

Synthesis and study of CsPbBr₃ by using antisolvent recrystallization method for solar cell applications

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Abstract

The cesium lead bromide (CsPbBr₃) perovskite gets considerable attention due to its excellent stability and moisture-tolerance aspects. In this study, a structural, optical and morphological property of CsPbBr₃ was investigated. The CsPbBr₃ was synthesized at room temperature by an antisolvent recrystallization method using Cesium Bromide (CsBr), Lead Bromide (PbBr₂), Oleylamine (OAm) and Oleic acid (OA). The Oleic acid acts as the capping ligand. The synthesized CsPbBr₃ nanoparticles were confirmed by X-Ray diffraction pattern. The optical bandgap and absorption were investigated from UV-Visible spectroscopy. In this work sample showed a bright green photo-luminescence when the sample was excited by 365 nm UV lamp. The morphology and elemental compositions were analyzed using SEM and EDAX. The results obtained are important for the synthesis of perovskite materials at room temperature for optoelectronic devices.

Keywords: Nanocrystals, Perovskites, Photovoltaics, CsPbBr₃, Thin film, Capping ligands, Room temperature synthesis.

Introduction

The scientific communities are searching the semiconductor materials that are easy to fabricate, stable in operating devices, and abundant elements in nature for the next generation of optoelectronics.

In the recent years, Perovskite materials have gained much attention particularly in the field of photovoltaics due to its outstanding optoelectronic properties and it could compete with silicon. The success and fast improvement in perovskite optoelectronics mainly due to their facile fabrication, chemical versatility, and excellent optoelectronic properties. In all inorganic counterparts (CsPbX_3 , $X = \text{I, Br, Cl}$) with changing inorganic Cs cation shows progress in stability and charge carrier transfer properties [1]. The CsPbBr_3 perovskite material has excellent optoelectronic properties such as large light absorption coefficient, high carrier mobility, long diffusion length, long electron-hole diffusion length, tunable direct bandgap with low trap state density, and simple to manufacture [2,3]. Thus CsPbBr_3 is the excellent candidates for the application in solar cells [4], light emitting diode [5], photodetectors [6], lasers [7], high-energy ray detectors.[8]

There exists several methods to synthesize CsPbBr_3 including hot injection method, conversion method, solution temperature lowering (STL) method, inverse-temperature crystallization etc. The solution-processed semiconductor material synthesis has received tremendous attention in the field of photovoltaics. Herein, we report a quality CsPbBr_3 NPs synthesized at room temperature from oleic acid and oleylamine ligands by a simple Anti solvent recrystallization method. After synthesizing CsPbBr_3 , structural, optical, morphological and compositional properties have been investigated with various analytical techniques.

Methodology

The Cesium Bromide (CsBr , 99.999 %), Lead Bromide (PbBr_2 , 99.999 %), Oleylamine (OAm, 70 %), Oleic acid (OA, 90 %) were used with the purity level as mentioned in parenthesis. The chemicals mentioned above used for the synthesis of CsPbBr_3 were procured from Sigma-Aldrich and used without further purification and processing. The N, N- Dimethylformamide (DMF 99.8 %), n- hexane (Aldrich) and toluene (99.5 %) were purchased from HPLC India with AR grade.

a. Preparation of CsPbBr_3 nanoparticles and thin film

The CsPbBr_3 nanoparticles were synthesized at room temperature by a simple antisolvent recrystallization method using two different precursors (CsBr , PbBr_2), solvent (DMF) and ligands (OA & OAm). Nucleation starts immediately after the injection of solvent. The CsBr (0.2 mmol) and PbBr_2 (0.2 mmol) were dissolved in 5 ml of DMF and stirred until it converts into transparent solution at ambient temperature. Later, 500 μl of OA and 200 μl of OAm were added to the precursor solution to stabilize it. Then 2 ml precursor solution injected drop-wise into anti solvent toluene (10 ml), under continuous stirring. Within 5-10 second, the green colloidal solution was obtained. Figure 1 shows the schematic procedure for the CsPbBr_3 synthesis.

b. Purification of CsPbBr_3 Material:

The solution prepared by the procedure mentioned above containing CsPbBr_3 was then taken out and centrifuged at 4500 rpm for 10 min. The centrifuge sediment was given twice a toluene and n-hexane wash, and the final sediment of CsPbBr_3 was collected and redispersed in toluene for further characterizations. The soda-lime glass was used as a substrate to deposit a thin film of CsPbBr_3 . The substrates were carefully cleaned sequentially in acetone and double distilled water. The CsPbBr_3 nanoparticles solution was deposited on the soda-lime substrate by drop cast method, and the deposited films were dried at room temperature for 2 hour and used for further characterizations.

