovoltaic cells were initialized by varying materials like organic phenylammonium chloride/Methylammonium chloride and inorganic Strontium chloride. Thus the chlorine inclusion has been shown for morphological development of perovskite films which results in improved optoelectronic characteristics for high efficiency, high absorption coefficient, long carrier diffusion length and high tolerance of chemical defects with enhanced property.³ The evidence of organic material as absorber layer with polymer based aniline sensitized solar cells simplify solar cells production, increase open circuit voltage and stability of cells. Photovoltaic cells contrasted from amine halides and its related materials have also generated a lot of interest in last couple of years due to power conversion efficiency with reduced cost.⁶

The importance of perovskite absorb layer (intrinsic layer) $\text{CH}_3\text{NH}_3\text{I}$ as kinetic reactivity and thermodynamic stability of films shows well defined grain structure and grain size upto microscale with full surface coverage and small surface roughness are suitable for photovoltaic applications.⁵ Perovskite's charge accumulation property was identified by impedance measurement. Perovskite layer absorption determined by electrons and holes generation with long electron and hole diffusion length.

This report describe about the preparation of active absorb layer by perovskite structure made by phenylamine (aniline) and methylamine with strontium chloride to analyze the major properties of perovskite layer. The absorption range, crystal structure formation, long term stability were analyzed by various characterization techniques were also reported.

Experimental

Preparation of precursor solution

Phenyl ammonium chloride (PACl_2) was synthesized by reacting phenyl amine (0.5 mL) with HCl (0.4 mL) in ice bath (maintained at 0 °C) and stirred for 2 h. The formed precipitate was washed with diethyl ether (3x3 mL) and dried at room temperature. The methyl ammonium chloride (MACl_2) was synthesized by using the above mentioned procedure. The commercially available Strontium chloride was grained for 6 h.

Fabrication of perovskite layer

The $\text{C}_6\text{H}_8\text{NSrCl}_3$ precursor solution was prepared by dissolving PAC and SrCl_2 with a molar ratio in anhydrous DMF and sonicated for 60 min. The resulting solution was dropped on cleaned glass substrate by using spin coating technique at 1000, 2000, 3000, 4000, and 5000 rpm. The coated films then treated at 100°C for 60 min in hot air oven.

Characterization

XRD patterns were collected for PAC, MAC, PASrCl_3 , MASrCl_3 powder and thin films using a XRD diffractometer (Xpert Panalytical, Netherlands) [$\text{CuK}\alpha$ radiation, $\lambda=1.54\text{Å}$]. Absorption spectra and diffused reflectance were recorded on a UV-Vis spectrometer (Analytek Jena, Germany). FTIR spectra was recorded (Bruker, Germany) in the range 600-4000 cm^{-1} . The cross sectional structure, shape and crystalline size of perovskite material were characterized by using FESEM with EDAX. The Photoluminescence measurements were carried out in (FluoroMax, Horiba Jovin) to calculate the emission for perovskite material.

Results and discussion

Perovskite material synthesis was confirmed by FTIR spectral analysis with the appearance of the band at 3385 (N-H stretch), 1461 (N-H bend), 2795 (C-H stretch), 2956 (C-H stretch), 1523 (C-C stretch) and band at 941 cm^{-1} (C-H bend). The optical property shows absorbance at 608nm in visible region for phenylammonium chloride (band gap value of 2.04eV) and for perovskite layer at 332 and 385nm with the band gap value of 3.23eV. The optical microscope reveals the shape, uniformity, moisture content and impurities of coated perovskite substrate.

Perovskite layer morphology determined at the ratio of 3:4, solvent, spun rate and drying temperature. XRD analysis revealed a monoclinic structure for perovskite by peaks at 22.30, 24.56, 32.55, 34.78, 36.23, 42.11, 44.89 are indexed to (111), (200), (220), (312), (511), (421) and (602) planes. Field Emission Scanning

Electron Microscope (FESEM)determinescrystal size as 250nm and the porous morphology of perovskite layer may lead to less conductivity.EDAXpattern of coated layer confirmed the presence of inorganic material (Strontium chloride) but the organic material (Phenylammonium chloride) may disappear due to temperature (drying) or atmospheric condition. Photoluminescence emission obtained regarding absorption range and minimal loss of energy by emitted as wavelength of 344 nm and 437 nm for phenylammonium strontium chloride, methylammonium strontium chloride respectively.

