

Next-Generation Scintillation Materials: Low-Dimensional All-Inorganic Cu(I) Halides

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Halide perovskites have become leading candidates for high-performance optoelectronic devices and radiation detectors. Currently more widely adopted method for radiation detection is using scintillators, which convert the ionizing radiation into UV/VIS/NIR light. Recent studies have shown the great potential of low-dimensional all-inorganic halide perovskites as high-performance scintillators thanks to the nature their intense self-trapped exciton emission. In this work, we report a set of ultrabright and highly efficient one-dimensional (1D) and zero-dimensional (0D) perovskite-like halide scintillators in the form of single crystals and thin films, such as Cs₃Cu₂I₅, In⁺/Tl⁺ doped Cs₃Cu₂I₅, CsCu₂I₃, and Cs₅Cu₃Cl₆I₂, for X-ray imaging and gamma spectroscopy applications. They show simultaneously high effective atomic number (Z_{eff}), non-hygroscopic, self-absorption free, low afterglow, high scintillation yield, and excellent energy resolution characteristics which is a unique feature among scintillation materials. Thus, they can serve as versatile scintillators covering a wide range of radiation energies for various applications incl. high-energy physics, homeland security and medical imaging.

Summary

I. INTRODUCTION

Recently, low dimensional perovskite-like metal halides for light emitting and scintillation applications have drawn tremendous attention due to their extremely high photoluminescence quantum yields (PLQYs) and large Stokes shift, among which ternary copper(I) halides are the most studied ones because of their excellent photophysical properties and decent stability. For instance, Tang reported the ultrahigh LY (~90,000 photons/MeV) of Rb₂CuBr₃ scintillators with an emission peak at 385 nm [1]. Other copper halide scintillators have also been investigated, such as Rb₂CuCl₃, Cs₃Cu₂Cl₅ and (TBA)CuX₂ (TBA = tetrabutylammonium cation; X = Cl, Br) in the forms of single or poly-crystals. However, one serious shortage for Rb₂CuBr₃ scintillator is that the Rb element shows high natural radioactivity, which may hinder its practical application in scintillator materials.

This work reports a series of high-performance cesium copper(I) halide scintillators with strong self-trapping exciton (STE) emissions, such as Cs₃Cu₂I₅, CsCu₂I₃, and Cs₅Cu₃Cl₆I₂ [2-4]. They show simultaneously high effective atomic number (Z_{eff}), non-hygroscopic, self-absorption free, low afterglow, high scintillation yield, and excellent energy resolution characteristics which is absolutely unique feature among scintillation materials. Moreover, after doping with Tl⁺ and In⁺, the X-ray and gamma-ray detection performance of Cs₃Cu₂I₅ was further improved thanks to the enhanced harvesting of charge carriers (and excitons) [5,6].

II. RESULTS AND DISCUSSION

Low-dimensional perovskite-like halide single crystals Cs₃Cu₂I₅, CsCu₂I₃, and Cs₅Cu₃Cl₆I₂ with a diameter of 7 mm were grown by the Bridgman method. The thin films of these compounds were prepared via the vapor deposition method. All of them have high Z_{eff}, no hygroscopicity, and low melting point. Their crystal structure belongs to the orthogonal crystal system with the dipole-allowed direct bandgap of 3.5~3.7 eV. The valence band maxima are composed of the Cu 3d orbitals and the conduction band minima are composed of the Cu 4s. The halogen p orbitals also contribute to the valence and conduction bands.

Cs₃Cu₂I₅ single crystal has an orthorhombic crystal structure, Pnma space group and 0D electron structure. The density and Z_{eff} are 4.51 g/cm³ and 52.2, respectively. Its intense STE emission centered at 445 nm shows a large Stokes shift of 1.35 eV, which excludes self-absorption. Its scintillation yield is 32 000 photons/MeV with an ultra-low afterglow of 0.03% at 10 ms under X-ray radiation. Cs₃Cu₂I₅ also has excellent energy resolution of 3.4±0.2% at 662 keV, high light yield of 29,000 photons/MeV, and a principal decay time of 967 ns under ¹³⁷Cs γ-ray radiation. After doping Tl⁺ into the lattice, The PLQY of Cs₃Cu₂I₅:Tl crystal was further increased from 70% to 80%. A very low X-ray detection limit (66.3 nGyair/s) of Cs₃Cu₂I₅:Tl single crystal is only 1/83 of the medical X-ray diagnostic requirements. Extremely low X-ray afterglow of only 0.17% at 10 ms is one order of magnitude lower than commercial CsI:Tl crystals. Cs₃Cu₂I₅:Tl crystal also has excellent γ-ray detection capability, with a light yield of up to 87,000 photons/MeV and an energy resolution of 3.4% at 662 keV.