c. Film and Nanoparticles characterization:

The synthesised CsPbBr_3 thin film and nanoparticles has been investigated by different characterization techniques for the detailed study of Structural, Optical and Morphological Properties. The X-ray diffraction pattern was obtained by X-ray diffractometer (Bruker D8 Advance, Germany) using $\text{CuK}\alpha$ line ($\lambda = 1.54 \text{ \AA}$). The absorbance of the CsPbBr_3 was measured using a JASCO, V-670 UV-visible spectrophotometer in the range of 300-1200 nm. The steady-state photoluminescence (PL) spectra were recorded. The samples were excited using 430 nm line for recording steady-state PL. The surface morphology of the CsPbBr_3 film is investigated using scanning electron microscopy.

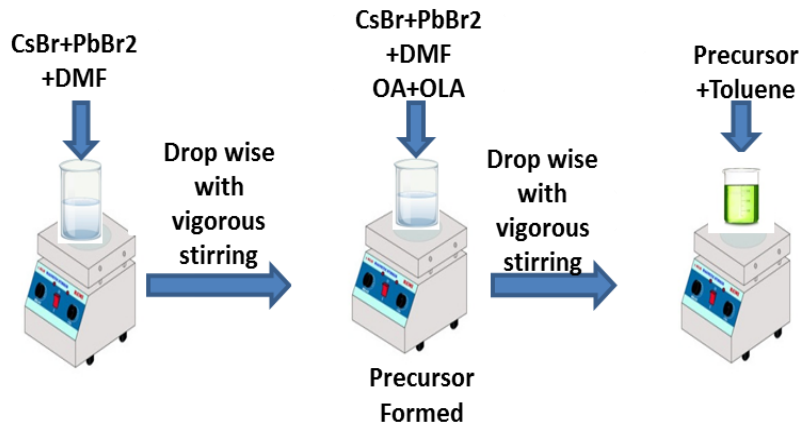


Figure 1. Schematic reaction procedure of CsPbBr₃ synthesis

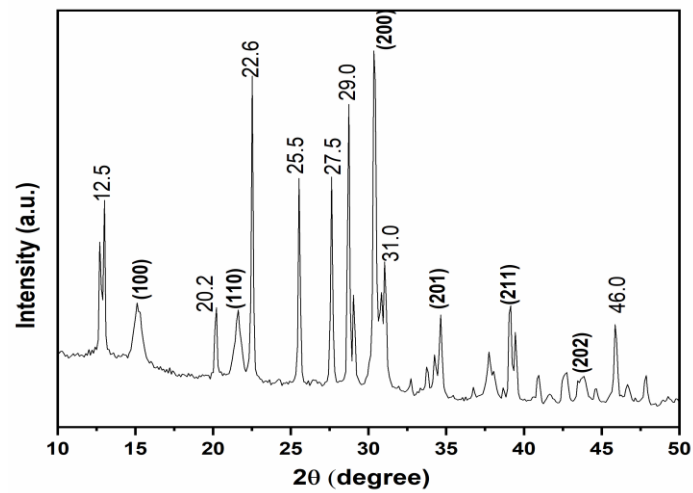


Figure 2. XRD pattern of the CsPbBr₃ thin film

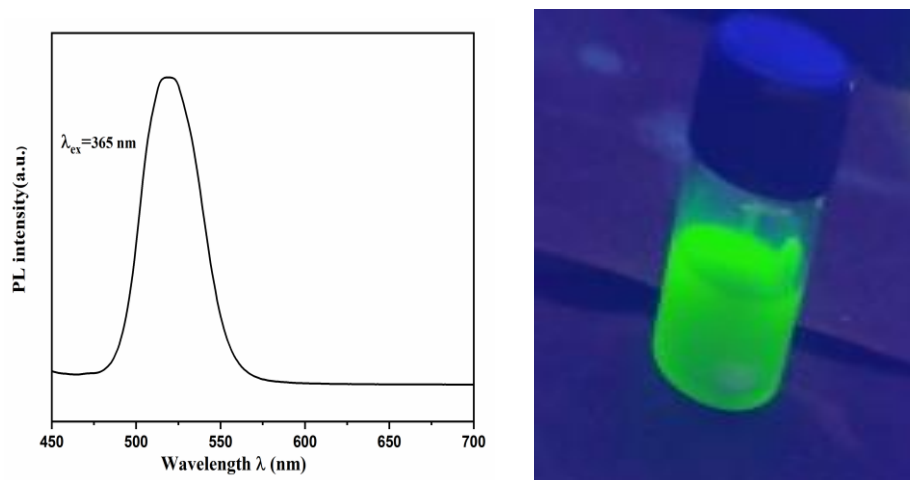


Figure 3 a) PL emission spectra b) digital image of CsPbBr₃ solution under the 365 nm UV lamp

