Density of bulk trap states of hybrid lead halide perovskite single crystals: temperature modulated space-charge-limited-currents

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Temperature-modulated space-charge-limited-current spectroscopy (TMSCLC) is applied to quantitatively evaluate the density of trap states in the band-gap with high energy resolution of semiconducting hybrid lead halide perovskite single crystals. Interestingly-multicomponent deep trap states were observed in the pure perovskite crystals, which assumingly caused by the formation of nanodomains due to the presence of the mobile species in the perovskites.

Organometallic and inorganic halide perovskites are prospective candidates to replace conventional inorganic materials not only in the photovoltaic application1–8 but also, in solid state lasers9, light-emitting diodes10, photodetectors11 and solar fuels production12. Lead halide perovskites possess high absorption coefficients, long-ranged ambipolar transport13 and low cost and facile deposition techniques such as coating and printing14–16. Moreover, it has been reported on facile growth of large monocrystals of lead halide17–19 (or even lead free20) perovskites by various techniques. Such single crystals, possessing very low defect density, are good candidates to disclose a variety of interesting and important properties of this group of materials. Perovskite single crystals have shown interesting properties, e.g., perovskite solar cells can harvest below the bandgap21, and perovskite photodetectors possess impressive characteristics for the detection of various wavelengths22. Furthermore, single crystals of lead halide perovskites are high-gain materials for lasing because of their high absorption coefficient, high photoluminescence quantum yield, slow Auger recombination rate, long carrier diffusion length and low defect density23,24.

Alongside with the other interesting properties of the lead halide perovskites, these materials possess two types of conductivity: electronic and ionic one25. Ionic conductivity in lead halide perovskite is the result of cations and/or anions migration across the perovskite under the influence of an electric field. As the result of the ionic diffusion, the open regions or the significant population of vacancies on the appropriate sublattice of perovskite lattice, which allow the ionic movement, appear. Aforesaid vacancy assisted ionic defects act as traps for charge carriers in the perovskite. Therefore the ionic diffusion in lead halide perovskites results in the appearance of lattice defects, which has important implications in terms of long-term stability and performance of perovskite-based devices (i.e. solar cells, LEDs, photodetectors etc.). Moreover polarization of the solar cell electrodes is usually associated with mobile ions and surface carrier recombination, and achievable open-circuit voltage26,27. In this regard, the understanding of the complex charge carrier dynamics induced by the ion migration is highly important. However it has to be noted, that kinetics of the mobile ions in the perovskites is a complex multicomponent phenomenon, which is still poorly understood. The existence of several ionic species, which can be a subject to diffusion, make the experimental evaluation rather obscure. As an example, it has been predicted theoretically and measured experimentally28, that, in fact three types of ionic species can be associated with vacancy-assisted ionic conductivity. The activation energy values to provoke the ionic movement were evaluated as: 0.58, 0.84 and 2.31 eV for I−, MA+ and Pb2+ respectively.

In the present communication the MAPbBr3 perovskite single crystals were studied by temperature-modulated space-charge-limited current (TMSCLC) method29–32. While regular SCLC technique is based on the measurement of current-voltage characteristic (steady-state regime) or time-of-flight of charge carriers (dynamic regime) to get information concerning the current non-linearity, charge carrier concentration, hole or electron mobility,  

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and charge trapping process in various device architectures and materials, the TMSCLC technique is suggested as a self-consistent spectroscopic method for the determination of both the distribution of localized states (traps) and their energy. The spectroscopic character of the method follows from the simultaneous measurement of space-charge current on both voltage and temperature (energy window associated with the Fermi-Dirac statistics and the shift of the Fermi level).

Results and Discussion

As it can be seen from the experimental current-voltage characteristic (Fig. 1), the current is influenced by the barrier up to 0.3 V, it is ohmic ($I \sim V$) in the voltage range (0.3–1.2) V. Then it is a superlinear dependence ($I \sim V^m$) with non-constant exponent $m$ ($m$ increases with voltage). It suggests the presence of charge carrier traps distributed in energy. The current decrease was observed in the voltage range (1.5–1.8) V. For higher voltages the $I$–$V$ characteristic is typical for the material with Gaussian distribution of traps for charge carriers$^{33,34}$. The last part of $I$–$V$ characteristic (voltages higher than about 2 V) can be expressed by Child’s law (trap-free SCLC conduction). Here, for the current density $j$ we can write

$$j = \frac{9}{8} \mu \varepsilon_0 \varepsilon_r V^2 L$$

where $\mu$ is the charge carrier mobility, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_r$ is the relative permittivity, $V$ is the voltage, and $L$ is the sample thickness. From this equation the trap free charge carrier mobility can be determined for $\varepsilon_r = 25.5^{35}$ as $\mu = 17.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

