



Research Highlight

Lead-free perovskites for X-ray detecting

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X-ray detection is of great importance for computed tomography scanning, security inspection, non-destructive testing of industrial products and other detection applications [1,2]. Due to the potential cancer risk caused by X-ray inspection, there is always room to achieve X-ray detectors with even better sensitivity and detection limit. There are two available approaches detecting X-rays, the first is indirect conversion using scintillators to convert X-ray photons into light and then a photodiode to convert light into charges; the other is direct conversion of X-ray photons into electrical current [3]. The drawback of scintillator-based detectors is the light scattering in active layer and thereby image blurring [4]. The direct conversion through amorphous or crystalline semiconductors effectively overcomes such shortcoming, and also enables high sensitivity and low detection limit due to a simpler system configuration [5].

Suitable semiconductors for the direct conversion X-ray detection should have: (1) high density and high atomic number, since absorption coefficient $\alpha \propto Z^4/E^3$, where Z and E denote respectively the atomic number of material and the radiation energy; (2) high $\mu\tau$ product of the carrier mobility and lifetime for efficient charge collection; (3) high resistivity to suppress the noise current; (4) good stability for long-term operation [3]. Thereby, the most studied semiconductors for direct conversion X-ray detecting are α -Se, HgI_2 and CdZnTe . Detectors based on α -Se have been commercialized for mammography, general radiography and fluoroscopy [6]. The main drawback, however, is its low quantum efficiency for high-energy X-rays due to its low attenuation efficiency [7]. As for HgI_2 and CdZnTe , the toxicity of Hg and Cd, as well as the difficulty in depositing a uniform film onto the thin-film transistors (TFT) arrays are the main limitations in applications.

Recent years, organic-inorganic hybrid lead halide perovskites, which have been demonstrated as an exceptional photovoltaic material, are also developed for X-ray detection because of their high X-ray attenuation efficiency, high $\mu\tau$ product, low-cost solution growth of single crystals (SCs) and convenience of depositing uniform films [8,9]. Han, Park and co-workers [10] recently reported a $10\text{ cm} \times 10\text{ cm}$ flat panel X-ray detectors from printable $\text{CH}_3\text{NH}_3\text{PbI}_3$ to obtain low-dose X-ray imaging.

Although lead halide perovskites have made remarkable progress in X-ray detection, there are still some remaining challenges

restricting their development and further commercialization. (1) The toxicity of lead limits the use of lead halide perovskite in electronic devices. Halide perovskites tend to decompose in water and their leaching into the environment could threaten local biological system. Moreover, Pb is accumulative in human body causing several brain related symptoms such as abdominal pain, constipation and headaches. A large dose of Pb ingest is fatal and children is particularly vulnerable to Pb poisoning [11]. (2) The stability of lead halide perovskite is still under debate, and long-term operation under a high voltage and radiation needs to be studied.

In a recent report published in *Nature Photonics*, Tang and co-workers [12] reported $\text{Cs}_2\text{AgBiBr}_6$ single-crystal X-ray detectors with a low detection limit. $\text{Cs}_2\text{AgBiBr}_6$ preserves the perovskite structure and abandons the use of toxic Pb^{2+} . The involvement of heaviest stable element Bi and inorganic composition enables $\text{Cs}_2\text{AgBiBr}_6$ a relatively high average atomic number ($Z = 53.1$), as well as good thermal and moisture stability compared to Pb based perovskites (Fig. 1a, b). More importantly, the indirect transition nature of $\text{Cs}_2\text{AgBiBr}_6$ makes its carrier lifetime (660 ns) [13] and thus $\mu\tau$ product ($6.3 \times 10^{-3}\text{ cm}^2\text{ V}^{-1}$) long enough for carrier collection (Fig. 1d). Also, the higher resistivity of the $\text{Cs}_2\text{AgBiBr}_6$ SCs (10^9 – $10^{11}\text{ }\Omega\text{ cm}$) than MAPbX_3 ($X = \text{Cl, Br, I}$; 10^7 – $10^8\text{ }\Omega\text{ cm}$), and suppressed ionic migration, both contribute to the reduced noise current and thereby low detection limit.

