Room Temperature Synthesis of Formamidinium Lead Iodide (FAPbI₃) Perovskite for Low-Cost Absorber in Solar Cells

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Abstract

We report room temperature synthesis technique for the formamidinium lead iodide (FAPbI₃) perovskite. The low-cost sequential room temperature chemical synthesis technique resulted in the formation of α -phase FAPbI₃, suitable for solar cell absorber application. The chemical precursors formamidine acetate (CH₄N₂·xC₂H₄O₂) and lead iodide (PbI₂) were used in the process. The drop cast and spin-coated films of FAPbI₃ on soda-lime glass were then annealed at a temperature of 80 °C. The FAPbI₃ materials films were characterized by X-ray diffraction, UV-Visible spectroscopy, photoluminescence (PL) measurements, and transmission electron microscopic (TEM) measurements. The X-ray diffraction pattern confirms the α -phase of FAPbI₃ perovskite. The crystallite size as calculated from x-ray diffraction was found to be 40 nm corresponding to (001) peak. The UV-Visible analysis showed broad absorption with a bandgap value of 1.55 eV. The PL analysis shows an emission peak at 727 nm with an estimated bandgap to be 1.57 eV, in agreement with the UV-Visible spectroscopy. TEM analysis confirms the crystalline phase of FAPbI₃ material and the inter-planar spacing was deduced to be 0.62 nm. We conclude the successful synthesis of FAPbI₃ perovskite with desirable properties in the α -phase composition of FAPbI₃ that are suitable for solar cell application.

Keywords: FAPbI₃ Perovskite; Photoluminescence of perovskites; Cubic FAPbI₃.

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1. Introduction

Thin film solar cell technology is actively researched due to its many advantages for use in special applications like flexible portable machines, building integrated photovoltaic (BIPV), and indoor applications due to ease of production and versatility at end-use. The present-day market leader, the CdTe thin film solar cell technology has been surpassed for champion cell efficiency of 23.4% by the Perovskite family of thin film solar cells.^[1] There are several advantages of perovskite materials to use as light-capturing active layers in thin-film solar cells cheaper production costs, less complex manufacturing processes, and highest efficiency in the thin-film family of photovoltaic cells.^[2-5] The hybrid organ lead trihalide perovskite material has an ABX₃ structure, where A is an alkali metal cation, B is a divalent cation (Pb²⁺, Sn²⁺) and X is halide anions (Br⁻, Cl⁻, I⁻), have attracted much more

attention from researchers all over the world. Because the materials exhibit the desired optical and electrical properties, with facile synthesis approaches and low-cost production, this ABX₃ family of perovskites has been actively researched for photovoltaic applications^[1,6] and light-emitting devices.^[7,8] The research efforts are mainly directed to utilize some or many of the advantages of high absorption coefficient, long charge carrier lifetimes, high charge carrier mobility, and long carrier diffusion distance of metal halide perovskites.

In comparison to another perovskite, the larger Formamidinium cations in a FAPbI₃ Perovskite occupy the A site of the ABX₃ structure, forming the symmetric crystal structure and reducing the electronic bandgap.^[9-11] Formamidinium lead Iodide (FAPbI₃) perovskite shows a wider absorption spectrum and better thermal stability.^[12,13] These research findings lead to wide acceptance that FAPbI₃ perovskite materials are a suitable candidate for absorber material in solar cell applications as well as photodetectors and light-emitting applications.^[14,15]

Recently Han *et al.* reported a 5 mm sized single crystal growth of FAPbI₃ perovskite using a modified inverse temperature crystallization method.^[16] They also fabricated

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single-crystal photodetectors and investigated photoconductivity and photoresponse. The FA and MA based perovskites have shown an efficiency of 20.1% by cation-Intermixing technique as reported by Mateen *et al.*^[6] Time-resolved PL measurements for the stability of MA based perovskite was reported by Guo *et al.*^[17] Niu *et.al.* have shown that RP/3D heterostructure combined with molecule passivation within α -phase FAPbI₃ films leads to better charge collection efficiency and better solar cells device performance and also the device becomes ambient-air stable.^[18] Despite many studies on FA-based perovskite structures, the intrinsic electrical, optical, and structural properties of FAPbI₃ still require further study. Besides this, the main problem in synthesizing FAPbI₃-based perovskites is α -phase purity. FAPbI₃ material has two phases, the desirable and important semiconducting perovskite phase (α -phase) and the as less suitable perovskite (δ – phase) which is mostly formed at room temperature.^[19,20]

In this article, we focus on a very simple and low-cost synthesis technique for the formation of the α -FAPbI₃ structure required for achieving high performance in optoelectronic devices. The synthesis was achieved at room temperature and post-synthesis annealing at a temperature of 80 °C. We introduce the synthesis of desirable and important semiconducting perovskite α -FAPbI₃ structure using a sequential room temperature synthesis method. The polycrystalline α -FAPbI₃ thin film was prepared by spin coating method followed by an annealing treatment. The structural and optical properties of FAPbI₃ thin film were studied using X-Ray diffraction, transmission electron microscopy, UV-Visible, and photoluminescence spectroscopy.

