Temperature Sensitive and Reversible Halide Ion Exchange in Inorganic-Organic Hybrid $CH_3NH_3PbI_{3-x}Br_x$ Mixed-halide Perovskite

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KEYWORDS: Temperature Sensitive, Reversible, Halide Ion Exchange, Perovskite

ABSTRACT: Ion exchange of organic-inorganic hybrid perovskite plays an important role in controlling the performance of materials ant its devices. In this study, we found an interesting phenomenon that the precipitate in the in suspension ($CH_3NH_3PbI_{3-x}Br_x$ in γ – butyrolactone) presented different colors at high and room temperature. The mechanism study shows that the phenomenon is controlled by temperature sensitive and reversible halide ion exchange in organic-inorganic hybrid $CH_3NH_3PbI_{3-x}Br_x$ mixed-halide perovskite. The results of structure phase, element composition morphology and band gap indicate that high temperature 55 °C is beneficial to the increasing of I content in $MAPbI_{3-x}Br_x$ and room temperature or lower is beneficial to increasing of Br content in $MAPbI_{3-x}Br_x$.measurement were carried out. Compared with $MAPbI_{0.76}Br_{2.24}$ precipitate obtained at room temperature, $MAPbI_{1.17}Br_{1.83}$ precipitate obtained at high temperature exhibit wider lattice spacing, better crystallinity, better morphology and narrower band gap. The results and findings in this study will arouse the interest of readers or experts in the field of organic-inorganic hybrid perovskite materials and related optoelectronic applications.

As a new semiconductor material, lead halide perovskite was first used in solar cells in 2009.[1] The photoelectric efficiency of solar energy has increased from 3.8 to 25.2%.[2] In the past two years, perovskites have attracted much attention in the fields of photocatalysis, photodiode and so on.[3-5] The synthesis methods of lead halide perovskite include solution synthesis, vapor deposition, solid phase synthesis and ion exchange. Ion exchange can be divided into two types, one is anion exchange, the other is cation exchange.[6]

Most common type of halogen ion exchange reaction is anion exchange reaction,[7, 8] which has many applications. The halogen ion exchange process can effectively slow down the grain growth efficiency, which is conducive to the full grain growth, and the final grain size of perovskite film reaches 2-3 microns.[9, 10] In terms of cation exchange,[11, 12] the first partial exchange of lead was achieved by using different divalent cations, which led to the change of band gap. Some studies have shown that dynamic halogen exchange can effectively open up the octahedral structure of perovskite and make cation exchange rapidly in a few seconds at room temperature.[13, 14] Meanwhile, the vertical grains of $FA_{1-x}MA_xPbI_3$ were obtained by cation exchange reaction, and the photo stability and thermal stability of $FA_{1-X}MA_XPbI_3$ were improved.[15]

In this study, we found an interesting phenomenon that the precipitate in the in suspension ($CH_3NH_3PbI_{3-x}Br_x$ in γ – butyrolactone) presented different colors at high and room temperature. The color of the precipitate in the suspension is orange at room temperature (25°C) or lower, as shown in Figure 1a, while it becomes black when the suspension was heated to 55 °C, as shown in Figure 1b. Interestingly, the precipitate returned to orange when the temperature is cooled down to room temperature, and it turned black again when the temperature was achieved to 55 °C. Thus, the color change of precipitate in suspension is reversible.

To explore the mechanism of color change of precipitation at different temperatures, we carried out solid-liquid separation and washing precipitation at room temperature and 55 °C. The precipitate obtained at room temperature is shown in Figure 1c, and that at high-temperature is shown in Figure 1d. Obviously, the precipitate obtained at room temperature is orange, and that at high temperature is crimson. Our hypothesis about color change is that halide ion exchange is different at different temperatures. To verify our hypothesis, structure phase, element composition morphology and band gap measurement were carried out.

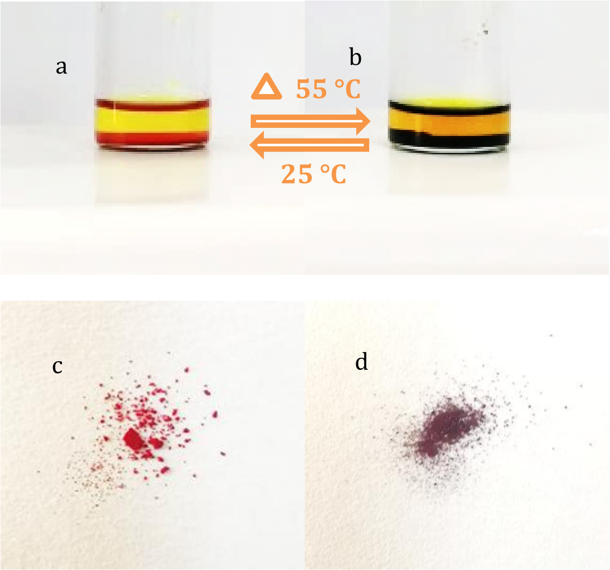

Figure 1. (a) Photo of the $\mathrm{MAPbI_{3-x}Br_x}$ suspension at room temperature; (b) Photo of the $\mathrm{MAPbI_{3-x}Br_x}$ suspension at high temperature (55 °C); (c) Photo of the $\mathrm{MAPbI_{3-x}Br_x}$ precipitate obtained at room temperature; (d) Photo of the $\mathrm{MAPbI_{3-x}Br_x}$ precipitate obtained at high temperature.

