

Real-time analysis of the crystallization dynamics of organolead halide perovskite

Organolead halide perovskite solar cells are expected to be highly efficient and inexpensive, and competition in the research and development of these solar cells is accelerating. A simple process for the fabrication of these solar cells would be of interest from an industrial perspective, such as the mixing of a lead halide and amine halide to produce perovskite crystals. High-performance solar cells with reduced cost are expected to be achieved with the use of perovskites. Intensive studies based on both solution processing and vacuum deposition have been carried out since 2013, and the power conversion efficiency reached more than 20% within a couple of years [1]. The study of the crystallization processes of the perovskites is important because their performance in solar cells is strongly affected by their crystal structure and morphology. In particular, the elucidation of the crystallization mechanism is of great importance. The author's group has been focusing on the real-time analysis of the formation process of organic thin films by X-ray diffraction using the SPring-8 large synchrotron radiation facility [2]. The use of synchrotron radiation is very useful for *in situ* analysis because high-speed X-ray diffraction measurement is possible using the high-intensity light source with a two-dimensional X-ray detector. We started the real-time analysis of the formation process of organolead halide perovskites in 2014. The solution-based reaction from source materials into the perovskite was investigated in order to elucidate the mechanism of crystallization.

In this study [3], SPring-8 **BL46XU** was used for the real-time observation of X-ray diffraction with a two-dimensional X-ray detector (PILATUS 300K). An organolead halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) was fabricated by the dropwise addition of a solution of $\text{CH}_3\text{NH}_3\text{I}$ in 2-propanol onto a PbI_2 thin film, which was mounted on a measurement stage (Fig. 1). Ten-frame-per-second real-time X-ray diffraction measurements were conducted to analyze the reaction process.

The measurement result in Fig. 2 shows the reduction in the amount of PbI_2 raw material over time and the formation process of the perovskite crystal. Analysis of the rate of progression of this reaction revealed that the reaction progression did not follow the normal diffusion phenomenon but instead followed an anomalous diffusion process. This is thought to be because when $\text{CH}_3\text{NH}_3\text{I}$ diffuses into the PbI_2 thin-film medium, the $\text{CH}_3\text{NH}_3\text{I}$ diffuses by branching, reflecting the heterogeneity of the medium.

Next, the angles of the X-ray diffraction patterns were analyzed (Fig. 3). In the early stage of the reaction the formed crystals were oriented in two specific directions, but with the progress of time they changed to a random orientation. This finding suggests that the crystals changed continuously during the process of formation of the perovskite crystal.

This is not the only study to have observed and reported on the formation process of a perovskite crystal by using X-ray diffraction. However, in this study, we measured this process with a high

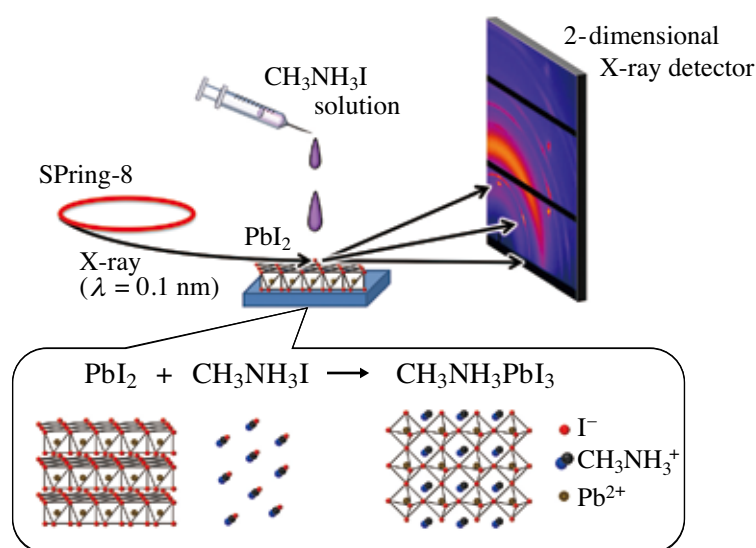


Fig. 1. Schematic illustrations of the measurement setup for real-time crystallization analysis.

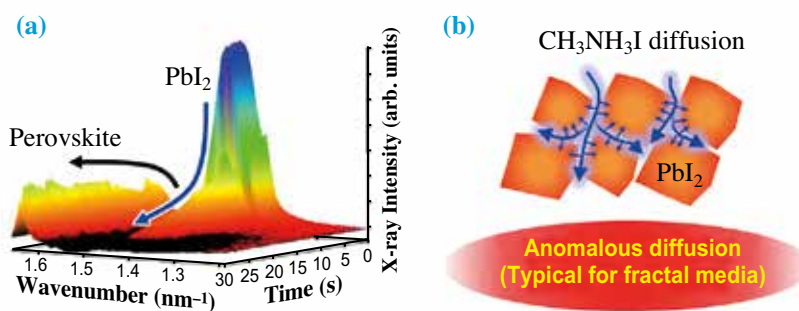


Fig. 2. (a) Changes in X-ray diffraction intensity over time and (b) schematic diagram of diffusion of $\text{CH}_3\text{NH}_3\text{I}$ into PbI_2 thin-film medium.

measurement speed of 10 frames per second; a detailed analysis of the reaction rate and crystal orientation was performed, which resulted in the finding of novel phenomena such as the anomalous diffusion and continuous changes in the crystal orientation. These behaviors appearing during the crystallization process are considered to be the cause of the poor reproducibility of perovskite thin-film formation. Therefore, achieving the control over these novel phenomena is the key to the highly

reproducible fabrication of highly efficient solar cells.

The X-ray diffraction method using synchrotron radiation has now been proven to be a valid method for analyzing the formation process of perovskite crystals. An increasing number of studies related to this topic have recently been reported [4,5]. It is important to conduct structural analysis and device development in a complementary manner in order to accelerate the research and development of organolead perovskite solar cells.

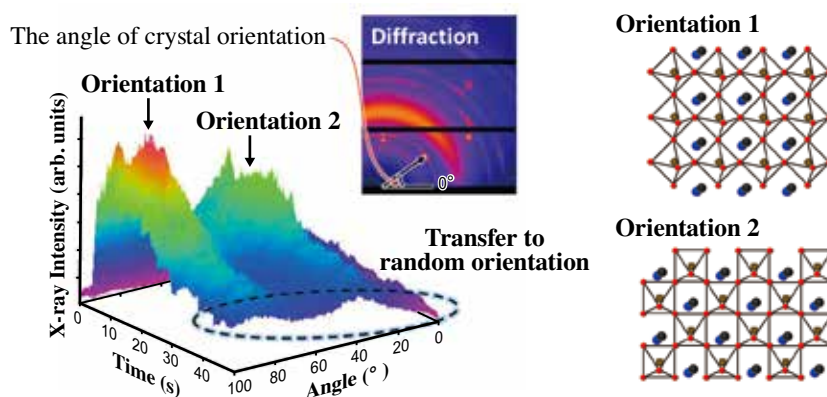


Fig. 3. Changes in the direction of the X-ray diffraction (reflecting the crystal direction) over time. In the early stage of the reaction, the crystals were oriented in two specific directions, but they later changed to a random orientation.

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