Alerts in High-resolution TEM characterization of perovskite material

Yu-Hao Deng

1 Academy for Advanced Interdisciplinary Studies, Peking University, Beijing, China

* Correspondence should be addressed to yuhaodeng@pku.edu.cn

Abstract

High-resolution TEM (HRTEM) is a powerful tool for structure characterization. However, MAPbI₃ perovskite is highly sensitive to electron beams and easily decompose into PbI₂. Universal mistakes that PbI₂ is incorrectly labeled as perovskite are widely exist in HRTEM characterizations, which negatively affect the development of perovskite research field. Here errors in MAPbI₃ perovskite calibration are statisticied and identified based on corresponding electron diffraction (ED) simulations. Corrected material phases, ED patterns of original PbI₂ and obvious crystallographic parameters are also presented. This approach paves the way to avoid misleadings in HRTEM characterization of perovskite and other electron beam-sensitive materials in the future.

Introduction

High-resolution transmission electron microscopy (HRTEM) is a very powerful characterization tool and has been extensively and successfully used for analyzing crystal structures on an atomic resolution scale [1]. Recently, halide perovskites have achieved substantial success in various optoelectronic devices owing to their solution-based growth method and remarkable physical properties [2-5]. However, MAPbI₃ perovskite is very sensitive to electron beam irradiation. As a rough estimation, MAPbI₃ begins to decompose into PbI₂ under 150 eÅ⁻² total dose irradiation [6, 7]. Figure 1 shows the MAPbI₃ degradation process under electron beam irradiation. Tetragonal perovskite decomposes into hexagonal lead iodide by the escape of methylamine and hydrogen iodide molecules.
Results and discussion

General phase calibration method of HRTEM data is to compare a group of interplanar spacings and angles. This method is easy to ignore the absent crystal planes, leading to mistaken calibration results. For instance, the lead iodide is generally labeled as perovskite \[^8\]. Figure 2 shows simulated ED patterns of MAPbI\(_3\) and PbI\(_2\) along different axis zones. These crystal planes are often confused in perovskite calibrations. Figure 2A is the ED pattern of MAPbI\(_3\) along [110] axis zone. (\(\bar{1}10\)), (002) crystal planes are existing in a perfect tetragonal perovskite, but they are missing in HRTEM characterizations in previous research papers. The absence of crystal planes indicates that the material is no longer MAPbI\(_3\) perovskite, but other phases and structures. Figure 2B shows the simulated ED patterns of PbI\(_2\) along [441] axis zone. (014), (\(\bar{1}04\)) crystal planes of PbI\(_2\) have the very closed interplanar spacing and angle with (\(\bar{2}20\)), (004) crystal planes of MAPbI\(_3\). Actually MAPbI\(_3\) has been damaged into PbI\(_2\) phase by electron beams and neglect of the lack of crystal planes results in the mischaracterization. Similarly, Figure 2C-H are ED patterns of MAPbI\(_3\) along [101] and PbI\(_2\) along [8101], MAPbI\(_3\) along [\(\bar{2}01\)] and PbI\(_2\) along [8\(\bar{8}1\)], MAPbI\(_3\) along [\(\bar{1}20\)] and PbI\(_2\) along [411] respectively.

Fig. 1. MAPbI\(_3\) degradation under electron beam irradiation. Tetragonal perovskite (A) decomposes into hexagonal lead iodide (B), followed by the escape of methylamine and hydrogen iodide molecules. Here, colors represent the following: green, iodine; red, lead; black, carbon; blue, nitrogen; pink, hydrogen.
Diffraction spots circled in red are missing crystal planes that were neglected in HRTEM characterizations. Moreover, these neglected planes are all present in X-ray diffraction (XRD) of MAPbI$_3$ [9-11].

Fig. 2. Simulated electron diffraction (ED) patterns of tetragonal MAPbI$_3$ and hexagonal PbI$_2$. (A) MAPbI$_3$ along [110] axis zone. (B) PbI$_2$ along [441] axis zone. (C) MAPbI$_3$ along [101] axis zone. (D) PbI$_2$ along [8 10 1] axis zone. (E) MAPbI$_3$ along [001] axis zone. (F) PbI$_2$ along [8 8 1] axis zone. (G) MAPbI$_3$ along [1 2 0] axis zone. (H) PbI$_2$ along [4 1 1] axis zone. Crystal planes marked in red circle are often missing in published articles.

