Carrier Concentration in Bulk Perovskite $CH_3NH_3PbI_3$ Thin Films

Cliff Orori Mosiori[1*], Mogunde Charles[2]

[1]Department of Mathematics and Physics, Technical University of Mombasa, Mombasa, **KENYA**
[2]Department of Mathematics and Physics, Kenyatta University, Nairobi, **KENYA**

[*]Corresponding Contact:
Email: corori@tum.ac.ke

ABSTRACT

Efforts are currently on going on the physics of photo electrics in methyl ammonium lead halide perovskites to unveil the secret of its success in photovoltaics. Since carrier concentration depends on impurity, temperature and other parameters of a semiconductor, herein, an attempt has been made address the relationship between these parameter and carrier concentrations. It was found out that the conventional band edge at 1.58 eV responsible for presenting a blue-shift depends on thickness, temperature and carrier concentration. Thus, in this work, the intrinsic carrier concentration was taken as the number of electrons and it was shown that the observed unusual optical band edge in $CH_3NH_3PbI_3$ perovskite bulk thin films is about 1.58eV. It was concluded that the band edge is beneficial for photo electric effect by making use of its inhibited radiative recombination.

Key words:
Bulk Perovskite, Thin Films, Band Edge, Photo Electric

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INTRODUCTION

Thermal excitation of a carriers from the valence band to the conduction band creates free carriers in both HOMO and LUMO bands (Carlos and Ignacio, 2008; D'Innocenzo et al., 2014; Eames et al., 2015; Habisreutinger et al., 2014; Hao et al., 2014; Haruyama et al., 2014) of both organic and hybrid semiconductors. Its concentration is referred to as intrinsic carrier concentration, denoted by n_i (Habisreutinger et al., 2014; Hao et al., 2014; Haruyama et al., 2014; Jeon et al., 2014; Juarez-Perez et al., 2014; Kasha, 2012). The number of carriers in the valence band in intrinsic material depends on the band gap of the material and the exposed temperature. A large band gap makes it more difficult for a carrier to be thermally excited across it meaning that increasing the temperature makes it more likely that an electron will be excited into the conduction band. This implies that the photo sensitivity and quantum efficiency of an optical device depends on carrier concentration and the operating temperature (Wilczek, 2014).

THEORY

Methyl ammonium lead tri-iodide is a hybrid perovskites. It forms a crystal structure of the type ABX_3 with an organic, ($A = CH_3NH^{+3}$), site cation contained within an inorganic framework ($BX_3 = PbI_3$) of the corner-sharing octahedral and in which CH_3NH^{+3} cause a unique but varying chemical and physical properties. Substitutions effected by Pb^{2+} ion leads to the formation of a double pair perovskite nature (Mosconi et al., 2013; Oga et al., 2014; Pekola et al., 2013; Roche et al., 2013; Roy and Bagchi, 1994; Zhao and Zhu, 2014). Thus using the Fermi-Dirac distribution gives the probability that an energy level, ε, will be occupied by an electron:

$$f(\varepsilon) = \frac{1}{\exp[\frac{(\varepsilon - \mu)}{k_B T}] + 1}. \quad (1)$$

and the number of electrons excited to the conduction band at given temperature, T we apply the Boltzmann Distribution (Habisreutinger et al., 2014; Hao et al., 2014; Haruyama et al., 2014),

$$f(\varepsilon) \approx \exp\left[\frac{(\mu - \varepsilon)}{k_B T}\right] \quad (2)$$

By simplifying Eq. (1) we obtain;

$$n = 2\left(\frac{m_e^* k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{(\mu - E_c)}{k_B T}\right) \quad (3)$$

By solving and simplifying Eq. (3) gives the intrinsic concentration n_i of conduction electrons as equal concentration p_i of holes (Juarez-Perez et al., 2014; Kasha, 2012; Lang et al., 2014; Memming and Bahnemann, 2015; Minemoto and Murata, 2014; Mosconi et al., 2013; Oga et al., 2014):

$$n_i = p_i = \sqrt{N_C N_V} \exp\left(\frac{-\Delta W}{2kT}\right) \quad (4)$$

Using simplification and material parameters, Eq. (4), can be reduced into Eq. (5) and Eq. (6) respectively for conduction and valence band respectively as (Carlos and Ignacio, 2008; D'Innocenzo et al., 2014; Eames et al., 2015);

$$N_C = 2\left(\frac{2\pi m_n kT}{h^2}\right)^{3/2} \quad (5)$$

$$N_V = 2\left(\frac{2\pi m_p kT}{h^2}\right)^{3/2} \quad (6)$$

where, N_C is the effective density of states in the conduction band, N_V is the effective density of states in the valence band, ΔW is the gap energy, k is the Boltzmann's

constant, T is the absolute temperature, h is the Plank's constant, m_n is the effective mass of an electron, and m_p is the effective mass of a hole. Therefore, the concentration n_n of electrons responsible for conduction in a donor-type at low temperatures can be expressed as (Jeon et al., 2014; Juarez-Perez et al., 2014; Kasha, 2012; Lang et al., 2014; Memming and Bahnemann, 2015; Minemoto and Murata, 2014; Mosconi et al., 2013);