The X-ray diffraction of $\mathrm{MAPbI_{3-x}Br_x}$ precipitation obtained at different temperatures are shown in the Figure 2. The diffraction pattern at room temperature is shown in Figure 2a, and that at high temperature is shown in Figure 2b. The diffraction peaks of the precipitation at room temperature appear at 14.70 °, 20.96°, 29.81°, 33.44°, 36.71°, 42.70° and 45.39°. The diffraction peaks of the precipitation at high temperature appear at 14.34°, 20.43°, 29.20°, 32.76°, 36.01°, 41.87° and 44.53° at high temperature. Compared with that of the precipitation at room temperature, the diffraction peaks at high temperature shift to low angle. The intensity of diffraction peaks at high temperature are two times stronger than that at room temperature. And peak width at half-height obtained at high temperature are narrower than that at room temperature. Therefore, the results indicate that the crystallinity of $\mathrm{MAPbI_{3-x}Br_x}$ at high temperature is better than that at room temperature.

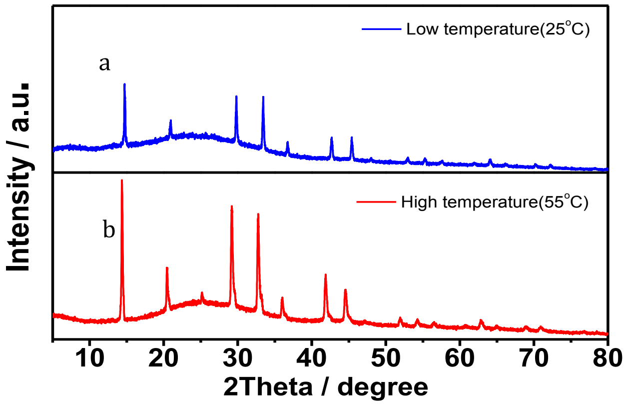

Figure 2. (a) X-ray diffraction of $\mathrm{MAPbI_{3-x}Br_x}$ precipitation obtained at room temperature; (b) X-ray diffraction of $\mathrm{MAPbI_{3-x}Br_x}$ precipitation obtained at 55 °C high temperature.

To observe the morphology of the precipitation of $\mathrm{MAPbI_{3-x}Br_x}$ system at different temperatures, the SEM images of precipitation at room temperature and high temperature are provided as shown in Figure 3a and 3b, respectively. The morphology of precipitation at room temperature and high temperature are both micron crystals. The size of grains is not uniform at room temperature. And the edge of the micron crystal is not clear. At high temperature, the micron crystals have regular morphology and clear edge. The crystallinity of grains at high temperature is better than that at room temperature, which is consistent with XRD results.

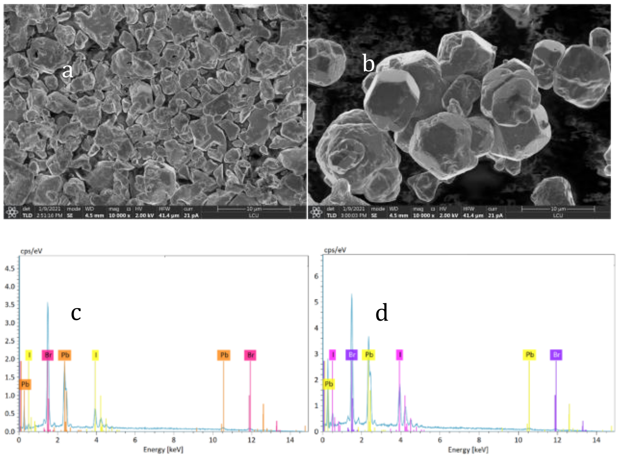

Figure 3. (a) SEM of room temperature precipitation of $\mathrm{MAPbI_{3-x}Br_x}$; (b) SEM of high temperature precipitation of $\mathrm{MAPbI_{3-x}Br_x}$; (c) EDS energy spectrum of room temperature precipitation of $\mathrm{MAPbI_{3-x}Br_x}$; (d) EDS energy spectrum of high temperature precipitation of $\mathrm{MAPbI_{3-x}Br_x}$.