The open question is the decrease of current in the voltage region (1.5–1.8) V. Here, we assume that the “negative differential resistance” is associated with the crystal polarization. As it was reported previously, lead halide perovskites can exhibit unipolar self-doping properties. Thus, depending on the composition of intrinsic point defects the material can be either n- or p-type$^{36,37}$. Hence, due to the presence of the mobile ionic species in lead halide perovskites, biasing the sample results in the crystal polarization, which in turn may be considered as an appearance of the depletion region between highly n-doped or n$^{++}$ (i.e. MA$^+$ rich or Br$^-$ poor) and highly p-doped or p$^{++}$ polar nanodomains$^{38}$. The increasing voltage at the “N-shaped” $I$–$V$ curve is presumably caused by the majority charge carriers tunneling through the depletion region between the MA$^+$ and Br$^-$ ion rich states at the bias voltage (1.2–1.8) V for the MAPbBr$_3$. At higher voltage the charge carriers injected across the depletion region can be observed.

It follows from equations below that each point in the SCL current-voltage characteristic comprises the information about the trap density which influences the current value at the given Fermi level $E_F$. The expression for the current density $j$ in the SCLC regime can be written as:

$$j = \mu \varepsilon_0 \varepsilon_r \Theta \frac{(1 - \gamma) (2 - \gamma) V^2}{L^3}$$

where $\gamma = \frac{d \ln V}{d \ln j}$ is the slope of logarithmic dependence of $I$–$V$ characteristics, and $\Theta = n_f/n_t$ is the ratio of the free ($n_f$) and trapped ($n_t$) charge carrier concentration.

The concentration of trapped charge carriers at the Fermi level ($E_F$) is equal

$$n_t = \frac{\varepsilon_0 \varepsilon_r (1 - \gamma) (2 - \gamma) V}{eL^2}$$

Traps below the Fermi level are usually all occupied and the relation is valid

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Figure 1. Dark $I$–$V$ characteristic (dark blue points) and $I$–$V$ characteristic under illumination (yellow points).
we can determine the density of
for heating and cooling cycle. Here,
where
. The shift of the Fermi level
and
(6)

where
is the trap energy,
is the concentration of electronic states, and
is the Heaviside step function. Thus, using the slope of the current-voltage characteristic
, we can determine the density of the localized electronic states.

Using the equation
, where
is electric conductivity and
is electric field, it is possible to determine the position of the Fermi level with the relation to the band energy levels (i.e. valence or conduction bands)

where
is energy of valence band and
is its states concentration. In ohmic region
is this position proportional to activation energy
, where
is position of Fermi level in thermodynamic equilibrium.

For this reason the activation energy of the current (conductance) was measured for each applied voltage in range of
, with step 28 mV. The temperature was changed (modulated) in the range of
. Figure 2 shows the level of accuracy at the measurement of activation energy according to the relation
, for heating and cooling cycle. Here, L is the distance between the electrodes of the certain area S. The slope of these dependences is directly activation energy.

An approximate relation can be considered:
, and
. The shift of the Fermi level
can be determined according to the relation mentioned above. Note, that Fermi level position represents the energy at which the localized state (trap) is filled during the measurement of current-voltage characteristic.

Figure 3 represents the activation energy and Fermi level shift for the dark (A) and illuminated (B) sample (each point in the plot is averaged from 300 experimental values). Note, that for the low voltages (subohmic regime, V < 0.3 V) where the Schottky barrier is predominant, traps also significantly influence the activation energy. Here, the dependence of the Fermi level on the initial voltage value (V0 ≈ 0.03 V)

and the dominant energy determined as the difference between the activation energy and the shift of the Fermi level
, both in the dark and under the illumination. From the Fig. 3C in which the two dominant energies are plotted together, it can be observed that the dominant energy under illumination being shifted by 0.46 eV to higher values, which indicates that the charge trapping takes place in the same states.

From the Fig. 3 follows that three main trap states (
) influence the electric behavior of the sample under study
. The activation energy
is associated with the thermodynamic equilibrium position of the Fermi level. During the charge injection (the superlinear I–V characteristic), the charge carriers are influenced by traps. The deepest trap
, can be related to the vacancy assisted mobile ionic species (presumably MA+); thus in the range of
the current-voltage characteristic we observe trap filled limit for p-type charge carriers. At higher voltages the interchange of dominant charge carriers is influenced by traps. The deepest trap
, can be observed as a tunneling through the depletion region between p++ and n++ sites.

