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On the growth of $CH_3NH_3PbI_{3-x}Cl_x$ single crystal and characterization

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ABSTRACT

In this paper, $CH_3NH_3PbI_{3-x}Cl_x$ crystal was grown by solution cooling method with CH_3NH_3I and $PbCl_2$ as raw materials. Lead compounds and $CH_3NH_3PbI_{3-x}Cl_x$ crystal with size about 6 mm × 4 mm × 2 mm were obtained. The chemical reactions with different $CH_3NH_3I/PbCl_2$ ratios were analyzed. XPS shows the content of chlorine in $CH_3NH_3PbI_{3-x}Cl_x$ is about 0.91%. PXRD, FT-IR, Raman and absorbance spectra were used to study the structure and optical properties of $CH_3NH_3PbI_{3-x}Cl_x$ by comparing with $CH_3NH_3PbI_3$ crystal. The $CH_3NH_3PbI_{3-x}Cl_x$ crystal grown is of tetragonal structure with the lattice constants a = b = 8.8165 Å, c = 12.7920 Å and the bandgap value of 1.57 eV.

1. Introduction

The organic-inorganic hybrid perovskite materials $CH_3NH_3PbX_3$ (X = halide) have attracted great interest due to their superior optical and electrical properties. The solar cells based on these materials have the advantages of low cost, self-assembly and high power conversion efficiencies (PCEs), etc. [1–3]. Since the first organic-inorganic halide perovskite solar cell was reported, the PCEs have been upgraded from 3.81% to 21% within a few years [4–6]. In addition, by changing the components of the $CH_3NH_3PbX_3$, the band gap can be easily modified [7]. For example, a continuous band gap would be got by replacing halogen elements in $CH_3NH_3PbX_3$. In the previous reports the band gap value of $CH_3NH_3PbI_{3-x}Br_x$ or $CH_3NH_3PbBr_{3-x}Cl_x$ films varies with the change of x values [8–10].

Halide perovskite solar cells based on $CH_3NH_3PbI_{3-x}Cl_x$ has attracted much attention for its high power conversion efficiency (PCE). As a result, the fabrication of $CH_3NH_3PbI_{3-x}Cl_x$ films has also become a hot issue [11–16]. For solar cells, the carrier diffusion length is an important factor to evaluate its application potential. The carrier diffusion length of $CH_3NH_3PbI_{3-x}Cl_x$ films increases from 100 nm to over 1 μm [17]. Some reports think the improvement in the electrical performance of $CH_3NH_3PbI_{3-x}Cl_x$ film should be due to the electronic effect by the doped Cl [17,18], some think the Cl is not doped in the film, while the presence of Cl in the precursor can influence film formation, which leads to a larger crystalline domain [19,20]. Until now, all studies on the properties of $CH_3NH_3PbI_{3-x}Cl_x$ are based on $CH_3NH_3PbI_{3-x}Cl_x$ film. It is well known that the single crystal is an ideal candidate for exploring its intrinsic structure and optical properties. In order to get accurate structural optical and electrical properties of $CH_3NH_3PbI_{3-x}Cl_x$, the growth of $CH_3NH_3PbI_{3-x}Cl_x$ single crystal becomes necessary.

In this paper, different molar ratios of CH_3NH_3I and $PbCl_2$ were used to grow $CH_3NH_3PbI_{3-x}Cl_x$ single crystal. The growth conditions, structure and optical properties were analyzed.

2. Experiments

2.1. Synthesis of CH_3NH_3I

CH_3NH_3I was synthesized by reacting methylamine (40 wt.%, aladdin) and hydroiodic acid (58 wt.%, aladdin) with the molar ratio of 1.2: 1 in an ice bath for 2 h whit stirring. Then it was dried at 100 °C for 24 h.