The mischaracterizations have negatively affected the development of perovskite scientific research field. Statistically, these errors occur in the following fields: phase identification and structure determination [12], grain, nanowire and microwire orientation [13-17], morphology analysis and shape control of nanocrystals [18], growth direction of perovskite materials [19], degradation process and kinetics of perovskite [20], phase transition research in perovskite [21] and ion migration characterization in photoelectric devices [22]. Not only in the field of single MAPbI$_3$ material system, misleading information also occurs in the research field of heterostructure materials. Such as lattice matching and kinetic study in epitaxial growth of perovskite films on 2D material [23], PbS quantum dots in perovskite material [24, 25] and lattice anchoring stabilizes perovskite research [26]. To make the comparisons and corrections clearer, Table 1 shows the detailed parameters of the MAPbI$_3$ and PbI$_2$ along different axis zone, missing crystal planes have been marked in brown. Even remarkably, the [110] and [001] zone axis are equivalent in tetragonal MAPbI$_3$ perovskite.
Table 1. Detailed crystallographic parameters of MAPbI₃ and PbI₂.

| Material and zone axis | Characteristic crystal planes | Interplanar spacing | Interplanar Angle | References |
|------------------------|--------------------------------|---------------------|-------------------|------------|
| **MAPbI₃ [110]**       | (110), (220) (002), (004)    | d(110) = 6.2 Å.     |                  |            |
|                        |                               | d(220) = 3.1 Å.     |                  |            |
|                        |                               | d(002) = 6.3 Å.     |                  |            |
|                        |                               | d(004) = 3.2 Å.     |                  |            |
|                        |                                | <(110), (002)> = 90° |                  | 12-23      |
| **PbI₂ [441]**         | (014) (104)                   | d(014) = 3.2 Å.     |                  |            |
|                        |                               | d(104) = 3.2 Å.     |                  |            |
|                        |                                | <(014), (104)> = 87.5° |              |            |
| **MAPbI₃ [101]**       | (020), (040) (202)            | d(020) = 4.4 Å.     |                  |            |
|                        |                               | d(040) = 2.2 Å.     |                  |            |
|                        |                               | d(202) = 3.6 Å.     |                  |            |
|                        |                                | <(020), (202)> = 90° |              | 27, 28     |
| **PbI₂ [8 10 1]**      | (108) (112)                   | d(108) = 2.2 Å.     |                  |            |
|                        |                               | d(112) = 3.7 Å.     |                  |            |
|                        |                                | <(108), (112)> = 88.0° |              |            |
| **MAPbI₃ [201]**       | (112), (224) (112), (224)    | d(112) = 4.4 Å.     |                  |            |
|                        |                               | d(224) = 2.2 Å.     |                  |            |
|                        |                               | d(112) = 4.4 Å.     |                  |            |
|                        |                               | d(224) = 2.2 Å.     |                  |            |
|                        |                                | <(112), (112)> = 60.5° |              | 14, 24-26  |
| **PbI₂ [881]**         | (018) (108)                   | d(018) = 2.2 Å.     |                  |            |
|                        |                               | d(108) = 2.2 Å.     |                  |            |
|                        |                                | <(018), (108) = 57.2° |              |            |
| **MAPbI₃ [120]**       | (002), (004) (211)            | d(002) = 6.3 Å.     |                  |            |
|                        |                               | d(004) = 3.2 Å.     |                  |            |
|                        |                               | d(211) = 3.8 Å.     |                  |            |
|                        |                                | <(002), (211)> = 72.7° |              | 29-32      |
| **PbI₂ [411]**         | (104) (011)                   | d(104) = 3.2 Å.     |                  |            |
|                        |                               | d(011) = 3.9 Å.     |                  |            |
|                        |                                | <(104), (011)> = 73.7° |              |            |

Conclusions

Above statistics and corrections are very helpful for researchers to avoid mistakes in perovskite research field. Others that incorrectly label metallic lead as perovskite can also be identified and corrected using the same method[33]. Lessons learned from the mistakes alert us it is unreliable to calibrate material phase only by measuring interplanar spacings and angles. We also need to refer simulated ED or XRD specimen data to ensure the crystal planes are complete. In addition, low dose irradiation[6, 34, 35] and low temperature[7, 36] can reduce the damage of electron beam irradiation to perovskite, and may help us get the real structure of perovskite.
This work provides a sober-minded brain for further characterization in organic-inorganic hybrid perovskite and other electron beam-sensitive materials.

**Methods**

The Electron diffraction (ED) simulations of MAPbI$_3$ and PbI$_2$ were obtained using CrystalMaker Software. Corresponding crystal structures cif files were downloaded from Crystallography Open Database (COD) website. COD IDs of MAPbI$_3$ and PbI$_2$ are 4124388 and 9009141 respectively. MAPbI$_3$ is I4/mcm space group with tetragonal structure, cell parameters: a=b=8.839Å, c=12.695Å; α=β=γ=90°. PbI$_2$ is P-3m1 space group with hexagonal structure, cell parameters: a=b=4.555Å, c=20.937Å; α=β=90°, γ=120°.

**Data availability**

All data are available from the corresponding author(s) upon reasonable request.

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