We report the detection of high energy electrons of some hundreds of MeV, crossing a methylammonium lead bromide single crystal device with sensitivity down to a single electron. In the device, the released energy is close to the energy released by minimum-ionizing particles. This is the first demonstration of a perovskite-based device that can be used for tracking and counting minimum-ionizing charged particles. The device reaches single particle sensitivity with a low bias voltage of 5 V. It also shows a good linearity of the response as a function of the number of electrons in a dynamic range of approximately $10^4$.

Organometal halide perovskite (OMHP) based devices are of high interest for radiation detection due to their strong stopping power, defect tolerance, large mobility-lifetime products, tunable bandgaps and simple single crystal growth from low-cost solution processes. There is copious literature on the potential of OMHPs to detect X-rays. In contrast, literature on the detection of charged particles is far less numerous. However, the interest in this field is also steadily growing, as there are many possible medical and scientific applications, like beam monitoring, dosimetry, therapies based on charged particle beams, and particle physics experiments. A recent review can be found in ref. 5 covering both direct and indirect detection through scintillation processes of $\alpha$ and $\beta$-particles. In direct detection, the electron–hole (e–h) pairs generated from the energy loss of charged particles in the material through ionization are collected on the electrodes. Indirect detection is based on scintillation processes; the material emits visible light when the charged particles lose energy while crossing the crystal. Therefore, indirect detection requires an additional external photo-detector.

Direct detection of charged particles from OMHP detectors has been investigated using either thin poly-crystalline films or, most commonly, thick single crystals (SCs). In the first case, the amount of energy released through ionization loss from the charged particles is limited due to the small thickness, therefore limiting sensitivity to high fluxes of particles. In 2017, Xu et al. reported for the first time the detection of $\alpha$-particles using a single CH$_3$NH$_3$PbBr$_3$ (MAPbBr$_3$) crystal and measured the energy spectrum. Some years later, $\alpha$-particles were detected also using a CsPbBr$_3$ crystal and HC (NH$_3$)$_2$PbBr$_3$ crystals. Huang et al. recently reported a radiation tolerant proton detector based on a MAPbBr$_3$ SC with a thickness of 1 mm. The detector is able to detect 3 MeV proton beams, which are completely stopped in the crystal, from a beam with a fluence between $2.65 \times 10^{10}$ cm$^{-2}$ s$^{-1}$ and $2.26 \times 10^{11}$ cm$^{-2}$ s$^{-1}$. A 100–228 MeV proton beam with flux between $4 \times 10^7$ and $2 \times 10^9$ p s$^{-1}$ was measured with a flexible CsPbCl$_3$ thin-film detector by Bruzzi et al. In ref. 12 L. Basiricò et al. developed a device based on a mixed 3D–2D perovskite film, 1 $\mu$m thick, to detect a 5 MeV proton beam with the flux in the range of $4.5 \times 10^5$–$1.4 \times 10^9$ cm$^{-2}$ s$^{-1}$.

So far, $\beta$-particles, i.e. high-energy, high-speed electrons or positrons, have been detected from OMHP-based devices only through scintillation. The first OMHP-based scintillator for $\beta$-particles was developed by Yu et al. More recently Hunyadi et al. developed a scintillator made of thin poly-crystalline perovskite films, up to 100 $\mu$m thick, able to detect single events from electrons, protons, $\alpha$-particles, and heavy ions. Direct detection of single charged particles with energy in the range of hundreds of MeV crossing a perovskite device has not been reported yet. It is worth noting that the energy released...
through ionization in a crystal from higher energy particles is smaller than that released from lower energy particles, which most of the studies so far have reported. In particular, the energy loss through ionization for electrons of some 100 MeV is very close to the minimum energy loss, according to the well-known Bethe–Bloch formula applied to electrons.\(^{15,16}\) The minimum energy loss through ionization inside a material is almost independent of the type of the particle, and occurs when the value of the momentum of the particle divided by the rest mass times the velocity of light, \(p/mc\), is \(\sim 3\). In this condition, the particles are referred to as minimum ionizing particles. In general, electrons lose energy in a material also due to bremsstrahlung, which is the emission of photons from electrons deflected by the Coulomb field of the nuclei. However, the energy released due to the latter process in the volume of our perovskite crystals has been estimated to be negligible based on Geant4 simulations,\(^{17}\) as shown in ESI Fig. S5.\(^\dagger\) Therefore, the energy loss in the device studied here is similar to the energy loss by other charged particles like muons, pions, protons and deuterons, when their \(p/mc\) is \(\sim 3\), i.e. by minimum ionizing particles.

