Abstract

Recently, halide perovskites have emerged as a promising material for device applications. Lead-based perovskites have been widely explored while investigation of optical properties of lead-free perovskites remains limited. Lead-halide perovskite single crystals have shown light-induced positive photoconductivity, and as lead-free perovskites are optically active, they are expected to demonstrate similar properties. However, we report here light-induced negative photoconductivity with slow recovery in lead free Cs$_3$Bi$_2$Cl$_9$ perovskite. The femtosecond transient reflectance (fs-TR) spectroscopy studies further reveal these electronic transport properties were due to the formation of light-activated metastable trap states within the perovskite crystal. The figure of merits of Cs$_3$Bi$_2$Cl$_9$ single-crystal detectors such as responsivity (17 mA/W), detectivity (6.23 × 10$^{11}$ Jones) and the ratio of current in dark to light (~7160) was calculated. This observation for Cs$_3$Bi$_2$Cl$_9$ single crystals, which were optically active but showed retroactive photocurrent on irradiation, remained unique for such materials.
Halide perovskites have recently drawn significant research interest for their large absorption coefficient, tunable bandgap and long carrier diffusion length.\textsuperscript{1-4} These optoelectronic materials are now at the forefront of current research for both light-emitting and photovoltaic applications.\textsuperscript{5-8} Halide perovskite research has predominantly focused on Pb-based materials perovskites because of their excellent properties, greater stability, and widely understood formation process observed in nanocrystals to bulk micron size single crystals and 0D, 2D and 3D materials.\textsuperscript{9-13, 5, 14-19} Recent studies of Pb-free materials have also demonstrated acceptable optical properties in double perovskites containing group (I) and group (III) metal ions and Sn, Sb and Bi ions.\textsuperscript{20-22, 17, 23-25} Further research has already been focused on developing such new materials without compromising the properties of the material.\textsuperscript{26-29}

As these materials are photoactive, their photoconductivity has been widely studied. These were expected to show enhanced photocurrent or positive photoconductivity (PPC) on irradiation and the same were reported for nanocrystals as well as some bulk single-crystal materials. Ding et al. showed the PPC in CsPbBr\textsubscript{3} single-crystal with high detectivity and rapid response.\textsuperscript{30} Saidaminov et al. also presented the PPC and self-powered photodetection in CsPbBr\textsubscript{3} single crystals.\textsuperscript{31} These results suggested that in lead halide single crystals positive photoconductivity could be observed with different anion and cation variation with their different response and detectivity.\textsuperscript{32-40} Similarly, Bin Yang et al. demonstrated in lead-free MA\textsubscript{3}Sb\textsubscript{2}I\textsubscript{9} single crystals exhibiting PPC with fast response and sensitive detection.\textsuperscript{41} Chengmin Ji et al. showed the high performance of lead-free (TMHD)BiBr\textsubscript{3} single crystals with positive photoconduction and rapid response.\textsuperscript{42} Jun Zhou et al. presented the narrowband photodetection with the positive photoconductivity in lead-free perovskite derivative Cs\textsubscript{2}SnCl\textsubscript{6-x}Br\textsubscript{x} single crystals.\textsuperscript{43} In some cases the conductivity upon illumination was reduced below the level of conductivity in the dark - termed negative photoconductivity (NPC), this phenomenon is often considered an anomaly; there have been reports on the NPC phenomenon.\textsuperscript{44-51} Intriguingly, negative photoconductivity was observed herein for Cs\textsubscript{3}Bi\textsubscript{2}Cl\textsubscript{9} single crystals. The significant current reduction was observed with an illumination time of 15 minutes, and in the dark, the current recovered slowly to its original value. Analysis of impedance spectroscopy and transient absorption spectroscopy revealed that the formation of metastable states may have caused negative photoconductivity and dark self-recovery, by trapping charge carriers which were slowly released in the dark. Evidence of phase change or crystal deformation was not be observed, as optical
features remained similar to the original single crystal material. Bi-based perovskites were largely accepted as lead-free materials and reported with their thermal and moisture stability. Besides, these materials have been demonstrated the high sensitivity for X-ray detectors. However, negative photoconductivity here adds a new feature to the electronic properties in the perovskite family of material.