2. Synthesis Method

For the synthesis of FAPbI₃, Formamidinium acetate (FA) ($\text{CH}_4\text{N}_2 \cdot \text{x}\text{C}_2\text{H}_4\text{O}_2$), lead iodide (PbI₂), and N, N-dimethylformamide (DMF) were procured from Sigma-Aldrich and used without further processing. The entire range of chemicals used in the synthesis process was of analytical grade and was used without further purification. The FAPbI₃ perovskite was synthesized using the one-step method with Formamidinium acetate ($\text{CH}_4\text{N}_2 \cdot \text{x}\text{C}_2\text{H}_4\text{O}_2$) as a FA precursor and lead iodide (PbI₂) as a Pb and I source and N, N-dimethylformamide (DMF) is used as capping agent or reactant. In the experiment, 0.12 gm FA and 0.32 gm PbI₂ were dissolved into 2 ml N, N-dimethylformamide (DMF) under magnetic stirring for 8 hours to clear the solution. Strong green emission was observed after adding both precursors into the DMF. After completion of the reaction, the FAPbI₃ solution was used for the preparation of films of the material.

The soda-lime glass was used as a substrate for the FAPbI₃ film preparation. The substrates were cleaned sequentially with DI water, acetone and ethanol, and DI water for 5 min each. After dry nitrogen flush, the substrate was deposited with FAPbI₃ film by spin coating. Then the FAPbI₃ coated film was dried under vacuum at 80 °C for 30 min. These dried films were used for further characterization. Fig. 1 represents the schematic of the steps in the synthesis of FAPbI₃ reported in this article.

3. Characterization techniques

The synthesized FAPbI₃ perovskite was systematically investigated by a range of characterization techniques including x-ray diffraction, UV–Visible spectroscopy and photoluminescence (PL) spectroscopy, and transmission

Fig. 1 Steps in the synthesis process of FAPbI₃ perovskite using sequential room temperature technique.

electron microscopy (TEM). The average crystalline size, lattice parameter, and phase identification of FAPbI₃ perovskite were studied in depth using x-ray diffraction (Bruker D8 Advance, Germany make) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at grazing angle 1° . The optical bandgap of the FAPbI₃ perovskite was estimated from absorbance spectra measured using a JASCO, V-670 UV-visible spectrophotometer in the range of 200–1500 nm. The photoluminescence spectra were recorded using a spectrophotometer (Horiba FluoroLog Spectrophotometer) at an excitation wavelength of 430 nm. The microstructural information of the FAPbI₃ Perovskite was obtained using transmission electron microscopy (TEM) by JEOL, JEM-2200FS at an acceleration voltage of 200 kV.

4. Results and Discussion

4.1 X-ray diffraction analysis

The x-ray diffraction pattern of spin-coated thin film FAPbI₃ perovskite synthesized using the one-step solution method is shown in Fig. 2.

Fig. 2 X-Ray diffraction pattern of FAPbI₃ material.

The most intense peaks located at $2\theta = 13.7^\circ, 19.8^\circ, 26^\circ, 28.3^\circ, 31.5^\circ, 34.1^\circ, 39.7^\circ, 42.9^\circ, 45.1^\circ, 47.9^\circ, 50.4^\circ, 52.4^\circ$, and 56.7° which are attributed to the diffraction of (100), (110),

(111), (002), (210), (220), (221), (310), (113), (222), (320), (321) and (004) planes of the cubic phase of α -FAPbI₃ perovskite thin film respectively. As observed, the peak position of FAPbI₃ perovskite thin film was confirmed and in good agreement with other reported data^[21,14] Also peaks located at $23.4^\circ, 24.5^\circ, 38.5^\circ$ and 47.9° which are attributed to unconverted PbI₂ in FAPbI₃ material.^[21] No any δ -FAPbI₃ phases were detected in the sample thus, confirms the synthesis of high-quality α -FAPbI₃ perovskite thin film. The sharp diffraction peak of α -FAPbI₃ indicates the high crystallinity of the as-synthesized compound. The crystalline size ($d_{x\text{-ray}}$) of the synthesized α -FAPbI₃ perovskite thin film was calculated by measuring full-width half maxima (FWHM) corresponding to (100) peak using the Debye-Scherrer equation.

