Lead-Free Perovskite $FA_3Bi_2I_9$ Single Crystals for Radiation Detectors (May 2022)

Doup Kim, *Graduate Student, Department of Nuclear Engineering at North Carolina State University*, Ge Yang*, *Associate Professor, Department of Nuclear Engineering at North Carolina State University*, Ralph James, *Senior Scientist and Lab Fellow, Savannah River National Laboratory*

Abstract—**Perovskite semiconductors have attracted impressive attention in radiation detector fields over the past few years. The research regarding lead-based perovskites, such as $MAPbX_3$ and $CSPbX_3$ ($MA = CH_3NH_3; X = I, Cl, and\ Br$), have shown that they are promising candidates as a radiation detector. However, the intrinsic toxicity of lead to human body and the environment has been restricting use of the materials in various applications. In this regard, environmentally friendly, i.e., lead-free, perovskite semiconductors, have been in the spotlight as an emerging detector material. Here, we report our efforts to develop $FA_3Bi_2I_9$ ($F = CH(NH_2)_2$) for radiation detector applications. In this study, we grow $FA_3Bi_2I_9$ single crystals, characterize their physical properties and examine their potential as an X-ray and γ-ray detector. Large $FA_3Bi_2I_9$ single crystals were grown, and Ag/$FA_3Bi_2I_9$/Ag detector was fabricated. Their bandgap (~2.03 eV) and trap-filled limit (TFL) voltage V_{TFL} (0.66 V) were measured. A high resistivity ($4.97 \times 10^{11} \Omega \cdot cm$) was achieved. The X-ray response shows a good linearity with a dose rate range from $0.02 mGys^{-1}$ to $1.83 mGys^{-1}$. Our results demonstrate that as-grown $FA_3Bi_2I_9$ single crystals exhibit bias dependence and have excellent stability during X-ray exposure. Furthermore, we also achieved the direct response of $FA_3Bi_2I_9$ single crystals to gamma-rays and alpha particles. Our results indicate that the $FA_3Bi_2I_9$ single crystals have excellent potential for high energy radiation detection.**

Index Terms—**Radiation Detectors, Alpha particle, Gamma-ray, X-ray, Perovskites**

I. Introduction

Advanced detector technologies for high energy radiation, such as X-rays and γ-rays, have played an important role in a wide range of applications including nuclear security [1-2], medical imaging [3-4] and diagnosis [5], non-destructive defect inspection [6], and homeland security [7-8]. Accordingly, research on developing innovative technologies to better detect high energy radiation, especially detecting materials, have been active. Among them, room temperature semiconductor radiation detectors have attracted special attention due to their high intrinsic efficiency, high energy resolution and their capabilities to operate at ambient temperature.

One class of room temperature semiconductor detector materials that has been in the spotlight over the past few years is perovskites, which are usually operable at room-temperature, has high absorption coefficient, high carrier mobility and lifetime, and can be produced at a relatively lower cost. In order to explore the use of perovskite materials as radiation detectors, there have been many on-going studies, such as $MAPbX_3$ ($MA = CH_3NH_3; X = I, Cl, and\ Br$) [9-10] and $CsPbX_3$ [11-12] that use lead (Pb) with a high Z number as a key component. However, these lead-based perovskites have adverse effects, i.e., the toxicity of lead on the human body and environment. Therefore, various lead-free perovskite materials are being actively pursued. In this regard, bismuth (Bi)-based perovskites, e.g., $Cs_2AgBiBr_6$, which could replace lead-based perovskites, have been studied intensively, and a series of important results have been demonstrated regarding their radiation detector applications.

Here, among lead-free perovskites, we report our efforts to develop $FA_3Bi_2I_9$ ($F = CH(NH_2)_2$) for radiation detector applications. In this study, we grow $FA_3Bi_2I_9$ single crystals, characterize their physical properties and examine their potential as an X-ray and γ-ray detector. Methods

II. Results and Discussion

A. Optical Properties

UV-vis transmission spectrum of $FA_3Bi_2I_9$ single crystals was performed. By using the transmission spectrum, the absorbance and absorption coefficient can be used for getting optical bandgap via the Tauc equation [15-16]:

$$(\alpha h\upsilon)^{1/n} = A(h\upsilon - E_g) \qquad (1)$$

The transmission cutoff edge is about 610 nm, which is corresponding with the result of an optical bandgap of 2.033 eV. This is consistent with the work reported by another group [14]. The current-voltage characteristics within a bias range from -100 V to +100 V were collected. The estimated resistivity of $FA_3Bi_2I_9$ single crystals was about $4.97 \times 10^{11} \Omega \cdot cm$, which ensures a low leakage current and low electronic noise.

