Study on the Effect of Synthesis Temperature on the Structural, Surface Morphological and Optical Properties of Methyl Ammonium Lead Iodide Nanoparticles by Sol-Gel Method

K A Benazeera Beegum 1,2, Maria Paulose1, V J Peter3, Rakhy Raphael1, V G Sreeja1 and E I Anila1*

1Optoelectronic and Nano Materials’ Research Lab, Department of Physics, Union Christian College, Aluva, Kerala, India, 683102
2 PJMSGHSS, Kandassankadavu, Thrissur, Kerala, India, 680613
3 St. Pauls College, Kalamassery, Kerala, India, 683503

*Corresponding author email: anilaei@gmail.com

Abstract

Lead halide perovskite solar cells have recently attracted tremendous attention because of their excellent photovoltaic efficiency. The quality and stability of perovskite films are critical for solar cells. We report the synthesis of methyl ammonium lead iodide (MAPbI3) nanoparticles from methyl amine, hydroiodic acid and lead iodide by sol-gel method. Three powder samples of Methyl ammonium Lead Iodide were prepared at 50°C, 90°C, and 100°C. The powder samples were characterised by X ray diffraction (XRD), Diffuse reflectance spectroscopy (DRS), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX) and Photoluminescence (PL). The presence of carbon, hydrogen and nitrogen were examined through CHN studies. The surface morphology, band gap, and elemental contents change with temperature. The XRD pattern exhibited major reflections from [110], [220], [310], [224] and [314] planes in agreement with JCPDS file No.00-021-1276, revealing tetragonal structure.

1. Introduction

In a perovskite solar cell a perovskite structured compound, most commonly a hybrid organic-inorganic lead or tin halide-based material is used as the light harvesting active layer. Perovskite materials such as methyl ammonium lead halides are cheap to produce and simple to manufacture. As per the NREL efficiency chart, solar cell efficiency of devices using these materials have increased from 3.8% in 2009 to 21.0% in 2015, making this the fastest-advancing solar technology to date [1]. They also show tremendous promise in a variety of optoelectronic applications including light emitting diodes and lasers. With the potential of achieving even higher efficiencies and the very low production costs, perovskite solar cells have become commercially attractive.

The perovskite structure has the general crystal structure ABX3 where “A” and “B” are cations and “X” is an anion. The most commonly studied perovskite absorber is methyl ammonium lead trihalide (CH3NH3PbX3, where X is a halogen atom such as iodine, bromine or chlorine), with an optical band gap between 1.5 and 2.3eV depending on halide content and temperature of preparation [2,3].
It was Miyasaka et al. in 2009[1], who developed a solar cell with perovskite material as the active layer and they could get an efficiency of 3.8%. But the stability of the cell was very poor. It lasted for a few minutes. Henry Snaith and Mike Lee from the University of Oxford in 2012[4] conducted studies on the stability of perovskite solar cells and realised that hole transport layer with Spiro-OMeTAD over the active layer can improve the stability and efficiency of the cell. Guangda Niu et al. reported that Metal oxide (e.g. Al₂O₃) as the hole transport layer improve the stability [6].

We prepared powder samples of Methyl Ammonium Lead Iodide at different temperatures by sol-gel method. Out of the many perovskites available, we selected MAPbI₃ because of the easiness of the preparation. The variation in band gap and photoluminescence with temperature were studied. The structural studies were carried out by X-ray diffraction and optical charactarisations by Diffuse reflectance spectroscopy (DRS) and Photoluminascence (PL) study. MAPbI₃ is highly moisture sensitive. The stability of the sample over time was examined by EDAX and CHN analysis. The structural studies were carried out by SEM analysis. The band gap increased with temperature. The photoluminescent charactaristics were different for the three samples.

2. Experimental section

Synthesis of methyl ammonium lead iodide nanoparticles from methyl amine, hydroiodic acid and lead iodide was done by sol-gel method. All the chemicals used were of analytical grade. 30ml of 1M hydroiodic acid [ Sigma-Aldrich 99.95% ] in water and 28ml of 1M of methyl amine [Spectrochem] in methanol were prepared by continuous stirring for 30 minutes using a magnetic stirrer. Methyl amine was added to hydroiodic acid dropwise and the solution was stirred for two hours. Then the solution was kept in oven at a temperature of 50°C for 2 days. The resulting powder was washed using diethyl ether and filtered. 1 mol.% lead iodide (PbI₂) is added to methyl ammonium iodide and mixed with few drops of DMF using agate mortar and pestle to get methyl ammonium lead iodide. The whole process was repeated by changing the temperature to 90°C and 100°C to prepare other two samples. The nanopowder of CH₃NH₃PbI₃ was structurally studied by Regaku Miniflux600 X-ray diffractometer and optical characteristics were studied using UV-Vis-NIR Spectrophotometer (Varian, Cary 5000) and spectrofluorometer (Fluoromax-4).

3. Results and discussion

X-ray diffraction of the given material is taken using diffractometer and a graph was plotted by taking 2θ along X axis and intensity along Y axis as shown in figure1. The pattern shows major reflections from planes (110), (220), (310), (224) and (314) matching with JCPS file number:00-021-1276 having tetragonal structure. The other unknown peaks are expected to be due to the presence of impurity particles.

