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Thermal stability of CsPbBr$_3$ perovskite as revealed by $\textit{in situ}$ transmission electron microscopy

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ABSTRACT

The thermal stability of all-inorganic halide perovskites is their key advantage over organic/hybrid halide perovskites. Here, $\textit{in situ}$ high-resolution transmission electron microscopy (HRTEM) was used to directly investigate crystallography dynamics of a CsPbBr$_3$ perovskite at high temperature (up to 690 K). In high vacuum TEM conditions ($\sim 10^{-5}$ Pa), CsPbBr$_3$ nanocrystals possessed superb stability at temperatures below 690 K. By sealing the crystals in amorphous carbon, their melting and solidification processes were directly observed at temperatures of 840 K and 838 K, respectively. This study should be valuable for future perovskite-containing solar cells, lasers, light-emitting diodes, and photodetectors working at high temperatures.

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In recent years, inorganic metal halide perovskites have attracted great research interest due to their extraordinary potential for high-performance optoelectronic devices with a variety of band gaps, excellent defect tolerance, low-cost, and trouble-free solution processing. As compared to organic halide perovskites, as well as to organic-inorganic hybrid halide perovskites, all-inorganic halide perovskites show decent stability against temperature, oxygen, and moisture. The applications of inorganic metal halide perovskites include light absorbers, solar cells, light-emitting diodes, photodetectors, and laser diodes.

A CsPbBr$_3$ perovskite was reported to have an orthorhombic Pbnm structure at room temperature, a tetragonal P4/mmbm phase between 361 and 403 K, and a cubic Pm-3m structure above 403 K. However, Burwig et al. were able to detect a cubic phase between 458 and 633 K, but not the tetragonal phase. In a recent report, Zeng et al. have discovered that CsPbBr$_3$ transforms from an orthorhombic to a tetragonal phase under photon irradiation with a negligible temperature increase. The material melting point was reported to be 840 K, as confirmed by differential-thermogravimetric-analysis (DTA) and melting-regrowth. In $\textit{in situ}$ photoluminescence spectroscopy performed in a temperature range of 80–550 K revealed that CsPbBr$_3$ nanocrystals had irreversibly degraded at a temperature higher than 450 K. $\textit{In situ}$ Raman spectroscopy combined with $\textit{in situ}$ X-ray diffraction (XRD) experiments performed between 83 and 773 K showed that CsPbBr$_3$ had exhibited a highly disordered state with featureless Raman spectra before thermal decomposition at 593 K. The measurements carried out below 773 K indicate that orthorhombic CsPbBr$_3$ would undergo phase transitions at different temperatures of 421, 361, 403, 450, 458, or 593 K. These very different temperatures imply that the thermal stability of this material is largely affected not only by temperature but also pressure.
humidity, and even light illumination. Therefore, it is essential to directly investigate the thermodynamics-related crystallography of CsPbBr$_3$ under direct, real time in situ transmission electron microscopy (TEM) heating in high vacuum conditions and without light illumination.

In this work, the CsPbBr$_3$ pervoskite was synthesized via a simple solution method through stirring CsBr and PbBr$_2$ in methanol. CsBr (99.9% metals basis) and PbBr$_2$ (99.999% trace metals basis) were purchased from Sigma Aldrich without further purification. The powder was mixed in a beaker at a molar ratio of 1:1. Then, an adequate amount of methanol was added to the materials. The beaker was set to 353 K, and the mixture was stirred at 800 rpm for 4 h. The solution was then fully dried in a vacuum oven at 333 K overnight. Powder samples were always sealed and kept away from the atmosphere. The crystal structure and phase composition of the materials were determined by X-ray diffraction (XRD) using a PANalytical X’Pert Pro multipurpose diffractometer (Co K$_\alpha$ radiation, $\lambda = 0.179095$ nm). Thermal analysis was carried out using an STA 449 F3 Jupiter by holding 288 mg of CsPbBr$_3$ under N$_2$ atmosphere with a measurement temperature range of 298–923 K. The heating rate was 5 K/min.

