Scintillation properties of \(((\text{CH}_3)_4\text{N})_3\text{BiCl}_6\) as a novel lead-free perovskite halide crystal

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Abstract

Two-dimensional hybrid organic-inorganic perovskites (2D-HOIPs) possess intriguing structural properties which makes them promising materials for diverse optical, electronic and scintillation applications. Recently, several classes of hybrid perovskites exhibit potential candidate for radiation detection. However, the scintillation properties of corrugated-type 2D-HOIPs have not been studied so far. In this work, we investigate the scintillation performance of bismuth chloride \(((\text{CH}_3)_4\text{N})_3\text{BiCl}_6\) perovskites for the lead-free candidate. No strong RL intensity at room temperature is observed due to a strong thermal quenching. A small negative thermal quenching is also observed, which infer the presence of trap states characterized by two activation energies: \(E_1 = 25.71\) meV and \(E_2 = 129.27\) meV. In addition, low temperature afterglow of \(((\text{CH}_3)_4\text{N})_3\text{BiCl}_6\) at 10 K is estimated to be 70 s (14.5%) and 1200 s (85.5%). In low temperature thermoluminescence \(((\text{CH}_3)_4\text{N})_3\text{BiCl}_6\) exhibits a broad band, which is attributed to a quasi-continuous distribution of shallow traps. All these results shed some light on the fundamentals of scintillation properties of bismuth-based perovskites.

1. Introduction

Scintillator materials have received a great deal of attention and have been utilized for radiation detection applications in many areas like security, detection of interstellar particles, medical imaging, and nuclear cameras due to their capability of transforming the high energy radiation into many low energy photons such as visible and ultraviolet photons [1–5]. Metal halide perovskites are more advantageous for scintillators because of their low cost, adjustable bandgap and structural dimension, and excellent photophysical properties [6–12]. Metal halide perovskites have also low trap densities, long minority carrier diffusion lengths, high charge carrier mobilities, and high photoluminescence quantum yields (PLQYs), especially for nanocrystals counterparts [13–16]. For instance, CsPbCl\(_3\) exhibits nanosecond free excitons (FEs) radioluminescence (RL) and has been considered as a potential material for fast scintillators [17–20]. Recently, lead halide perovskite x-ray scintillator
detectors have achieved lower detection limits (13 nGy s⁻¹), faster response speeds (44.6 ns) and higher spatial resolution compared to the CsI:Tl based commercial flat-plane x-ray detectors [17].

Despite the great benefits of lead halide perovskites, the high concentrations of lead (Pb) in the perovskite can cause serious harm to the human body and biological system due to higher solubility of Pb in water [21, 22]. Consequently, a non-toxic element must be sought to replace Pb. Bismuth halide perovskites have been developed as lead-free halide perovskites for optoelectronics materials due to their lower toxicity, good stability, and lead isoelectronic 6s lone-pair electron [23–26]. Bismuth halide perovskites consist of a large structure group due to their various connection possibilities between the adjacent Bi halide octahedral, which can fabricate polynuclear or mononuclear through face, edge and corner sharing [27]. Thus, bismuth should be a useful component for x-ray scintillation. The first studies of bismuth-based x-ray scintillator materials were focused on oxide compounds, including Bi4Ge3O12 (BGO) [28] and Bi4Si3O12 (BSO) [29–31]. Moreover, bismuth perovskites are the best options for lead-free perovskite x-ray detector candidates in comparison to manganese [32, 33] and tin [34, 35] perovskites. Since the atomic number (Z(Bi) = 83) is comparable to lead (Z(Pb) = 82), its x-ray absorption performance can be more promising than that of manganese (Z(Mn) = 25) and tin (Z(Sn) = 50). Bismuth has also been utilised as a dopant in Cs2Ag0.4Na0.4In1.4(Bi)6Cl6 perovskite material, which demonstrated a strong RL intensity [20]. Jin et al reported the chloro-bismuth perovskite incorporated with ionic liquid, which exhibited the stronger interchain hydrogen bonding and more rigid structure, and resulted in a long lifetime of 99.8 ms at 298 K [36]. Later, Cao et al has reported the 0D (TMEDA)3Bi3Cl12·H2O, which demonstrated low quantum efficiency (1%) and there was no RL at room temperature (RT) [37]. However, there are not so many reports on scintillation properties from full-bismuth compound as it is known that bismuth doping can decrease the scintillation performance in some perovskite crystals [38]. In another aspect, bismuth-based layered double halide perovskite (Cs4MnBi2Br12, M = Cu, Mn, Pb and Sr) is reported with a longest lifetime for Cs4MnBi2Br12, and demonstrated a strong reversal orbital polarization at low temperature, which holds promises in the photo-physics applications beside scintillators [39].