2.2. Crystal growth

$CH_3NH_3PbI_3$ were grown as reported previously [21]. For the growth of $CH_3NH_3PbI_{3-x}Cl_x$ single crystal, firstly, CH_3NH_3I and $PbCl_2$ (99.99%, aladdin) were dissolved in 90 ml hydrochloride acid (37 wt. %, Alfa Aesar) with the molar ratio $CH_3NH_3I/PbCl_2$ 1: 3, 1: 1, 3: 1, 6: 1 respectively. Then these solutions were kept at 90 °C for 12 h, followed by cooling the solutions to 40 °C at the rate of 1–2 °C/d. Different color solid products were obtained, as shown in Fig. 1.

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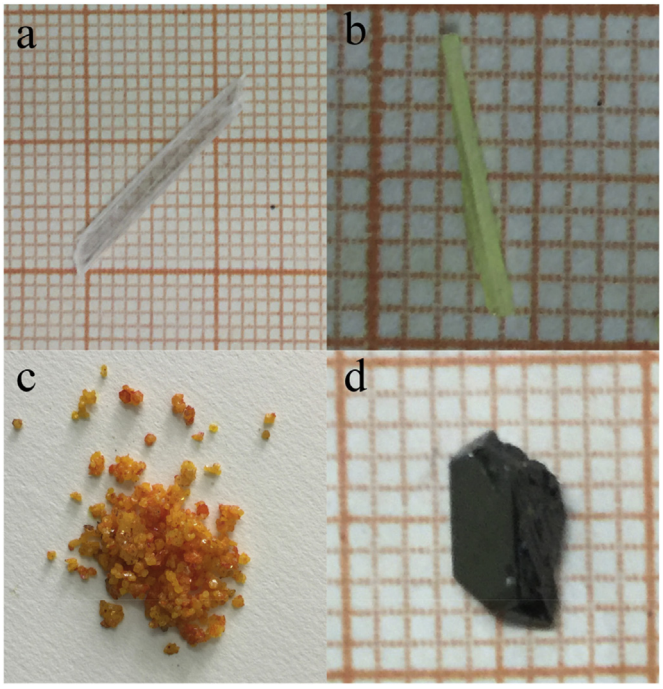

Fig. 1. Products obtained by solution cooling method with $CH_3NH_3I/PbCl_2$ ratio: (a) 1: 3, (b) 1: 1, (c) 3: 1, (d) 6: 1.

2.3. Measurements

Powder X-ray diffraction was performed on a Bruker D8 diffractometer using Cu-Kα radiation in the 2θ range of 5-90° with a step size of 0.02°. The steady-state absorption was recorded using UV2700 spectrophotometer in the range of 200 nm–800 nm. XPS spectra were measured by K-Alpha X-ray photoelectron spectrometer with monochromatized Al Kα (1486.6eV) X-ray radiation source. The Fourier transform infrared spectroscopy was detected by Nicolet-460 spectrometer in the range of 400 cm^{-1} - 4000 cm^{-1}. The Raman spectroscopy was detected by Renishaw inVia 2000 with excitation at 514 nm in the range of 50 cm^{-1} - 4000 cm^{-1}. All the experiments were performed at room temperature.

3. Results and discussion

In order to define the phase of the products as Fig. 1 shown, the powder X-ray diffraction (PXRD) (Fig. 2) was used to characterize their structure. As Fig. 2 (a) shown, while the molar ratio of $CH_3NH_3I/PbCl_2$ is 1: 3, the X-ray diffraction peaks of the product [Fig. 1 (a)] are corresponding to orthorhombic $PbCl_2$, with space group Pnam (JCPDS No.26–1150), the lattice constants are determined as a = 7.6059 Å, b = 9.0274 Å, c = 4.5250 Å. As the molar ratio of $CH_3NH_3I/PbCl_2$ changes to 1:1, the PXRD of product [Fig. 1 (b)] is confirmed to be orthorhombic PbClI with space group Pnam (JCPDS No.73–0361), and a = 8.1423 Å, b = 9.6001 Å, c = 4.5749 Å. PbClI crystal has not been reported in the fabrication of $CH_3NH_3PbI_{3-x}Cl_x$ films, and our results show PbClI crystal could be obtained as the I^-/Cl^- ratio changes to a