The MAPbBr\(_3\) perovskite single crystal used in this study was grown from a DMF solution by the inverse temperature crystallization method (ITC) over a temperature range of 50–88 °C.\(^{18}\) The sample has an area of 6 mm × 6 mm and is 1.4 mm thick. An accurate single crystal X-ray structure determination was carried out on a fragment cut from a mm-long bulk MAPbBr\(_3\) single crystal. The purpose was to determine the crystallographic quality of the synthesized material. A complete discussion can be found in the ESI.\(^\dagger\) The quality of the specimen was very high, allowing a complete \textit{ab initio} structural solution from the diffraction data. The compound has the usual ABX\(_3\) perovskite structure with A = positively charged methylammonium (MA\(^+\)), B = Pb\(^{2+}\) and bromide species as counterions. The phase is the expected cubic centric apolar \(Pm\bar{3}m\) one, with the unit cell length (\(a = 5.9175(3)\) Å) in very good agreement with other recent experimental estimates.\(^{19-21}\)

180 nm-thick ITO contacts have been deposited on the top and bottom faces of the crystal using an industrial RF magnetron sputter machine (Inline RF Magnetron Sputter, Kenosisteec). A hard mask is applied to avoid undesirable deposition on the lateral faces of the crystals. The deposition was performed at 1.1 × 10\(^{-3}\) mbar as the chamber pressure, at a low temperature (40 °C), and at a low power density (0.58 W cm\(^{-2}\)).

We have performed basic electrical characterisation on the contacted sample. First, we extracted the static relative permittivity through capacitance measurements, and then the trap density and mobility from dark current–voltage measurements. The capacitance was found to be 9.84 pF (see ESI Fig. S6).\(^\dagger\) Using the crystal dimensions given above, we deduced a relative permittivity of \(\varepsilon_r = 43.2\), which is in good agreement with experimental data.\(^{22}\) Since both contacts are made of ITO, our device can be considered as a hole-only device, and we analyzed the dark current–voltage characteristics (see ESI Fig. S7)\(^\dagger\) using the space-charge-limited current (SCLC) method.\(^{23,24}\) In this approach, the voltage at the transition between the third SCLC regime and the second regime with rapidly increasing current, known as trap-filled limit voltage \(V_{\text{TFL}}\), allows estimation of the trap density via \(V_{\text{TFL}} = \frac{e_n L^2}{2\varepsilon_0 \varepsilon_r}\), where \(L\) is the device thickness and \(n_t\) is the trap density. It has to be noted, though, that this procedure might not necessarily provide reliable values, in particular due to the non-negligible ionic mobility of the different atomic species in the perovskite crystal.\(^{23}\) In our case, we estimated \(V_{\text{TFL}} \approx 1.85\) V, leading to \(n_t \approx 4.5 \times 10^{13}\) cm\(^{-3}\), which is in the range of values reported in the literature.\(^{24,25}\) Furthermore, we estimated the hole mobility from the third region in the current–voltage characteristic with quadratic voltage dependence via the Mott–Gurney law\(^{26}\) as \(\mu = \frac{8J^2}{9\varepsilon_0 \varepsilon_r V^2}\), where \(J\) is the current density, obtaining a value of 12 cm\(^2\) V\(^{-1}\) s\(^{-1}\), which is also compatible with other literature.\(^{27}\)

To record the small amount of charges released from minimum ionizing electrons, the crystal is connected to a Cremat CR-110-R2 charge-preamplifier\(^{28}\) which converts the charge released in the crystal from the particles into a voltage signal, as shown schematically in Fig. 1.

High-energy electrons of 300 MeV were provided by the Beam Test Facility (BTF) at the Frascati National Laboratories.\(^{29}\) The BTF uses a secondary beam produced using the primary DAFNE Linac pulses hitting a dedicated target on the BTF extraction line. The BTF architecture allows the control of charge (electron/positron), energy (50–500 MeV), and multiplicity (1–10\(^4\)) of particles in the beam. The maximum beam repetition rate is 50 or 25 Hz according to the DAFNE usage. An initial setup was realized using BTF diagnostics only (FITPix detectors\(^{10}\)) to measure the beam profile along the longitudinal coordinate, especially at the nominal position of the crystal under test. The setup used for the test is schematically shown in Fig. 1. The placement of FITPix detectors allowed continuous monitoring of the transverse dimensions during the data acquisition, and the initial calibration of the beam profile has been used to properly extrapolate the beam size at the crystal position.\(^{31}\) Depending on the beam conditions the widths ranged between 2.5 mm–2.8 mm and.

