Analysis of misidentifications in TEM characterization of perovskite material

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Abstract

Organic-inorganic hybrid perovskites (OIHPs) have recently emerged as groundbreaking semiconductor materials owing to their remarkable properties. Transmission electron microscopy (TEM), as a very powerful characterization tool, has been widely used in perovskite materials for structural analysis and phase identification. However, the perovskites are highly sensitive to electron beams and easily decompose into PbX₂ (X= I, Br, Cl) and metallic Pb. The electron dose of general high-resolution TEM is much higher than the critical dose of MAPbI₃, which results in universal misidentifications that PbI₂ and Pb are incorrectly labeled as perovskite. The widely existed mistakes have negatively affect the development of perovskite research field. Here misidentifications of the best-known MAPbI₃ perovskite are summarized and corrected, then the causes of mistakes are classified and ascertained. Above all, a solid method of phase identification for perovskite materials has also been proposed. This review aims to provide the causes of mistakes and avoid misinterpretations in perovskite research field in the future.

Keywords: Organic-inorganic hybrid perovskites (OIHPs), MAPbI₃, transmission electron microscopy (TEM), electron diffraction (ED), phase identification

Introduction

Organic-inorganic hybrid perovskites (OIHPs), which can be synthesized via low-cost solution-based methods, have emerged as groundbreaking semiconductor materials with remarkable performance in various optoelectronic devices such as solar cells, light-emitting diodes (LED), lasers and photodetectors [1-6]. In terms of structural characterization and phase identification of perovskite materials, transmission electron microscopy (TEM) is considered
to be the powerful characterization tool and has been widely used in these fields [7]. Unfortunately, the extreme sensitivity of OIHPs to electron beam irradiation inhibits us from obtaining the real structure of perovskite. For example, the best-known MAPbI$_3$ perovskite (Fig. 1A, B) begins to decompose into PbI$_2$ and Pb under 150 eÅ$^{-2}$ total dose irradiation [8]. The degradation process shows in Fig. 1C. However, the value of the electron dose in normal high-resolution transmission electron microscopy (HRTEM) is around 800-2000 eÅ$^{-2}$ s$^{-1}$, which is much higher than the critical dose of MAPbI$_3$ perovskite. Due to the neglect of electron beam-sensitive property of perovskite, the decomposition products, such as PbI$_2$, Pb and other intermediates have been widely misidentified as perovskite in TEM characterizations.

Fig. 1. The atomistic structure and degradation process of tetragonal MAPbI$_3$. (A) The atomic models of MAPbI$_3$ along [001] zone axis. (B) The atomic models of MAPbI$_3$ along [100] zone axis. (C) Tetragonal perovskite decomposes into hexagonal PbI$_2$, followed by the escape of methylamine and hydrogen iodide molecules. Furthermore, PbI$_2$ will decompose into cubic metallic Pb by further irradiation of the electron beam. Here, colors represent the following: green, iodine; red, lead; black, carbon; blue, nitrogen; pink, hydrogen.

The widely existed misidentifications have negatively influenced the development of perovskite research field, such as structural determination, material growth, phase transition, heterostructure and so on [4, 9-39]. Although the mistakes are being taken seriously [8, 40], analyzing the causes of misidentifications, and proposing a solid method of phase identification
for electron beam-sensitive materials is still highly urgent.

In this review, we focus on the best-known MAPbI$_3$ perovskite and aim to present an overall analysis of existing misidentifications in TEM characterization, other perovskites with similar components can be analyzed with the same approach. Firstly, we will highlight the summary and classification of the mistakes, whose HRTEM images mismatch intrinsic perovskites and electron dose is much higher than the critical dose. Subsequently, analyzing the causes of these misidentifications. The causes are specifically highlighted in this paper and are summarized as ignoring the absent crystal planes, systematic extinction and parameter proofreading. Furthermore, a solid method of phase identification for perovskite materials will be proposed. Finally, the available strategies to obtain intrinsic structure of perovskites are discussed. This review aims to provide the causes of mistakes and avoid misidentifications in perovskite research field in the future.

1. Ignoring the absent crystal planes

All supposed crystal planes should be present in HRTEM and electron diffraction (ED) pattern for a complete crystal structure. However, lacking of crystal planes exist extensively in TEM characterizations in previously published articles. The absence of crystal planes indicates that the structure and composition of perovskite are no longer intrinsic under electron beam irradiation.

