



Synthesis of $\text{NH}_2\text{CH}_2=\text{NH}_2$ based mixed halide Perovskite nanoparticles using single step low temperature microwave assisted heating

Rajib Saha and Samrat Paul*

Advanced Materials Research and Energy Application Laboratory (AMREAL), Department of Energy Engineering, North-Eastern Hill University, Shillong-793022, India.

Abstract: The present paper reports the synthesis and characterization of mixed halide based formamidinium lead Perovskite nanoparticles having general formula $[\text{HC}(\text{NH}_2)_2]\text{PbI}_n\text{Br}_{3-n}$. A single step low temperature chemical route using microwave reactor is reported. The Perovskites synthesized were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and Transmission electron microscopy (TEM). The X-ray diffraction revealed phase purity and tetragonal structure whereas TEM micrographs found that the synthesized particles are at 10-12 nm, 12-15 nm, 15-20 nm and 20-22 nm for FAPbI_3 , FAPbBr_3 , FAPbBrI_2 and FAPbIBr_2 respectively. Optical properties and molecular bonding of the Perovskites was investigated by Fourier transform infra-red spectroscopy.

Keywords: Formamidinium, Low temperature synthesis, Mixed halide, Microwave reactor, Perovskite.

1. Introduction: Perovskite nanoparticles are gaining importance research in the field of solar cell. This material exists in the form of halides, oxides and nitrides and has not only shown remarkable performance in the field of solar cells but also other solid-state device. Perovskite, such as formamidinium lead halide (FAPbX_3 , where FA is Formamide and X is a halogen or combination of halogens) have been considered as a promising photoactive compound for photovoltaic application after the Methylammonium lead halide based Perovskites. At high temperature, in formamidinium based Perovskite, a phase transition occurs making it relatively stable compared with Methylammonium based Perovskite [1]. Koh *et al.* found that formamidinium based Perovskite display a bandgap of 1.47 eV leading to a broader absorption compared to the Perovskites containing methylammonium [2]. Eperon and his group investigated the effect of the A cation size upon the optical and electronic properties of the Perovskite by replacing methylammonium with formamidinium and achieved a power conversion efficiency upto 14.2 %. The thermal behaviour of formamidinium iodide ($\text{CH}_5\text{N}_2\text{I}$) was studied by Petrov and his team by using different physicochemical methods such as thermogravimetry, differential scanning calorimetry and powder diffraction [3]. For the first time a highly efficient wide bandgap planar heterojunction formamidinium lead bromide based solar cells was presented by a research team and they found that material exhibits much longer diffusion lengths of the photo excited activity than the methylammonium based Perovskites [4]. However, a novel synthesis of Perovskite nanoparticles to achieve a low dimensional, nanosized organo-lead halide Perovskite is matter of research interest. Kimball *et al.* reported the synthesis of formamidinium lead halide (FAPbX_3) colloidal Hybrid organic–inorganic Perovskites (HOIPs) nanocrystal using in situ solid–liquid–solid cation exchange reaction found that nanocrystal exhibits a wide range of emissions spanning from 395 nm to 700 nm [5]. Moreover, a research group has proposed a facile and highly reproducible room temperature method for the preparation of a few-layer formamidinium lead bromide nanoplatelets. The obtained nanoplates of FAPbBr_3 NPs exhibit ultrapure-green PL at 532 nm with a photoluminescence quantum

yield as high as 88 % [6]. A simple and highly reproducible roomtemperature synthesis of device grade high quality formamidinium lead bromide (FAPbBr₃) colloidal nanocrystals (NC) was reported and which achieved a high photoluminescence quantum efficiency (PLQE) of 55 % – 65 % [7]. Microwave assisted synthesis or heating flourished firstly in the field of nanoparticles synthesis. Microwave heating refers the use of electromagnetic waves ranging from 0.01m to 1m wave length of certain frequency to generate heat in the material. Rapid heating and selective heating of materials are the important characteristic of microwave assisted heating. Several researchers have performed microwave assisted synthesis to produce different kind of Perovskite oxide materials. Li *et al.* reported the synthesis of single-crystalline BiFeO₃ (BFO) nanoplates using simple and very rapid microwave-assisted hydrothermal technique and found that that the microwave treatment gives improvement in crystallinity of BFO nanocrystals in compare to traditional hydrothermal process [8]. Another research group highlighted the synthesis of Indium-doped zinc oxide (IZO) nanoparticles using microwave-assisted method and achieved a good device performance, with low fabrication cost and impressive light-soaking stability [9]. Perovskite nanoparticles have been synthesized by researcher using various method and process such as sol-gel process [10], co-precipitation process [11], solid state reaction technique [12], etc. to achieve highly crystalline nanoparticles.

