Ion Migration Controlled Stability in α -Particle Response of CsPbBr_{2.4}Cl_{0.6} Detectors

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ABSTRACT: Halide perovskites have been considered as nuclear radiation detection materials due to their high mobility, long carrier lifetime, and high absorption coefficient. However, it has been reported that the ion migration increases the dark current of halide perovskite detectors and hinders the stable response to high energy photons or particles. In this work, we report the utilization of the “voltage cycling” technique to obtain the stable α -particle spectra in a CsPbBr_{2.4}Cl_{0.6} device. Also, by measuring the time-dependent stability and the effect of electric field strength, we can gain insight into the phenomena causing instability in these devices. Accordingly, the influence of ion migration on the charge transport properties and energy spectra in CsPbBr_{2.4}Cl_{0.6} detectors was also revealed. Our investigation demonstrates the strong correlation between ion migration processes and stable energy spectra in halide perovskite materials.

1. INTRODUCTION

Recently, lead-based perovskite halides APbX₃ (A = Cs⁺/MA⁺ = CH₃NH₃⁺/FA = HC(NH₂)₂⁺, X = Cl/Br/I) received more attention as nuclear radiation detection materials. Kovalenko and co-workers studied the use of cesium formamidinium lead halide perovskite (Cs_xFA_{1-x}PbI_{3-y}Br_y (x = 0–0.1, y = 0–0.6)) single crystals for γ -ray detection.¹ The special mixed cation and mixed halide composition of this Cs_{0.1}FA_{0.9}PbI_{2.8}Br_{0.2} single crystal device achieved a spectroscopic response to γ -ray photons (59.6 keV ²⁴¹Am). Huang demonstrated use of the dopant-compensated methylammonium perovskite alloy MAPbBr_{2.94}Cl_{0.06} as a room-temperature γ -ray detector, which gave a 10-fold improvement in bulk resistivity of 3.6 × 10⁹ Ω·cm compared to the pure bromide equivalent perovskite.² The use of a guard ring electrode in the detector reduced the crystal surface leakage current and the corresponding device dark current, and a distinguishable ¹³⁷Cs energy spectrum was obtained with a resolution of 6.5%. Kanatzidis and co-workers demonstrated that devices with symmetric electrode metals based on halide perovskite crystals show large leakage currents and ion migration effects, which impeded the detection of γ -ray photons and charged particles. They found that devices fabricated with asymmetric contacts, such as (Ga or In)/CsPbBr₃(MAPbI₃)/Au acted as Schottky-type detectors, which could effectively reduce the leakage currents.^{3–5} Finally, various reports have shown that CsPbBr₃ single crystals exhibit a good energy spectra resolution (3.9% @122 keV ⁵⁷Co and 3.8% @662 keV ¹³⁷Cs) for γ -ray photons.⁵

Although great achievements have been made in these previous works, there remains a major challenge for halide perovskite devices to obtain stable radiation spectra. On the basis of the halide perovskite single crystals, such as Cs_{0.1}FA_{0.9}PbI_{2.8}Br_{0.2},¹ MAPbBr_{2.94}Cl_{0.06},² CsPbBr₃,^{4–6} MAPbBr₃,^{7,8} and MAPbI₃,³ the detectors demonstrated high energy spectral resolution of γ -rays or α -particles at room temperature. These successes were dependent on the complex and delicate designs of the materials and devices. Because typical nuclear radiation detectors are usually operated under high voltages, perovskite materials tend to be more susceptible to severe ion migration^{9–11} in comparison to the applications of solar cells^{12,13} and light-emitting diodes (LEDs).¹⁴ The exact nature of the species of mobile ions is still unclear. In a representative halide perovskite material MAPbI₃, I[–],^{15,16} hydrogenic impurities,¹⁷ and MA⁺¹⁸ were experimentally and theoretically identified as the possible mobile ions. Br[–] or Cs⁺ was proposed as the possible mobile ions in CsPbBr₃ by different people.^{11,19} The defects in the perovskites are deemed to provide the ion migration paths.^{9,15} Thus, halide perovskite crystals with different types and concentrations of defects show variable ion migration behavior. The ion migration happened in the halide perovskite optoelectric devices and induced “I–V

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Figure 1. (a) The energy band diagram and photograph of the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device. (b) The diagram of Ga/CsPbBr_{2.4}Cl_{0.6}/Au structure device. (c) The linear current–voltage curve of CsPbBr_{2.4}Cl_{0.6} device. (d) The current–voltage loops from –50 to 50 V at the scan rates of 100 and 1 V/s.