Fig. 2A shows the HRTEM image of intrinsic MAPbI$_3$ perovskite along [001] axis zone at total doses of 1.5 eÅ$^{-2}$ s$^{-1}$ [41]. Obviously, (1$\bar{1}$0), (110) planes with 0.62 nm interplanar spacing are existing in the image, which matches the ED pattern (Fig. 2B) and XRD data of intrinsic MAPbI$_3$ [42, 43]. Fig. 2C is the HRTEM image of the pseudo MAPbI$_3$ perovskite in previously published paper at high total doses under normal TEM condition [10]. (1$\bar{1}$0), (110) planes are missing and only (2$\bar{2}$0), (220) planes remains. Actually, the perovskite has decomposed to PbI$_2$, according to the matched ED pattern along [4$\bar{4}$1] axis zone (Fig. 2D). Similarly, Fig. 2E and Fig. 2F show the HRTEM image and ED pattern of intrinsic MAPbI$_3$ along [\bar{2}01] axis zone [44] at dose rate is about 1.5 eÅ$^{-2}$ s$^{-1}$ for two seconds. The phase composition in Fig. 2G under normal TEM condition is identified as PbI$_2$ rather than MAPbI$_3$. 
due to the lacking of (1\(\bar{1}2\)), (112) planes and the matched ED pattern (Fig. 2H) [37].

Fig. 2. Analysis of ignoring the absent crystal planes. (A) HRTEM image of intrinsic MAPbI\(_3\) along [001] axis zone. (B) Simulated ED pattern of intrinsic MAPbI\(_3\) along [001] axis zone. (C) HRTEM image of pseudo MAPbI\(_3\) along [001] axis zone, (1\(\bar{1}0\)), (110) planes are missing. (D) Simulated ED pattern of corrected PbI\(_2\) phase along [4\(\bar{4}\)1] axis zone. Similarly, HRTEM images or Simulated ED patterns of intrinsic (E, F), pseudo (G) MAPbI\(_3\) along [201] axis zone and corrected PbI\(_2\) phase (H) were also be analysed. The words marked yellow in figures mean pseudo parameters of perovskite. (A) Reproduced with permission from Ref. [41], ©WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2020. (B) Reproduced with permission from Ref. [10], ©WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2014. (E) Reproduced with permission from Ref. [44], © 2020 Elsevier B.V. 2020. (G) Reproduced with permission from Ref. [37], © Springer Nature 2015.

Ignoring the absent crystal planes results in the misidentifications. In addition to the [001] and [201] axis zones of perovskite, other errors in other axis zones have also been corrected [40]. Even remarkably, all above intrinsic HRTEM images of MAPbI\(_3\) perovskite were captured under low temperature or low-dose electron beam irradiation. The words marked yellow in figures mean pseudo parameters of perovskite. To make the comparisons and corrections clearer, Table 1 shows the detailed parameters of the MAPbI\(_3\) and PbI\(_2\) in Fig. 2.

Table 1. Detailed crystallographic parameters of MAPbI\(_3\) and PbI\(_2\).

| Material and zone axis | Characteristic crystal planes | Interplanar spacing | Interplanar Angle |
|------------------------|-------------------------------|---------------------|-------------------|
| MAPbI\(_3\) [001]      | (1\(\bar{1}0\)), (2\(\bar{2}0\)) | d(1\(\bar{1}0\))= 0.62 nm. | <(1\(\bar{1}0\)), (110)> |
|                        | (110), (220)                 | d(2\(\bar{2}0\))= 0.31 nm. | = <(2\(\bar{2}0\)), (220)> =90.0° |

|                        | d(110)= 0.62 nm.           |                     |                   |
| Material     | Plane       | d(014)   | d(104)   | Bragg's angle |
|--------------|-------------|----------|----------|--------------|
| PbI₂ [441]   | (014)       | 0.32 nm  | 0.32 nm  | 87.5°        |
|              | (104)       |          |          |              |
| MAPbI₃ [201] | (112), (224)| 0.44 nm  | 0.22 nm  |              |
|              | (112), (224)|          |          |              |
| PbI₂ [881]   | (018)       | 0.22 nm  | 0.22 nm  | 57.2°        |
|              | (108)       |          |          |              |

### 2. Ignoring the systematic extinction effect

Lattice fringe image and ED pattern in TEM are based on the Bragg's law, described by

\[ n\lambda = 2d\sin\theta \]  

where \( n \) is a positive integer, \( \lambda \) is the wavelength of the incident wave, \( d \) is the interplanar spacing in a crystal and \( \theta \) is the glancing angle of incidence. Only the crystal planes that satisfy the Bragg diffraction equation can diffract electron beams and appear in TEM image. Besides, some crystal planes satisfying the Bragg's law will still disappear due to the microscopic symmetric elements in crystal structure, such as screw axis, slip plane, centered lattice and so on. We call this phenomenon systematic extinction effect which is often overlooked during phase identification [45].

