Contract No:

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Novel Perovskite Semiconductors for the Detection of Special Nuclear Material

Highly efficient and compact detectors are required for portable, discrete radiation detection for nonproliferation monitoring as well as for radioactive 3D imaging and neutron spectroscopy. To create low-profile detectors with increased efficiency, the goal of this project is to create a novel solid-state neutron detector composed of boron based single crystal perovskites. Unlike traditional detectors that rely on separate layers to capture and detect neutrons (i.e. indirect conversion materials), directly incorporating a neutron capturing element into the perovskite unit cell combines both the neutron absorber and charge carrier generator in one material. This eliminates the energy diminishing routes (e.g. self-absorption, interlayer energy transfer, etc.) that typically occurs in indirect conversion materials. The development of novel materials for neutron detection can bolster an industry heavily dependent on ^{3}He, and offer a means for highly efficient, cost effective, and portable detection. In this project, we successfully synthesized and characterized perovskite crystals for future incorporation into boron-based neutron detectors.

Awards and Recognition

No awards or recognition were received for this seedling funding

Intellectual Property Review

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

SRNL Legal Signature

Signature **Date**

Novel Perovskite Semiconductors for the Detection of Special Nuclear Material

Project Team: K.J. Lawrence, J. D. McNamara, A. Duncan

Subcontractor: N/A

Thrust Area: NS

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Special nuclear material (SNM) detection using portable, highly efficient detectors is of paramount importance to national security for treaty verification and nonproliferation monitoring. The most mature technology for neutron detection is the ^{3}He proportional counter; however, despite its high efficiency and ubiquitous use, ^{3}He detectors have significant drawbacks, including long absorption lengths, high voltage requirements, and dependence on the availability of ^{3}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}B eliminates the need for a conversion layer and leads to high neutron absorption coefficients. In this seedling project, we successfully synthesized millimeter sized crystals using inverse temperature crystallization with sizes of 1.73 mm in length and 480 µm in thickness.

FY2019 Objectives

- Synthesize perovskite crystals using inverse temperature crystallization

Introduction

Perovskite photovoltaic devices ($CsPbX_3$ and $CH_3NH_3PbX_3$; X = Cl, I, or Br) have experienced an unprecedented and meteoric rise in device efficiency due to their unique and tunable optoelectronic properties, including exceptionally high carrier mobility-lifetime products (µτ; higher µτ 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.[1-5] Typical µτ 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.[6] 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.[7] 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.[6,8-9] Perovskites have a band gap (depending on composition) 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.[10] The customizable size of solution processed single crystal perovskites is ideal for portable, low profile detection and for 3D imaging pixelated arrays to detect the presence of radioactive material in containers. Upon the successful creation of highly efficient perovskite neutron detectors, the detectors can be mounted in a variety of packages, including on drones or in hand held detection devices to create small, stealthy detectors. For 3D imaging, the crystals can be configured into a pixel-type array for radiation source imaging with increased detector sensitivity and signal to noise ratios.

Directly incorporating boron (^{10}B) into the perovskite unit cell 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}B atoms capture incoming neutrons, the emission of charged particles (alpha particles, ^{7}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}He gas detectors, which is much larger than the difference in neutron absorbing efficiency (^{3}He is 28% more efficient than ^{10}B). Additionally, since the atomic density is much lower for ^{3}He compared to ^{10}B, the thermal neutron absorption length is much larger for ^{3}He. Therefore, at this replacement level, the fabricated crystals will exceed the sensitivity and performance of current ^{3}He detectors and do so with smaller size requirements. In this project, we successfully synthesized and characterized perovskite single crystals using ITC for future incorporation into boron-based neutron detectors.

Approach

To accomplish the goals of this project, single crystal perovskites were synthesized using inverse temperature crystallization (ITC). Perovskites exhibit an inverse temperature solubility correlation in certain solvents, where crystallization occurs at higher temperatures.[11] This is a characteristic unique to the crystal structure, so impurities and defects will be minimized by tailoring the temperature and crystalline growth rate. To enhance neutron sensitivity, ^{10}B will be directly incorporated into the unit cell by taking the place of the halogen, since BF_4 has a similar radius and chemical reactivity to the halogen.

Results/Discussion

Perovskite crystals ($CsPbBr_3$) were synthesized using inverse temperature crystallization (ITC) to create the initial synthesis procedure before incorporating boron into the crystal structure. The synthesis was carried out in dimethyl sulfoxide (DMSO) at 120 °C and was attempted both with and without seed crystals. Crystals formed in both scenarios within a few hours in solution and with no major difference in size. One challenge to synthesizing $CsPbBr_3$ crystals includes the appearance of other, non-desired phases, including Cs_4PbBr_6 and $CsPb_2Br_5$.[12] To overcome this, the solutions were filtered after heating after the appearance of yellow precipitates. The fast processing of crystals at relatively low temperatures makes this crystal growth technique a competitive candidate for industrial applications, including neutron detectors. After the crystals were successfully synthesized, they were characterized using polarized field light microscopy (**Figure 1**), scanning electron microscopy (**Figure 2**), and energy dispersive x-ray spectroscopy (EDX) (**Figure 3**).