Table 1.Optimization of Phenylammonium chloride perovskite structure formation

Batch name	Precursor ratio PAC:SrCl ₃	Sonication time (min)	Stirring time (min)	Spun rate (rpm)
(a)	1:1	60	360	1000-3000
(b)	2:1	60	360	500-2000
(c)	3:1	60	360	2000-4000
(d)	4:1	60	360	2000-4000
(e)	3:4	60	480	1000-4000
(f)	2:1	120	720	2000-5000

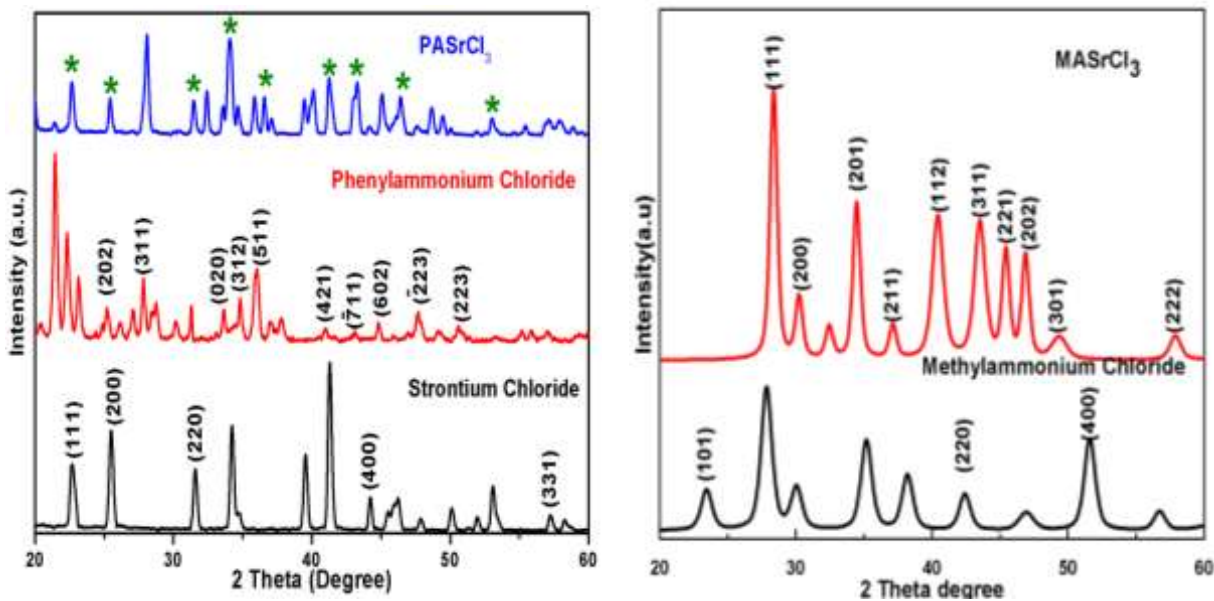


Figure1.XRD pattern for Phenylammoniumstrontium chloride and Methylammonium strontium chloride