Under the illumination, the Fermi level is strongly influenced by the light generated charge carriers (electrons). From the overall thermal conductivity measurement the Drude-like behavior is expected38. The dominant energy is significantly lower (0.17 V); no contact barrier was observed (Fig. 3B). The dominant states close to the valence band (0.09 eV) are taken over by the charge carrier traps above the edge of the valence band (−0.08 eV). As a result (see Fig. 3C), three trap states with the energies
, and
are formed under
illumination. These are the same relationships as in the dark, but they are related to the other position of the edge of the valence band (shifted by 0.46 eV to lower values).

Under the assumption, that the concentration of states in the valence band of the MAPbBr3 crystal equals to $N \approx 10^{17}$ cm$^{-3}$ and crystal thickness is $L \approx 10^{-3}$ m, the mobility for holes was determined in the dark conditions as $\mu_p = 1.78 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Using the expression for trapped charge carriers (equation 3) it is possible to calculate their concentration for various energies and therefore to get energy distribution of traps. For the more representative dependence of the charge carriers on individual traps the charge carrier concentration vs. activation energy $g(E) \approx \frac{dn_{\text{tr}}}{dE}$ (Fig. 4A) can be plotted. The red dashed vertical lines represent individual charge carrier traps as it was estimated from the $I$-$V$ characteristics. It can be clearly seen how the concentration of the charge carrier increases at each individual trap states, which means charge carriers accumulation at the trap density. For the above-mentioned calculation the relative permittivity of the MAPbBr3 was taken as $\varepsilon_r \approx 25.5$.

Generally, the values for the

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**Figure 3.** Dependence of activation energy $E_a$, Fermi level shifts $\Delta E_F$ and dominant energy $E_d = E_a - \Delta E_F$ on the applied voltage in the dark (A), under illumination (B) and dependence of both dominant energies (dark/illumination) on the voltage. Note that under light illumination the dominant energy is shifted for 0.46 eV, see the text for details.
concentrations and charge carrier mobilities obtained by the TMSCLC method are close to the values reported before40–44. In the Fig. 4B the concentrations were calculated using the equation (2).

Interestingly, the band diagram (see Fig. 4C) shows, that the charge transfer is associated only with holes in the valence band. Trap state $E_{t1}$ is located above the edge of the valence band, when no light illumination is applied, however, under light illumination it shifts under the edge of the valence band.

The results for all the determined traps are summarized In the Table 1: their position (dominant energy is equal to activation energy when the trap is fulfilled $E_{d} \approx E_{a}$), the concentration of trap states for this case

Table 1. Dominant energies, concentrations of trap states, and drift mobilities of charge carriers MAPbBr$_3$ $E_{F0} = 0.8$ eV).

| Dark | Light | Dark/Light |
|------|-------|-----------|
| $E_{t}$ (eV) | $E_{t}$ (eV) | $N_{t}$ (cm$^{-3}$) | $\mu$ (cm$^{2}$V$^{-1}$s$^{-1}$) |
| 0.63 | 0.17 | 2.4 $\times$ 10$^{9}$ | 1.6 |
| 0.55 | 0.09 | 4.5 $\times$ 10$^{7}$ | 9.1 |
| 0.38 | -0.08 | 6.2 $\times$ 10$^{10}$ | 17.8 |

Figure 4. Dependences of concentration of the charge carriers (A) and drift mobility versus the dominant energy. Concentration of states and mobility at dominant energies (B) of the traps are depicted as dashed (see Table 1). Band gap diagram of carbon/MAPbBr$_3$ (C) Schottky barrier blue and red lines for the dark and illuminated conditions respectively, dominant energies of the traps depicted as dashed.
Mechanism of carrier accumulation in perovskite thin-absorber solar cells.

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Figure 5. XRD pattern of the single crystal MAPbBr$_3$ perovskites (A). Graph inset: single crystal device prepared with the patterned ITO covered glass and contacted with carbon paste.
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Author Contributions
J.P. – conducted the experiments. S.N. and O.Z. – contributed with the theoretical part of the manuscript and calculations. J.K. – provided the synthesis of single crystals. M.W., as a head of the lab, provided materials and necessary equipment. A. K. – designed the experiments and wrote the main text of the manuscript.

Additional Information
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