The lattice parameters are determined from the XRD pattern by taking the hkl values of the peaks using the equation

\[ d = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}} \]  \hspace{1cm} (1)
Figure 1. XRD pattern of MAPbI$_3$ synthesised at 50°C, 90°C and 100°C.

In equation (1), d is the interplanar distance, a and c are lattice parameters and h, k and l are the miller indices. The lattice parameters are determined to be a=b=8.936Å, 4.499Å and 4.679Å and c=12.635Å, 7.222Å and 17.567Å for 50°C, 90°C and 100°C respectively.

The grain size (D) is determined using Debye-Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

Here $\lambda$ is the wavelength of X-ray used, $\beta$ is the full width at half maximum and $\theta$ is the glancing angle. The grain sizes are calculated to be approximately 31nm, 31.1nm and 35nm respectively for samples prepared at 50°C, 90°C and 100°C respectively.
Figure 2. WH Plot-(βcosθ Vs 2sinθ).
The graph shows all the samples have negative strain.

W-H plot between βcosθ and 2sinθ is drawn.(Fig 2). The slope of the curve is the lattice strain parameter. All the curves have negative strain which means that the samples have compressive strain.

Figure 3. (hν*k/s)^2 Vs hν graph of MAPbI₃ nanoparticles synthesised at different temperatures.
The bandgap of the samples are found from the \((h\nu^2/k) vs h\nu\) graph (Fig.3) by extrapolating the linear portion of the graph to the Xaxis and obtained as 1.49eV, 1.53eV and 1.56eV for 50\(^\circ\)C, 90\(^\circ\)C and 100\(^\circ\)C respectively. The continuous blue-shift of the band gap is due to the down-shift of the valence band [5]. The blue-shift is observed on increasing the temperature because of tetragonal-cubic phase transition [3] for MAPbI\(_3\).

Figure 4 is the photoluminescence spectrum of the three samples. The photoluminescence emission occurs nearly at 880nm for 50\(^\circ\)C, and at 820 nm for 90\(^\circ\)C and 100\(^\circ\)C. The variation in emission wavelength for the samples may be due to the change in band gap energy. Samples prepared at 90\(^\circ\)C and at 100\(^\circ\)C have emission nearly at 820nm because their band gap energies are almost equal.

Figure 5. SEM images for of MAPbI\(_3\) nanoparticles synthesised at 50\(^\circ\)C, 90\(^\circ\)C and 100\(^\circ\)C

SEM analysis was done to study the surface morphology of the samples. The three powder samples have different types of surface morphologies (Figure 5). For the sample synthesised at 50\(^\circ\)C the surface is smooth over a large area and it looks like combination of different sheets. On increasing synthesis temperature to 90\(^\circ\)C irregular smaller sheets with fine particles attached to it can be seen and at 100\(^\circ\)C agglomerated particles are observed.
Table 1. The atom percentage and mass percentage of each element in the samples

| Element | Mass % | Atom % |
|---------|--------|--------|
|         | At 50\(^{\circ}\) C | At 90\(^{\circ}\) C | At 100\(^{\circ}\) C | At 50\(^{\circ}\) C | At 90\(^{\circ}\) C | At 100\(^{\circ}\) C |
| C       | 0.83   | 1.28   | 0.96   | 8.95   | 13.00   | 10.47   |
| O       | 0.36   | 0.81   | 0.69   | 2.94   | 6.22    | 5.61    |
| I       | 67.19  | 61.71  | 54.94  | 68.40  | 59.40   | 56.55   |
| Pb      | 31.62  | 36.00  | 43.42  | 19.71  | 21.35   | 27.37   |

Table 1 illustrates the mass % and atom % of each element in the samples at different temperature. There is no much variation in the elemental composition at different temperature. The data shows the presence of oxygen in the sample which may be due to the oxidation of the metal cation. The presence of nitrogen and hydrogen can’t be detected by EDAX analysis. Hence the CHN analysis was carried out. The result showed only a small percentage (below 2%) for N and H. As per the molecular formula of MAPbI\(_3\), there must be 50% hydrogen atom, and 8% nitrogen atom while considering the atom percentage. The decay of solar cell efficiency with MAPbI\(_3\) as the active layer in perovskite solar cell may be due to the loss of these elements from the material.

3. Conclusion

The samples of MAPbI\(_3\) prepared at 50\(^{\circ}\) C, 90\(^{\circ}\) C and 100\(^{\circ}\) C by sol-gel method have different characteristics like band gap energy, photoluminescence, SEM and EDAX. The XRD pattern shows major reflections from planes (110), (220), (310), (224) and (314) matching with JCPDS file number: 00-021-1276 having tetragonal structure. The band gap energy of MAPbI\(_3\) increases with temperature. PL emission occurs at 820nm for 90\(^{\circ}\) C and 100\(^{\circ}\) C and at 880nm for 50\(^{\circ}\) C. The structural morphology is different but the EDAX analysis gives almost same result for the three samples. The CHN analysis reveals the loss of Hydrogen and Nitrogen from the sample. We hope to find a solution to attain stability for the material by providing protective layer with a metal oxide.

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