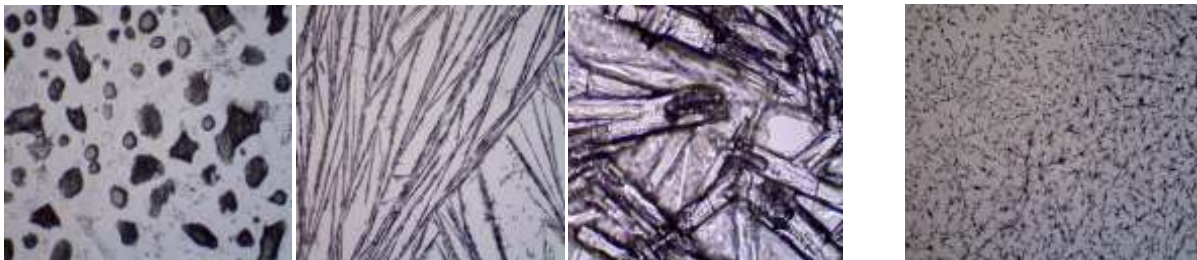


Figure2. Microscope images for the formation of perovskite layer

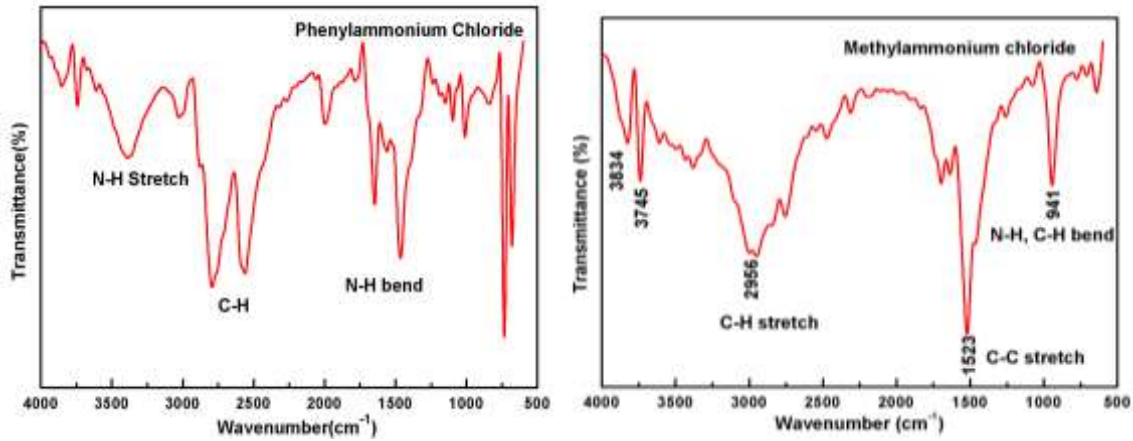


Figure 3. FTIR spectra of Phenyl ammonium chloride and Methyl ammonium chloride

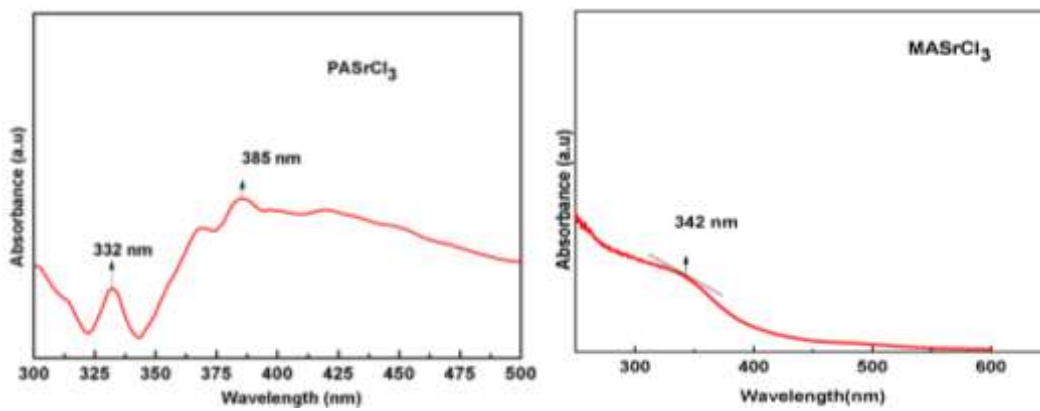


Figure 4. UV-Visible absorption for Phenyl ammonium strontium chloride and Methyl ammonium strontium chloride

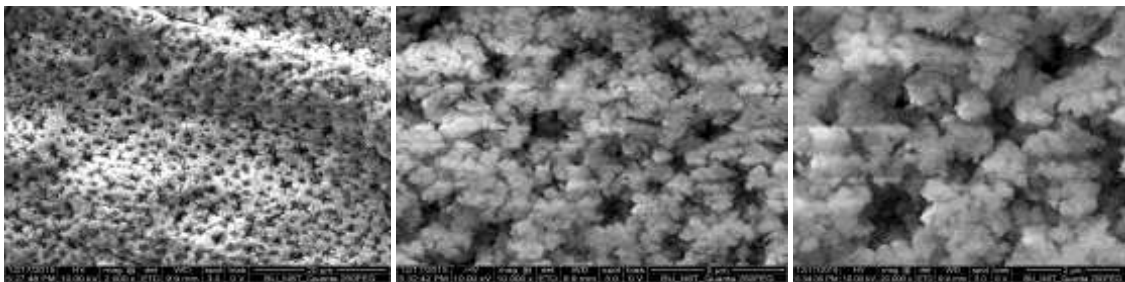


Figure 5. Field Emission Scanning Electron Microscope (FESEM) of perovskite layer