hysteresis” behavior^{9,10,20} and unstable leakage current,^{21,22} which was normally deemed as a negative factor. To our best knowledge, it was difficult to restrain the ion migration in halide perovskite materials due to the weak bonding strength especially under extreme environments such as high electric field and irradiation with strong light.^{11,22,23}

In this study, a Schottky-type Ga/CsPbBr_{2.4}Cl_{0.6}/Au device was designed based on solution-grown high quality CsPbBr_{2.4}Cl_{0.6} single crystals for the application of nuclear radiation energy spectra. In order to restrain the ion migration, the “voltage cycling” technique was applied to stabilize the leakage of the device and then the stable α -spectra in the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device can be obtained for a period of time. Furthermore, the influence of ion migration on the α -particle energy spectra was investigated and discussed.

2. METHODS

Preparation of Precursor Solution. Six millimoles of CsBr ($\geq 99.9\%$), 9 mmol of CsCl ($\geq 99.9\%$), together with 30 mmol of PbBr₂ ($\geq 99\%$) purchased from Aladdin Reagent Ltd. without purification were dissolved in 30 mL of dimethyl sulfoxide (DMSO, $\geq 99.5\%$) with continuous stirring for 2 h at room temperature. After all of the raw materials were dissolved, the solution was filtered using a membrane with a pore size of 0.2 μm to remove the insoluble impurity particles. Upon this step, a mixture of dimethylformamide (DMF, $>99.5\%$) and cyclohexanol (CyOH, $>98\%$) with a volume ratio of 1.8:1 was added into the filtered solution.

Crystal Growth. Sixty milliliters of prepared precursor solution was transferred into a 100 mL conical flask with rubber plug. After that, the flask was put in a water tank with an initial temperature of 40 $^{\circ}\text{C}$, which was then heated with the rate of 1 $^{\circ}\text{C}/\text{day}$. A water bath was adopted to provide a uniform thermal field inside the solution. The nucleation and growth occurred at 40–70 $^{\circ}\text{C}$,²⁴ which was below the phase transition temperature (88 $^{\circ}\text{C}$),²⁵ guaranteeing a better crystalline quality. After the growth, many millimeter-sized CsPbBr_{2.4}Cl_{0.6} crystals with a greenish-yellow color were obtained as shown in Figure S1b.

Crystal Surface Treatment. The crystal surface was polished by sandpaper with absolute ethyl alcohol to make the crystal surface smooth. The crystals were transferred to the polishing pad and polished by hand for about 5 min using the

magnesium oxide powder. When no obvious scratches could be observed on the crystal surface, 2–3 drops of absolute ethyl alcohol were added to the polishing pad and polishing was continued for about 30 s until the scratches could not be seen directly. Finally, the crystal surface was cleaned with anhydrous ethanol and then dried for later use.

Characterization. Current–voltage (I – V) and current–time (I – t) were measured by Keithley 6517B. The energy spectra were obtained by exposing the sample under the irradiation of ²⁴¹Am 5.49 MeV α -particle source. The pulse shape information was simultaneously recorded by connecting the preamplifier output to a high-speed waveform digitizer card. The signals from the preamplifier (ORTEC 142) were further amplified and shaped by the shaping amplifier (ORTEC 570). Finally, a standard multichannel analyzer (Imdetek AMCA-01) was used for the pulse height spectra acquisition.

3. RESULTS AND DISCUSSION

3.1. The Ion Migration in CsPbBr_{2.4}Cl_{0.6} Device.

According to our previous report,²⁴ as-grown greenish-yellow CsPbBr_{2.4}Cl_{0.6} single crystals (Figure S1) are n-type semiconductors with an electron carrier concentration of $2.96 \times 10^8 \text{ cm}^{-3}$ and a mobility of $146 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which were evaluated by Hall measurements. Gallium (Ga) and gold (Au) electrodes with a thickness of 70 nm and a diameter of 4 mm were deposited by thermal evaporation onto opposite sides of the CsPbBr_{2.4}Cl_{0.6} crystal with a thickness of 1.44 mm (as shown in Figure 1a,b). In our Ga/CsPbBr_{2.4}Cl_{0.6}/Au device, the bias was applied on the Ga electrode and the Au electrode was connected to the ground. This CsPbBr_{2.4}Cl_{0.6} device in Figure 1c revealed the linear dark current–voltage curve at a bias range of –1 to approximately +1 V. The evaluated resistivity is about $1.19 \times 10^9 \Omega \cdot \text{cm}$. By scanning the I – V curve in both directions, a strong hysteresis behavior of the I – V curves was observed in Figure 1d, Figure S4, and Figure S5 and whose origin comes from ion migration.¹¹ The ion migration induced leakage current is influenced by the voltage scanning speed, measurement time, and the magnitude of the applied electric field. The coexistence of ion and electron/hole conductivity in CsPbBr_{2.4}Cl_{0.6} crystal tends to limit the ability to acquire stable pulse height spectra for nuclear radiation detection. However, we found there are two states of high