MAPbI₃ perovskite is I4/mcm space group with tetragonal structure, (100), (011) crystal planes are extinctive and will not appear in TEM image and ED pattern. But in some published papers, extinctive crystal planes appear [46]. As shown in Fig. 3A, (011) and (011) crystal planes appear in the HRTEM image of pseudo MAPbI₃ but disappear in the intrinsic ED pattern along [100] axis zone (Fig. 3B). Similarly, the extinctive (100) crystal plane exists in pseudo perovskite (Fig. 3C) but disappear in intrinsic ED pattern along [011] axis zone (Fig. 3D). These materials cannot be identified as PbI₂ or Pb, and more likely to be other intermediates [46]. Ignoring the systematic extinction effect will also lead to misidentifications. In the identification of electron beam-sensitive materials, we should pay more attention to the
systematic extinction effect to avoid mistakes.

![HRTEM image of pseudo MAPbI3](image1)

![Simulated ED pattern of intrinsic MAPbI3](image2)

![HRTEM image of pseudo MAPbI3](image3)

![Simulated ED pattern of intrinsic MAPbI3](image4)

**Fig. 3.** Analysis of ignoring the systematic extinction effect. (A) HRTEM image of pseudo MAPbI3 along [100] axis zone. (B) Simulated ED pattern of intrinsic MAPbI3 along [100] axis zone. HRTEM image of pseudo MAPbI3 (C) and simulated ED pattern of intrinsic MAPbI3 (D) along [01\(\bar{1}\)] axis zone. (011), (0\(\bar{1}\)1) and (100) crystal planes are extinctive and should not appear in TEM image and ED pattern. (A, C) Reproduced with permission from Ref. [46], © Springer Nature 2020.

3. Ignoring the parameter proofreading

General phase identification of HRTEM and ED data is to compare a group of interplanar spacings and angles. As an electron beam-sensitive material, the critical electron dose of MAPbI3 perovskite is much lower than the radiation level of normal experimental HRTEM and ED [47], so we need to proofread whether the parameters are intrinsic perovskite, PbI2 or Pb. As shown in Fig. 4A [18], the decomposed metallic Pb was incorrectly labeled as perovskite and ED pattern of the corrected phase shows in Fig. 4B. The same misidentification in Fig. 4C and has been corrected in the corresponding ED pattern in Fig. 4D. Moreover, it is also not rigorous to only measure one crystal plane to identify the phase, because the decomposed materials have approximate interplanar spacings with intrinsic perovskite. As shown in Fig. 4E-H [13, 16, 18, 27], we completely cannot identify whether these materials are MAPbI3
perovskite, PbI₂, Pb or other intermediates based on one crystal plane. Ignoring the parameter proofreading makes it impossible to get the reliable result, so rigorous parameter proofreading is necessary and can help us avoid the misidentifications of electron beam-sensitive materials.

Fig. 4. Analysis of ignoring the parameter proofreading. (A) HRTEM image of pseudo MAPbI₃. (B) Simulated ED pattern of corrected Pb phase along [112̅] axis zone. (C) HRTEM image of pseudo MAPbI₃. (D) Simulated ED pattern of corrected Pb phase along [01̅1] axis zone. (E-H) HRTEM images of pseudo MAPbI₃ with only one crystal plane measured. (A, C, E) Reproduced with permission from Ref. [18], © Multidisciplinary Digital Publishing Institute (MDPI) 2019. (F) Reproduced with permission from Ref. [16], © American Chemical Society 2017. (G) Reproduced with permission from Ref. [13], © Springer Nature 2017. (H) Reproduced with permission from Ref. [27], © IOP Publishing 2014.

4. The solid method of phase identification

The misidentifications of perovskite material lead to wrong results, which have negatively affected the development of perovskite research field. To avoid misleadings in HRTEM characterization of perovskite in the future, we propose a solid method of phase identification for electron beam-sensitive materials here. Table 2 shows the crystallographic parameters of intrinsic MAPbI₃. Interplanar spacings from experimental data should match the data in the table. The interplanar spacing outside of this table indicates that the phase is not MAPbI₃ perovskite and would be other decomposition products. Once a group of alternative crystal planes ((h₁ k₁ l₁), (h₂ k₂ l₂)) have successfully corresponded to the intrinsic values, then we need to confirm that the experimental angle between (h₁ k₁ l₁) plane and (h₂ k₂ l₂) plane should also match the intrinsic value. The intrinsic angle between crystal planes can be obtained from
\[
\cos \theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{\left(\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2}\right)\left(\frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2}\right)}}
\]  

(2)

where \(a, b, c\) are the parameters of the unit cell. Finally, proofreading the fast Fourier transform (FFT) of the experimental HRTEM image or experimental ED pattern according to intrinsic ED simulation, only when the experimental data matches the ED simulation perfectly can the identification be proved to be successful. Schematic diagram of the method shows in Fig. 5. This method of phase identification is solid and can avoid the problems of ignoring the absent crystal planes, systematic extinction effect and parameter proofreading.

