Non-aqueous Ultra-microtome of Cesium Lead Halide Perovskite Crystals for Defect Analysis

Kyle Sendgikoski1*, Brendon T. Jones2, Sarah Brittman3, Todd Brintlinger3

1National Research Council Postdoctoral Associate at U. S. Naval Research Laboratory, Washington, DC 20375 USA
2Department of Physics, Florida State University, Tallahassee, Florida 32306 USA
3U. S. Naval Research Laboratory, Washington, DC 20375 USA
*Corresponding author: kyle.sendgikoski.ctr@nrl.navy.mil

Metal halide perovskites (MHP) have drawn increasing focus in the semiconductor community because of their defect tolerant optoelectronic properties, chemical versatility, and varied fabrication methods [1]. Specifically, CsPbBr3 has demonstrated significant promise as a photodetector and radiation detector with CsPbBr3 photovoltaic solar cells having the potential to surpass the efficiency of their polycrystalline counterpart [1,2]. Understanding the effects that defect density, distribution, and type have on the optoelectronic properties of single crystal MHPs can facilitate improved fabrication processes and performance of CsPbBr3 in applications. In this work, ultra-microtome is used to create thin, electron transparent sections of bulk single crystal CsPbBr3, and HRTEM and EDS are used to identify defects and elemental composition.

Ultra-microtome is typically used to create ultra-thin sections of organic material such as viruses or cells at room temperature but has had notable success with cryo-wet and -dry sectioning [3]. This is often done by embedding the organic specimen in a cooperative supporting material, such as epoxy, and shaping a trapezoidal pyramid with a 100µm maximal edge dimension. Sections are made with a diamond knife with an edge radius of roughly 10nm with sections supported by the surface tension of a liquid: water. The water-filled boat is used to separate the sections from the knife to prevent adhesion, shape alteration, and facilitate ease of transfer. Because CsPbBr3 is ionic, alternative liquids to water are investigated as section-suspending liquids to determine ultra-microtome viability when compared to standard wet-section ultra-microtome with water. Single crystals of CsPbBr3 were grown using inverse temperature crystallization to sizes of at most 1mm [4]. Larger crystals were cut into smaller (<400µm) pieces, embedded in epoxy, and sectioned to thicknesses from 100-500nm.

Dry-sectioning ultra-microtome at room and cryogenic temperatures eliminates all effects from the suspending liquid but increases cutting compression and electrostatic charging. Unfortunately, liquid is still required to transfer dry-cut sections from the blade to the TEM grid. In the process of shaping embedded CsPbBr3 crystals, a fine particulate spray of cut crystal was observed and captured on TEM grids for comparison to wet-sectioned specimens. HRTEM and EDS were performed on both standard wet-cut sections and non-aqueous particulate capture CsPbBr3 to determine crystallinity, elemental composition, and section thickness. Mass transfer was observed under sufficient electron dose/dose rate by changes in phase contrast and individual nodule movement. This mass transfer is explained by electron radiation causing a chemical interaction throughout a local region of the specimen and is confirmed by site-specific EDS to be lead migration.

Metal halide perovskite single crystal CsPbBr3 is a defect robust optoelectronic material that has significant potential for applications in photo- and high-energy detectors, light emitters such as LEDs and
lasers, photovoltaics, and nanocrystal quantum dots. Thin sections of CsPbBr$_3$ are made by wet-cut ultramicrotome and a novel non-aqueous method from microtome pillar shaping. HRTEM and EDS are performed on the sections identifying crystal structure, boundaries, and eventual lead mobilization due to the electron radiation.