Figure 2. (a) The time dependent current curves under the negative bias of -20 V for a series of time, which was applied for conditioning the device. The inset is the accumulated charges and numbers of anions and cations with the conditioning time. (b) After conditioning the device, the time-dependent current curves of the device were measured. (c) Schematic illustrations for a typical ion migration process under a negative bias and the initial band structure of the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device. (d) Schematic illustrations of the accumulation of the cations and anions near two electrodes of the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device, which changed its initial energy band structure.

resistivity and low resistivity under the positive bias from I - V curves in Figure 1d. The low and high resistivities can be calculated as $2.90 \times 10^7\text{ }\Omega\cdot\text{cm}$ and $1.02 \times 10^9\text{ }\Omega\cdot\text{cm}$ at the scanning rate of 1 V/s using the different slopes of I - V curves. The high resistivity is close to the intrinsic resistivity of $1.19 \times 10^9\text{ }\Omega\cdot\text{cm}$, which indicates that no ion migration participated in the charge transport process. However, the low resistivity is attributed to the contribution of ion and electron/hole transport together. This is the ion migration controlled “volatile resistive switching behavior”.²⁶ Furthermore, the states of resistivities in the CsPbBr_{2.4}Cl_{0.6} device were controlled by the bias voltage scanning direction. Can we utilize or stabilize the high resistivity to obtain the stable pulse height spectra for nuclear radiation detection? The answer is yes and the detailed experiment and discussion are shown below.

To decrease the ion migration-induced dark current and obtain stable pulse height spectra for nuclear radiation detection, the “voltage cycling” technique was applied.^{7,27,28} As shown in Figure 2a, the same negative voltage of -20 V was applied on the CsPbBr_{2.4}Cl_{0.6} device for 10, 30, 60, 120, and 240 s. The negative current gradually increased with the duration and saturated at about $13\text{ }\mu\text{A}$. The transition time in current–time curves under the bias of $+10\text{ V}$ was increased from about 20 s to about 200 s (Figure 2b) when the negative voltage was applied for a longer time. It indicated this “voltage cycling” technique was effective to reduce the leakage current in a period of time. Also, we applied the variable negative biases of -10 , -20 , -30 , -40 , and -50 V with the same

duration of 60 s. The similar results were achieved in Figure S6. The larger negative bias would induce more ions to gather at two electrodes in the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device, which enhanced the stability of the device.

A voltage of opposite polarity (negative bias) was applied to condition the device prior to use in order to drive the anions and cations to gather around the interface of two electrodes, as shown in Figure 2c,d. After this process, the accumulated anions and cations would partly stay near electrodes. According to our previous study in CsPbBr₃ crystals,¹¹ the possible mobile anions are halide ions of Br^- or Cl^- and mobile cations are Cs^+ ions. Furthermore, it is assuming that the current is induced by ion migration under negative bias, thus the total migrated charge under different durations could be calculated by integrating the I - t curve (Figure 2a). As we inferred that the mobile anions should be Cl^- or Br^- and the mobile cations should be Cs^+ , they are monovalent ions and therefore the accumulated numbers of anions and cations can be calculated as $N = Q/e$. The numbers of the accumulated ions near the electrodes are increased from 2.12×10^{13} to 1.45×10^{16} when the duration is increased from 10 to 240 s, as shown in the inset of Figure 2a. The more accumulated charges will lead to the longer stable time of the device when it is tested under positive biases. It told us that the accumulated charges can change the initial energy band structure of the device near the electrodes (Figure 2c,d), which can effectively restrain the leakage current of the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device.