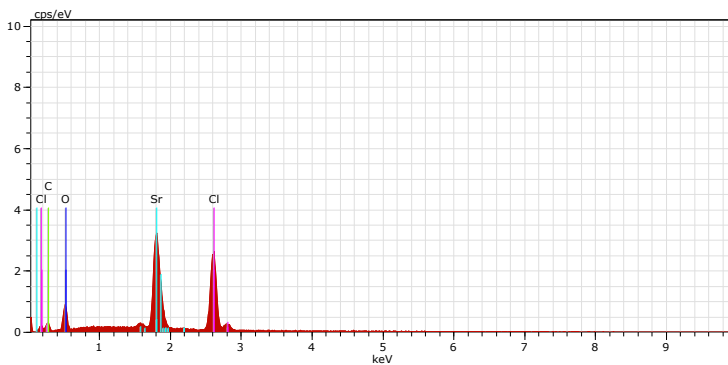


Figure 6. EDAX spectrum of perovskite layer (PASrCl₃)

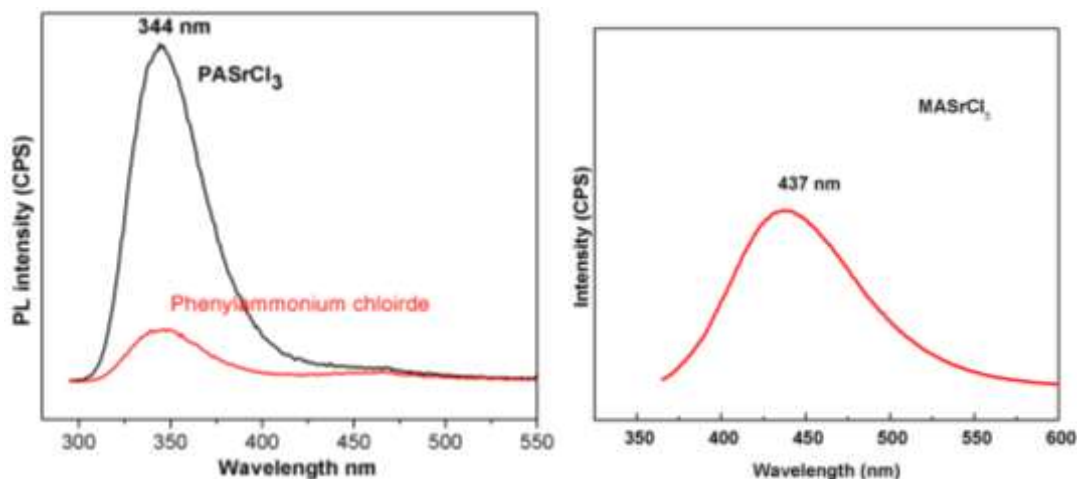


Figure 7. Photoluminescence emission spectrum of Phenylammonium and Methylammonium

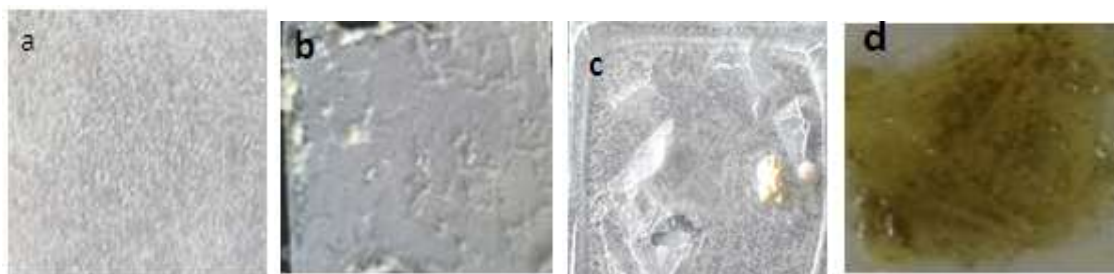


Figure 8. (a) PASrCl_3 coated film with good formation and uniformity, (b) PASrCl_3 coated film with excess chlorine content and crystal formation, (c) MASrCl_3 coated film with very less thickness and crystal formation, (d) Crystalline form of PASrCl_3 synthesized.

Conclusion

The hybrid organic-inorganic perovskite absorber layer exhibit stability for phenylammonium based perovskite layer and very thin film orientation for methylammonium at low temperatures. The obtained band gap value for phenylammonium chloride and methylammonium chloride are (3.23 eV), (3.45 eV) respectively. The high crystalline nature of perovskite material obtain from precursor with higher content of chlorine leads to more crystalline formation and less stability in methylammonium strontium chloride.

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