Replicating the success of hybrid organic–inorganic scintillators [19, 34, 35], we attempt to explore methylammonium (MA) as it is the most common organic cation in the perovskite crystals. However, MAPbX3 crystals, especially MAPbI3, degrade into PbI2 in the presence of air, which reveals a rather poor stability because of the weak interaction of organic–inorganic in MAPbI3, while both MAPbBr3 and MAPbI3 crystals show high stability [32, 33]. Consequently, a non-toxic element must be sought to replace Pb. Bismuth halide perovskites have been developed as lead-free halide perovskites for optoelectronics materials due to their lower toxicity, good stability, and lead isoelectronic 6s lone–pair electron [23–26]. Bismuth halide perovskites consist of a large structure group due to their various connection possibilities between the adjacent Bi halide octahedral, which can fabricate polynuclear or mononuclear through face, edge and corner sharing [27]. Thus, bismuth should be a useful component for x-ray scintillation. The first studies of bismuth-based x-ray scintillator materials were focused on oxide compounds, including Bi4Ge3O12 (BGO) [28] and Bi4Si3O12 (BSO) [29–31]. Moreover, bismuth perovskites are the best options for lead-free perovskite x-ray detector candidates in comparison to manganese [32, 33] and tin [34, 35] perovskites. Since the atomic number (Z(Bi) = 83) is comparable to lead (Z(Pb) = 82), its x-ray absorption performance can be more promising than that of manganese (Z(Mn) = 25) and tin (Z(Sn) = 50). Bismuth has also been utilised as a dopant in Cs2Ag0.4Na0.4In1.4(Bi)6Cl6 perovskite material, which demonstrated a strong RL intensity [20]. Jin et al reported the chloro-bismuth perovskite incorporated with ionic liquid, which exhibited the stronger interchain hydrogen bonding and more rigid structure, and resulted in a long lifetime of 99.8 ms at 298 K [36]. Later, Cao et al has reported the 0D (TMEDA)3Bi3Cl12·H2O, which demonstrated low quantum efficiency (1%) and there was no RL at room temperature (RT) [37]. However, there are not so many reports on scintillation properties from full-bismuth compound as it is known that bismuth doping can decrease the scintillation performance in some perovskite crystals [38]. In another aspect, bismuth-based layered double halide perovskite (Cs4MnBi2Br12, M = Cu, Mn, Pb and Sr) is reported with a longest lifetime for Cs4MnBi2Br12, and demonstrated a strong reversal orbital polarization at low temperature, which holds promises in the photo-physics applications beside scintillators [39].