In this article, we report, the synthesis and characterization of formamidinium based mixed halide Perovskite nanoparticles. Low temperature microwave assisted heating within a single step chemical route for the synthesis is described. The single step is simple, low-cost approach to obtain highly crystalline nanocrystals within a very short reaction time with high yields and good reproducibility than the classical techniques used to synthesize Perovskite nanoparticles.

2. Materials and methodology:

2.1 Chemicals and reagents: Formamidine acetate salt (HN=CHNH₂·CH₃COOH, Sigma-Aldrich), hydroiodic acid (HI, Alfa Aesar), hydrobromic acid (HBr, Alfa Aesar), N, N-Dimethylformamide (C₃H₇NO, Sisco Research Laboratories Pvt. Ltd. India), lead (II) Iodide (PbI₂, Alfa Aesar) and lead (II) Bromide (PbBr₂, Alfa Aesar) were used as initial precursors for the synthesis of formamidinium based Perovskite respectively.

2.2 Instruments: The Transmission Electron Microscope (TEM), model no. JEM-100CX II (JEOL, Japan) was used to study the internal structure and morphology of the synthesized particles. X-ray Diffractometry (XRD) analysis was performed using BRUKER AXS, D8 FOCUS (Germany) with wavelength 0.154 nm to investigate the crystallinity of the Perovskite nanoparticles. Fourier Transform Infrared Spectroscopy (FTIR) Analysis using IMPACT 410, NICOLET (USA) was performed to identify the functional groups in the compound.

2.3 Synthesis of Perovskite using chemical technique: The formamidinium based Perovskite nanoparticles was synthesized by chemical technique synthesis method as described elsewhere [13-14] with some modifications. For the synthesis of formamidinium lead iodide (and NH₂CH₅=NH₂PbI₃, FAPbI₃), Formamidine acetate salt (HN=CHNH₂·CH₃COOH in absolute methanol is added to hydroiodic acid (57 wt. %) under continuous stirring (2 hours) at room temperature. The white precipitate (formamidinium iodide) obtained was filtered. Lead (II) Iodide (PbI₂) was also dissolved in anhydrous N, N-Dimethyl formamide and finally the solution was added to formamidinium iodide at 3:1 molar ratio, to synthesize formamidinium lead iodide (NH₂CH₅=NH₂PbI₃, FAPbI₃) Perovskite solution. The Perovskite solution was then dried to get Perovskite nanocrystals. The FAPbBr₃, FAPbIBr₂ and FAPbI₂Br have been synthesized using similar methods as discussed above.

The obtained nanoparticles was heated at of 60 °C for 5 minutes and was allowed to settle down (Hold time) for 5 minutes. The materials were given time to cool down at temperature of 60 °C as shown in Table (1).

Table 1: Steps for heating of Perovskite nanoparticles by microwave heating

Step	Program	Temperature (°C)	Time (hh:mm:ss)	Power (W)	Cooling	Stirrer Speed (rpm)
1	Heat to temperature in time	60	00:05:00	850.0	Off	600
2	Hold	-	00:05:00	850.0	Off	600
3	Cool down	50	-	-	On	600

The Perovskites nanoparticles absorbed microwave energy differently. They have shown a different degree of polarity within the molecule, and therefore, will be affected either more or less by the changing microwave field. Heating mechanism involved dielectric polarization and conduction of the nanomaterials. Reaction mixture heating proceeds directly inside mixture of the nanomaterials. The reaction mixture and heating mechanism of microwave is shown with help of the graph as shown below-

