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A Stepwise Synthesis of Methylammonium Lead Bromide (MAPbBr3) Perovskite Using Lead Acetate Trihydrate as a Precursor

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Abstract. Methylammonium lead bromide (MAPbBr3) has been successfully synthesized in an aqueous solution using lead acetate trihydrate as a precursor. The synthesis process was conducted in a stepwise manner, first lead acetate was combined with hydrogen bromide to produce lead bromide. Subsequently, methylammonium bromide, which was obtained from the reaction of methylamine and hydrogen bromide was added to the lead bromide to form methylammonium lead bromide. The red-orange solid product has a chemical formula of CH3NH3PbBr3 based on SEM-EDS (scanning electron microscopy with energy dispersive spectroscopy), AAS (atomic absorption spectroscopy), and argentometric titration. The perovskite structure of the product has been confirmed by PXRD (powder X-ray diffraction) measurements and the thermal stability of the product was performed by TGA (thermal gravimetric analysis). The yield of each reaction step was found to be approximately 80%.

Keywords: *acetate; bromide; lead; mapbbr3; methylammonium; perovskite; synthesis*.

1 Introduction

Organometal halide perovskites possess a unique combination of characteristics that make them highly attractive for use in optoelectronic devices. Specifically, they exhibit excellent charge carrier mobility similar to inorganic semiconductors, while also retaining the flexibility and low-temperature processability of organic materials. Among these, methylammonium lead trihalide (MAPbX3) perovskites stand out due to their cost-effectiveness and the ability to be processed using low-cost solutions. Additionally, they exhibit a broad absorption range across the solar spectrum, high photoluminescence efficiency, facilitate easy, rapid generation and transport of both electrons and holes, which are desirable qualities for optoelectronic devices as written by Gonzalez-Carrero S., et. al. in [1].

Over the past decade, there has been a significant improvement in the application of perovskite materials in photovoltaic technology. The conversion efficiency of lead-based hybrid perovskites has undergone a remarkable improvement, increasing from 3.8% to 25.8% as reported by Min H., *et. al.* in [2]. In tandem application with silicon cells, the transparent perovskite cells can achieve a power conversion efficiency of 28.3% as reported by Yang D., *et al* in [3]. This has now surpassed that of conventional silicon-based photovoltaic cells currently available in the market, which typically offer power conversion rates of about 21%-22%.

The ease of synthesis and wide range of applications have further increased the use of perovskite materials. A cost-effective spin coating process for solar cell application has been reported by Kim, M., *et al*. in [4]. Another method involving vapor-assisted deposition of methylammonium bromide into $PbBr_2$ film on a TiO_2 layer for solar cell applications has been reported by Sheng R., *et al*. in [5] and for efficient light emitting diode Leyden M. R., *et al*. in [6].

The synthesis of lead-based perovskite is usually done in aprotic solvent such as N, N-dimethylformamide (DMF), as reported by Singh R.K., *et.al* in [7], Jancik Prochazkova A., *et. al.* in [8], Mayer A., *et. al.* in [9], Chen F., *et. al*.in [10]. Dimethyl sulfoxide (DMSO) has also been reported as a solvent by Jancik Prochazkova A., *et. al.* in [8], García-Aboal R., *et. al.* in [11], Swain B.S., *et. al.* in [12]. Other solvents used for synthesis include γ-butyrolactone (GBL) and acetonitrile (ACN), as well as combination of the aprotic solvent as reported by Radicchi E., *et. al.* in [13] and Yao F., *et. al.* in [14]. Another method for preparing stable lead halide-based perovskite nanoparticles also has been reported by Schmidt L.C., *et. al.* in [15].

The reason for employing aprotic solvents lies in the fact that the product can degrade in the presence of water and oxygen. However, the perovskite synthesis in aqueous solution is possible as long as pH is maintained lower than 4 and the formation of perovskite crystal can be controlled by controlling the temperature of crystallization as reported by Geng C., *et. al.* in [16] and Dimesso L., *et. al*. in [17].

Here, we reported our work on synthesizing methylammonium lead bromide ($MAPbBr_3$) perovskite using water as the solvent, promoting green chemistry and developing an educational module that introduces the concept of perovskite as a potential material for photovoltaic or optoelectronic devices, within the scope of chemistry education for upper secondary to junior college students.

