Preliminary Study on Synthesis of Organolead Halide with Lead Derived from Solder Wire

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Abstract. Organolead halide has attracted great attention for application in perovskite solar cells due to its high power conversion efficiency (PCE) of up to 20.1%. One of the most common perovskite materials is lead based reagent. In this research, we have synthesized organolead halide with lead extracted from solder wire. In the preparation procedure, first PbCl2 and PbI2 are produced by reacting lead from the solder wire with NaCl and KI, which are used as the basic substance for the perovskite material. Then, in order to get perovskite solution, the powders are reacted with methylamine iodide (MAI) in dimethylformamide (DMF) using a solution based method. Further, the spin coating method is used to fabricate perovskite thin film. The XRD peak results agreed with JCPDS Powder Diffraction of PbCl2 and PbI2. Based on FTIR, the transmittance spectra of the organolead mixed halide that was prepared using solder wire lead exhibited absorption peaks identical to organolead mixed halide using commercial lead. The UV-Vis absorbance spectra of the organolead mixed halide from solder wire lead also exhibited the same absorption ability as from commercial lead. Moreover, EDS measurement showed that the element composition of the perovskite thin film using lead from solder wire identical to that from commercial lead. This indicates that solder wire lead is suitable enough for organolead halide material synthesis.

1. Introduction
Organolead halide has attracted great attention for application in perovskite based solar cells (PBSC) due to its high power conversion efficiency (PCE) of up to 20.1% [1]. It acts as light absorber in PBSC applications. The general formula of organic-inorganic perovskite material is AMX3, where A is the organic part and MX3 (M = a metal such as Pb or Sn, X = I, Br, and Cl) is the inorganic part. Fabrication of this material is relatively simple and inexpensive. Because of the organic part, this material can be synthesized by solution method.

Lead is the most common metal used in perovskite materials. Generally, lead comes from lead ore (galena). The extraction process requires very high temperatures and potentially generates hazardous vapors as by-product [2]. It is relatively difficult to obtain the lead raw material. As an alternative, lead from lead-acid batteries is often used, which are widely used in automotive vehicles. In 2014, Chen et al. [2] have successfully used lead from car batteries for perovskite solar cell fabrication. Chen has
reported that the perovskite material using lead either from car batteries or high-purity commercial reagents had identical material characterization. However, the extraction process of lead from car batteries is relatively difficult and dangerous.

Solder wire is another candidate as a lead source. Solder wire, which consists of tin and lead alloy, is easily found on the market [3]. In addition, this material is relatively inexpensive. Therefore, in this study we attempted to synthesize perovskite using lead from solder wire with mass concentrations at 60% and 40%, respectively (Sn60/Pb40).

2. Experimental Procedure

2.1. Materials Preparation

MAI was synthesized by mixing 5 mL hydroiodic acid (HI) with 12 mL methylamine and stirred for 1 hour at room temperature, drying at 100 °C for 12 hours in an oven. Then, the powder was recrystallized with absolute ethanol under drying at 60 °C for 12 hours [4]. Solder wire was cleaned using aceton to remove unwanted polymers and then dissolved in HNO₃ (2 M) at room temperature. The reaction produced SnO₂ (solid) and Pb(NO₃)₂, which were separated using a centrifuge and filtration equipment. Pb(NO₃)₂ was then mixed with NaCl (2 M) in order to get PbCl₂. NaNO₃ as by-product was separated by washing the reaction product using 95% ethanol three times and then dried at 85 °C for 12 hours to yield PbCl₂ powder. In order to get PbI₂, Pb(NO₃)₂ was mixed with KI (2 M). KNO₃ as by-product was separated by washing the reaction product using cold water for three times and then dried at 85 °C for 12 hours to yield PbI₂ powder.

The composition of MAI, PbCl₂, PbI₂ and DMF was variated according to the procedure reported in [4]. In order to get mixed halide perovskite solution (CH₃NH₃PbI₃-xClₓ), MAI and PbCl₂ was dissolved in 1 mL DMF at 3:1 molar ratio of MAI and PbCl₂, with final concentrations at 2.64 M MAI and 0.88 PbCl₂. Triiodide perovskite solution (CH₃NH₃PbI₃) was produced by dissolving MAI and PbI₂ in 1 mL DMF at 1:1 molar ratio of MAI and PbI₂, with final concentrations at 0.88 M MAI and 0.88 M PbCl₂. The solution was stirred at room temperature for 2 hours. FTO substrate was coated with perovskite thin film by spin coating each perovskite solution at 1500 rpm for 30 seconds and dried at 100 °C for 45 minutes.