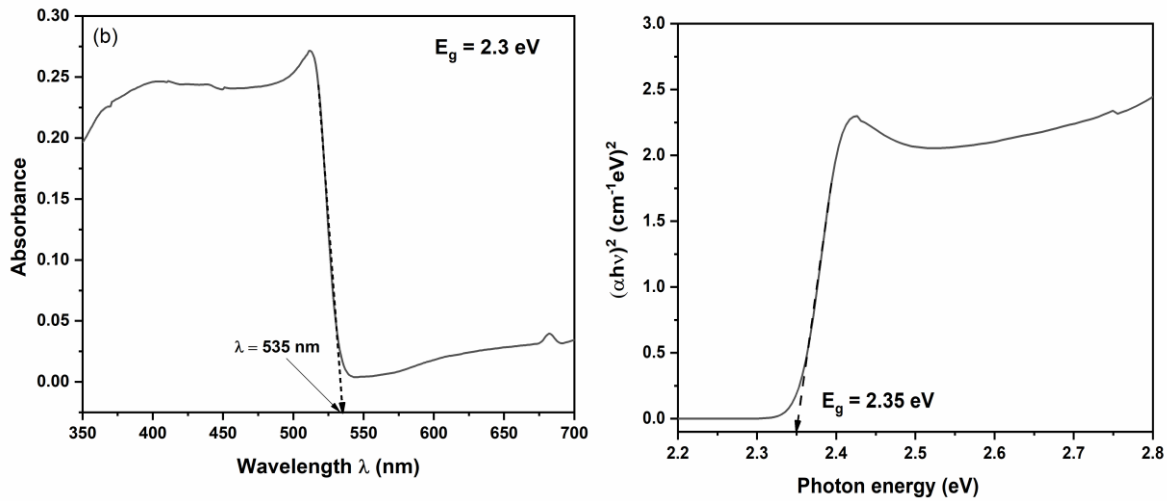


Figure 4 a) UV- Visible absorption Spectra b) Tauc plot of CsPbBr₃

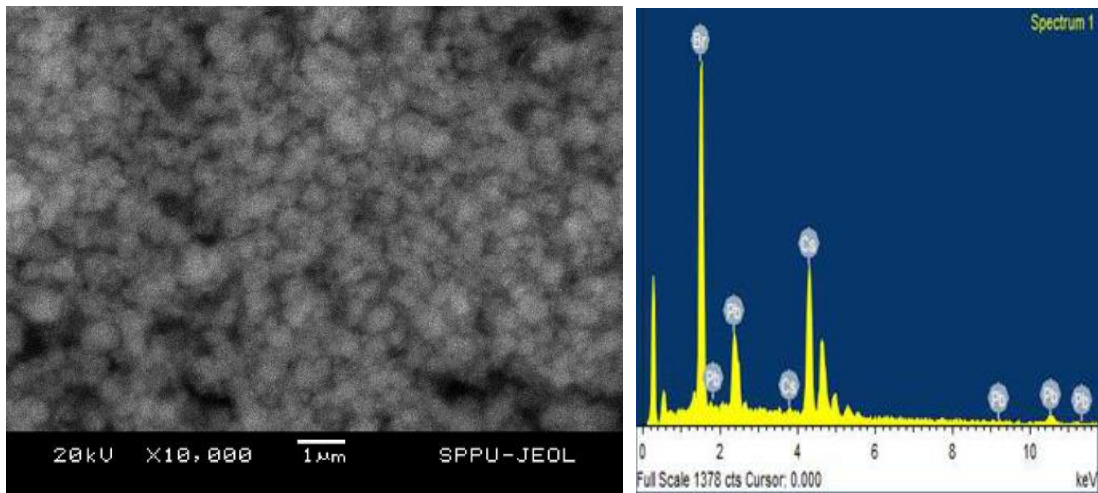


Figure 5 (a) SEM images of CsPbBr₃ Thin Film (b) EDAX pattern of CsPbBr₃ Thin Film

