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## Novel Perovskite Semiconductors for the Detection of Special Nuclear Material

**Project highlight.** Portable, discrete radiation detection is imperative for nuclear safeguards applications, radioactive 3D imaging, and neutron spectroscopy. Current neutron detectors, including gas proportional counters and scintillators, are not suitable for discrete or portable monitoring due to size, weight, and power limitations. Perovskite based semiconductors have the potential to overcome existing issues with current nuclear detectors and exceed the performance of traditional semiconducting detecting materials. The goal of this project is to create novel boron ( $^{10}\text{B}$ ) based single crystal perovskites for low-profile solid-state neutron detection. Directly incorporating the neutron capturing element ( $^{10}\text{B}$ ) into the unit cell of the detector eliminates the energy diminishing routes that typically occur in indirect conversion materials, including self-absorption and interlayer energy transfer routes.

## Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

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Date

## Novel Perovskite Semiconductors for the Detection of Special Nuclear Material

Project Team: Joy McNamara (Primary) and Kaitlin Lawrence

Project Type: Seedling

Project Start Date: October 1, 2019

Project End Date: September 30, 2020

*Special nuclear material detection using portable, highly efficient detectors is of paramount importance to national security and environmental monitoring. Current neutron detectors, including gas proportional counters and scintillators, are not suitable for discrete or portable monitoring due to size, weight, and power limitations. For example,  $^3\text{He}$  gas proportional detectors have significant drawbacks, including long absorption lengths, high*

*voltage requirements, and dependence on the availability of  $^3\text{He}$ . The goal of this project is to synthesize a novel, boron-based perovskite semiconductor crystals to create a more efficient and more portable neutron detector. This innovative material will lead to a significant decrease in power and size requirements with higher operating temperatures than other traditional solid-state detectors. Directly incorporating  $^{10}\text{B}$  eliminates the need for a conversion layer and leads to high neutron absorption coefficients. In this seedling project, we used inverse temperature crystallization with boron precursors to create  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{BF}_4)_x$ . The crystals were analyzed with X-ray diffraction, but the results were inconclusive. Future work will focus on tailoring the solution growth and selecting appropriate solvents and precursors.*

### FY2020 Objectives

- Synthesis of boron perovskite crystals
- Characterization of boron perovskite properties

### Introduction

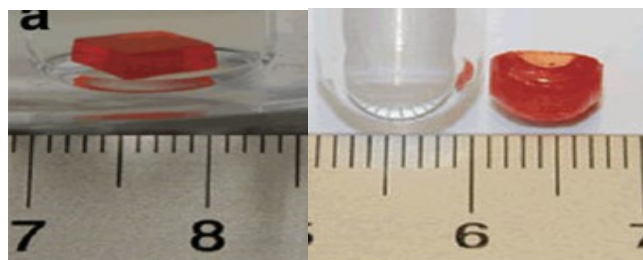
Perovskite photovoltaic devices ( $\text{CsPbX}_3$  and  $\text{CH}_3\text{NH}_3\text{PbX}_3$ ;  $\text{X} = \text{Cl, I, or Br}$ ) have experienced an unprecedented and meteoric rise in device efficiency due to their unique and tunable optoelectronic properties. These include exceptionally high carrier mobility-lifetime products ( $\mu\tau$ ; higher  $\mu\tau$  values lead to higher charge collection efficiencies), low defect density, long carrier diffusion lengths, larger band gap, and high absorption coefficients that match and even exceed most traditional solid-state detectors.<sup>1-5</sup> Typical  $\mu\tau$  products and band gaps for perovskites are 2-5 orders of magnitude larger than common solid state detectors, such as boron nitride (h-BN), high purity germanium (HPGe) and single crystal silicon.<sup>6</sup> Since the bias voltage required for efficient charge collection is inversely proportional to charge carrier mobility lifetime products, perovskites can be operated at lower bias voltages, utilizing less energy.<sup>7</sup> Additionally, traditional solid state detectors require expensive and time consuming fabrication techniques that can lead to interfacial strain due to lattice mismatch and require cryogenic cooling for efficient operation.<sup>6,8,9</sup> Depending on the composition, perovskites have a band gap that is 2-3 times larger than the band gap for HPGe, allowing for operation without active cooling due to the suppression of thermal excitation of charge carriers. The electronic and optical properties of perovskites lead to higher charge collection efficiencies and lower detection limits, which can be harnessed to create more efficient, smaller nuclear detection devices. Although there is extensive research from the photovoltaic community

on the progress and achievements of perovskite based photovoltaic devices, radiation detection using perovskites is scarce and focused on gamma detection.<sup>10</sup>