Figure 1. (a) Digital image of nearly 3 mm single-crystal Cs$_3$Bi$_2$Cl$_9$ perovskite. (b) Single crystal X-ray diffraction of the grown Cs$_3$Bi$_2$Cl$_9$ crystal. Assignments of peaks and the CIF file are provided in supporting information. (c) An atomic model of the unit cell of Cs$_3$Bi$_2$Cl$_9$ perovskite was obtained using the obtained CIF data. (d) Absorption spectra, (e) corresponding photoluminescence spectra, and (f) excited state decay plot of Cs$_3$Bi$_2$Cl$_9$ single crystal. The exciting wavelength is 340 nm and the emission is at 379 nm for the decay plot.

The lead-free perovskite Cs$_3$Bi$_2$Cl$_9$ single crystals were grown following a modified method reported in our previous paper. The slow cooling led to an approximate 4 mm Cs$_3$Bi$_2$Cl$_9$ single crystal. Figure 1a presents the digital image of the single crystal and the scanning electron microscope image is shown in Figure S1, which shows a grain-boundary free surface. Figure 1b shows the single-crystal X-ray diffraction pattern of Cs$_3$Bi$_2$Cl$_9$ crystal. Details of the analysis of these peaks are provided in the supporting information and from their positions, these were confirmed orthorhombic phase. Crystal information file (CIF) from the obtained single crystal is also provided in supporting information. The atomic model showing the unit cell for the obtained
Cs$_3$Bi$_2$Cl$_9$ crystal is presented in Figure 1c. The optical absorption spectra (Figure 1d) of this single crystal showed the band edge around 410 nm and the calculated bandgap is shown in Figure S2. The photoluminescence spectra excited at 340 nm is shown in Figure 1e which featured a narrow band and also blue-shifted in comparison to the band edge. Similar blue shifted and narrow emissions were also reported for CH$_3$NH$_3$PbX$_3$ (X= Cl, Br, I) single crystals$^{58}$ and this characteristic was suggested because of minimized or trap free single crystal. Interestingly, the decay lifetime (Figure 1f) remained in picoseconds indicating atomic or small clusters like transition in these single crystals.

![Image of device structure](image)

**Figure 2.** (a) The device structure of Cs$_3$Bi$_2$Cl$_9$ single crystal, which is used for the electrical measurements. (b) Current-Voltage characterization of Cs$_3$Bi$_2$Cl$_9$ single crystal under 1-sun illumination. Photocurrent profile under different applied voltages as a function of device light-illumination time and dark-storage time. It shows photocurrent degradation of the device under constant light-illumination and self-recovery of the photocurrent in the dark. (c) Current (at 1 V) vs time curve in dark and light illumination conditions. Here D represents the dark condition. L represents the light illumination condition. O represents light off condition.

The current-voltage characteristics of the Cs$_3$Bi$_2$Cl$_9$ single crystal device were measured under 1-sun illumination (Air Mass 1.5) in the planar device structure as shown in Figure 2a. Figure 2b shows the typical I-V characteristics with different light exposure time and corresponding self-recovery again in dark. As observed, the dark current starts decreasing when the light incident on the single crystal. Current decreases completely after 15 minutes of constant 1-Sun illumination and after then current recovers to its original steady-state value in 180 minutes after resting the device in the dark (Figure 2c). The current below the dark level demonstrates the negative photoconductivity in the Cs$_3$Bi$_2$Cl$_9$ crystal.
To confirm the observations in Figure 2, we also perform the impedance spectroscopy (IS) in Cs$_3$Bi$_2$Cl$_9$ single crystal. Figure 3a illustrates the representative Nyquist ($Z' - Z''$) plots of impedance spectra of the Cs$_3$Bi$_2$Cl$_9$ perovskite single-crystal device in the dark, with light exposure and with dark recovery. The diameter of the semicircle increases with illumination indicating increased resistance ($R(\omega) = \text{Re}(Z)$), which is consistent with the trend observed in the bode plots (Figure 3b). Greater resistance is correlated to the reduction of capacitance in the low-frequency region. With the light off, the diameter of the semicircle decreases, returning to the diameter observed in the dark. The equivalent circuit is depicted in the inset of Figure 3a, in which a constant phase element with a parallel resistor element is added with series resistance. The EIS data were fitted using ZSimpWin Software and obtained the element values (Table S1). The impedance of the device increases with light exposure time, contrary to the expected decrease in impedance with increased observation photo-generated current upon light excitation. The behavior of real and imaginary components of impedance with light exposure and recovery time is displayed in Figure S5. This unusual photo-impedance observation is explained using a two-terminal ionic device with deep trap states, consisting of Cs$_3$Bi$_2$Cl$_9$ perovskite as the active layer, a metal electrode as the contact layer, and light-activated deep level traps inside the single crystal. If the perovskite-electrode contact is perfectly reflective, the impedance becomes a Warburg like coefficient at high frequency and purely capacitive at low frequency due to ion accumulation at the interface. At the other extreme, if the charge carriers are allowed to diffuse through the perovskite-metal electrode interface, the contact becomes partially absorptive and there will be an additional semicircular arc at the lower frequency response of the impedance spectrum. In the observed case, the radius and height of the semicircular arc increase gradually with light exposure, becoming more resistive and capacitive, respectively, implying a transition from a photoconductive to a photo resistive state.