In order to obtain the high resistivity, the researchers studied the cation disordering (Ag_{Bi} and Bi_{Ag} antisites) in the $\text{Cs}_2\text{AgBiBr}_6$ SCs and found that inert atmosphere annealing could decrease such disordering. Then the trap density decreased from 4.54×10^9 to $1.74 \times 10^9\text{ cm}^{-3}$, while the carrier mobility increased from 3.17 to $11.81\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ through annealing process (Fig. 1c). Moreover, through surface treatment with an isopropanol or ethyl acetate rinse, they also removed the surface conduction channel and further increased the resistivity of the $\text{Cs}_2\text{AgBiBr}_6$ SCs to 10^9 – $10^{11}\text{ }\Omega\text{ cm}$.

The ionic migration of $\text{Cs}_2\text{AgBiBr}_6$ SCs was compared with MAPbBr_3 through experimental and theoretical studies. The field-driven ionic migration has been reported as a non-negligible problem that will not only increases the dark current of the device but also makes it unstable under bias voltage. Tang and co-workers [12] found the $\text{Cs}_2\text{AgBiBr}_6$ SCs exhibited an effective migration barrier of 348 meV, nearly three times that of MAPbBr_3 SCs (127 meV), indicating the more difficult ionic migration in $\text{Cs}_2\text{AgBiBr}_6$. Theoretical calculations found Br vacancies (V_{Br}) in $\text{Cs}_2\text{AgBiBr}_6$ and

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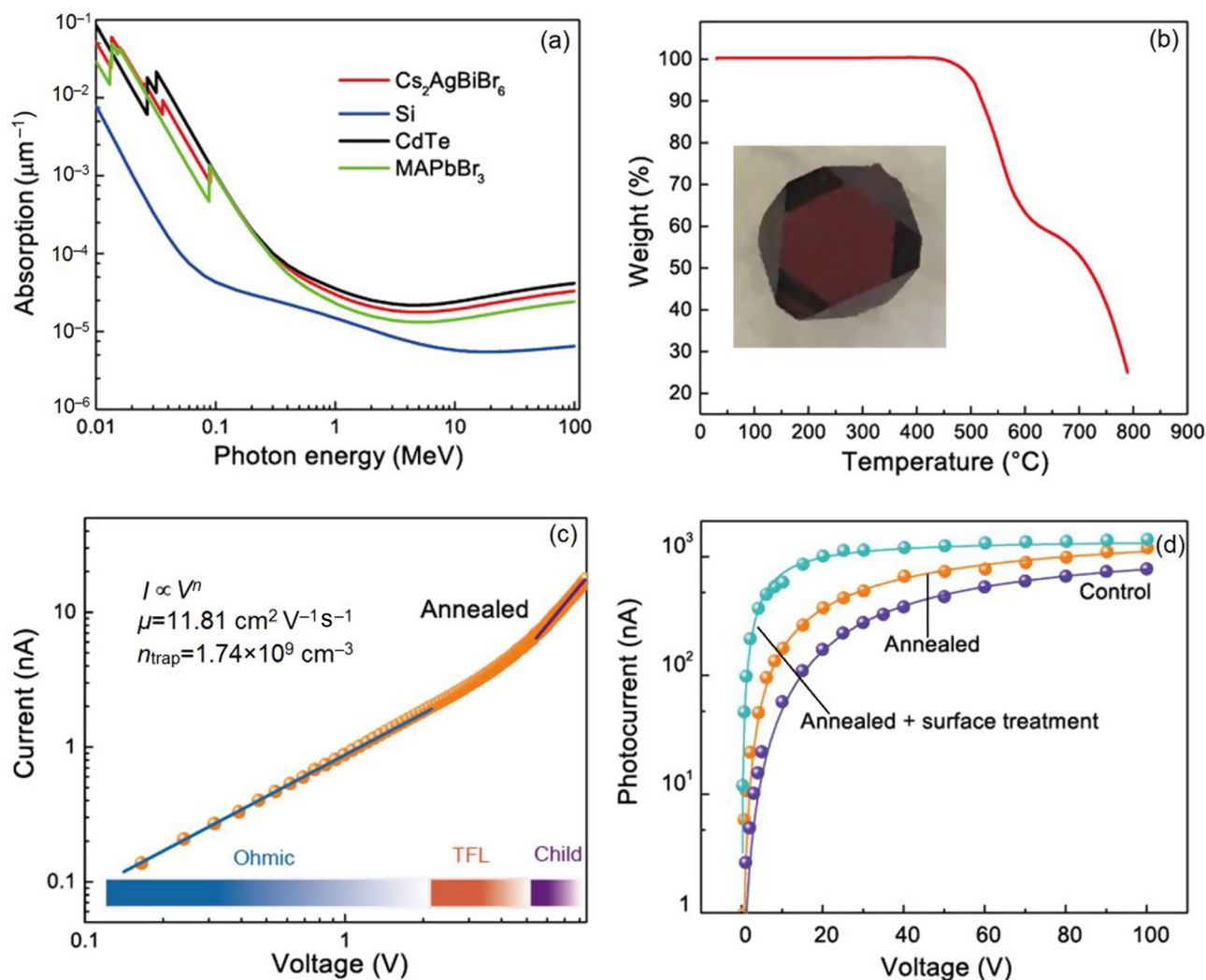