The as-synthesized material was then studied under in situ Micro-Electro-Mechanical System (MEMS) heating in a TEM holder from Zeptools using a JEOL 2010 TEM with a LaB$_6$ filament. The images and videos were acquired by using a TVIPS TemCam-XF416 camera with 4k × 4k resolution and 20 000:1 dynamic range. The usual column pressure of the microscope was 1.1–1.4 × 10$^{-5}$ Pa. Energy-dispersive X-ray spectroscopy (EDS) data were taken by an Oxford AZtecTEM system with an 80 mm$^2$ X-Max detector and a SATW window. The heating MEMS chips with four contacts were controlled by the proportional-integral-derivative (PID) program and by a high-resolution source-measure unit Keithley 2634B. To prepare a sample for the in situ TEM heating experiments, a minimum amount of the powder sample was added to a small container with ethanol. The container was sonicated for 30 min at room temperature. The container was then kept still for 30 min, and the supernatant fluid was collected using a 2 ml pipette. The liquid was applied to the MEMS heating chip placed on a filter paper. Excess fluid was removed by gently applying the edge of another filter paper on top. The MEMS heating chip was then mounted onto the MEMS chip holder under an optical microscope.

The produced material was first characterized by XRD, TEM, selected area electron diffraction (SAED), and EDS to confirm its initial orthorhombic structure. It was then transferred onto the MEMS heating chip of a dedicated in situ TEM holder to observe the crystallography changes at different temperatures.

It was demonstrated that a 200 kV electron beam with low to medium electron flux doses ($10^{15}$–$10^{19}$ e$^{-} \text{cm}^{-2} \text{s}^{-1}$) had not affected CsPbBr$_3$ or a Si$_3$N$_4$ substrate in our experiments. However, when the dose was higher than $8 \times 10^{19}$ e$^{-} \text{cm}^{-2} \text{s}^{-1}$, perovskites became unstable and crystals started to degrade into lead islands. Therefore, the beam was always set at a low dose condition when the temperatures became higher than 500 K. In addition, the electron beam was tilted away from the samples unless images or videos were being acquired.

To seal the crystal with amorphous carbon, a low electron dose was applied using a small TEM electron beam spot size. First, a piece of paraffin wax as a source of carbon (the minimum amount possible) was placed on the side of the MEMS chip (accessible to the electron beam). After the sample was located, the electron beam was focused onto the paraffin spot for 2 s at a high dose to release carbon in a controllable amount. Then, the electron beam was quickly spread over to illuminate the sample at a very low dose, using a small condenser aperture and a small electron beam spot size. By controlling the beam brightness and duration of its exposure, an adequate amount of the amorphous carbon was attracted to the designated sample area at room temperature.

Under vacuum conditions within the TEM (∼10$^{-5}$ Pa), a CsPbBr$_3$ nanocrystal was perfectly stable at temperatures ranging from room temperature to 690 K, revealing no phase transformations. Then, at 690 K, the crystal started to sublime while maintaining crystallinity, and then became amorphous and evaporated, starting from local regions before extending to the whole particle. However, when the crystals were sealed in amorphous carbon, they started to melt at 840 K. Upon decreasing the temperature back to 838 K, the crystal solidification took place. This process was repeated several times to show its reversible nature.

The MEMS heating chip is presented in Fig. 1(a). The heating zones are made from electrically insulating silicon nitride (Si$_3$N$_4$). Four contacts are used for heating and PID control. The thicker membrane is not transparent to the electron beam, while the thinner “windows” are the transparent regions for direct observations. One “window” is marked by a red square in Fig. 1(a) and expanded in Fig. 1(b). The window is 5 μm wide, 25 μm long, and ∼100 nm thick. As an example, a nanoparticle marked in Fig. 1(b) is presented in Fig. 1(c). The single crystal showing lattice fringes of 0.31 nm stands on the amorphous membrane at room temperature. Such distance corresponds to (122) or (212) planes of the orthorhombic CsPbBr$_3$. The detailed characterization is illustrated in Fig. 2, where Fig. 2(a) shows a high-resolution (HRTEM) image of a nanoparticle edge, revealing lattice fringes of 0.29 nm and 0.33 nm, which correspond to (220), (004) and (113), (202), (022) planes, respectively. The power spectrum of Fig. 2(a) is depicted in Fig. 2(b) by fast Fourier transform (FFT). The powder XRD spectrum of the sample is shown in Fig. 3(c). The experimental spectrum is a perfect match with the calculated result from a PDF 04-014-9676 card. There is no residue of CsBr or PbBr$_2$ phases in the sample. The structure from the PDF card no. 04-014-9676 was then imported to the SingleCrystal program for electron diffraction simulation. The result obtained along the (111) zone axis is presented as the inset in Fig. 2(b), which is fully consistent with the indexing of power spectrum in zone (111).

