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Study on the effect of chlorine on the growth of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ crystals

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1. Introduction

Organic-inorganic hybrid halide perovskites have attracted great interest for scientists and entrepreneurs due to their intrinsic properties and considerable business prospects in recent years. Perovskite single crystal can determine its properties well because of no grain boundaries for itself, so it is necessary to study the nucleation and growth process of perovskite crystals. In this work, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ single crystals with about 10 mm sized are prepared. It’s found that chlorine can restrict the nucleation and slow crystallization during the perovskite grown process. Moreover, the number of perovskite crystals can be controlled by tuning the content of chlorine in the precursor solutions, because chlorine can restrict the perovskite crystal nucleation as an inhibitor.

Keywords: perovskite, crystal growth, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$, chlorine
2. Experimental

2.1. Materials
Lead iodide (PbI$_2$) powder (99.0%), CH$_3$NH$_3$Cl (MACI, 99.5%) and CH$_3$NH$_3$I (MAI, 99.5%) were purchased from Xi’an Polymer Light Technology Corp. Lead chloride (PbCl$_2$) powder (99.0%) was purchased from Shanghai No.4 Reagent & H.V. Chemical Limited Company. γ-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) was purchased from Aladdin. All reagents and materials from commercial sources were used in this work without further purification.

2.2. Single crystal growth
In this work, CH$_3$NH$_3$Pb$_x$I$_{3-x}$ single crystal and all the CH$_3$NH$_3$Pb$_{1-x}$Cl$_x$ (MAPb$_{1-x}$Cl$_x$) single crystals were grown via inverse temperature crystallization (ITC) method as the previous literature reported [23].

For obtaining CH$_3$NH$_3$Pb$_x$I$_{3-x}$ single crystals, CH$_3$NH$_3$I and PbCl$_2$ with the molar ratio of 1:1 were dissolved in 5 ml of γ-butyrolactone (GBL), and then the precursor (1 M, refer to as Precursor I) heated and stirred for 12 h at 70 °C. Some small MAPbI$_3$ crystal seeds were appeared in the bottom of vial after the solution being heated for several hours at 120 °C. Then, a selected seed was placed in the bottom of the vial with fresh precursor solution. The bulk MAPbI$_3$ single crystal (refer to as PI) was formed within several hours.

For obtaining MAPb$_{1-x}$Cl$_x$ single crystals, the precursor solution was made by adding CH$_3$NH$_3$Cl and PbCl$_2$ in 1:1 molar ratio in Precursor I solution to replace a part of the solute, then the precursor solution with mole I:Cl ratio of 30:1, 22:1 and 14:1 were obtained (refer to as Precursor I$_{30}$Cl$_1$, Precursor I$_{22}$Cl$_1$ and Precursor I$_{14}$Cl$_1$). The precursor solution was heated and stirred for 12 h at 70 °C. Followed, the solution was heated for several hours at 120 °C. Some small MAPb$_{1-x}$Cl$_x$ crystal seeds were appeared in the bottom of the vial. For preparing bulk MAPb$_{1-x}$Cl$_x$ single crystal, a selected seed was placed in the bottom of the vial with fresh precursor solution. The bulk MAPb$_{1-x}$Cl$_x$ single crystal was formed from the precursor with I:Cl = 14:1, 22:1 and 30:1 (refer to as PICl 1, PICl 2, PICl 3, respectively) within several hours.

By changing a part of solvent of the precursor, the precursor (refer to as Precursor I$_{50}$Cl$_1$-D) with I:Cl = 30:1 was replaced a part of GBL with 2.5 vol% DMSO to obtain CH$_3$NH$_3$Pb$_{1-x}$Cl$_x$ single crystal (refer to as PICl 4D) by using the same method.

2.3. Characterization
Energy dispersive spectroscopy (EDS) spectra of perovskite single crystal powders were measured by ZEISS EVO 18 scanning electron microscope (SEM). Powder x-ray diffraction (Powder XRD) patterns were measured by Rigaku/Smartlab diffractometer equipped with a Cu Kα radiation source in the range of $10^\circ$–$60^\circ$ with a step size of 0.01°. The Fourier transform infrared (FTIR) spectrum was measured by Nicolet/iS 50 spectrometer in the range of 400 cm$^{-1}$–4000 cm$^{-1}$. XPS spectra were measured by Thermo ESCALAB 250 with the excitation source of a monochromized Al Kα source.

3. Results and discussion
As shown in figure 1, high quality MAPb$_{1-x}$Cl$_x$ single crystals have been successfully grown in their precursor solution, which size can be reach to nearly 10 mm length.