Furthermore, the leakage currents of the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device under positive bias from +10 to +50 V were compared with and without the “voltage cycling” technique. As shown in Figure 3, under the condition of −50 V for a duration

Figure 3. Comparison of the time-dependent leakage currents of Ga/CsPbBr_{2.4}Cl_{0.6}/Au device without and with the voltage cycling technique.

of 500 s, the leakage currents under variable voltages of +10, +20, +30, +40, and +50 V can be two orders lower than that without the utilization of the “voltage cycling” technique. Therefore, based on the “voltage cycling” technique, the device could be operated within this stable region by controlling the conditioning bias and the duration of the applied voltages. It is expected that this technique can be applied to acquire stable energy spectra.

3.2. The Stable Detection of α -Particle Based on “Cycling Voltage” Technique. An ²⁴¹Am α -particle source with an activity of 187 kBq was used and kept at a distance of 5 mm from the Ga/CsPbBr_{2.4}Cl_{0.6}/Au detector. As shown in Figure 4a, α -particles were incident onto the Ga electrode of the device and produced large amounts of electron–hole pairs under the Ga electrode. When a positive voltage is applied to the Ga electrode, only the holes produced close to the Ga electrode (anode) will transport across the device to the Au electrode (cathode). The drifting carriers will induce charge pulse signals in the preamplifier. The output pulses from the preamplifier are processed by the shaping amplifier to form pulses with a Gaussian shape. The height of the Gaussian pulses was measured using a Multi Channel Analyzer to produce energy spectra. The “cycling voltage” technique (applying −20 V bias for 1 min) was also used to condition the device prior to each measurement using positive voltage. Figure 4b demonstrated the pulses at variable positive biases (+10, +20, +30, and +50 V) from the preamplifier. It is noted that the ion migration is constrained provided that the measurements are made within the duration of the critical time as explained above. Therefore, in order to evaluate the intrinsic transport properties of the holes, the pulses from the preamplifier were collected during the first 5 s of the measurement. From Figure 4b, the amplitude of the pulses was increased, and the rise time of the preamplifier output pulses was decreased as the voltage was changed from +10 V to

+50 V. This systematic change indicated that the collection efficiency of hole carriers was increased and the drift velocity was enhanced. As shown in Figure 4c, the mobility (μ) could be extracted by a linear fitting of the carrier drift velocity V_{dr} versus the electric field (E) with the formula^{29–31}

$$\mu = \frac{V_{dr}}{E} = \frac{d^2}{U \cdot \tau} \quad (1)$$

where d is the thickness of CsPbBr_{2.4}Cl_{0.6} crystal ($d = 1.44$ mm) and U is the applied voltage. Accordingly, the corresponding hole mobility of CsPbBr_{2.4}Cl_{0.6} crystal was calculated to be $52.2 \pm 5.7 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which is similar to that of intrinsic p-type CsPbBr₃ ($49 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) obtained by using the same α -particle time-of-flight technique.⁴

Besides the pulses from the preamplifier, stable pulse height spectra due to the α -particle irradiation of the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device can also be acquired using the “cycling voltage” technique, as shown in Figure 4d. By controlling the signal collecting time from 120 s (+5 V) to 9 s (+50 V), the full energy peaks were observed. The peak centroids in the pulse height spectra moved to higher channels with increasing the bias. Because of the short acquisition time at high voltages, the spectra contain relatively few counts and hence show some variation due to random fluctuations. The energy resolution of the full energy peak in the α -particle spectra is shown in Figure 4e and increases with increasing bias voltage. The best energy resolution was obtained as 42% FWHM with a bias voltage of +50 V. However, in comparison to the reported 15% energy resolution for the α -particle spectra-based Ga/CsPbBr₃/Au device,⁴ our results are still quite limited. Here, we want to emphasize that if the ion migration influencing the leakage current can be controlled, stable energy spectra can be obtained. It may help us harvest better energy resolution in further research. The higher energy resolution was attributed to the higher charge collection efficiency (CCE), as shown in Figure 4f. On the basis of the single carrier transport model, the mobility-lifetime product ($\mu\tau$) can be evaluated by the Hecht formula³⁰

$$\text{CCE} = \frac{\mu\tau U}{d^2} \cdot (1 - e^{-d^2/\mu\tau U}) \quad (2)$$

Figure 4f shows the corresponding data which is fitted well by eq 2 and the resulting value of $\mu\tau$ product of $(3.26 \pm 0.22) \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1}$. Accordingly, the lifetime (τ) of the hole was obtained as 6.24 μs , which is smaller than that of intrinsic CsPbBr₃ crystal (19 μs) reported previously.⁴