As shown in Fig. 3(a), the original state of a CsPbBr$_3$ nanocrystal at room temperature reveals 0.33 nm lattice fringes, corresponding to (113), (202), and/or (022) planes of the orthorhombic phase. By heating the MEMS chip holder to 690 K, the nanoparticle was eventually evaporated, as shown in Fig. 3(b). By comparing the EDS data of the nanocrystal at room temperature with that of the final product, as shown in Fig. S1, no significant amounts of residual elements, i.e., Cs, Pb, or Br, were observed. The remaining contrast in Fig. 3(b) should be attributed to the inhomogeneous thickness of the Si$_3$N$_4$ membrane due to the process of heating and evaporation of the nanoparticle. Under a low dose electron beam, before a sublimation point at 690 K, the sample had no changes in morphology or crystallography. In Fig. 3(c), a series of clip images represents the dynamic process at 690 K, from 0 to 10 s. When the temperature
FIG. 1. (a) Low magnification TEM image of the MEMS heating chip. (b) TEM image of the red square area from image in (a) displaying a window with a thinner Si$_3$N$_4$ membrane. (c) An individual CsPbBr$_3$ single-crystalline nanoparticle on the amorphous Si$_3$N$_4$ membrane.

FIG. 2. (a) High-resolution TEM image and (b) the Fast Fourier transform (FFT) pattern of an individual CsPbBr$_3$ perovskite nanoparticle. The FFT image perfectly fits the simulated diffraction pattern of orthorhombic CsPbBr$_3$, as shown in the inset. (c) XRD pattern of the sample at room temperature confirming a perfect match with the orthorhombic Pbnm62 CsPbBr$_3$ (PDF 04-014-9676) structure.
reaches 690 K, the central part of the crystal immediately starts to reveal a dark contrast, while transforming from the crystalline to the amorphous state. The amorphous matter in the centre can be attributed to material melting at high temperature. The rest remains crystalline but exhibits a weaker contrast. The fading contrast can be related to the sublimation of surface atoms without melting. Such sublimation at the surface takes heat away. In the beginning, this can stabilize the dynamic surface without its melting. During continuous heating, the edge of the crystal tends to become amorphous, displaying a weaker contrast as compared to that of the Si$_3$N$_4$ background membrane. This can be attributed to the start of general melting and evaporation at the left crystal part. At 690 K and 4 s, the central amorphous part becomes larger, while the left part of the nanocrystal totally loses its crystallinity. It becomes amorphous with a similar contrast to the Si$_3$N$_4$ background, implying that the material partially melted. At the same time, the rest part of the crystal keeps its overall crystallography, while its sublimation happens solely at the surface. In the image of 6 s at 690 K, the upper part of the nanocrystal is sublimated, showing two voids. The central amorphous part (showing dark contrast) is moving toward the right side. The bottom side of the crystal still presents some crystalline features with lattice fringes of 0.33 nm, but the contrast sharpness gradually decreases over a period from 0 to 6 s. The edge of the crystal also gradually becomes amorphous and featureless. At 690 K and 10 s, the nanoparticle loses all crystal features and becomes totally amorphous, with several voids remaining in its body. After 10 s, the particle shifts away from the camera view due to the heating drift. The final product, after 1 min at 690 K, is shown in Fig. 3(b). The sublimation process is well captured by the present in situ TEM heating experiment. The dynamics of the whole process is available in the supplementary material (Video 1). From the video, it is clear that the crystal undergoes a mix of sublimation and evaporation. Some parts of the particle become thinner, maintaining crystallinity at the beginning, whereas other parts of the particle become amorphous and then evaporate. The data show that in vacuum TEM conditions ($\sim 10^{-5}$ Pa), the perovskite single crystal becomes amorphous and evaporates immediately at 690 K. The particle becomes completely amorphous and partly evaporates just after 10 s. After 1 min, the particle is completely evaporated without any Cs, Pb, or Br residual traces. De-sublimation was not observed due to high vacuum conditions and cold trapping of the microscope. It should be noticed that the in situ evaporation temperature recorded in our experiment is an approximate number which is influenced by not only temperature but also pressure, the cold trap, and the low-dose electron beam. Additionally, the temperature was recorded for a single nanoparticle with a size of 20 nm. Thus, the observed scenario can represent a mixed process of sublimation along with melting plus evaporation.