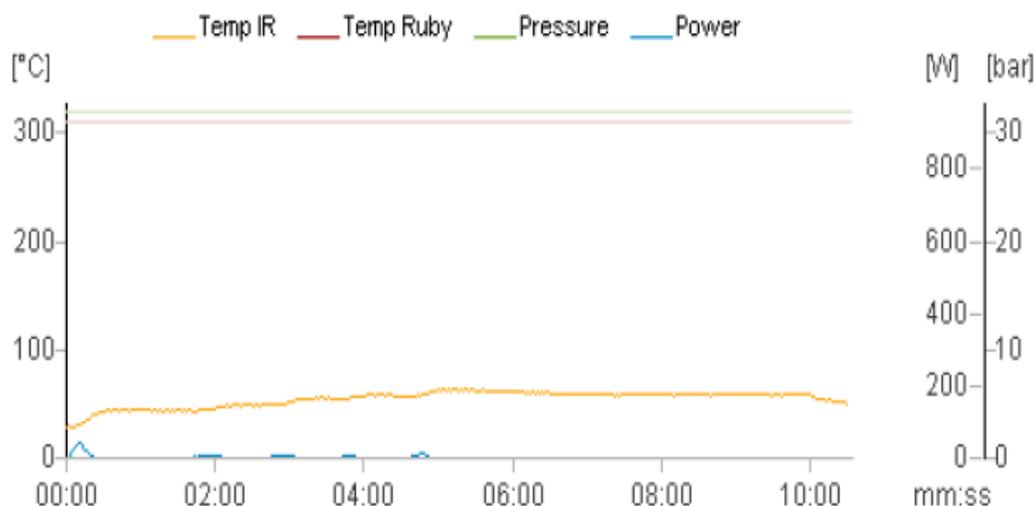


Figure (1): Reaction mixture and heating mechanism graph of microwave heating.

3. Results and Discussion:

3.1 X-ray Diffraction: X-ray Diffraction graph of formamidinium based Perovskite nanoparticles synthesized are shown in Figure (2). The diffraction pattern indicates the formation of FAPbI₃ Perovskite shows two highest peak at 2θ angles of 12.24 ° and 24.42 °, that is assigned in tetragonal lattice with planes (110) and (220) respectively. XRD patterns for FAPbBr₃ Perovskite shows two strong diffraction peaks at 2θ angles 21.96 ° and 44.60 °, which could be assign to (200) and (220) planes in the tetragonal lattice. The diffraction pattern for FAPbBr₂ Perovskite shows two strong diffraction peaks at 2θ angles of 31.16 ° and 55.36 °, which could be attributed to (300) and (330) planes in the tetragonal lattice. The sample C is characterized to be mixed halide FAPbIBr₂ Perovskite with peaks at 20.09 °, 27.07 °, 32.06 ° and 42.52 ° respectively. It shows one strong diffraction peaks at 2θ angles of 20.09 ° in the tetragonal lattice plane of (200). The complete phase transformation occurred for Perovskite nanoparticles at 80 °C

followed by microwave heating at low temperature which is in good agreement with the earlier reports. The crystallite size for the four different Perovskite nanoparticles was calculated from X-ray diffraction peaks by measuring the full width at half maximum (FWHM). The FWHM (β) for FAPbI₃, FAPbBr₃, FAPbBrI₂ and FAPbIBr₂ Perovskite was found to be 0.07 rad, 0.11 rad, 0.14 rad and 0.08 rad respectively.

The Debye-Scherrer equation for calculating the crystallite size is given by:

$$D = K\lambda/\beta\cos\theta \dots\dots\dots(1)$$

where K is the Scherrer constant, λ is the wavelength of light used for the diffraction, β the ‘full width at half maximum’ of the sharp peaks, and θ the angle measured. The Scherrer constant (K) in the above formula accounts for the shape of the particle and is generally taken to have the value 0.9. The results revealed that the crystallite size of FAPbI₃, FAPbBr₃, FAPbBrI₂ and FAPbIBr₂ Perovskite was found to be 21 nm, 13.4 nm, 11 nm and 19 nm respectively.