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According to the observation mentioned above, we report a new lead-free bismuth chloride compound of ((CH3)4N)3BiCl6 as a candidate for a low temperature lead-free scintillator. This study aims to gain the fundamental scintillation properties of full bismuth-perovskite crystals, as most of the previous studies for bismuth are related with the mixing-cation compounds. ((CH3)4N)3BiCl6 consists of isolated [BiCl6]4– anions encircled with (CH3)4N+ cations. A large-size single crystal of ((CH3)4N)3BiCl6 with a size of 5 × 5 × 3 mm3 has been successfully grown in ambient conditions. The x-ray diffraction analysis gathered with computational simulation confirms that the crystal has a triclinic structure with the P1 space group. The temperature-dependent RL reveals that ((CH3)4N)3BiCl6 shows strong thermal quenching (TQ) at RT. However, a small negative thermal quenching (NTQ) is also observed at much lower temperature of 50 K, similar with that in MAPbI3. Interestingly, the absorption length of ((CH3)4N)3BiCl6 is close to the lead-based chloride perovskite system and higher than of manganese-based chloride perovskite system, which reveals that ((CH3)4N)3BiCl6 crystal is suitable for low-energy x-ray detection. This study will give a more understanding of the bismuth-based halide perovskite system for scintillation process, so that the optimized-light-yield bismuth-based compounds can be the future for the environmental-friendly scintillators.

2. Experimental design

2.1. Synthesis of ((CH3)4N)3BiCl6

All reagent were purchased from Sigma Aldrich, namely hydrochloric acid (HCl, 37%), Bismuth(III) chloride (BiCl3), and tetramethylammonium chloride ((CH3)4NCl, reagent grade, 98%). 1 mol of BiCl3 was dissolved with 2 mol of 37% HCl. 3 mol of ((CH3)4N)3BiCl6 was dissolved with 4 mol of 37% HCl and stirred until a homogeneous solution was obtained. The BiCl3 solution was concentrated at 120 °C followed by the addition of (CH3)4NCl solution and stirred for 2 min. The mixture was kept at RT until the crystals were grown. The obtained crystal was separated, washed with ethanol and dried at RT. The crystal was kept in desiccator before used for further characterization.
2.2. Characterization
Powder X-ray diffraction (PXRD) of ((CH$_3$)$_3$N)$_3$BiCl$_6$ was performed on a PANanalytical diffractometer with Cu Kα radiation (λ = 1.54178 Å) at RT. The diffraction patterns were collected in the 2θ range of 5°–60°. The microstructure of ((CH$_3$)$_3$N)$_3$BiCl$_6$ was observed using scanning electron microscopy (SEM, JEOL). The surface element compositions of ((CH$_3$)$_3$N)$_3$BiCl$_6$ were analysed using energy dispersive x-ray (EDX) and Raman spectroscopy (laser wavelength of 532 nm, recorded from 1000 to 20 cm$^{-1}$), which was confirmed by x-ray photoelectron spectroscopy (XPS). XPS analysis was done using magnesium Kα as a source of x-rays with typical excitation energy output of 1254 eV.

Photoluminescence (PL) properties were investigated at RT based on epifluorescence method using free-space excitation and collection through a visible-near-infrared microscope objective (Nikon 20 ×, NA = 0.4), where the measurement parameter refers to research in [43]. The time resolved PL (TRPL) decay traces were obtained by a time-correlated single-photon counting acquisition module at emission selected wavelength of 500 ± 25 nm. The absorption properties of crystals were measured by ultraviolet-visible diffuse reflectance spectrophotometer (UV–vis DRS, Shimadzu UV-2450). The radioluminescence (RL), afterglow (AG) and thermoluminescence (TL) measurements are carried out using one integrated setup following the previous research in [35]. Then, the RL is measured at various temperatures between 10 and 350 K, starting from the highest temperature to the lowest temperature, to avoid the possible contribution of thermal emission of charge carriers to the emission efficiency.