2 Experimental

The chemicals used in this experiment are lead acetate trihydrate (Pb(CH3COO)2.3H2O), methylamine (CH3NH2) 40% in aqueous solution, and hydrobromic acid (HBr) 47% all reagents are purchased from Merck and is used without further purification. Three steps are involved in synthesis of MAPbBr3.

First, the formation of lead bromide (PbBr2) from Pb(CH3COO)2.3H2O. Second, the formation of methylammonium bromide (MABr) from CH3NH2, and finally the formation of MAPbBr3 from MABr and PbBr2. The schematic illustration of synthesis MAPbBr3 was drawn in Figure 1. Characterization was conducted to evaluate the properties of the perovskite using this method. Physical characterization involves the colour, appearance under a microscope and the thermal decomposition profile, while chemical characterization involves the perovskite's formula and structure.

2.1 Synthesis of Lead Bromide (PbBr2)

Pb(CH3COO)2.3H2O (2.00 g, 5.3 mmol) was dissolved in distilled water (150 mL), and to this solution HBr 47% (2.0 mL, 17.3 mmol) was added in excess. The solution mixture was heated until becomes saturated and allowed to cool at room temperature. PbBr2 was crystalized from the saturated solution after three hours. The product then was filtered using filter paper, washed with water and dried in air. The filtrate was evaporated until the solution becomes saturated and left overnight for crystal formation and harvest it for the second time.

2.2 Synthesis of Methylammonium Bromide

HBr 47% (5.0 mL, 43.3 mmol) was slowly added to an excess of CH3NH2 (5.0 mL, 57.9 mmol) in an ice bath (at 0 oC) with strong stirring. This was done while stirring the mixture. The resulting solution was stirred for another 30 minutes, then the container was sealed using rubber septa stopper to prevent further evaporation of CH3NH2.

2.3 Synthesis of Methylammonium Lead Bromide

PbBr2 (1.00 g, 2.7 mmol) was dissolved in HBr 47% (5.0 mL) and after the dissolution was complete, distilled water (30.0 mL) was added and the solution mixture was heated (± 70 oC) until clear solution was obtained. The solution was heated until all PbBr2 was dissolved (at about 70 oC). While being stirred, MABr (5.0 mL) solution was added. The stirring and heating were stopped at the time the first orange solid appeared, then the solution was allowed slowly to cool at

room temperature. MAPbBr3 was crystallised from the saturated solution after three hours. The product then was filtered using filter paper and dried in air. The filtrate was evaporated until the solution becomes saturated and left overnight for crystal formation and harvest it for the second time.