The proposed neutron detecting perovskites also increase efficiency by directly incorporating boron ( $^{10}\text{B}$ ) into the perovskite unit cell. This combines both the neutron absorber and charge carrier generator in one material, eliminating the energy diminishing routes (e.g. self-absorption, interlayer energy transfer, etc.) that can occur in indirect conversion materials. After  $^{10}\text{B}$  atoms capture incoming neutrons, the emission of charged particles (alpha particles,  $^7\text{Li}$ , and gamma rays) generates electron-hole pairs in the perovskite semiconductor. The density of boron atoms in a solid-state detector is an order of magnitude larger than that found in  $^3\text{He}$  gas detectors, which is much larger than the difference in neutron absorbing efficiency, since  $^3\text{He}$  is 28% more efficient than  $^{10}\text{B}$ . Additionally, since the atomic density is much lower for  $^3\text{He}$  compared to  $^{10}\text{B}$ , the thermal neutron absorption length is much larger for  $^3\text{He}$ . Therefore, at this replacement level, the fabricated crystals will exceed the sensitivity and performance of current  $^3\text{He}$  detectors with smaller size requirements. In this project, we attempted the synthesis and characterization of boron perovskite crystals using the inverse temperature crystallization (ITC) method.

## Approach

Solution crystal growth is traditionally accomplished through the process of cooling heated solutions, since solutes are typically more soluble at higher temperatures. Growth using this method is slow and time consuming and is dependent on the solubility of the precursors in the solvent. Using the appropriate solvent will allow more precursors to be dissolved when heated, and will induce supersaturation upon cooling the solution, thereby causing crystallization to occur. Choosing an appropriate solvent therefore determines the quality of crystal growth. For organo-metal halide perovskites ( $\text{CH}_3\text{NH}_3\text{PbX}_3$ , where  $\text{X} = \text{Br}, \text{Cl}, \text{or I}$ ), solvents which lead to successful crystal growth are commonly  $\gamma$ -butyrolactone (GBL),  $\text{N,N}$ -dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The solubility of the  $\text{PbX}_2$  precursor varies based on the specific halogen, and successful crystal growth is only achieved upon selecting the appropriate solvent. It has been reported that for perovskites with iodine, crystallization is more successful using GBL as the solvent.<sup>11</sup>



**Figure 1.** ITC grown  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  perovskite single crystals. Taken from Ref. 13.

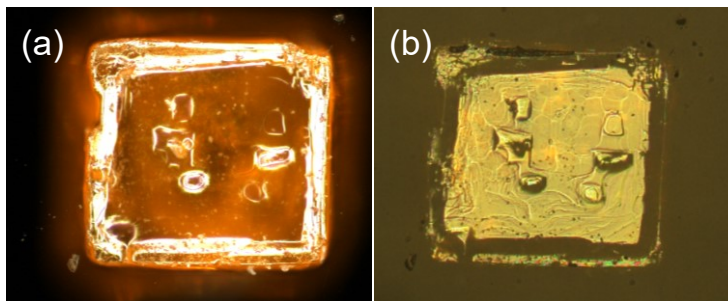
Interestingly, perovskite solution crystal growth exhibits retrograde solubility; that is, the precursors have a higher solubility at low temperatures, and a lower solubility at high temperatures.<sup>12</sup> This rare phenomenon that is only seen in a few materials,<sup>12</sup> is referred to as inverse temperature crystallization (ITC). The ITC method is capable of growing high-quality single crystals very rapidly in a matter of hours as opposed to days (Figure 1).<sup>13</sup> In this work, we have attempted the growth of  $\text{CsPbBr}_3$  (Figure 2) in FY19 and  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{BF}_4)_x$  in FY20, and we explored the use of different solvents for the growth of organometal halides with boron substitution.

## Results/Discussion

The goal of this work was to synthesize boron substituted perovskites with the elemental composition of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{BF}_4)_x$ . This perovskite structure was grown in Ref. 14 using vapor deposition and solid-state synthesis. A perfunctory search of the literature does not reveal if this specific perovskite form has ever been grown using solution crystal growth methods.

Following the approach of Ref. 13, 1 molar (M) solutions of  $\text{PbI}_2$  and  $\text{CH}_3\text{NH}_3\text{BF}_4$  were prepared in GBL. The solutions were stirred at  $60^\circ\text{C}$  until dissolved. Both solutions were filtered and combined into one solution, which was then heated to  $110^\circ\text{C}$  for 2-3 hours. No observable crystallites formed even upon increasing the temperature to  $140^\circ\text{C}$ . Since  $\text{PbI}_2$  did not readily dissolve in GBL, the synthesis was carried out in a GBL/DMF mixture to ensure the lead was dissolved. Small crystallites began to form after heating to  $110^\circ\text{C}$ . After increasing the temperature to  $140^\circ\text{C}$ , the crystallites rapidly grew to 1-2 millimeters in size and were bright orange colored (Figure 3). The crystals were rinsed with GBL and washed with ethanol to remove the solvent before drying overnight. These crystals were analyzed via X-ray diffraction (XRD). The data showed peaks for  $\text{PbI}_x$  structures, but peaks for the desired form of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{BF}_4)_x$  were not observed (Figure 4). Upon analyzing the data, it was determined that  $\text{PbI}_x$  crystallites had most likely formed from the solution, since the  $\text{PbI}_2$  solute was not able to fully dissolve in the GBL.