2.3. Density functional theory calculation
DFT calculations were performed using Quantum Espresso software package version 6.7 [44] The initial crystal structure of ((CH$_3$)$_3$N)$_3$BiCl$_6$ used in this calculation adopted and modified the crystal structure reported by Zheng, et al [45], where a = 8.190; b = 8.190; c = 10.613; α = 90; β = 90; γ = 120. Furthermore, geometry (atomic coordinates) and lattice crystal optimization were carried out using variable cell relaxation (VC–RELAX) method in the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [46–49] with a convergence criteria for ionic minimization were satisfied when all components of all forces were smaller than 2.57 × 10$^{-2}$ eV/Ångstrom and the total energy changes less than 2.72 × 10$^{-3}$ eV. The relaxation of the compound will result in new lattice constants as the result of the vc-relaxation calculation. The resulting lattice constants will be used as the subsequent lattice constants in next calculation. This iteration will continue until the lattice constant doesn’t change considerably. The k-point size ($k_x \times k_y \times k_z$) for this calculation was set to 4 × 4 × 2. This k-point value was then enlarged to 12 × 12 × 12 to obtain denser curve of the electronic band structure. The calculation of the electronic band structure was carried out by selecting the k-point path of Γ-X-Γ-Y-Γ-Z-Γ-R-Γ-Γ-U-Γ-V-Γ in the corresponding Brillouin zone with P1 symmetry group. The VC–RELAX calculation was performed using Vanderbilt ultrasoft pseudopotential and scalar relativistic Generalized Gradient Approximation–Perdew–Burke–Ernzerhof (GGA-PBE) exchange-correlation functional [50]. This calculation used kinetic energy cut-off for wavefunctions of 680.28 eV and a kinetic energy cut-off for charge density and potential of 6802.85 eV, the convergence threshold for self-consistent field calculations was set to 10$^{-6}$ eV atom$^{-1}$.

3. Results and discussion
Trimethylammonium bismuth(III) hexachloride, ((CH$_3$)$_3$N)$_3$BiCl$_6$, crystallizes as a colourless triclinic diamond-like from the precursors solution. According to the simulated results in figure 1(a), a ((CH$_3$)$_3$N)$_3$BiCl$_6$ crystal has a triclinic crystals system with the P1 space group. ((CH$_3$)$_3$N)$_3$BiCl$_6$ is arranged by isolated [BiCl$_4$]$^{3-}$ anions encircled with (CH$_3$)$_3$N$^{++}$ cations [51]. The anionic sublattice is composed of three independent octahedrons of [BiCl$_6$]$^{3-}$ surrounded by six independents of (CH$_3$)$_3$N$^{++}$ via a R–N–Cl ionic bond. The octahedrons of [BiCl$_6$]$^{3-}$ are only slightly distorted in ((CH$_3$)$_3$N)$_3$BiCl$_6$ with varying bond length of Bi–Cl from 2.695 Å to 2.801 Å and varying bond angles of Cl–Bi–Cl from 35.6° to 71.0°. The simulated supercell shows that the crystal built a two-dimensional networks. The diffraction pattern of ((CH$_3$)$_3$N)$_3$BiCl$_6$ in figure 1(c) shows the characteristic peaks at 7.91°, 11.16°, 11.61°, 15.94°, 19.02°, 23.04°, 25.20°, 31.28°, 34.46°, 36.02° and 49.59°. The experimental pattern is slightly different than the simulated pattern shown in figure 1(b). The results show that the targeted compound has minor contamination a precursor contribution. One of the possible entities originates from BiOCl, since BiCl$_3$ as a precursor pose low chemical stability. We confirm the finding by comparing several peaks that prove the presence of BiOCl (JCPDS No 00-06-0249) rather than BiCl$_3$ (JCPDS No 01-071-0666). Thus, we consider BiOCl inserted into the crystal networks.

To investigate the chemical states of the perovskites, XPS measurements are presented in figure 2. As shown in figure 2(a), the XPS spectra exhibit peak at 165.21 eV and 159.87 eV corresponding to the binding energies of Bi 4$f_{5/2}$ and 4$f_{7/2}$ core levels [52]. The photoemission peaks at 285.33 eV, 402.59 eV and 198.50 eV were assigned to the carbon, quaternary nitrogen and chloride binding energies as shown in figures (b)–(d). The
deconvolution of O peaks is carried out to investigate the presence of O species in the crystal. The deconvolution of O peaks exhibits three peaks of binding energies of 531.67, 532.26 and 533.37 eV. The binding energy of 531.67 eV is attributed to the surface hydroxyl group [53]. Those binding energies also indicate the normal O of BiOCl crystal structure [54]. The peak at 532.26 eV indicates the presence of defects such as oxygen vacancies on the crystal surface, which promote the potential adsorption of O2 [55]. The peak at binding energy of 533.37 eV corresponds to the water on top [56].