$$d_{x\text{-ray}} = \frac{0.9 \lambda}{\beta \cos(\theta)} \quad (1)$$

where $d_{x\text{-ray}}$ is the crystalline size, λ is the wavelength of diffracted radiation which is equal to $1.54 \text{ \AA}$, θ is the Bragg angle, and β is the full width at half maximum (FWHM) line width of the diffraction peak. The calculated crystalline size α -FAPbI₃ perovskite thin film corresponding to (001) peak is found to be 40 nm. An inter-planar distance of α -FAPbI₃ perovskite thin film for the first-order diffraction is $6.38 \text{ \AA}$. The estimated lattice constant for α -FAPbI₃ perovskite cubic structure is $a = b = c = 6.376 \text{ \AA}$,^[22] the estimated values are a good agreement with the values reported in the literature.^[23]

4.2 UV-Visible-NIR spectroscopic analysis

The basic requirement for a high-performance solar cell is optical properties such as band gap (E_{opt}) and absorbance. The UV-Visible-NIR spectroscopic measurements of the α -FAPbI₃ perovskite synthesized using the one-step solution method are shown in Fig. 3. To record the UV-Visible-NIR spectroscopic measurements, the thin film of FAPbI₃ was spin-coated on soda lime glass. The FAPbI nanoparticles were dispersed uniformly in the DMF with adequate viscosity and spin-coated on a thoroughly cleaned soda lime glass. The absorption spectra of FAPbI₃ perovskite were then recorded in the wavelength range of 300-1500 nm.

Fig. 3 a) Absorbance Spectra b) Tauc's plot of FAPbI₃ perovskite.

As shown in Fig. 3a, the synthesized α -FAPbI₃ perovskite shows absorption up to 900 nm. For the direct allowed transition of α -FAPbI₃ perovskite, the absorption coefficient (α) and band gap can be expressed as equation (2) below:

$$(\alpha h\nu) = B(h\nu - E_g)^n \quad (2)$$

where, B is Tauc's constant, α is the absorption coefficient, h is Planck's constant, ν is photon frequency, and E_g is the optical band gap energy of the material. To determine the band gap, $(\alpha h\nu)^{1/2}$ is plotted against energy $E(h\nu)$ as shown in Fig. 3b. A straight line is fitted through the data points. The band gap of α -FAPbI₃ perovskite was estimated to be 1.55 eV which is in good agreement with reported values in the literature.^[24] The synthesized FAPbI₃ perovskite in the present study has good crystallinity and is thus a better candidate for use in semiconducting devices like absorber layers in solar cells, batteries, sensors, etc.

4.3 Photoluminescence spectroscopic analysis

The photoluminescence (PL) measurement of α -FAPbI₃ perovskite thin film prepared using a one-step deposition method was recorded at an excitation wavelength of 430 nm. Fig. 4 shows the PL spectra of FAPbI₃ perovskite which is obtained by diluting the sample in two ml N, N-dimethylformamide (DMF). This result is confirmed by the evolution of the wavelength for FAPbI₃ perovskite from 710 nm - 740 nm, thus it involves the passage to the most stable α phase, which is confirmed by the results of X-ray diffraction. The result supports further the claim that the α -FAPbI₃ perovskite is a promising material for the application in light-emitting diode and photovoltaic solar devices. The deviation in the bandgap value of the material by UV-VIS-NIR and PL measurement is due to the slightly different size distribution of nanocrystallite during the two measurements.

Fig. 4 Photoluminescence (PL) spectra of FAPbI₃ perovskite material.

4.4 Transmission electron microscopic analysis

Transmission electron microscopy (TEM) was employed to deduce microscopic, crystallographic, and compositional information about the FAPbI₃ material. The microstructural information of the FAPbI₃ perovskite as obtained from transmission electron microscopy (TEM) at an acceleration voltage of 200 kV is shown in Fig. 5a. Morphology with agglomerate of FAPbI₃ perovskite nanocrystals shows the presence of particles with differently oriented crystallites. Fig. 5b shows a sample estimation of the inter-planar distance to be 0.657 nm, which is very close to the inter-planar distance measured from XRD measurements.

Fig. 5 a) Low magnification Transmission electron microscopic image and b) high-resolution Transmission electron microscopic image with fringe analysis for interplanar spacing measurement of FAPbI₃ perovskite sample.

5. Conclusion

In summary, we report a successfully synthesized FAPbI₃ perovskite, using a simple room temperature one-step chemical method. The synthesized FAPbI₃ materials were thoroughly investigated for structural, and optical properties using XRD, photoluminescence, UV-Visible absorption, and transmission electron microscopy. The confirmation of cubic α -FAPbI₃ structure was confirmed using XRD and the crystallite size of the nanoparticle was found to be 40 nm. The UV –Visible spectra were used to deduce the bandgap value of the direct transition to be 1.55 eV of FAPbI₃. The transmission electron microscopic analysis shows the conglomerate of crystallites and the inter-planar spacing of 0.625 nm. This leads to the conclusion that the FAPbI₃ perovskite synthesized by a simple low-temperature chemical technique is a better candidate for applications in optoelectronic and photovoltaic device applications.

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Supporting information

Not Applicable.

Conflict of interest

There are no conflicts to declare.

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