2.2. Characterization

An X-ray diffractometer (Philips Analytical PW1710 BASED) was used to identify the PbCl₂ and PbI₂ crystal structure. The vibrational mode in the molecules was investigated using a spectrometer (Bruker ALPHA FT-IR). The element composition of the perovskite materials was investigated using EDS characterization (JEOL JSM-6510LA). The optical and electrical characterization (absorbance and bandgap) were measured using a UV-VIS (Ocean Optik HR2000CG-UV-NIR).

3. Results and discussion

White lead (II) chloride (PbCl₂) powder from solder wire was successfully synthesized. The powder had identical physical appearance with commercial PbCl₂. Furthermore, the resulting powder was characterized by X-ray diffractometer (XRD) to verify the crystal structure. The XRD pattern had diffraction patterns identical to those of JCPDS Powder Diffraction as shown in Figure 1(a). This shows that the powder was successfully synthesized and had a cotunnite structure and orthorhombic symmetry. The XRD results indicated that solder wire lead is suitable enough for organolead halide synthesis. Figure 1(b) shows the XRD pattern of PbI₂. The powder had an identical physical appearance to commercial PbI₂ and the XRD pattern had diffraction peaks identical to those of JCPDS Powder Diffraction. The XRD pattern being identical shows that the powder had hematite structure and rhombohedral symmetry. This confirms that solder wire lead is suitable enough for organolead halide synthesis.

After PbCl₂ and PbI₂ were synthesized, organolead mixed halide and triiodide materials were synthesized by one-step deposition as reported in [4]. Moreover, we also synthesized organolead
mixed halide material from commercial lead to compare their physical appearance and characteristics. These perovskite solutions had an identical physical appearance (yellow transparent solution).

Figure 2 shows the FTIR analysis of the organolead halide solution. The transmittance spectra of the organolead mixed halide from solder wire lead exhibited absorption peaks identical to those of organolead mixed halide from commercial lead. For further analysis, we used the DMF infrared spectrum from Ref. [] NIST Standard Reference Database 69: NIST Chemistry WebBook to compare the transmittance spectra of organolead mixed halide with their solvent. The transmittance spectra of the perovskite solution showed all absorption peaks of DMF, but there was a peak at ±3429 cm⁻¹, which is the NH symmetric stretching mode. This peak cannot be found in the DMF transmittance spectra and may indicate that perovskite CH₃NH₃PbI₃₋ₓClₓ and CH₃NH₃PbI₃ was formed [5, 6].

![Figure 1. XRD pattern of (a) PbCl₂ and (b) PbI₂ powder with lead extracted from solder wire.](image1)

The organolead mixed halide thin film from solder wire lead and commercial lead were characterized using a UV-VIS spectrophotometer to measure the absorption ability of both thin films. Figure 3 shows the absorbance spectra of the organolead mixed halide from solder wire lead exhibiting the same absorption ability as commercial lead, which is able to absorb UV-visible light to near infrared region [1, 7-12]. The identical absorption ability shows that the thin films were successfully synthesized.

![Figure 2. FTIR study of organolead halide using high-purity commercial lead and lead from solder wire.](image2)
To identify the element composition, we used EDS measurement for each perovskite thin film. The EDS measurements showed that organolead mixed halide from solder wire lead had the same element composition as from commercial lead. Both consisted of C, N, Pb, I, and Cl as basic elements. The CH$_3$NH$_3$Pb$_{1.3-x}$Cl$_x$ perovskite thin film using lead from solder wire consisted of 1.20% wt of element C, 0.28% wt of element N, 0.3% wt of element Cl, 60.94% wt of element I, 37.27% wt of element Pb. Meanwhile, the CH$_3$NH$_3$Pb$_{1.3-x}$Cl$_x$ perovskite thin film from commercial lead consisted of 1.66% wt of element C, 0.17% wt of element N, 0.37% wt of element Cl, 59.64% wt of element I, 38.17% wt of element Pb. This confirms that synthesis of organolead mixed halide using PbCl$_2$ from solder wire lead was successfully carried out.

![Figure 3. UV-Vis spectra of perovskite thin film.](image)

4. Conclusion
PbCl$_2$ and PbI$_2$ powders using lead from solder wire was successfully synthesized. The formed powders’ color was identical to that of the commercial powders. The XRD peak results agreed with JCPDS Powder Diffraction of PbCl$_2$ and PbI$_2$. Moreover, based on FTIR, UV-Vis and EDS measurements, perovskite solution and thin films were also successfully synthesized. They had identical physical appearance and characteristics compared to using commercial lead.

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