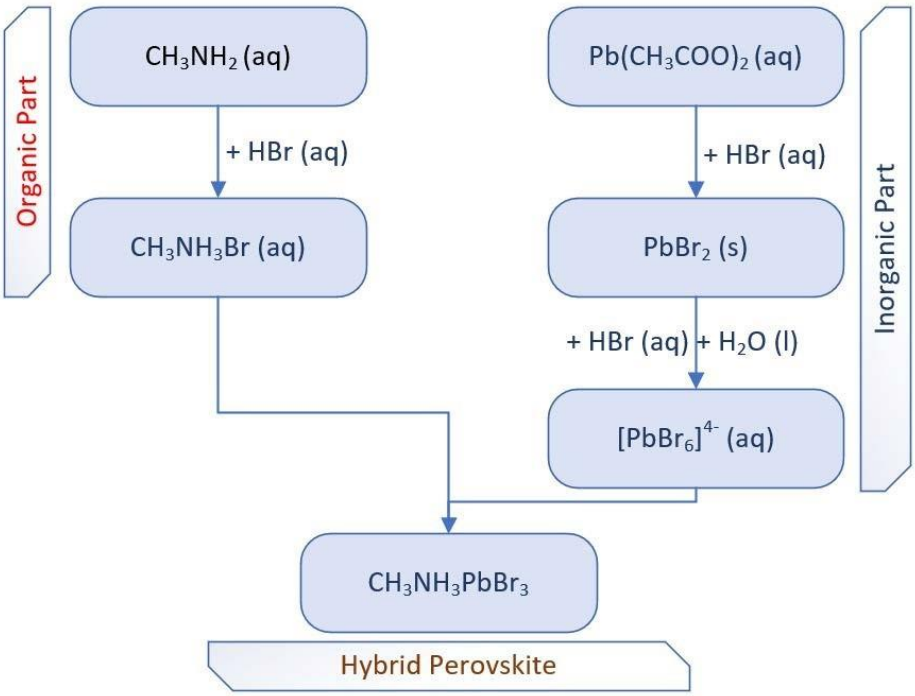


Figure 1 Schematic illustration of the perovskite synthesis procedure

2.4 Characterization

The characterization of the product was done to identify the product formed. Agilent 200 Series AA Atomic Absorption Spectrometry (AAS) was used for measuring the quantity of metal present in the sample. Volhard's method argentometric titration is used to determine the quantity of bromide. JEOL JSM 6510LA Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) was performed to measure the elemental composition of the product. Rigaku Miniflex 600 Powder X-Ray Diffraction (PXRD) was performed to prove the structure and compare it from the previous published paper. And Netzsch STA 449 Thermal Gravimetric Analysis (TGA) was used to determine thermal stability of the product.

3 Results and Discussion

The initial step of solvation of Pb(CH3COO)2.3H2O in water produced white cloudy solutions due to the nature of the salt. The acetate ion readily hydrolised in water producing OH- that react with Pb2+ ion to form Pb(OH)2. Therefore, 50 mL of distilled water and excess HBr was used to dissolve all the solid to make sure there is no unreacted Pb(OH)2 left in the solid due to sudden formation of PbBr2 when HBr was added. The PbBr2 formed is white coloured solid, the crystal has needle like image taken under microscope shown in Figure 2. PbBr2 obtained from the synthesis was 1.59 g (81.6% yield) and it contained 43% bromide (Ar = 79.9), according to argentometric titration. From this data, the PbBr2 (Mr = 367.0) was produced in pure compound and does not contain water molecules.

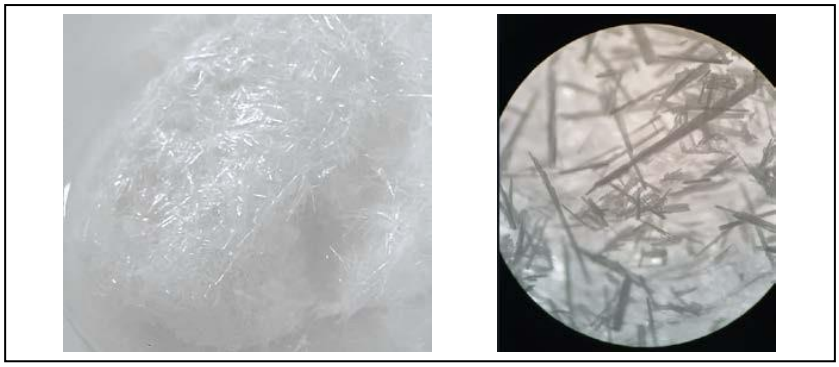


Figure 2 PbBr2 crystal (left) lead bromide crystal 100x magnification (right)

The preparation of MABr, excess CH3NH2 was used and the solution was keep at low temperature (0 oC) using ice bath due to volatility of CH3NH2 (b.p -6.3 oC [18]). A small amount of white fumes of CH3NH2 was produced during the addition of HBr, and it stayed on the surface of the solution. Therefore, the container needs to be sealed and stirred strongly to prevent the loss and to re-dissolve the CH3NH2 fumes. We found MABr was difficult to be isolated as a powder due to its hygroscopic nature, it was obtained as colourless solution and directly being used for the synthesis of MAPbBr3.

The solid PbBr2 was easily dissolved in HBr to form [PbBr6]4- complex ion [16]. When this solution is reacted with MABr, the MAPbBr3 crystal produced as orange solid. With controlled rate and cooling process, a large crystal with hexagonal form able to isolated as shown in Figure 3. From the synthesis, 1.05 g MAPbBr3 was obtained in 81.5% yield. In this preparation, the addition of excess HBr is necessary to produce acidic condition (pH < 4). In higher pH, the white crystal of PbBr2 or Pb(OH)2 will also be crystallised. In low pH, the hydrogen

ions in the solutions is used to force MA ions to enter the lattice of PbBr2. The MAPbBr3 produced could not be washed by water as it will dissolve and remove the MA ions from the lattice to make a white coloured solid.