$$n_n = \sqrt{N_D N_C}\exp\left(\frac{-\Delta W_D}{2kT}\right) \tag{7}$$

where N_D is donor concentration, ΔW_D – ionisation energy of donor atom and is less than T_s. Thus, at medium temperatures, the concentration n_n equals concentration of donors (Jeon et al., 2014; Juarez-Perez et al., 2014; Kasha, 2012; Lang et al., 2014; Memming and Bahnemann, 2015; Minemoto and Murata, 2014; Mosconi et al., 2013):

$$n_n = N_D . \tag{8}$$

At high temperatures, an *n*-type semiconductor has properties of an intrinsic semiconductor; the concentration of intrinsic carriers exceeds n_n. Then, temperatures T_s and T_i can be easily be expressed as;

$$T_S = \frac{\Delta W_D}{k\ln(\frac{N_C}{N_D})} \tag{9}$$

and

$$T_i = \frac{\Delta W}{k\ln(\frac{N_C N_V}{N_D^2})} . \tag{10}$$

The concentration of holes in an acceptor-type semiconductor can be determined using Eq. (1) to Eq. (6) by substituting N_V for N_C, N_A as well as acceptor concentration in place of N_D respectively; hence the concentration of minority carriers is calculated using mass action law (Memming and Bahnemann, 2015):

$$np = n_i^2 = p_i^2 . \tag{11}$$

It becomes then clear The Fermi level in an *n*-type semiconductor in the extrinsic range is always over the middle of the forbidden band. Its distance from the bottom of the conduction band is given by (Lang et al., 2014);

$$W_c - W_F = kT\ln\frac{N_c}{N_D} . \tag{12}$$

Therefore, using Eq. (5), Eq. (6), Eq. (12) and Eq. (13), the Fermi level in a *p*-type semiconductor in the extrinsic range is found to below the middle of the forbidden band while its distance from the top of the valence band is given by (Lang et al., 2014);

$$W_F - W_v = kT \ln \frac{N_v}{N_A} \quad . \tag{13}$$

$CH_3NH_3PbI_3$ transits from orthorhombic to tetragonal at temperature of 162 K while it transits into cubic structure at approximately 328 K (Habisreutinger et al., 2014; Mosconi et al., 2013; Pekola et al., 2013). When such transitions take place, the effective mass of both electrons and holes in these three states is approximate less than $0.2m_e$, with a carrier mobility of less than 100 $cm^2\ V^{-1}\ s^{-1}$. Therefore, since $CH_3NH_3PbI_3$ has a higher dielectric constant with low effective mass, there is a higher tendency to obey the hydrogen atomic model (Jeon et al., 2014; Juarez-Perez et al., 2014; Kasha, 2012; Lang et al., 2014; Memming and Bahnemann, 2015; Minemoto and Murata, 2014) represented basically in Eq. (14);

$$E_n = -\frac{m^*}{m_o}\frac{1}{2n^2\varepsilon_o^2} \tag{14}$$

where $\frac{m^*}{m_o}$ is the effective mass ratio, $\epsilon 0$ is the static dielectric constant, and n is an integer quantum number for the given energy level in Hartrees.

RESULTS AND DISCUSSIONS

Numerical calculations were carried out and a summary of the results obtained are presented in Tables 1. It can be observed that in some cases, the exact value of the intrinsic carrier concentration in $CH_3NH_3PbI_3$ are similar or equal to the values obtained by modeling in literature or by other approaches like computational analysis (Carlos and Ignacio, 2008; Eames et al., 2015; Jeon et al., 2014; Juarez-Perez et al., 2014; Memming and Bahnemann, 2015). At 300 K, the approximate accepted value for the intrinsic carrier concentration was n_i, is $1.101 \times 10^{29}\ cm^{-3}$ which varied to 9.976×10^{29}about at 169 K which is below room temperature. Values were calculated or obtained by using computation model formula as given by Altermatt and Misiakos (Mosconi et al., 2013);

$$n_i(T) = 5.29 \times 10^{19}\left(\frac{T}{300}\right)^{2.54} \exp\left[\frac{-6726}{T}\right] \tag{15}$$

Table 1: Calculated parameters of $CH_3NH_3PbI_3$ thin films

Average thickness (*nm*)	Temp. (*K*)	Carrier concentration (n_i)×10^n	Band gap (*eV*)	Mobility ($cm^2V^{-1}S^{-1}$)	Diffusion length (μm)	Auger recombination rate (cm^6S^{-1})
223	400	5.472×10^{12}	1.48	20	1.0	**1.130** ×10^{29}
219	375	1.514×10^{12}	1.49	23	1.3	**1.121** ×10^{29}
209	350	3.521×10^{11}	1.50	28	1.7	**1.113**×10^{29}
194	325	6.666×10^{10}	1.51	36	2.1	**1.112** ×10^{29}
188	300	9.696×10^{9}	1.53	42	2.6	**1.101** ×10^{29}
176	275	1.013×10^{9}	1.56	45	3.0	**9.997** ×10^{29}
169	250	6.888×10^{7}	1.58	46	3.1	**9.976** ×10^{29}

CONCLUSION

It was concluded that impurity atoms in $CH_3NH_3PbI_3$ enter the structure by either substitution of the lattice atoms of Pb or by fitting into *interstitial* sites in either tetrahedral, octahedral, or cubic interstices directly. As a result, they modify crtain optical and electrical parameters of methyl ammonium iodide. In general, it was suggested that, atoms which have similar size to the host structure atoms occupy the substitutional sites rather than *interstitial* sites in $CH_3NH_3PbI_3$ samples and concluded that some dopants used on $CH_3NH_3PbI_3$ occupy substitutional sites.

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