Fig. 1. (Color online) Cs₂AgBiBr₆ perovskite properties. (a) The absorption coefficient of Cs₂AgBiBr₆, MAPbBr₃, CdTe, and Si as a function of photon energy. (b) Thermogravimetric analysis of Cs₂AgBiBr₆. (c) Current-voltage curves for the annealed Cs₂AgBiBr₆ SC. (d) Bias-dependent photoconductivity of as-received, thermally annealed, thermally annealed and then surface-rinsed Cs₂AgBiBr₆ SCs. Reprinted with permission from Ref. [12], Copyright © 2017 Nature Publishing Group.

MAPbBr₃ as the most possible migration species. The diffusion barrier for V_{Br} in Cs₂AgBiBr₆ is 0.33 eV, higher than that of MAPbBr₃ (~0.2 eV), which echoes the experimental results.

Under 30 keV X-ray photons, the Cs₂AgBiBr₆ SCs based X-ray detectors achieved a sensitivity of 8 μC Gy_{air}⁻¹ cm⁻² (1 V bias). With bias increasing to 50 V (field of 25 V mm⁻¹), the sensitivity could be enhanced to 105 μC Gy_{air}⁻¹ cm⁻² (Fig. 2b), which is four times higher than α-Se detectors (20 μC Gy_{air}⁻¹ cm⁻², bias 10 V μm⁻¹). Cs₂AgBiBr₆ SC detectors exhibited a low detection limit of 59.7 nGy_{air} s⁻¹ with 5 V bias (Fig. 2c), which is much lower than that required for regular medical diagnostics (5.5 μGy_{air} s⁻¹). The device also exhibited excellent radiation stability. The detection limit (59.7 nGy_{air} s⁻¹) of the Cs₂AgBiBr₆ SCs detector without any encapsulations remained unchanged under continuous X-ray radiations (total dosage of 9,257 mGy_{air}, dose rate of 138.7 μGy_{air} s⁻¹) with a constant 5 V bias (Fig. 2d). Such good stability is very important for real applications.

More work on Cs₂AgBiBr₆-based X-ray detectors is still needed, such as further improvement of the detector sensitivity, evaluation of the response speed and ghosting effect, and integrating Cs₂AgBiBr₆ with thin-film-transistor active matrix arrays and read-out integrated circuits.

Overall, the Cs₂AgBiBr₆-based X-ray detectors are competitive to lead halide perovskite detectors and also commercial products, and have the potential to become a game changer for X-ray imaging field. In addition, although lead-free perovskites always show inferior performance when applied in solar cells and LEDs etc., the results of Tang and co-workers will undoubtedly inspire more researchers to develop and engineer lead-free perovskites for some specific applications.

Conflicts of interest

The authors declare that they have no conflicts of interest.