To ensure the element composition of ((CH3)4N)3BiCl6 crystal, the Raman and EDX analysis were carried out. The Raman spectra in figure 3(a) (Raman and SEM) is dominated by seven bands at 75.54, 96.91, 114.46, 176.57, 234.85, 279.63 and 755.77 cm⁻¹. According to the [57, 58], the bands at 75.54, 96.91 and 114.46 cm⁻¹ are assigned to bending modes of Bi–Cl. The terminal stretching vibrations of Bi–Cl are observed at 176.57 and 279.63 cm⁻¹. The bridging stretching vibration of Bi–Cl is observed at 234.85 cm⁻¹. The band at 755.77 cm⁻¹ is associated with the asymmetric stretching vibration of (CH3)4N. The weak band at 954 cm⁻¹ is attributed to the rocking vibration of (CH3)4N [57].

The SEM of ((CH3)4N)3BiCl6 single crystal showed the smooth surface of ((CH3)4N)3BiCl6 crystal, which is composed of rod-shaped particles that merge together to form a triclinic structure as shown in figure 3(c). The EDX analysis (figure S1 available online at stacks.iop.org/MRX/9/096202/mmedia) also confirms the presence of Bi, Cl, C and N elements in the ((CH3)4N)3BiCl6, exhibiting the homogeneous distribution of four elements over the particles. The potential of x-ray scintillation of ((CH3)4N)3BiCl6 crystal is determined by the absorption length calculation. One of the x-ray scintillation material requirements is posed the short absorption length to guarantee an effective radiation absorption during the conversion process [2] in scintillation. The calculation result is shown in figure 3(d). The ((CH3)4N)3BiCl6 has an absorption length of 0.2 cm at 50 keV. This value is not different enough compared to the series of lead-based chloride compounds which have an absorption length of 0.19 cm at 50 keV. However, the absorption length value of ((CH3)4N)3BiCl6 is lower than manganese based IOHP [59], which reveals that ((CH3)4N)3BiCl6 crystal is appropriate for low-energy x-ray or gamma radiation.

The photophysical properties of ((CH3)4N)3BiCl6 were investigated by UV–vis absorption and PL spectroscopy. The absorption spectra of ((CH3)4N)3BiCl6 exhibit an absorption band below the bandgap, as shown in figure 3(a). We attribute this finding to localized state formation due to intrinsic disorder prior to photoexcitation. This in turns promotes exciton trapping after excitation and yields a broad photoluminescence spectrum [60]. The optical bandgap of ((CH3)4N)3BiCl6 was determined using direct Elliot formalism [61] to be 3.44 eV (see figure S2). This result is in agreement with the bandgap from the DOS calculation in figure 1(b) of 3.73 eV and the bandgap of another white-light-emission perovskite chloride crystal, EDBEPbCl4 of 3.45 eV [40]. Upon excitation under a 356 nm laser, ((CH3)4N)3BiCl6 exhibits a broadband spectrum of PL at 100 K and 300 K. The peak energies at 100 K and 300 K are 451.52 eV and 532.61 eV, respectively. At 100 K, a strong PL emission is generated, which reveals more self-trapped excitons (STEs) formation due to enhancing the
electron-phonon interaction. On the contrary, a weak PL emission is observed at 300 K, indicating the reducing of electron-phonon interaction, which leads to a small quantity of STEs. Time-resolved photoluminescence (TRPL) spectroscopy was further conducted to investigate the carrier lifetime of \((\text{CH}_3)_4\text{N})_3\text{BiCl}_6\). As shown in figure 4(c), the decay curve of \((\text{CH}_3)_4\text{N})_3\text{BiCl}_6\) shows a biexponential feature with lifetimes of 13.6 μs and 3 μs at 100 K and 300 K, respectively. At 100 K, the strong interaction of electron-phonon leads to domination of STEs radiative recombination in the PL decay curve. Then, as the increasing temperature to 300 K, a nonradiative recombination by FEs becomes prominent due to the weak electron-phonon interaction.