**Fig. 5.** Schematic diagram of the solid method of phase identification. Interplanar spacings and angle between alternative crystal planes must be matched. Moreover, proofreading the fast Fourier transform (FFT) of the experimental HRTEM image or experimental ED pattern according to ED simulation is necessary.
Table 2. Crystallographic parameters of tetragonal MAPbI$_3$.

| Sequence number | Index (h k l) | $2\theta$ (°) | Interplanar spacing (Å) | Relative intensity (%) |
|-----------------|---------------|---------------|-------------------------|------------------------|
| 1               | 002           | 13.9513       | 6.3425                  | 57                     |
| 2               | 110           | 14.2216       | 6.2225                  | 100                    |
| 3               | 112           | 19.9730       | 4.4418                  | 7                      |
| 4               | 200           | 20.1647       | 4.4000                  | 10                     |
| 5               | 211           | 23.6509       | 3.7587                  | 25                     |
| 6               | 202           | 24.6041       | 3.6152                  | 17                     |
| 7               | 004           | 28.1149       | 3.1713                  | 43                     |
| 8               | 220           | 28.6684       | 3.1113                  | 61                     |
| 9               | 213           | 31.0176       | 2.8808                  | 11                     |
| 10              | 114           | 31.6405       | 2.8255                  | 30                     |
| 11              | 222           | 32.0148       | 2.7933                  | 22                     |
| 12              | 310           | 32.1387       | 2.7828                  | 46                     |
| 13              | 204           | 34.8441       | 2.5727                  | 6                      |
| 14              | 312           | 35.1881       | 2.5483                  | 11                     |
| 15              | 321           | 37.4940       | 2.3967                  | 2                      |
| 16              | 224           | 40.5874       | 2.2209                  | 38                     |
| 17              | 400           | 40.9903       | 2.2000                  | 13                     |
| 18              | 215           | 42.3526       | 2.1323                  | 3                      |
| 19              | 323           | 42.6932       | 2.1213                  | 1                      |
| 20              | 006           | 42.7343       | 2.1142                  | 2                      |
| 21              | 411           | 42.9354       | 2.1047                  | 16                     |
| 22              | 314           | 43.2169       | 2.0917                  | 34                     |
| 23              | 402           | 43.5043       | 2.0785                  | 5                      |
| 24              | 330           | 43.5998       | 2.0742                  | 2                      |
| 25              | 116           | 45.2084       | 2.0041                  | 1                      |
5. Conclusions and outlook

Phase identification plays a vital role in material science, which determines whether we can get correct results from the experimental data. Above summary, classification, correction and analysis of misidentifications in TEM characterization of MAPbI₃ perovskite are very helpful for researchers to avoid mistakes in perovskite research field. The alerts learned from the mistakes and the proposed solid method of phase identification here can not only be applied to OIHPs, but also to other electron beam-sensitive materials, such as metal-organic frameworks (MOFs), organic crystals, etc. In addition, in order to get the intrinsic structure of OIHPs, low dose irradiation [8, 47-49] and low temperature [44, 50] which can reduce the damage of electron beam irradiation to perovskite have become the practical approaches. This review provides a sober-minded brain for further TEM characterizations in OIHPs and other electron beam-sensitive materials.

Methods

Corresponding crystal structures cif files were downloaded from Crystallography Open Database (COD) website. COD IDs of MAPbI₃, PbI₂ and Pb are 4124388, 9009141 and 9008477 respectively. MAPbI₃ is I4/mcm space group with tetragonal structure, cell parameters: a=b=8.839Å, c=12.695Å; α=β=γ=90°. PbI₂ is P-3m1 space group with hexagonal structure, cell parameters: a=b=4.555Å, c=20.937Å; α=β=90°, γ=120°. Pb is Fm-3m space group with cubic structure, cell parameters: a=b=c=4.950Å; α=β=γ=90°. The Electron diffraction (ED) simulations of MAPbI₃ and PbI₂ were obtained using CrystalMaker Software. The interplanar spacing and interplanar angle can be calculated from the cell parameters. During the process of phase identification, I also tried other polytypes of PbI₂, but the results could not match well.

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

Acknowledgements: None.

Conflict of interest: The authors declare no competing financial interest.
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