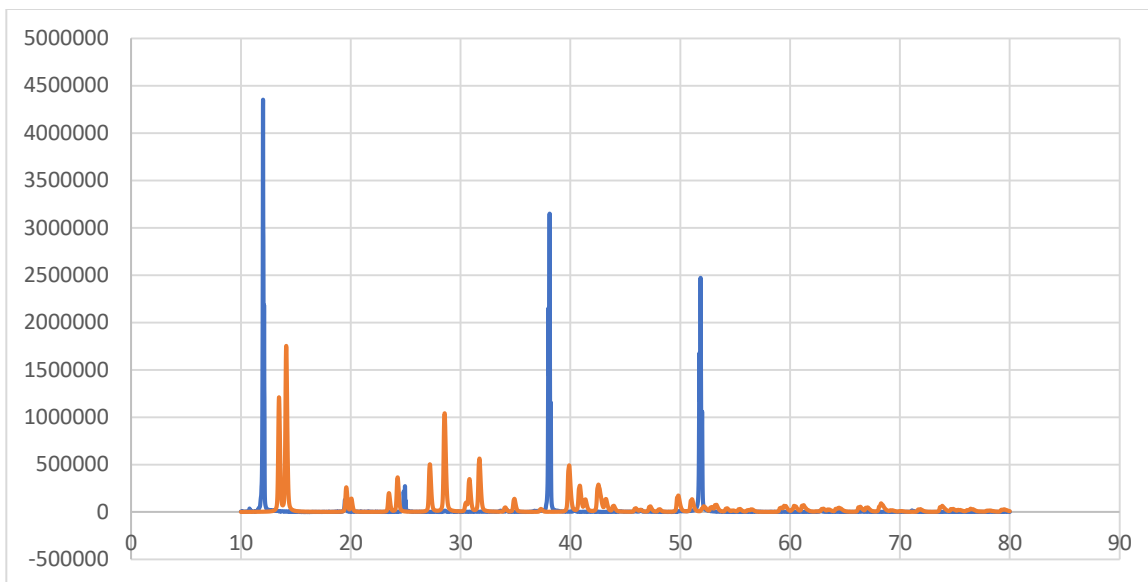
It appears that the  $\text{PbI}_2$  crystallites are forming from the mixture of GBL and DMF solvents, since the individual boiling points of the two solvents is  $153^\circ\text{C}$  for the DMF and  $205^\circ\text{C}$  for the GBL. Thus, heating the mixture of these two solvents caused the  $\text{PbI}_2$  products to crystallize, indicating that DMF, the solvent responsible for dissolving the  $\text{PbI}_2$ , was evaporating faster than the GBL. This resulted in the supersaturation of  $\text{PbI}_2$ , which caused crystallization of  $\text{PbI}_2$ . Future work may involve modeling the vapor liquid equilibrium curves for these two solutions or finding comparable systems from which comparisons can be made. Further studies must be conducted on the appropriate solvents, since successful crystallization of similar perovskite structures in the literature was accomplished using only one solvent (e.g., GBL for iodine containing perovskites<sup>13</sup>). Alternatively, different precursors can be explored such as  $\text{CH}_3\text{NH}_3\text{BF}_4$  salts mixed with  $\text{PbBF}_4$  solutions to increase the boron density and reduce the need for halogen substitution. Again, a search of the literature does not reveal that this technique has ever been tested.



**Figure 2.** (a) Dark field and (b) polarized light micrographs of a  $\text{CsPbBr}_3$  perovskite crystal grown at SRNL using ITC.



**Figure 3.** Vial containing presumed boron perovskite crystals after ITC growth.



**Figure 4.** XRD graph of presumed boron perovskite structures (blue lines) compared to desired theoretical composition (orange lines).

## FY2020 Accomplishments

- Determined the need for appropriate solvent and precursor usage in perovskite crystal growth.
- Successfully relocated setup from W-area to A-area laboratory and revised hazard analysis package.
- Procured materials and chemicals

## Future Directions

- Model vapor liquid equilibrium curves for solvents
- Optimize crystal growth by exploring the use of alternative precursors and solvents
- Optimize crystal growth by understanding time and temperature effects
- Partner with external sources (e.g., university) to grow reference crystal materials.
- Carry out electrical and device characterization using current-voltage measurements to obtain expected device performance
- Examine the neutron absorption ability and stability of the crystals in a neutron source

## Acronyms

- DMF: N,N-dimethylformamide
- DMSO: dimethylsulphoxide
- GBL:  $\gamma$ -butyrolactone
- HPGe: high-purity germanium
- ITC: inverse temperature crystallization
- $\mu\tau$ : mobility lifetime
- XRD: X-ray diffraction

## FY 2020 Peer-reviewed/Non-peer reviewed Publications

- Peer reviewed publications are anticipated upon the successful synthesis of novel perovskite structures.

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