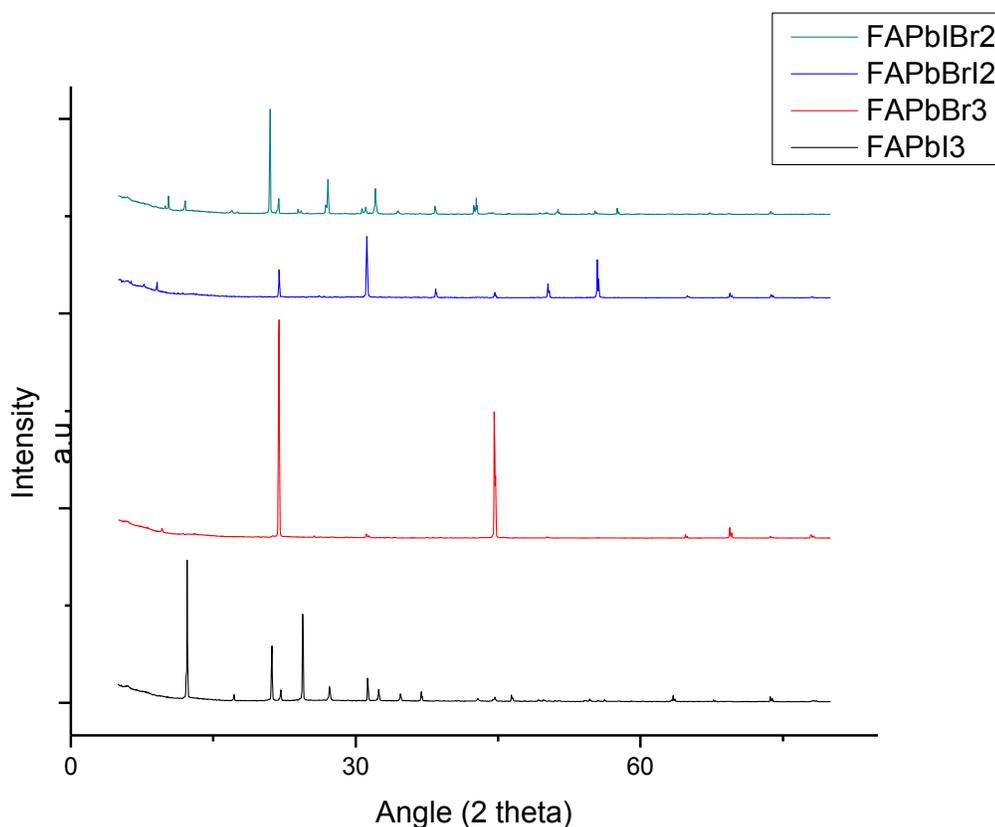


Figure (2): XRD graphs of Perovskite nanoparticles. Y-axis: Angle (degree).

3.2 FTIR: FTIR analyses were carried out to study the surface chemistry of the Perovskite nanoparticles in Dimethylformamide (DMF) as the solvent used in the precursor solutions which shown in Figure (3). All the four Perovskite nanoparticles possess the characteristic of CH₃ stretching, CH₃ deformation, CH₃ wagging and NH₂ wagging vibrational modes of NH₂CH₅=NH₂ respectively. In FAPbI₃, the 3500 – 3200 cm⁻¹ broad strong peak is assigned to N-H stretching and the peak at 1520 cm⁻¹ corresponds to the C=O.