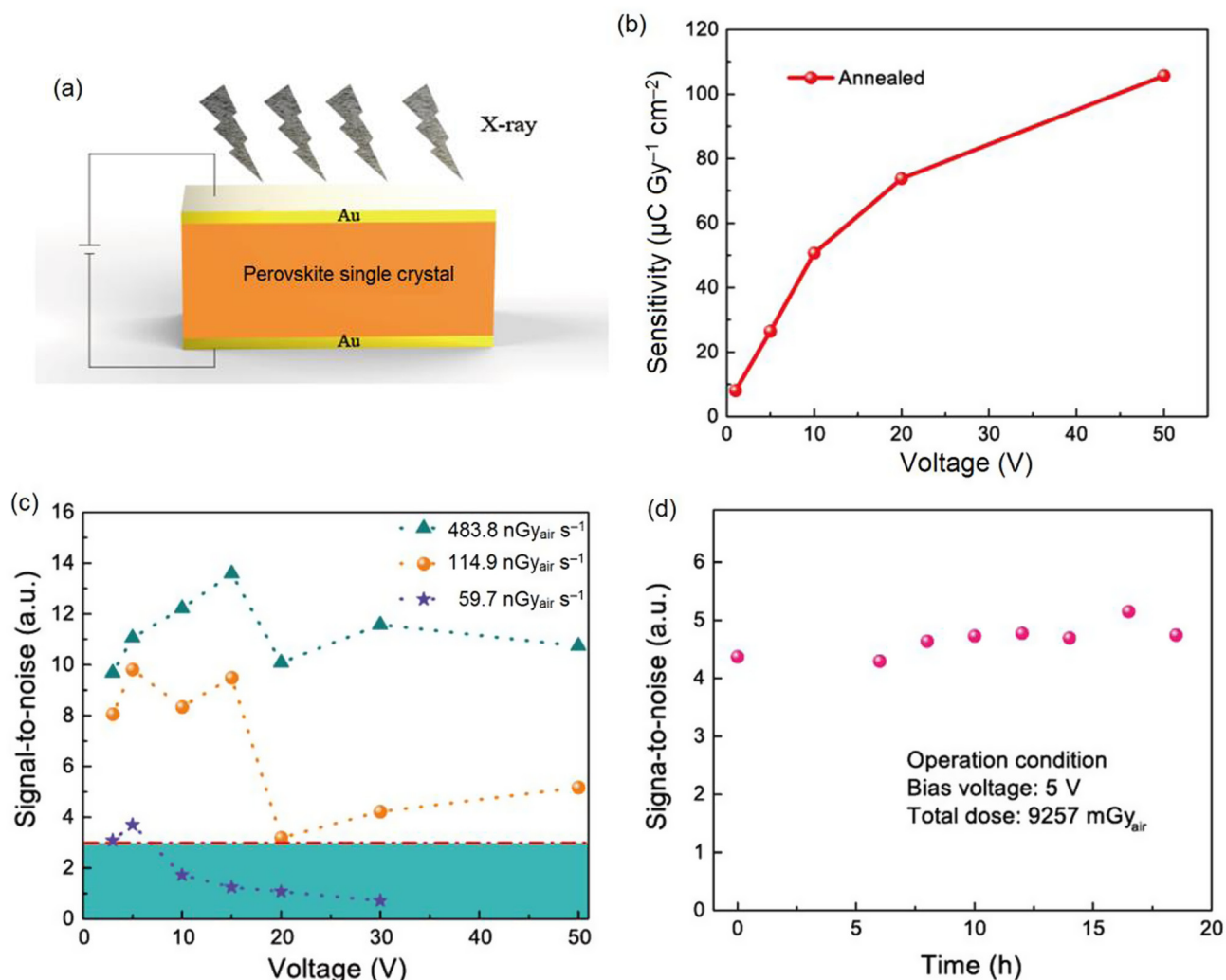


Fig. 2. (Color online) Performance of $\text{Cs}_2\text{AgBiBr}_6$ SC X-ray detector. (a) Schematic illustrations of the Au/ $\text{Cs}_2\text{AgBiBr}_6$ SC/Au device under X-ray radiation. (b) The obtained sensitivity under different bias of the annealed device. (c) The derived signal-to-noise ratio of the device through calculating the standard deviation of X-ray photocurrent. The dash line represents a signal-to-noise ratio (SNR) of 3, and thus the detection limit is $59.7 \text{ nGy}_{\text{air}} \text{ s}^{-1}$ at 5 V bias. (d) Operational stability of $\text{Cs}_2\text{AgBiBr}_6$ SC X-ray detector without any encapsulation. Reprinted with permission from Ref. [12], Copyright © 2017 Nature Publishing Group.

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