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![Fig. 1](image-url)
0.9 mm–1.7 mm in the horizontal and vertical directions, respectively. The multiplicity of the electrons in the beam was monitored at a single BTF pulse event level using a lead-glass calorimeter placed at the end of the line acting as a beam dump.

Waveforms were recorded at different electron multiplicities inside the bunch, from 1 electron up to $10^4$ electrons. To study the sensitivity to a single electron, the beam was configured to provide, on average, 1.4 and 5 electrons per bunch. The mean electron multiplicity provided by the beam is referred to as $\langle \mu \rangle$ in the following. The actual electron multiplicity in a bunch, denoted by $\mu$, follows a Poisson distribution with mean $\langle \mu \rangle$, as shown in the distribution of the calorimeter signals in the ESI, Fig. S9.† It is possible, therefore, to select various electron multiplicities for a given beam configuration.

In Fig. 2 the average waveforms from subsets with a fixed number of electrons are shown for beam configurations with $\langle \mu \rangle = 1.4$ and $\langle \mu \rangle = 5$, respectively. The signal from a single electron passing through the SC, indicated with red symbols in Fig. 2, is well visible. The applied bias voltage was 5 V, which has been chosen in order to detect the single particle signals. Higher bias voltage would further increase extraction efficiency; however, our perovskite crystals suffer from instability at higher voltages. Similar bias instability has been observed also in perovskite solar cells in reverse bias. Therefore, we preferred to use the lowest possible bias allowing to observe signals from single particles.

The waveforms have been fitted with a triple exponential function, using the known amplifier frequency response (see the ESI†). The resulting amplitudes are reported in Table 1 together with the corresponding number of single events used for averaging. The reported errors are statistical only and are estimated based on the root mean square (RMS) of the deviation calculated around the peak. The $\mu$ values between 1 and 3 can be studied with both beam configurations, and the reconstructed amplitudes are comparable in the two cases.

In particular, a slope of 0.3 mV is obtained in both cases, with less than 2% difference (see ESI Fig. S10†). This observation and the linearity of the amplitudes with the number of electrons passing through the crystal demonstrate that MAPbBr$_3$ has the capability of tracking and counting minimum ionizing particles.

In Fig. 3 the signal amplitude as a function of electron multiplicity in a bunch, from 5 up to $\sim 10^4$, is shown. To avoid saturation of the preamplifier at high multiplicity, the applied bias voltage was reduced to 2 V. The data are presented in terms of effective multiplicity, i.e. the actual number of electrons impinging on the SC. In fact, due to the spatial distribution of the electrons in the beam and the limited lateral size of the crystal, not all electrons in bunches of large multiplicity hit the detector. We have estimated a geometrical acceptance of 70% within the SC volume. During the test beam, the SC has been centered on the beam axis with a resolution of 0.5 mm which is the minimum step of the motorized platform used for beam-based alignment of the device. The acceptance uncertainty has been evaluated by convoluting the alignment uncertainty with the beam size and the SC active volume using a toy MC simulation. The horizontal error bars in Fig. 3 indicate the systematic uncertainty resulting from the simulation. For the linear fit, represented by the red line, we have considered the latter by weighting the data points accordingly.

Table 1: Fitted amplitudes for electron multiplicities between 1 and 5 using two beam configurations with the mean electron multiplicity per bunch ($\langle \mu \rangle$) equal to 1.4 and 5. For the first sample, the collected events with $\mu > 3$ are not used in the analysis because of the lack of statistics.

<table>
<thead>
<tr>
<th>Multiplicity ($\mu$)</th>
<th>Output signal (mV) and number of events</th>
<th>$\langle \mu \rangle = 1.4$</th>
<th>$\langle \mu \rangle = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0.25 \pm 0.03$</td>
<td>974</td>
<td>$0.36 \pm 0.09$</td>
</tr>
<tr>
<td>2</td>
<td>$0.34 \pm 0.03$</td>
<td>522</td>
<td>$0.66 \pm 0.08$</td>
</tr>
<tr>
<td>3</td>
<td>$0.85 \pm 0.05$</td>
<td>141</td>
<td>$0.95 \pm 0.08$</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>—</td>
<td>$1.23 \pm 0.05$</td>
</tr>
<tr>
<td>5</td>
<td>—</td>
<td>—</td>
<td>$1.60 \pm 0.06$</td>
</tr>
</tbody>
</table>