Ge Yang and Doup Kim. Authors are with the Department of Nuclear Engineering at North Carolina State University, Raleigh, NC 27695 USA (e-mails: gyang9@ncsu.edu; dkim33@ncsu.edu).

Ralph James. Author is with Savannah River National Laboratory, Aiken, SC 29808 USA (e-mail: ralph.james@srnl.doe.gov).

The trap-filled limit (TFL) voltage (V_{TFL}) of $FA_3Bi_2I_9$ single crystals is about 0.66 V. The detailed cathodoluminescence (CL) and photoluminescence (PL) measurements together with their mechanical properties will be presented in the presentation.

B. X-ray Response

Figure 1 shows the response of $FA_3Bi_2I_9$ single crystals to X-rays. Figure 1 (Left) describes the X-ray response of $FA_3Bi_2I_9$ single crystals to X-rays with a dose rate range from $0.02\ mGys^{-1}$ to $1.83\ mGys^{-1}$ under a bias voltage of 10 V. The data indicate that the current increased linearly as the dose rate was increased. Figure 1 (Right) demonstrates the response of $FA_3Bi_2I_9$ single crystals to X-rays with a dose rate of $0.02\ mGys^{-1}$ under different bias voltages. Our X-ray response tests of $FA_3Bi_2I_9$ single crystals demonstrated their bias dependence showed a good stability during X-ray exposure.

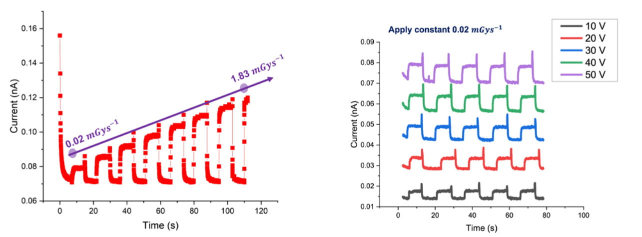

Figure. 1. (Left) X-ray response of $FA_3Bi_2I_9$ single crystal to X-rays with dose rate range from $0.02\ mGys^{-1}$ to $1.83\ mGys^{-1}$ with a bias voltage of 10 V. (Right) The bias dependence of X-ray response of $FA_3Bi_2I_9$ single crystal with constant dose rate of $0.02\ mGys^{-1}$.

III. Conclusion

In summary, we successfully grew $FA_3Bi_2I_9$ single crystals and demonstrated their potential for radiation detection. Our results confirm that as-grown $FA_3Bi_2I_9$ single crystals have appropriate bandgap, high resistivity, and excellent stability during X-ray exposure and demonstrated the high potential of the crystals for X-ray and gamma detection.

References

[1] Swoboda, M., R. Arlt, V. Gostilo, A. Lupilov, M. Majorov, M. Moszynski, and A. Syntfeld. "Spectral gamma detectors for hand-held radioisotope identification devices (RIDs) for nuclear security applications." IEEE transactions on nuclear science 52, no. 6 (2005): 3111-3118.

[2] Johns, Paul M., and Juan C. Nino. "Room temperature semiconductor detectors for nuclear security." Journal of Applied Physics 126, no. 4 (2019): 040902.

[3] Darambara, Dimitra G. "State-of-the-art radiation detectors for medical imaging: Demands and trends." Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 569, no. 2 (2006): 153-158.

[4] Kandarakis, I., D. Cavouras, P. Prassopoulos, E. Kanellopoulos, C. D. Nomicos, and G. S. Panayiotakis. "Evaluating Zn2SiO4: Mn phosphor for use in medical imaging radiation detectors." Applied Physics A 67, no. 5 (1998): 521-525.