Table 1. Various element contents in the precipitation of $\mathrm{MAPbI_{3-x}Br_x}$ at high and room temperature.

Element	Room temperature precipitation	High temperature precipitation
Pb	23.29	23.12
I	19.33	30.05
Br	57.38	46.83

To analyze the components of $\mathrm{MAPbI_{3-x}Br_x}$ precipitation at different temperatures, EDS of precipitation at room and high temperature are provided, as shown in Figure 3c and 3d. The contents of various elements in the precipitation of $\mathrm{MAPbI_{3-x}Br_x}$ micron crystal at high and room temperatures are shown in Table 1. By comparing the atomic content of precipitations at high and room temperatures, the iodine content of high temperature precipitation (30.05%) is 10.72% higher than that (19.33%) of room temperature precipitation. The bromine content of high temperature (46.83%) precipitation is 10.55% lower than that (57.38%) of room temperature precipitation. The lead content of precipitations at high and room temperatures is similar. At the same time, we calculated the ratio of bromine to iodine in the micron crystal precipitate. The ratio of bromine to iodine at room and high temperature is 4.57 and 1.56, respectively. Thus, the formula is $MAPbI_{1.17}Br_{1.83}$ at high temperature and $MAPbI_{0.76}Br_{2.24}$ at room temperature. The result is consistent with the color of precipitate. The results indicate that the ion exchange of $MAPbI_{3-x}Br_x$ is sensitive to temperature. High temperature is beneficial to the increasing of I content in $MAPbI_{3-x}Br_x$ and Low temperature is beneficial to increasing of Br content in $MAPbI_{3-x}Br_x$.

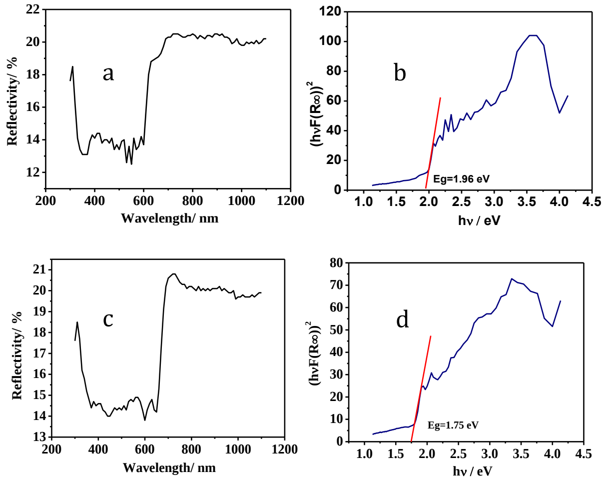

Figure 4. (a) Diffuse reflectance spectra of $MAPbI_{0.76}Br_{2.24}$; (b) hv-(hv F(R∞))^2 curve of $MAPbI_{0.76}Br_{2.24}$;(c) Diffuse reflectance spectra of $MAPbI_{1.17}Br_{1.83}$; (d) hv-(hv F(R∞))^2 curve of $MAPbI_{1.17}Br_{1.83}$

The diffuse reflectance spectra of $MAPbI_{0.76}Br_{2.24}$ micron crystal is shown in Figure 4a. The curve of hν-(F(R∞) hν)^n (where h, Planck constant, ν, frequency of light, n, process of absorbing light, $F(R\infty)=(1-R)^2/2R$, R represents reflectivity) were drawn according to Tauc plot as shown in Figure 4b. According to previous report,[16] the band gap of micron crystal precipitation at room temperature is 1.96 eV as shown in Figure 4b. The diffuse reflectance spectra of $MAPbI_{1.17}Br_{1.83}$ micron crystal is shown in Figure 4c. The band gap of $MAPbI_{1.17}Br_{1.83}$ micron crystal is 1.75 eV, as shown in Figure 4d. Thus, we can control the band gap of $MAPbI_{3-x}Br_x$ system by controlling the temperature for different optoelectronic applications.

In summary, we found an interesting phenomenon that the precipitate in the in suspension ($CH_3NH_3PbI_{3-x}Br_x$ in γ – butyrolactone) presented different colors at high and room temperature. The SEM, EDS, XRD patterns and band gap of the precipitates at high and room temperature were measured. It can be calculated that the molecular formula of the precipitate is $MAPbI_{0.76}Br_{2.24}$ at room temperature and $MAPbI_{1.17}Br_{1.83}$ at high temperature. The results demonstrate that the ion ex-change of the material is sensitive to temperature. Low temperature is beneficial to the increase of content of I element in $MAPbI_{3-x}Br_x$. High temperature is beneficial to the elevation of the content of Br element in $MAPbI_{3-x}Br_x$.Therefore, the color of the precipitate is black at high temperature and orange at room temperature.

ASSOCIATED CONTENT

Supporting informantion: Experiment section. This material is available free of charge via the Internet at http://pubs.acs.org.

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