The impedance spectroscopy was further utilized to investigate the frequency dependence of capacitance as shown in Figure 3c. We find that the high-frequency capacitive response does not change with light illumination with time. Previously, it is observed that high-frequency capacitance is usually dominated by geometrical and series resistance$^{60-61}$ and the present observation confirms that neither geometrical capacitance nor series resistance does play a major role here. On the other hand, the low-frequency capacitance is supposed to be increased rapidly under the photogeneration of carriers. However, in our case, the low-frequency response reduces
upon 15 minutes of light exposure and regains back in dark within 180 minutes as also observed in the I-V study of these single crystals. Therefore, both the I-V characteristics and impedance measurement study confirm the existence of negative photo-conductivity (NPC) behavior in the as-grown Cs$_3$Bi$_2$Cl$_9$ crystal.

**Figure 3.** Impedance spectroscopy characterization of Cs$_3$Bi$_2$Cl$_9$ single crystal. (a) The behavior of real and imaginary part of impedance (Nyquist plot) in the Dark, Light illumination, and again Light off condition. Inset: Equivalent circuit of this lead-free single crystal. In this circuit, resistance R1 is added in series and constant phase element CPE1 and resistor R2 are added in parallel. Here series resistance R1 is equivalent to contact resistance and R2 corresponds to bulk resistance of crystal. The constant phase element includes the bulk capacitance of the system. (b) The behavior of the real part of impedance with Frequency in the Dark, Light illumination and again Light off condition. (c) Capacitance vs frequency curve in the Dark, Light illumination and again Light off condition. In the low-frequency region, capacitance is decreasing in light illumination condition and again recovering in dark.

To understand the origin of the light-activated degradation and self-recovery behavior, photoluminescence spectra on single-crystal was performed in the dark and also after the exposure of 1-sun illumination for 15 minutes (Figure S3). However, no significant change in the PL position or intensity was observed which discards any light-induced structural or compositional changes. Furthermore, the role of ferroelectricity in the current degradation mechanism in the lead-free single crystal is eliminated in our study as observed timescales for current degradation and recovery are in minutes to hours. This timescale does not coordinate with the proposed domain migration time (milliseconds). Demonstration of a different underlying physical explanation of the photo-degradation/self-healing was also motivated by recently published reports which suggest the difference in the dielectric constant is associated with structural fluctuations, where photo-induced charge carriers change the polarizability. The Raman measurement in dark and after 15 minutes of the light illumination (Figure S4) show no significant change, which eliminates the
possibility of the local structural distortion and light-induced local distortions. All these experimental results directly eliminate photo-induced structural changes, ferroelectricity or the local polarization effects as a plausible mechanism of the observed NPC phenomena.

To further explore the origin of observed NPC, we performed femtosecond transient reflectance (fs-TR) spectroscopy. The fs-TR measurements were carried out using ultrafast transient absorption (TA) spectrometer, where the negative TR signal (i.e., \( \frac{R(t_i) - R(t_0)}{R(t_0)} = \frac{\Delta R}{R(t_0)} < 0 \)) and positive TR signal (i.e., \( \frac{R(t_i) - R(t_0)}{R(t_0)} = \frac{\Delta R}{R(t_0)} > 0 \)) are assigned to the photobleaching (PB) and photoinduced absorption (PIA), respectively. \( R(t_0) \) and \( R(t_i) \) are the reflectance signals without and with pumping at the delay time \( t_i \). The FTRS analysis reveals the formation of the light-activated metastable trap states. Figure 4 shows the TR spectra of the Cs\(_3\)Bi\(_2\)Cl\(_9\) SC after exciting at 350 nm (above band-edge). The negative reflectivity with maximum signal intensity at 383 nm refers to ground state bleach (GSB) observed due to the depletion of the charge carrier population. The GSB recovery kinetic (Figure 4b) depicts two-time constants, a fast 1.5 ps and a long 480 ps, which we attribute as trapping and charge carrier recombination time, respectively. However, at 415 nm excitation (just below the band-edge, Figure 4c), instead of the GSB signal, only a broad PIA is noticed which can be referred to as trap state-assisted absorption. From TR spectra, it is clear that the intensity of trap states reflectivity close to bandgap is low whereas it gradually increases at low energy. The absence of a GSB signature on 415 nm excitation indicates no inherent mid-band state allows the two-photon absorption process.