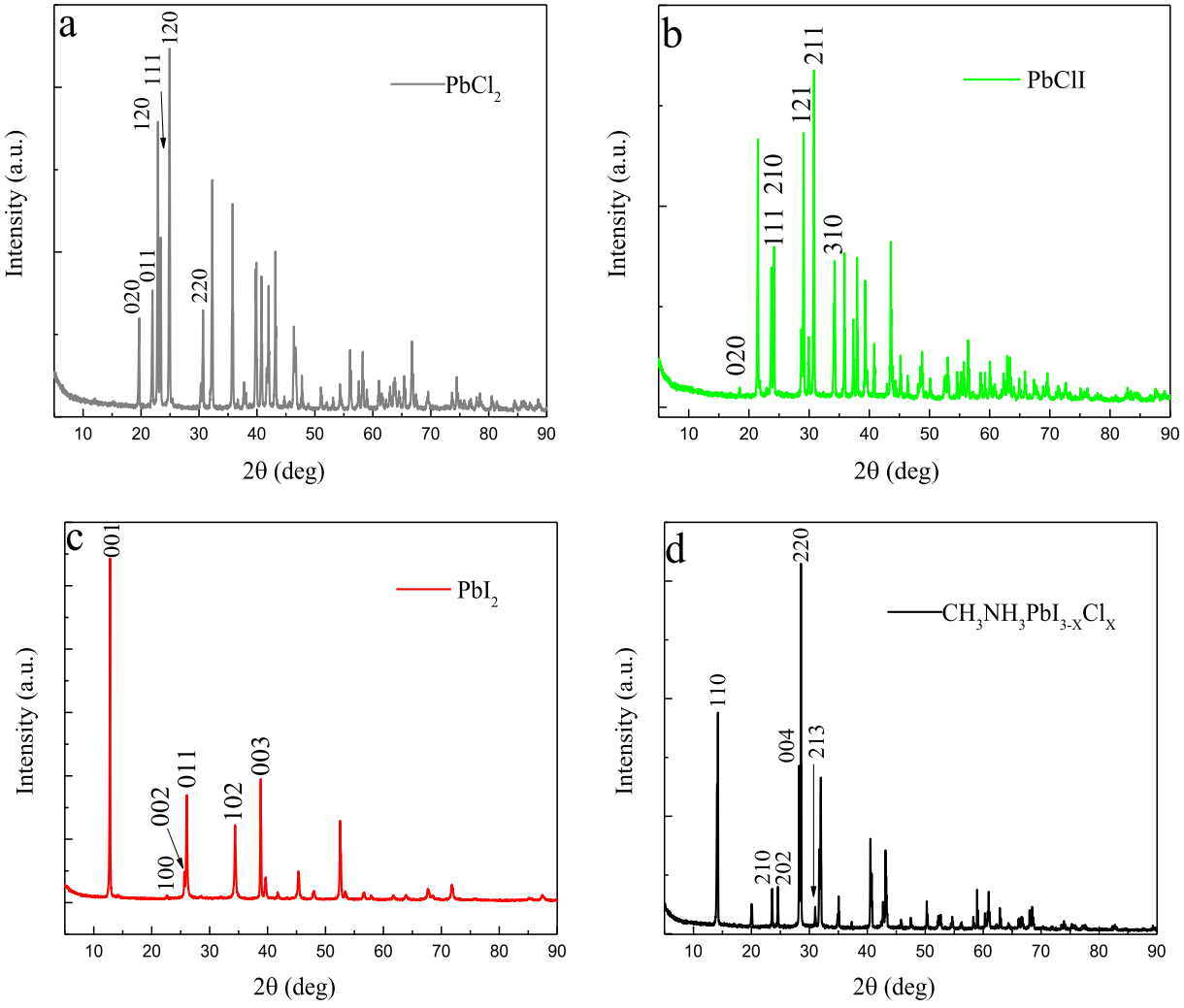

Fig. 2. Powder X-ray diffraction of crystals: (a) $PbCl_2$, (b) PbClI, (c) PbI_2, (d) $CH_3NH_3PbI_{3-x}Cl_x$.