During the MAPb$_{1-x}$Cl$_x$ single crystal growing process, it can be observed that the number of small crystals on the bottom of the vial decreases with increasing molar ratio of Cl: (Cl + I) in the precursor. The number of crystals on the bottom of a vial after heating for 5 h is shown in figures S1(a)–(d). Figure 2 shows the crystal quantity statistics with different molar ratio of Cl:(Cl + I) after heating for 5 h. It can be seen that 25 smaller crystals were precipitated from Precursor I. However, 22, 10 and 7 crystals were precipitated from Precursor I$_{30}$Cl$_1$, Precursor I$_{22}$Cl$_1$ and Precursor I$_{14}$Cl$_1$, respectively. Obviously, it can be indicated that Cl element in the precursor can restrict the formation of perovskite nucleus. Furthermore, the more time is needed for growing crystals with the more Cl...
element in the precursor. It is about 3 h that small crystals appeared for Precursor I, Precursor I30Cl1 and Precursor I22Cl1. However, more than 5 h is needed for Precursor I14Cl1. The molar ratio of Cl: (Cl + I) in Precursor I14Cl1 is 6.67% which is over than 5%. Comparing with Precursor I30Cl1 and Precursor I22Cl1, higher Cl content in Precursor I14Cl1, which slow down the CH3NH3PbI3−xClx crystal growing speed significantly. According to previous research [24], it is known that Cl atom can be coordinated to Pb atom, as a result, it is more difficult to form Pb-I-Pb. As shown from scheme 1, consequently, it therefore caused the slower nucleation and crystal growth. Cl can retard the formation of CH3NH3PbI3−xClx during perovskite film fabrication [17, 25], both of MACl and PbCl2 indicate that chlorine can slow down the rate of crystallization. In our work, we found that Cl can also slow down the rate of perovskite single crystal growth. Although we call the perovskite CH3NH3PbI3−xClx, the Cl content in perovskite crystal is very little in this work and the previous literatures. So we think that the formation of Pb-I-Pb is crucial to the crystal growth. The crystal growth prepared with Cl contained precursor is slower than without Cl. In addition, it takes more time to obtain the same size crystal with increasing Cl content in precursor.

In addition, as shown in figure S1e is available online at stacks.iop.org/MRX/7/015522/media only 3 MAPbI3−xClx crystals precipitated from the I30Cl1-D precursor solution, after heating for 5 h, which contained 2.5 vol% DMSO in GBL solvent. Only due to 2.5 vol% DMSO added in the precursor, the number of MAPbI3−xClx crystals was decreased significantly from over 20 to about 4, which may be attributed to the formation of complexes between DMSO and Pb [26]. With the volume of DMSO raised to 3.3 vol% and 5 vol% in the precursor replaced GBL, respectively, even no crystal can be obtained after heating for 5 h. Moreover, even the precursor was heated for 36 h, there was still no crystals appeared in the precursor with 3.3 vol% or 5 vol% DMSO, respectively.

The Cl content is calculated by using XPS datas (figure 3(a)) and EDS datas (figure 3(b)), respectively. Both of them show the same trend, the molar ratio of Cl: I increases in single crystal with increasing Cl content in precursor. Although the Cl content of the same sample is different by using two different measurements, it may due to under different test condition. Figure S2 shows XPS datas. Figures S3-S6 show EDS datas.
XRD is used to characterize the structure of MAPbI$_3$ and MAPbI$_{3-x}$Cl$_x$ single crystals, which were tested after grinding into powder. As shown in figure 4(a), the peaks at 20 of 14.1°, 28.4° and 43.2° are attributed to MAPbI$_3$ [27], moreover, they are also the main peaks of MAPbI$_{3-x}$Cl$_x$ assigned to the (110), (220) and (330) planes, respectively [28]. In fact, the difference of the XRD patterns between MAPbI$_{3-x}$Cl$_x$ and MAPbI$_3$ crystals is not significant, because the content of chlorine in MAPbI$_{3-x}$Cl$_x$ crystals is very little. However, figure 4(b) shows the peaks of MAPbI$_{3-x}$Cl$_x$ move to large angles compared to MAPbI$_3$. It verified that Cl incorporates into the perovskite crystals successfully.

The freshly crushed MAPbI$_{3-x}$Cl$_x$ single crystal powders were examined by EDS. It is verified that chlorine incorporates into the MAPbI$_{3-x}$Cl$_x$ single crystal. The signals of chlorine have been detected for all the MAPbI$_{3-x}$Cl$_x$ single crystal samples. As shown in figure 5, it is focused on one big particle, the homogeneous dispersion of chlorine elemental can be seen in the EDS spectrum.
4. Conclusions

In this work, high quality MAPbI$_3$-$x$Cl$_x$ single crystals with more than 10 mm have been successfully obtained by inversion temperature crystallization method. Chlorine element was incorporated into the MAPbI$_3$-$x$Cl$_x$ crystals by adding different amount of PbCl$_2$ and MACl in their precursor solution. It can be inferred that chlorine in the precursor should restrict the nucleation and growth of perovskite crystals, which is the inhibitor for the MAPbI$_3$-$x$Cl$_x$ single crystals growth.

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Conflicts of interest

There are no conflicts to declare.

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