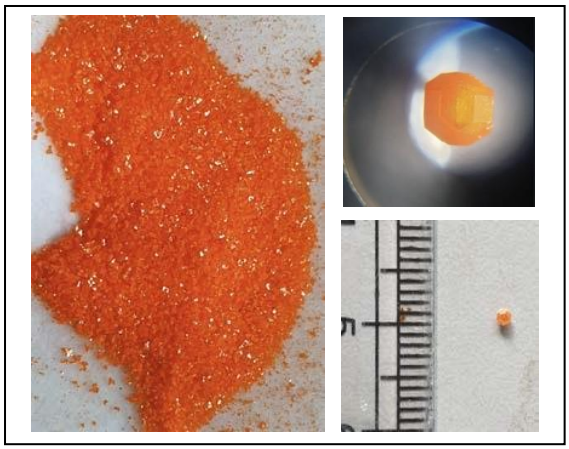


Figure 3 3 MAPbBr3 in powder form (left), in large crystal (1.5 mm) (right)

The mass percentage of Pb (Ar = 207.2) in the MAPbBr3 (Mr = 478.9) sample is 43%. This value was obtained using the calibration curve method as shown in Figure 4. The amount of Br (Ar =79.9) in the sample was 50% based on argentometric titration. Using these data we can conclude that chemical formula of the product is MAPbBr3. This composition was also confirmed by the EDS data that no oxygen was present in the sample and Pb to Br ratio in the sample was 1:3. Based on SEM picture on Figure 5., the crystal was not uniform and shows some defect, due to rapid crystallisation of the unsaturated solution.

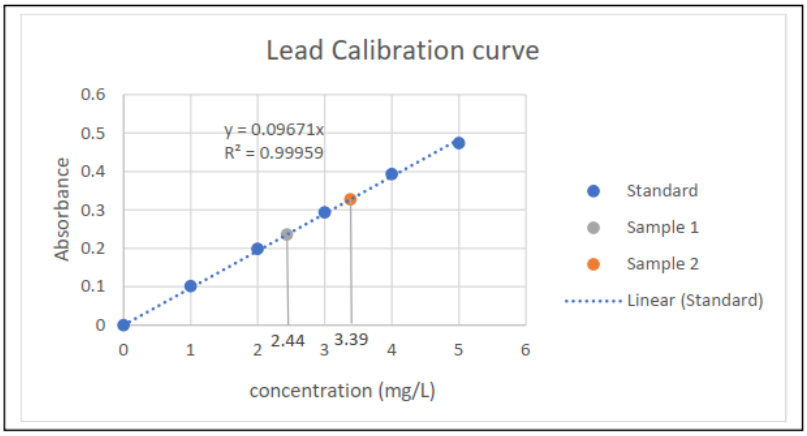
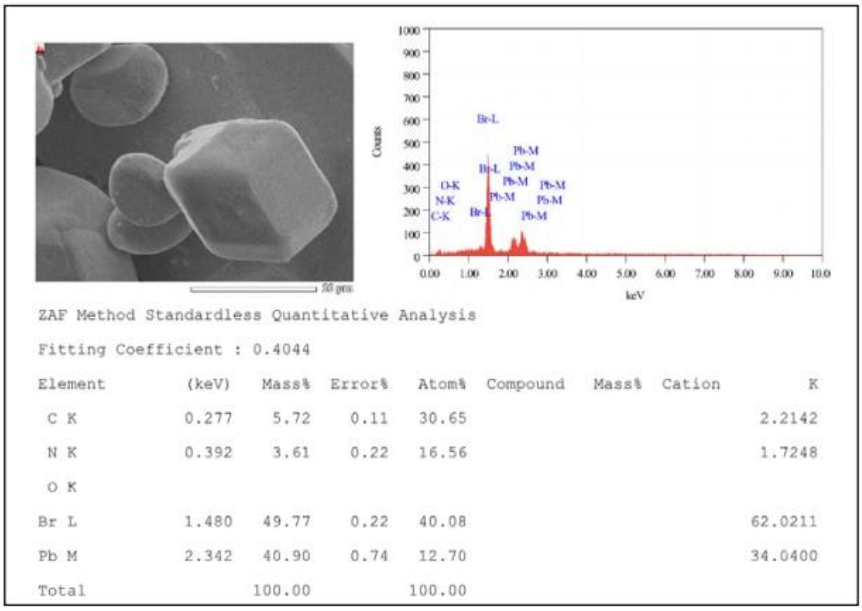