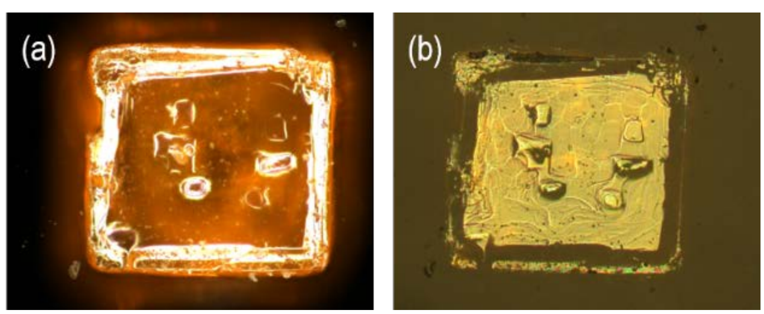

Figure 1. (a) Dark field and (b) polarized light micrographs of a perovskite crystal

Dark field and polarized light micrographs were measured for the perovskite crystals (**Figure 1a** and **Figure 1b**, respectively) and show some surface roughness of the crystals.

The size and composition of the crystals were measured using SEM/EDX. The average length of the crystals was 1.73 ± 0.08 mm and 480 µm thick. According to EDX, the average empirical formula of multiple different syntheses and crystals was found to be $CsPb_{1.1}Br_{3.3}$ (**Figure 3**). The percent difference between synthesis was 1% for bromine and 3.6% for the lead. The desired formula was created in this synthesis with high reproducibility. The appearance of other phases with undesired empirical formulas were not detectable by EDX.

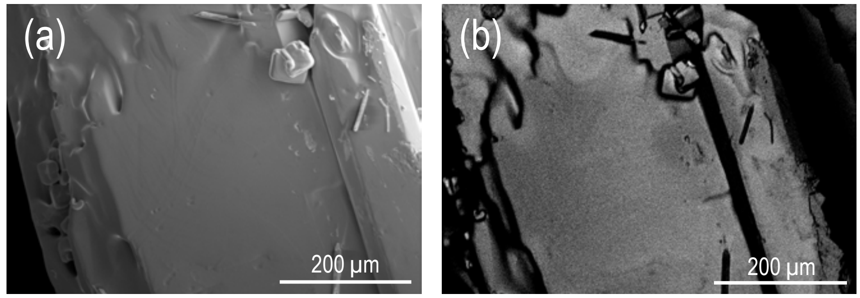

Figure 2. (a) SEM and (b) backscattered electron images of a perovskite crystal

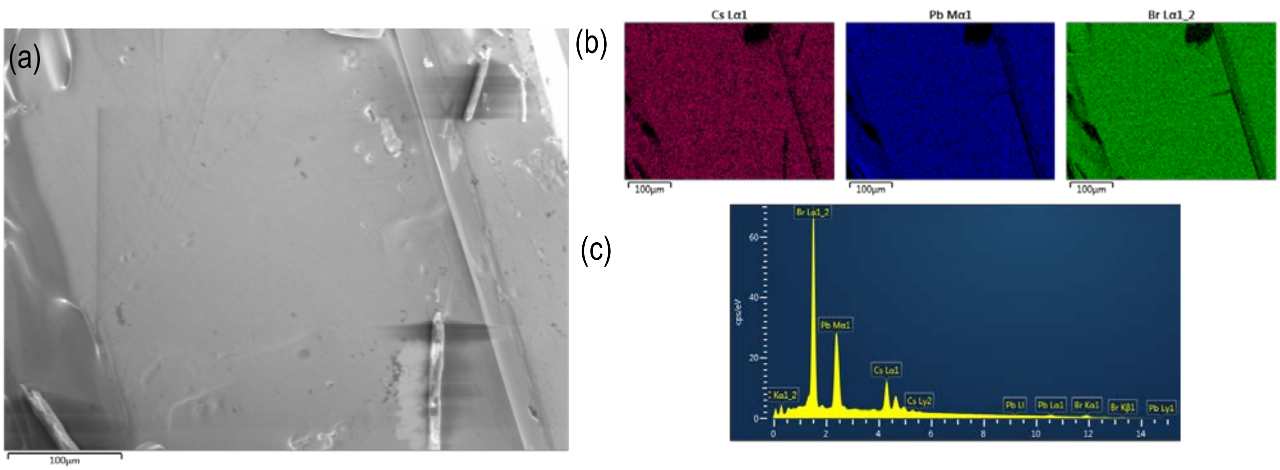

Figure 3. Representative SEM/EDX of perovskite crystals: (a) electron image; (b) elemental mapping; (c) EDX map sum spectrum for this image

FY2019 Accomplishments

Brief descriptions of accomplishments to date in bullet form. Whenever possible, accomplishments should be stated quantitatively, as in the examples below, and indicate the contribution to meeting the objectives as well as the magnitude of the improvement over past work.

- Successfully synthesized perovskite crystals using the inverse temperature crystallization technique

Future Directions

- Optimize crystal growth to directly incorporate boron into the crystal structure
- 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

FY 2019 Publications/Presentations

1. 1 publication anticipated based on perovskite synthesis

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Acronyms

μτ: carrier mobility-lifetime products
DMSO: Dimethyl sulfoxide
EDX: Energy dispersive X-Ray spectroscopy
HPGe: high purity germanium
ITC: Inverse Temperature Crystallization
SEM: Scanning Electron Microscopy
SNM: Special Nuclear Material

Intellectual Property

1 invention disclosure

Total Number of Post-Doctoral Researchers

0

Total Number of Student Researchers

0