Table 1: atomic percentages of Cs, Pb and Br

Element	Wt. (%)	At. (%)
Cs	39.38	32.30
Pb	17.91	9.42
Br	42.71	58.28

Result and Discussion

Growth Mechanism of CsPbBr₃ Nanoparticles:

To synthesis CsPbBr₃ nanoparticles, two different precursors (CsBr and PbBr₂) and ligands (OLA and OA) and two different solutions (DMF and Toluene) were

used. The 10 ml DMF solution was added drop-wise into two different precursors under continuous stirring. The precursors start to dissolve into DMF solution and convert it into transparent solution. At the initial stage, precursor concentration is too low to permit the growth of CsPbBr₃ nanoparticles, and no nucleation process occurs at this stage. After adding Ligands (OA, OAm)

precursor solution is formed. Then immediately, 2 ml precursor solution injected into 10 ml toluene with vigorous stirring, which can provide essential nutrients for crystallization and growth of larger CsPbBr₃ nanoparticles.

X-Ray diffraction analysis:

The X-ray diffraction (XRD) pattern of the CsPbBr₃ thin film is shown in figure 2. In the XRD pattern, the peaks at 2θ equal to 15.109°, 21.6204°, 31.037°, 34.543°, 37.748°, 44.660° are assigned to the (100), (110), (200), (201), (211) and (202) planes respectively. The XRD pattern shows the monoclinic crystal structure of the CsPbBr₃ with lattice parameter $a = b = c = 5.83 \text{ \AA}$. The results are well-matched with the previous reports and the JCPDS file no. (#18-0364) [9], the monoclinic CsPbBr₃ shows polycrystalline in nature. The diffraction peaks observed nearly at 2θ equal to 12.5°, 20.2°, 22.6°, 25.5°, 27.5°, 29.0°, 31.0° and 46.0° are correspond to the secondary phases and it will vanishes after the annealing of the sample. The diffraction peaks are sharp and narrower, indicating the better crystallinity of the material.

UV- visible and Photoluminescence spectroscopic analysis

To explore the optical properties of the CsPbBr₃ Photoluminescence (PL) was carried out. The PL studies shows that the emission from the CsPbBr₃ is in visible region with broad FWHM of 33 nm observed, as shown in Figure 3(a). The PL peak was located at 520 nm. The CsPbBr₃ nanoparticle showed bright green photo-luminescence when the sample was excited by 365 nm UV lamp as shown in fig. 3(b). After the confirmation of crystal structure of CsPbBr₃, the colloidal solution of the sample was used for UV-Visible spectroscopic measurements. The UV-Visible absorption spectra of CsPbBr₃ is shown in figure 4(a). The spectra shows a strong absorption peak at 535 nm, which is the bandgap absorption of CsPbBr₃ perovskite [10]. The optical band gap was estimated using the relation of $(\alpha h\nu)^2$ vs. $h\nu$, where α is an absorbance, h is the Planks constant and ν is frequency. The effective optical band gap energy is 2.3 eV.

Morphology and Composition Analysis of CsPbBr₃

The morphology and EDAX Spectra of the CsPbBr₃ sample is shown in figure 5(a) and 5(b). The SEM image of CsPbBr₃ sample shows the agglomeration of particles is visible in the mode under lower magnification. Table 1 shows the atomic percentages of Cs, Pb and Br. The EDAX confirms the presence of all elements in the materials. The excess in the lead (Pb) signal is due to the reabsorption of X-ray emission by cesium (Cs). Similarly, the excess in the bromide (Br) signal is due of the reabsorption of X-rays from Cs and Pb [11].

Conclusions

This work explains a detailed study of structural, optical and compositional analysis of CsPbBr₃ thin film and nanoparticles. We have successfully synthesized the CsPbBr₃ NPs at room temperature using antisolvent recrystallization method. The formation of CsPbBr₃ was confirmed from the XRD pattern. The UV-Visible spectroscopic analysis shows a strong absorption peak at 535 nm. The calculated bandgap energy of CsPbBr₃ was found to be 2.3 eV. The wavelength of PL emission spectra is at 520 nm with a narrow FWHM of 33nm have been observed. The EDAX pattern confirms the presence of all the elements in the material. The controlled room-temperature synthesis and formation of thin films of CsPbBr₃ nanoparticles with promising properties can open a novel path for low-cost optoelectronic devices.

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Conflicts of interest: The authors stated that no conflicts of interest.

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