Figure 4 Lead calibration curve and $MAPbBr_3$ sample plotted in the curve



ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.4044

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	5.72	0.11	30.65				2.2142
N K	0.392	3.61	0.22	16.56				1.7248
O K								
Br L	1.480	49.77	0.22	40.08				62.0211
Pb M	2.342	40.90	0.74	12.70				34.0400
Total		100.00		100.00				

Figure 5 SEM image of $MAPbBr_3$ and its elemental composition

The structure of MAPbBr3 is confirmed by PXRD, it has P m 3$\bar{}$ m structure with lattice parameter a = b = c = 0.5918 nm. The pattern of PXRD is match with 2θ position from crystallographic information file generated using VESTA and also compared with result from published paper by Shen H., et. al. in [19] (shown in Figure 6). However, there is a slight misalignment of the peak generated from crystallographic information file from CCDC reported by Jaffe A., et. al. in [20] due to the reported lattice parameter a = 0.59328 nm.

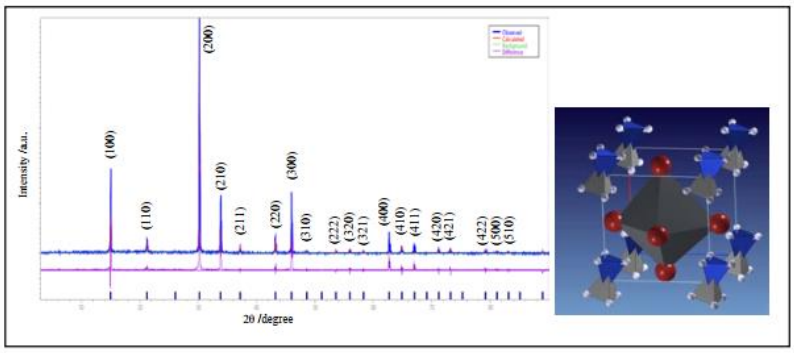


Figure 6 PXRD 2θ angle and model of $MAPbBr_3$ lattice used in matching

Thermal stability of MAPbBr3 was assessed through TGA in an inert atmosphere, following the method described by Loganathan S., et. al. in reference [21]. No mass loss was observed around 100 oC, indicating the absence of water molecules in the crystal. The crystal exhibited thermal stability up to 300 oC. The first 21.8% mass loss between 320-380 oC is nearly identical to the MABr (Mr = 111.9) molecule in the compound. And this decomposition is very close to melting point of PbBr2 (373 oC) corresponds to previous reports by Mayer A., et. al. in [9] and Dimesso L., et. al. in [17]. And based on study by Juarez-Perez, E. J., et. al. in [22] MABr released in this decomposition is released as methylamine (CH3NH2) and hydrogen bromide (HBr). The decomposition profile of MAPbBr3 can be seen in Figure 7.

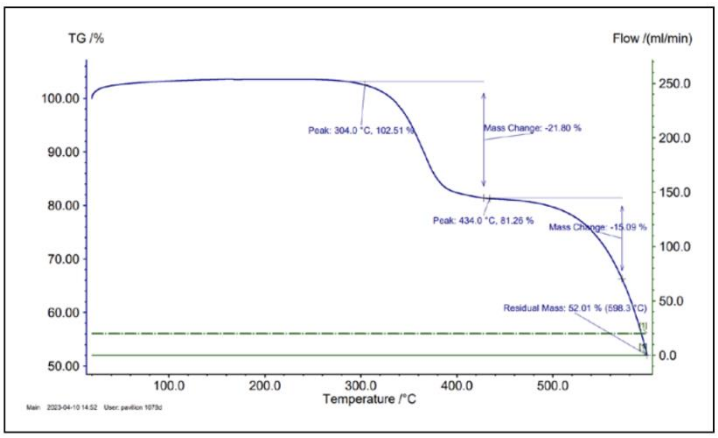


Figure 7 Temperature profile of MAPbBr3 in inert atmosphere

4 Conclusion

The synthesis of methylammonium lead bromide perovskite can be done in two step synthesis in aqueous solvent using lead acetate trihydrate as precursor and give 80% yield for each step which indicating a high level of success in the synthesis process. The product has the same characteristic compare to those produce using aprotic solvent. Although the crystal can be degraded by water, but water can be used as the solvent for the preparation as long as the pH is maintained below 4 and there is no water content found in the crystal. Overall, this study provides significant insights into the successful synthesis of MAPbBr3 using a stepwise aqueous solution method, which may have important implications for the development of perovskite-based solar cells and other optoelectronic devices.

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