RL properties of \((\text{CH}_3)_4\text{N})_3\text{BiCl}_6\) are shown in figure 5. According to figure 5(a), we do not observe strong RL spectra at RT due to strong TQ. The temperature-dependent RL exhibits a small increase in the RL intensity from 10 to 50 K, which is a typical behaviour of STEs in the reported metal halide crystals \[62\]. The higher RL intensity at low temperature due to the suppressed phono-assisted nonradiative recombination \[63, 64\]. The mechanism that could cause such observation is called NTQ and corresponds to some shallow trap states located near the edge of the bandgap \[65\]. The ionization energy of these states has to be smaller than thermal perturbations at room temperature, therefore it is sufficient to excite the trapped carriers in these shallow states. As the temperature increases above 100 K, the trapped carriers are less likely to be excited thermally to the energy band and consequently quench the RL signals. In order to analyse both NTQ and TQ from \((\text{CH}_3)_4\text{N})_3\text{BiCl}_6\) we assume that the temperature-dependent normalized intensity evolution follows the Shibata model behaviour.

![Figure 2. XPS spectra of (a) Bi 4f, (b) C 2s, (c) N 2s, (d) Cl 2p and (e) O 2p in the ((CH₃)₄N)₃BiCl₆ crystal.](image-url)
Figure 3. (a) Raman profile, (b) morphology and (c) absorption length of ((CH$_3$)$_3$N)$_3$BiCl$_6$ crystal.

Figure 4. Optical properties of ((CH$_3$)$_3$N)$_3$BiCl$_6$ crystal. (a) Absorption spectra, (b) PL spectra and (c) TRPL spectra of ((CH$_3$)$_3$N)$_3$BiCl$_6$ crystal.
where $D$ is the NTQ coefficient corresponding to the thermally excited electrons contributions, $C_1$ and $C_2$ are the TQ coefficients related to non-radiative electrons excitation leading to the thermal quenching, $E$ is the activation energy of NTQ, $E_1$ and $E_2$ are the activation energies of typical thermal quenching, $k_B$ is the Boltzmann constant, respectively. Equation (1) fits well with the temperature dependent-RL normalized intensity of \((\text{CH}_3\text{N})_3\text{BiCl}_6\) crystal. The depth of the trap states $E\approx 22.28\text{ meV}$ for \((\text{CH}_3\text{N})_3\text{BiCl}_6\) RL is similar to $k_B T\approx 26\text{ meV}$, consistent with the expected shallow trap state that may generate NTQ. A small NTQ value ($D$) is measured, which indicates that shallow traps are created. The trap states have to be associated with the RL-active component in the \((\text{CH}_3\text{N})_3\text{BiCl}_6\) to produce RL at room temperature, either at surface or in the bulk of \((\text{CH}_3\text{N})_3\text{BiCl}_6\). The first activation energy ($E_1 = 25.71\text{ meV}$) can be defined as the detrapping process of bound exciton, which manifests from higher RL intensity at low temperature. These bound excitons do not have sufficient energy to be returned to free excitons at low temperature [63]. The higher second activation energy ($E_2 = 129.27\text{ meV}$) is related to the fast RL quenching associated with nonradiative recombination [66]. The two processes of activation demonstrate that the radiative recombination consists of a sub-band gap states distribution, which is derived from excitons that are trapped at the different sites of distorted perovskite lattice. According to the integrated intensity of RL, we find that the thermal quenching behaviour also occurs above 100 K.