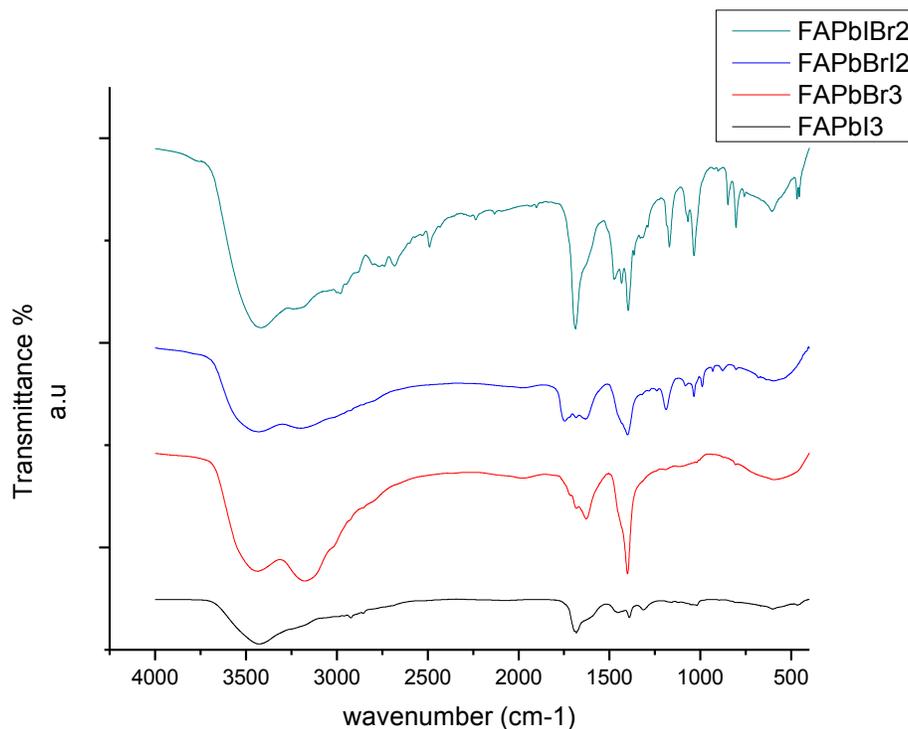


Figure (3): FTIR graphs of Perovskite nanoparticles.

The FAPbBr₃ spectrum shows broad strong peak at 3500 cm⁻¹ is assigned to N-H stretching, C-H stretching at 1510 cm⁻¹ and the peak at 1490 cm⁻¹ corresponds to the C=O, whereas, for FAPbI₃, the peaks are at 3400 and 1600 cm⁻¹ (N-H stretching modes). The FAPbBrI₂ Perovskite spectrum shows peaks at 3510 and 1494 cm⁻¹, which are in agreement with the characteristic CH₃ stretching and NH₂ wagging vibrational modes of NH₂CH₃=NH₂, respectively.

3.3 Transmission Electron Microscopy (TEM): The internal morphology of obtained Perovskite nanoparticles was studied using TEM as shown in Figure (4). The micrographs confirmed crystalline structure of Perovskites synthesized. An even particle size distribution can be observed in all the four samples. This confirms that the synthesis process resulted in similar crystalline structures of nano-scale has been successfully synthesized. TEM analysis of the FAPbI₃ showed the presence of ultra-small nanoclusters with a narrow size distribution. An average particle size was of 20 nm which was determined from the high- resolution TEM analysis (4a).

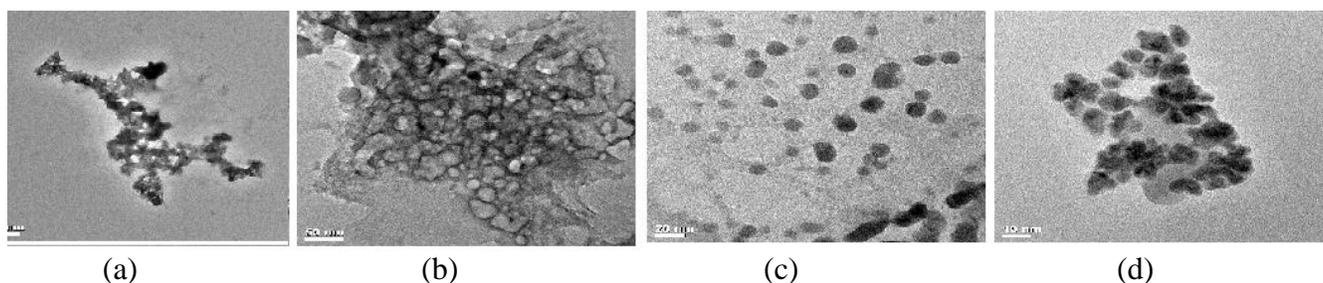


Figure (4): Micrographs of Perovskite synthesized, (a) FAPbI₃ (b) FAPbBr₃ (c) FAPbI₂ (d) FAPbBrI₂

The FAPbBr₃ (Figure-4b) nanoparticle formed from many FAPbBr₃ nanoparticles due to aggregation. However, there was no reaction between the nanoparticles. The particle size was found to be around 12 - 15 nm. The TEM analysis shows FAPbI₂ (Figure 4c) assemblies forming a dense mesoporous layer,

containing a high concentration of isotropic nanoparticles with $\text{NH}_2\text{CH}_5=\text{NH}_2\text{PbBr}_2$ materials with particle size of 20 - 22 nm. The particle size of FAPbBr_2 was found to be 11 nm.