Note that the slope of 0.058 mV is 5.2 times smaller than the one obtained from Table 1, due to the lower bias voltage. The acceptance uncertainty with the beam size and the SC active volume has been evaluated by convoluting the alignment uncertainty with the beam size and the SC active volume using a toy MC simulation. The horizontal error bars in Fig. 3 indicate the systematic uncertainty resulting from the simulation. For the linear fit, represented by the red line, we have considered the latter by weighting the data points accordingly. Note that the slope of 0.058 mV is 5.2 times smaller than the one obtained from Table 1, due to the lower bias voltage. The acceptance uncertainty has been evaluated by convoluting the alignment uncertainty with the beam size and the SC active volume using a toy MC simulation. The horizontal error bars in Fig. 3 indicate the systematic uncertainty resulting from the simulation. For the linear fit, represented by the red line, we have considered the latter by weighting the data points accordingly.

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good linearity over a dynamic range of $\sim 5 \times 10^5$ demonstrates the potential of MAPbBr$_3$ SCs as real-time non-destructive dosimeters.

In order to estimate the charge extraction efficiency, given as the ratio between extracted and generated charge $Q_{\text{extr}}/Q_{\text{gen}}$, we have simulated the energy deposit of 300 MeV electrons inside the SC using the Geant4 software.$^{17}$ The distribution of the released energy by a single electron, shown in Fig. 4, has an average of $\sim 0.75$ MeV.

Taking into account the energy to create an electron–hole pair, calculated using the formula$^{33} \ W = 2E_g + 1.43$ eV, where $E_g = 2.2$ eV is the band gap of MAPbBr$_3$, approximately 128 600 e–h pairs are generated from the energy released by one electron passing through the crystal. The collected charge could in principle be obtained by integrating the output signal. In our case, however, the presence of a high pass filter due to the output ac coupling does not allow us to follow this approach. Instead, we used the triple exponential fit to deduce the charge in the input signal. Two of the exponentials can be associated with the electronics, with known coefficients, while the third has been used for fitting and models the current pulse at the amplifier input (see the ESI† for details). An exponential pulse is in fact expected if the electric field is constant in the device and the carrier lifetime is lower than the transport related extraction time, which at 5 V can be estimated as 327 $\mu$s using the extracted mobility of 12 cm$^2$ V$^{-1}$ s$^{-1}$. For the decay time, we obtained a value of roughly 32 $\mu$s. The collected charge at the electrodes can then be calculated as the product of the peak current and the decay time. For the low multiplicity data, we obtained an extracted charge of approximately 5600 e$^-$ per incident electron (see ESI Fig. S12†). Combining with the slope of the signal amplitude, we calculated a conversion factor of roughly $5.4 \times 10^{-5}$ mV per extracted electron.

Deconvolution of the output signal leads to substantially the same values (see ESI Fig. S13†). The extraction efficiency $Q_{\text{extr}}/Q_{\text{gen}}$ is therefore $\sim 4.35\%$. Using the above mobility and decay time in the Hecht equation, we estimated an efficiency of 9.2%, which is reasonably close, considering the uncertainties in the parameter extraction and the approximations of the model itself. The low efficiency is related to the small electric field inside the SC due to the large thickness and the low applied voltage.

Drift-diffusion simulations using Synopsys Sentaurus TCAD$^{14}$ have been performed in order to qualitatively corroborate the assumptions made in the above analysis. Adjusting the main model parameters to approximately reproduce the steady-state bias current, and using the extracted trap density, carrier life time, mobility and permittivity, we obtained similar current signals after passage of single or multiple ionizing particles, as shown in Fig. S15–S17.† Although the simulated extraction efficiency results to be larger, signal shape and linearity show similar behaviour to the measured data. The simulations also suggest that screening due to the generated electron–hole pairs does not seem to contribute to the low extraction efficiency, even at high multiplicity.

Additional measurements have been performed at a multiplicity of $\mu = 20$, for various bias voltages between 5 and 25 V. The charge extraction efficiency obtained by the same approach as above in this case leads to values compatible with a Hecht curve when assuming an electron mobility of 6 cm$^2$ V$^{-1}$ s$^{-1}$, as shown in ESI Fig. S14.†

In conclusion, we report for the first time the direct detection of minimum ionizing particles from a perovskite single crystal. The response is around 0.3 mV for a single minimum ionizing particle. The small response is related to the small charge extraction efficiency, due to the large thickness of the SC and the low voltage bias applied. Larger signals from MIPs are expected from thinner SCs, which will be the subject of a future study.

Conflicts of interest

There are no conflicts to declare.
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