The known melting points of PbBr$_2$ and CsBr reagents are 644 K and 909 K (Sigma Aldrich), respectively; whereas the melting point of CsPbBr$_3$ is not stated on the PDF 04-014-9676 card. The reported melting point is 840 K for the ISCD 97851 orthorhombic phase, as revealed by differential scanning calorimetry (DSC), and also under Differential Thermal Analysis (DTA). Then, the thermogravimetry (TG)—DSC analysis was additionally carried out on the present sample. The result represents a broad peak centred at 839.1 K, as shown in Fig. S2. This is in good agreement with the previous results, considering a relatively large full peak width at half maximum (FWHM) of 12 K. However, the phase transitions are not clearly seen during either TG-DSC scanning or in situ TEM observations.

In high vacuum conditions, the material is stable up until 690 K. After reaching 690 K, it immediately evaporates. In order to confirm the melting point at a meaningful pressure, the crystals were sealed by amorphous carbon using a special technique, as detailed previously. In this case, the crystals were triple-sealed using three different focusing at different beam diameters. As shown in Fig. S3, three crystals were covered by three layers of amorphous carbon. The sandwichlike sealed structure between Si$_3$N$_4$ and amorphous carbon provides sufficient pressure to the material and prevents its evaporation. In Fig. 4, a series of clip images showing the states of three sealed crystals at temperatures of 300 K, 840 K, and 838 K are presented. The heating was carried out from room temperature to 840 K at a rate of 2 K/min. When approaching the target...
FIG. 4. TEM images of three individual CsPbBr$_3$ perovskite crystals sealed in amorphous carbon at room temperature, then heated in the TEM to 840 K, cooled to 838 K, and then heated back to 840 K, displaying an operando reversible processes of melting, solidification, and repeatable melting. The red arrows point to the starting stages of melting (840 K, 15 s) and recrystallization (838 K, 10 s).

TABLE I. Melting point, solidification point, and boiling/sublimation point of CsPbBr$_3$ compared to relevant materials.

| Material | Melting point (K) | Solidification point (K) | Boiling point (K) | Condition | Reference |
|----------|-------------------|--------------------------|-------------------|-----------|-----------|
| CsBr     | 909               | ...                      | 1573              | Not stated | Sigma Aldrich |
| PbBr$_2$ | 644               | ...                      | 1165              | Not stated | Sigma Aldrich |
| 840      | 823               | ...                      | DSC 10 K/min N$_2$ atm | Reference 25 |
| 840      | 825               | ...                      | DSC 5 K/min Ar atm | Reference 25 |
| CsPbBr$_3$ | ~840             | ~787                     | DTA details not stated | Reference 26 |
| ~839     | ...               | ...                      | DSC 5 K/min N$_2$ atm | This work |
| 840      | 838               | 690 (sublimation)        | In situ MEMS heating ~2 K/min high vacuum | This work |

The results regarding the melting, solidification, boiling, and evaporation of the CsPbBr$_3$ perovskite compared to relevant materials are summarized in Table I.

To summarize, in high vacuum TEM conditions ($\sim 10^{-5}$ Pa), CsPbBr$_3$ perovskite nanocrystals revealed superb stability at temperatures below their sublimation point of 690 K. By sealing the crystals in amorphous carbon, melting and solidification were observed at temperatures of 840 K and 838 K, respectively. The present in situ dynamic observations of CsPbBr$_3$ should be an important reference for future solar cells, lasers, light-emitting diodes, and photodetectors working at high temperature and using this prospective material. Yet, it is planned to further expand direct in situ real time TEM observations to other inorganic halide perovskites with respect not only to their thermodynamics but also to light illumination conditions and to study the related mechanisms relevant to emerging applications.

See supplementary material for the detailed videos of in situ experiments, EDS data, TG-DSC data, and TEM images of the produced in situ setups.

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