A low temperature afterglow and thermoluminescence curve \((\text{CH}_3\text{N})_3\text{BiCl}_6\) is shown in figure 6(a). The long tail of the afterglow is observed at 10 K and is extended to thousands of seconds. This afterglow decay of \((\text{CH}_3\text{N})_3\text{BiCl}_6\) was fitted with a two-exponential model and those extracted components are 70 s (14.51%) and 1200 s (85.49%). To determine the parameters (concentrations, depths and frequency factors) of traps
appearing in TL, we first deconvoluted the glow curve into three peaks according to the classic Randall-Wilkins equation [40]:

\[
I = \sum_i n_{0i} \exp\left(-\frac{E_i}{k_B T}\right) \exp\left(-\frac{s}{\beta} \int_{T_i}^T \exp\left(-\frac{E_i}{k_B T'}\right) dT'\right)
\]

(2)

where \(I\), \(n_{0i}\), \(s\), \(E\), \(T\), \(k_B\) and \(\beta\) are the TL intensity, initial traps concentration, factor of frequency, trap depth, temperature, the Boltzmann constant and heating rate, respectively. We note that TL signal is observed at relatively low temperatures in a form of a rather broad inhomogeneous band. Therefore, not surprisingly, this effort exhibited a very low, non-physical values of the frequency factor. Similar cases are reported in literature for various materials, including oxide scintillators like GAGG:Ce, LuAG:Pr or YAM:Pr [67]. The Auvoirs and Morgan [68] postulate have been considered by Brylew et al [69] and Drozdowski et al [70, 71] to explain the TL peak, which reveal that broad glow peaks derived from trapping levels instead of discrete traps in the form of quasi-continuous Gaussian distributions [67]. Based on this approach, a fitting series was carried out to determine the trap parameters and the calculated curve with the highest possible accuracy was used to reproduce the experimental points. We obtained the best agreement between the measurement and the fit when assuming that the distribution had a triple Gaussian structure. The derived parameters are listed in table 1, while the fitted curves are displayed in figure 6(b). The traps, although shallow, are still quite significant, capturing about 25% of charge carriers generated during irradiation. If it was possible to optimize the crystal by decreasing the capturing role of traps and reducing the afterglow, the light yields of bismuth-based halide perovskites would certainly go higher.
4. Conclusion

We investigated trimethylammonium bismuth(III) hexachloride perovskite as the candidate for a lead-free scintillation material. The RL study reveals the existence of the trapping states with activation energies of 25.71 meV and 129.25 meV. The afterglow decay at 10 K has a composition of 70 s (14.51%) and 1200 s (85.49%). ((CH₃)₄N)₃BiCl₆ demonstrates two activation processes. A strong TQ at RT is observed in which the bright signal is persistent at low temperature with a small NTQ at 50 K. According to the calculated absorption length the proposed material is comparable to the existing series of lead-based chloride compounds at 50 keV. Interestingly, this parameter is higher than the manganese-based chloride system, which reveals that ((CH₃)₄N)₃BiCl₆ crystal is suitable for low-energy x-ray detection. Although the RL only shows the intensity at low temperatures, this is the initial study for full bismuth compounds as most of the previous studies for bismuth are related with the mixing-cation compounds. Such study will pave the way towards high light yield and heavy lead-free perovskite scintillators, which can be interesting for many radiation detection applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

RS: Synthesis crystal, Characterization, Writing—original draft. AA: Characterization, Review and editing. LJ D: Review and editing. AL I: Simulation DFT. ME W: Characterization. MM: Characterization. DK: Characterization. WD: Characterization. MDB: Characterization, Supervision, Review and editing. YK: Supervision, Funding acquisition, Review and editing.

Declaration of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1. Trap parameters derived from the fit based on a triple-Gaussian quasi-continuous distribution of traps (n₀—initial concentration, E—the trap depth, σ—halfwidth, s—frequency factor).

| i | n₀ (10⁶) | Eᵢ (meV) | σᵢ (meV) | s (s⁻¹) |
|---|---------|---------|---------|---------|
| 1 | 6.29 × 10⁶ | 351 | 149 | 10⁻¹² |
| 2 | 1.09 × 10⁵ | 237 | 58.9 | 10⁻¹² |
| 3 | 1.28 × 10⁵ | 284 | 86.2 | 10⁻¹² |
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