3.3. The Influence of Ion Migration on α -Particle Energy Spectra. The “voltage cycling” technique can restrain ion migration in halide perovskites for a certain time. However, when the duration of the applied bias voltage exceeds the critical time, the dark current tends to increase quickly as shown in Figure 2b and Figure 3 above, which influences the stability of the detection process. The detailed influence of ion migration on the measured α -pulse height spectra was investigated below. As shown in Figure 5a, an operating bias of +10 V was applied after initial conditioning of the device (−20 V bias for 1 min). The spectra were recorded at variable collecting times until the detector no longer functioned. As shown in Figure 5a, a clear full energy peak was maintained for collections less than 200 s, after which it gradually disappeared. This phenomenon was expected according to the critical time that was previously measurement from the dark currents in

Figure 4. (a) Diagram of the hole transport process in the Ga/CsPbBr_{2.4}Cl_{0.6}/Au device illuminated under α -particles. (b) After ion migration under high electric field. On the basis of the “voltage cycling” technique, ²⁴¹Am α -preamplifier pulses of Ga/CsPbBr_{2.4}Cl_{0.6}/Au device were obtained from +10 V to +50 V during the initial stable time (less than 5 s). (c) Hole drift velocity as a function of electric field strength. The extrapolated hole mobility value is 52.2 ± 5.7 cm²·V⁻¹·s⁻¹. (d) The bias-dependent ²⁴¹Am α -particle spectra under positive voltage using a Ga/CsPbBr_{2.4}Cl_{0.6}/Au detector. (e) The energy resolution of the α -particle spectra improved by increasing the bias. (f) The mobility-lifetime product calculation for holes according to the single carrier Hecht equation.

However, the analysis of the time evolution of the pulse height spectra showed a more detailed situation. As revealed in Figure 5b, the position of the full energy peak and the energy resolution both gradually reduced with the increasing collection time. This indicates that the ion migration process always exists during the period of signal collection. During the measurement period when the bias voltage is applied, two processes can in principle account for the degraded detector response. On the one hand, the cations and anions can transport to the respective electrodes, which form an opposite internal electric field. This internal field reduces the actual electric field inside the detector and thus reduces the CCE. On the other hand, ion migration from the

lattice will increase the point defect concentration in the bulk material of the device, leading to a reduced amplitude as well as an increase rise time of the pulse from the preamplifier. The time-dependent peak intensity and dead time was also shown in Figure 5b. The peak intensity, which can also refer to the total counts within the full energy peak, increases linearly as a function of acquisition time, indicating that the counting rate is almost stable. The dead time is obtained by dividing the live collection time by total collection time, where a rapid increase indicates the failure of the detector. On the basis of the discussions above, the voltage and time-dependent phase diagram was plotted and stable and unstable regions can be distinguished as shown in Figure 5c.

Figure 5. (a) The ^{241}Am α -particle spectra of Ga/CsPbBr $_{2.4}$ Cl $_{0.6}$ /Au detector under +10 V change with increasing the testing time. (b) With the increasing collecting time, the position, counts, and energy resolution of the peaks were reduced, increased, and decreased, respectively. The dead time of the device was increased with increasing time. (c) The bias and time-dependent phase diagram for the α -particle energy spectra.

4. CONCLUSIONS

Schottky-type Ga/CsPbBr $_{2.4}$ Cl $_{0.6}$ /Au detectors were prepared for α -particle pulse height spectra testing. To minimize the ion migration in CsPbBr $_{2.4}$ Cl $_{0.6}$, the “voltage cycling” technique was applied and stable α -particle spectra from +5 to +50 V were obtained below a critical acquisition time. The highest FWHM energy resolution of the full energy α -peak is 42%. The hole mobility evaluated by the TOF technique, the hole mobility-lifetime product, and the hole lifetime were obtained as $52.2 \pm 5.7 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, $(3.26 \pm 0.22) \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1}$, and $6.24 \mu\text{s}$, respectively. Though the “voltage cycling” technique can effectively increase the stable time of halide perovskite detectors, the leakage current would start to increase due to the start of ion migration beyond the critical time. Accordingly, the reduced amplitude and increased rise times of the preamplifier pulses and the disappearance of the full energy peak were both observed and discussed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c10758>.

Experimental results of the crystal growth and characterization, XRD patterns, optical properties, electric properties of CsPbBr $_{2.4}$ Cl $_{0.6}$ devices (PDF)

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Notes

The authors declare no competing financial interest.

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