1D CsCu₂I₃ is composed of Cs⁺ and [CuI₄]_n³ⁿ⁻ tetrahedral chains. It has a high density of 5.01 g/cm³ and a high Z_{eff} of 50.6. Its STE emission peaks at 570 nm and has a large Stokes shift of 1.54 eV. Its scintillation yield is 16,000 photons/MeV with a principal decay time of 97 ns. It is very worth noting that it has an extremely

low afterglow level of 0.008% at 10 ms, which is three orders of magnitude lower than that of commercial CsI:Tl scintillator.

The crystal structure of Cs₅Cu₃Cl₆I₂ can be described as 1D zigzag [Cu₃Cl₆I₂]_n chains separated by Cs⁺ cations. The 1D chains of [Cu₃Cl₆I₂]_n consists of connected [CuCl₂I]₂ units and single [CuCl₂I]₃ units. Due to the strong exciton-phonon coupling, Cs₅Cu₃Cl₆I₂ emits bright cyan light (475 nm) associated with STE emission with a large Stokes shift of 1.2 eV. High crystal quality and large exciton binding energy of 1 eV render a high PLQY of 70% for Cs₅Cu₃Cl₆I₂. The scintillation yield of Cs₅Cu₃Cl₆I₂ can reach 87,000 photons/MeV, which is one of the highest value ever reported for self-activated scintillators.

III. CONCLUSIONS

We developed a series of bright and sensitive low-dimensional perovskite-like Cu(I) halide scintillators and demonstrated their excellent X-ray imaging and gamma spectroscopy capability. They show the desirable and rare combination of high Z_{eff}, non-hygroscopic, self-absorption free, high scintillation yield, and excellent detection limit characteristics which are unique among scintillation materials. Moreover, cheap raw materials, low temperature melting point, and possibility to scale-up the crystal size in industrial manufacturing will result in very competitive pricing which is critically important for applications. Thus, the low-dimensional Cu(I) halides could be regarded as next-generation scintillation materials.

REFERENCES

- [1] B. Yang, L. Yin, G. Niu, J.-H. Yuan, K.-H. Xue, Z. Tan, X.-S. Miao, M. Niu, X. Du, H. Song, E. Lifshitz, and J. Tang, "Lead-Free Halide Rb₂CuBr₃ as Sensitive X-Ray Scintillator," *Advanced Materials*, vol. 31, no. 44, pp. e1904711, Nov, 2019.
- [2] S. Cheng, A. Beitlerova, R. Kucerkova, M. Nikl, G. Ren, and Y. Wu, "Zero-Dimensional Cs₃Cu₂I₅ Perovskite Single Crystal as Sensitive X-Ray and γ -Ray Scintillator," *physica status solidi (RRL) –Rapid Research Letters*, vol. 14, no. 11, pp. 2000374, 2020.
- [3] Q. Wang, M. Nikl, S. Cheng, G. Ren, Y. Wu, "Undoped and Tl-doped Cs₃Cu₂I₅ thin film as potential X-ray scintillators," *physica status solidi (RRL) –Rapid Research Letters*, vol.15, pp. 2100422, 2021.
- [4] S. Cheng, A. Beitlerova, R. Kucerkova, E. Mihokova, M. Nikl, Z. Zhou, G. Ren, and Y. Wu, "Non-Hygroscopic, Self-Absorption Free, and Efficient 1D CsCu₂I₃ Perovskite Single Crystal for Radiation Detection," *ACS Appl Mater Interfaces*, vol. 13, no. 10, pp. 12198-12202, Mar 17, 2021.
- [5] S. Cheng, M. Nikl, A. Beitlerova, R. Kucerkova, X. Du, G. Niu, Y. Jia, J. Tang, G. Ren, and Y. Wu, "Ultra-bright and Highly Efficient All-Inorganic Zero-Dimensional Perovskite Scintillators," *Advanced Optical Materials*, vol. 9, no. 13, 2021.
- [6] Q. Wang, Q. Zhou, M. Nikl, J. Xiao, A. Beitlerova, S. Cheng, X. Wen, J. Wang, G. Niu, J. Tang, G. Ren, Y. Wu, "Highly resolved X-ray imaging enabled by In(I) doped perovskite-like Cs₃Cu₂I₅ single crystal scintillator," *Advanced Optical Materials* DOI:10.1002/adom.202200304.

Primary author: Prof. WU, Yuntao (Shanghai Institute of Ceramics, Chinese Academy of Sciences)

Presenter: Prof. WU, Yuntao (Shanghai Institute of Ceramics, Chinese Academy of Sciences)

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