To explore the nature of the trap state, we compare the TR kinetics at three different wavelengths (Figure 4d) that can be fit using a bi-exponential function with sub ps time scales. As can be seen from the kinetics, the excited state decay is the relatively slower rate in closed to bandgap (at 600 nm) than below bandgap (700 and 890 nm) states.
Figure 4. (a,c) fs-TR spectra at a different time delay of Cs$_3$Bi$_2$Cl$_9$ SC in response to 350 and 415 nm excitation, respectively. (b) GSB dynamic monitored at 383 nm after exciting at 350 nm. (d) Normalized decay kinetics following 415 nm excitation. Solid black lines represent the exponential fitting of experimental data.

We further studied through exciting at 500 nm (below the band-edge) and the figures are summarized in Figure S6. Unlike 415 nm excitation, a relatively less broad and weak PIA is observed after 500 nm excitation. More importantly, the TR kinetics decay monitored in 735 nm to 800 nm in a similar way (Figure S6b). Furthermore, we compare the TR kinetics at 752 nm following 415 and 500 nm excitation (Figure S6c), which shows a significant difference in their decay rate. From the above discussion, it is obvious that the generation of trap states in Cs$_3$Bi$_2$Cl$_9$ SC is sensitive to light. The wavelength-dependent trap-assisted absorption can possible only when the trap states are generated through a light-induced process.
Figure 5. Schematic diagram of the proposed dark self-healing-mediated negative photoconductivity mechanism in lead-free Cs$_3$Bi$_2$Cl$_9$ perovskite single crystal. Here diagram shows the evolution of the valence (VB) and conduction (CB) bands in three different situations. (i) During the dark condition (ii) during light-induced degradation and accumulation of charges and (iii) during recovery or self-healing in dark in dark. The dashed lines between bands represent the light-activated metastable trap states.

To demonstrate the observations in Figure 2-4, a mechanism is proposed based on the changes in the sub-band-gap density of states over the light-exposure duration in the Cs$_3$Bi$_2$Cl$_9$ perovskite single-crystal. As shown in Figure 5, broken lines show an enhanced number of light-activated meta-stable states under constant light exposure. These meta-stable trap states accumulate over time evolution and form charged islands in the bulk of the single crystal, which, in turn, leads to the degradation of the observed dark current. On the other hand, when the device is kept in the dark, the majority of these light-activated trap states dissipate away, and self-healing occurs. However, a more detailed analysis about the depth distribution of these trap states and the detailed microscopic origin needs to be explored.

The observed negative photoconductivity phenomenon in Cs$_3$Bi$_2$Cl$_9$ single crystals can be used in the photodetection application with high responsivity and large detectivity. The responsivity and detectivity were calculated according to formula (SI) and values are estimated as 17 mA/W and $6.63 \times 10^{11}$ Jones at 5V bias voltage. We have observed enhancement in the responsivity and
detectivity with the bias voltage as displayed in Figure S7a and S7b respectively. The ratio of “current in dark” to “current after light incident 15 minutes” was estimated as ~7160 which is very higher in comparison to reported positive photodetectors. We observed that the responsivity and detectivity of the Cs$_3$Bi$_2$Cl$_9$ single crystals are comparable to other reported lead-halide perovskite single crystals based positive photodetectors.$^{30,65-66}$

In summary, the intrinsic photo-stability of lead-free perovskite Cs$_3$Bi$_2$Cl$_9$ single crystal was studied. From I-V and impedance measurements, this is concluded that these materials showed light-induced degradation and negative photoconductivity. From the transient reflectivity spectroscopy, it is assumed here light-illumination could induce meta-stable trap states generation, which stated as responsible for this observed negative photoconductivity as well as the dark self-healing of photocurrent. This resistive switching behavior in perovskite single-crystal provides a deep understanding of the carrier trapping or de-trapping under the light on and off condition. These findings open up the need for further study about the interesting photophysical phenomena in these lead-free perovskite single crystals.

ASSOCIATED CONTENT

Supporting Information:

The supporting Information is attached separately. Crystal synthesis method, characterization details, SEM image, Tauc plot, PL and Raman spectra before and after illumination, analysis of impedance data and fitting parameters, additional TA data, responsivity and detectivity graph.

Data availability
The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.
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