Atomic structure of lead-free $Cs_3Bi_2Br_9$(001) perovskite surface

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Perovskites have found great potential in their promising applications in electronics and optoelectronics [1]. While moving forward from research to productization, many concerns remain about the stability and the toxicity of this class of materials, particularly the organic–inorganic hybrid lead-halide perovskites [2]. Therefore, making inorganic and/or environmental-friendly Pb-free perovskite materials, e.g. Bi-based halide ones, is a stimulating research field [3]. Although the development of Bi-based halide perovskites with novel optical and (opto)electronic properties makes rapid progress and the bulk structures of these materials have been intensively studied, the information regarding the surface and interface structures, which defines the final device performances, has rarely been studied directly so far [4].

With an aim to reveal the structure-property relationship of a class of Bi-based halide perovskite of relevance for optoelectronics, we focus on the synthesis and surface structural characterization, as well as the bandgap measurement. Herein, orthorhombic $Cs_3Bi_2Br_9$ nanofilm with precise stoichiometric ratio is synthesized inside an ultra-high vacuum (UHV) chamber onto an Au(111) substrate using physical vapor deposition (PVD) method. By means of atomic-resolution scanning tunneling microscopy (STM), the as-prepared atomically defined $Cs_3Bi_2Br_9$/Au(111) is first compared with bulk $Cs_3Bi_2Br_9$ nanoplatelets prepared by wet-chemistry method to confirm the structure relevance. We further investigate the resulting atomic structure, particularly the different layer-terminated surfaces. Ultimately and by means of I-V characteristics measured by STM and its numerical derivative, we analyze the bandgap properties of the as-prepared $Cs_3Bi_2Br_9$ nanofilm.

Our results show that the $Cs_3Bi_2Br_9$/Au(111) nanofilm prepared by surface science method is terminated by either Cs-Br or Bi-Br layers, while structurally matching well with the bulk $Cs_3Bi_2Br_9$ nanoplatelets. The observed energy gap varies with film thickness, which allows for the creation of desirable electrical properties and indicates the possibility of tunable photo-responsivity. This model further naturally permits elucidation of the termination (site)-specific properties and allows detailed evaluation of stability and photo-reactivity.

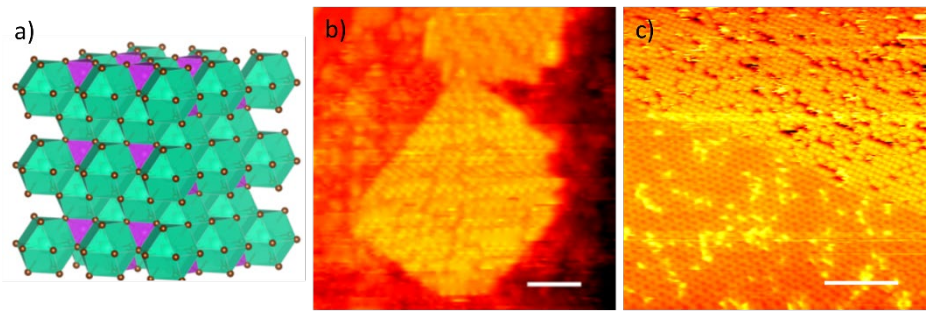

Fig. 1. (a) Model of the $Cs_3Bi_2Br_9$ structure. STM images of perovskite synthesized by (b) wet-chemistry method and (c) PVD method. (c) shows an area with adjacent different terminated layers. Scale bar 5nm.

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