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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 (Zeff), 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 (Zeff), 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 Zeff, 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 Zeff 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 Zeff 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 $Cs_5Cu_3Cl_6I_2$ can be described as 1D zigzag $[Cu_3Cl_6I_2]_n^{5n-}$ chains separated by Cs^+ cations. The 1D chains of $[Cu_3Cl_6I_2]_n^{5n-}$ consists of connected $[CuCl_2I]_2^{4-}$ units and single $[CuCl_2I_2]^{3-}$ units. Due to the strong exciton-phonon coupling, $Cs_5Cu_3Cl_6I_2$ 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 $Cs_5Cu_3Cl_6I_2$. The scintillation yield of $Cs_5Cu_3Cl_6I_2$ can reach 87,000 photons/MeV, which is one of the highest value ever reported for self-activated scintillators.

III. CONCLUSIONS

We developed a serious 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 Zeff, 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.

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