[5] Van Eijk, Carel WE. "Radiation detector developments in medical applications: inorganic scintillators in positron emission tomography." Radiation protection dosimetry 129, no. 1-3 (2008): 13-21.

[6] Lu, Yuzhen, and Renfu Lu. "Non-destructive defect detection of apples by spectroscopic and imaging technologies: a review." Transactions of the ASABE 60, no. 5 (2017): 1765-1790.

[7] Klann, Raymond T., Jason Shergur, and Gary Mattesich. "Current state of commercial radiation detection equipment for homeland security applications." Nuclear technology 168, no. 1 (2009): 79-88.

[8] Park, Hye Min, and Koan Sik Joo. "Performance characteristics of a silicon photomultiplier based compact radiation detector for Homeland Security applications." Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 781 (2015): 1-5.

[9] Wu, Haodi, Yongshuai Ge, Guangda Niu, and Jiang Tang. "Metal halide perovskites for X-ray detection and imaging." Matter 4, no. 1 (2021): 144-163.

[10] Fan, Zhengfang, Jiang Liu, Wentao Zuo, Guoqiang Liu, Xulin He, Kun Luo, Qinyan Ye, and Cheng Liao. "Solution-Processed MAPbBr3 and CsPbBr3 Single-Crystal Detectors with Improved X-Ray Sensitivity via Interfacial Engineering." physica status solidi (a) 217, no. 9 (2020): 2000104.

[11] He, Yihui, Matthew Petryk, Zhifu Liu, Daniel G. Chica, Ido Hadar, Charles Leak, Weijun Ke et al. "CsPbBr3 perovskite detectors with 1.4% energy resolution for high-energy γ-rays." Nature Photonics 15, no. 1 (2021): 36-42.

[12] Zhang, Hongjian, Fangbao Wang, Yufei Lu, Qihao Sun, Yadong Xu, Bin-Bin Zhang, Wanqi Jie, and Mercouri G. Kanatzidis. "High-sensitivity X-ray detectors based on solution-grown caesium lead bromide single crystals." Journal of Materials Chemistry C 8, no. 4 (2020): 1248-1256.

[13] Szklarz, Przemysław, Anna Gągor, Ryszard Jakubas, Piotr Zieliński, Anna Piecha-Bisiorek, Jakub Cichos, Mirosław Karbowiak, Grażyna Bator, and Agnieszka Ciżman. "Lead-free hybrid ferroelectric material based on formamidine:[NH 2 CHNH 2] 3 Bi 2 I 9." Journal of Materials Chemistry C 7, no. 10 (2019): 3003-3014.

[14] Li, Wei, Deyu Xin, Shujie Tie, Jiwei Ren, Siyin Dong, Lin Lei, Xiaojia Zheng, Yiying Zhao, and Wen-Hua Zhang. "Zero-Dimensional Lead-Free FA3Bi2I9 Single Crystals for High-Performance X-ray Detection." The Journal of Physical Chemistry Letters 12, no. 7 (2021): 1778-1785.

[15] Makuła, Patrycja, Michał Pacia, and Wojciech Macyk. "How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV–Vis spectra." The Journal of Physical Chemistry Letters 9, no. 23 (2018): 6814-6817.

[16] Jubu, P. R., F. K. Yam, V. M. Igba, and K. P. Beh. "Tauc-plot scale and extrapolation effect on bandgap estimation from UV–vis–NIR data–a case study of β-Ga2O3." Journal of Solid State Chemistry 290 (2020): 121576.

[17] Zheng, Xiaojia, Wei Zhao, Peng Wang, Hairen Tan, Makhsud I. Saidaminov, Shujie Tie, Ligao Chen, Yufei Peng, Jidong Long, and Wen-Hua Zhang. "Ultrasensitive and stable X-ray detection using zero-dimensional lead-free perovskites." Journal of Energy Chemistry 49 (2020): 299-306.

[18] Steele, Julian A., Weicheng Pan, Cristina Martin, Masoumeh Keshavarz, Elke Debroye, Haifeng Yuan, Subhasree Banerjee et al. "Photophysical Pathways in Highly Sensitive Cs2AgBiBr6 Double-Perovskite Single-Crystal X-Ray Detectors." Advanced Materials 30, no. 46 (2018): 1804450.