4. Conclusions: $\text{NH}_2\text{CH}_5=\text{NH}_2$ based mixed halide Perovskite nanoparticles were successfully synthesized at lower temperatures in a single step chemical process followed by microwave heating. The synthesized samples results suggest that the mixed halide Perovskite nanoparticles are composed of both $\text{NH}_2\text{CH}_5=\text{NH}_2$ and $\text{PbI}_2/\text{PbBr}_2$. By changing the molar ratio Br/I in the precursor solution has a significant effect on the morphology and size of the nanoparticles. XRD analysis shows occurrence of complete phase transformation of Perovskite nanoparticles. TEM analysis of the Perovskite showed the cubic phase of the material with a narrow size distribution. Optical properties and molecular bonding of the Perovskite nanoparticles was shown using FTIR analysis.

5. Acknowledgements: The authors acknowledge SERB, DST, New Delhi (File no-SERB/F/9654/2016-17, PDF/2016/002390) for the financial support to carry out this work. The Sophisticated Analytical Instrument Facility (SAIF) at NEHU, Shillong and SAIC at Tezpur University, Tezpur is gratefully acknowledged for assistance in characterization.

6. Reference:

- 1) Z. Shi and A. H. Jayatissa, *Materials*. 11 (2018) 729.
- 2) T. M. Koh, K. Fu, Y. Fang, S. Chen, T. C. Sum, N. Mathews, Subodh G. Mhaisalkar, Pablo P. Boix and Tom Baikie, *J. Phys. Chem. C* 118 (2014) 16458–16462.
- 3) Andrey A. Petrov, Eugene A. Goodilin, Alexey B. Tarasov, Vladimir A. Lazarenko, Pavel V. Dorovatovskii and Victor N. Khrustalev, *Acta Cryst. E* 73 (2017) 569
- 4) F. C. Hanusch, E. Wiesenmayer, E. Mankel, A. Binek, P. Angloher, C. Fraunhofer, N. Giesbrecht, J. M. Feckl, W. Jaegermann, D. Johrendt, T. Bein, and P. Docampo, *J. Phys. Chem. Lett.* 5 (2014) 2791.
- 5) K. H. Kimball, Y. Nagaoka, C. Cao, E. Chaykovsky and O. Chen, *J. Mater. Chem. C* 5 (2017) 5680.
- 6) H. Fang, W. Deng, X. Zhang, X. Xu, M. Zhang, J. Jie, and X. Zhang, *Nano Res.* 12 (2019) 1.
- 7) A. Perumal, S. Shendre, M. Li, Y. K. E. Tay, V. K. Sharma, S. Chen, Z. Wei, Q. Liu, Y. Gao, P. J. S. Buen consejo, S. T. Tan, C. L. Gan, Q. Xiong, T. C. Sum & H. V. Demir, *Scientific Reports* 6 (2016) 36733.
- 8) S. Li, R. Nechache, I. A. V. Davalos, G. Goupil, L. Nikolova, M. Nicklaus, J. Laverdiere, A. Ruediger, and F. Rosei, *J. Am. Ceram. Soc.* 96 (2013) 10.
- 9) Y. H. Chiang, C. K. Shih, A. S. Sie, M. H. Li, C. C. Peng, P. S. Shen, Y. P. Wang, T. F. Guoa and P. Chen, *J. Mater. Chem. A* 5 (2017) 25485.
- 10) K. A. B. Beegum, M. Paulose, V. J. Peter, R. Raphael, V. G. Sreeja and E. I. Anila, *IOP Conf. Series: Materials Science and Engineering* 149 (2016) 012078.
- 11) Wankassama Haron, Anurat Wisitsoraat, and Sumpun Wongnawa, *International Journal of Chemical Engineering and Applications* 5/2, April 2014.
- 12) C. Ramírez, F. E. C. Pastrana, J. R. Rojas, D. A. L. Tellez and F. Fajardo, *Journal of Physics: Conference Series* 687 (2016) 012104.
- 13) Zhelu Hu, Hengyang Xiang, Mathilde Schoenauer Sebag, Laurent Billot, Lionel Aigouy and Zhuoying Chen, *Chem. Commun.* 54 (2018) 2623.
- 14) N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Nature* 517 (2015) 476 - 480.
