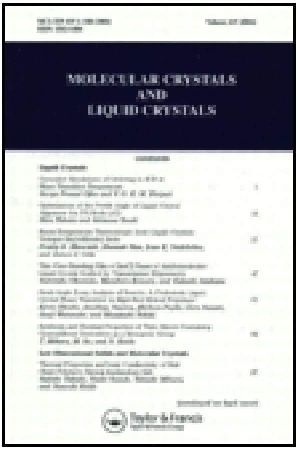

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Electric Field Dependence of the Probability of Charge Carriers Recombination

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The influence of an external electric field on the probability of charge carriers recombination in molecular solid state was investigated. From analytical approximations, the probability of charge carriers recombination is found to decrease with increasing electric field. The results could be useful to explain the decrease of electroluminescence efficiency in single layer organic light emitting diodes (OLEDs) at high electric field.

Keywords: bimolecular recombination; external electric field; molecular materials; OLED

INTRODUCTION

The charge carriers recombination is the key device process in organic light emitting devices (OLEDs) [1]. Electroluminescence occurs via Langevin bimolecular electron-hole pair recombination [2,3], which leads to singlet or triplet excitons formation. Experimental results concerning the electroluminescence in organic materials show that strong electric field induces the decrease of electroluminescence efficiency [e.g., 4,5]. The aim of this work is to analyse the influence of an external electric field on the probability of charge carriers recombination. The results could be used to explain the decrease of electroluminescence efficiency in OLEDs at high external electric field.

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FORMULATION OF THE PROBLEM

The understanding of the behaviour of two oppositely charged particles moving randomly under the influence of their mutual Coulomb attractive potential and an external electric field is of theoretical and practical interest [6–8]. It follows from the fact that the final product of opposite charge carriers encounter – the recombination is recognized as the essential event in OLEDs converting current into light.

It is usually assumed that the recombination process occurs when two oppositely charged particles approach each other to a certain distance, which is called the encounter distance. According to the Langevin formalism [9], which is usually taken to explain the phenomenon of charge carrier bimolecular recombination in OLEDs, the encounter distance must be equal to the Coulombic capture radius, which is defined as a distance at which the kinetic energy of particle is equal to the Coulombic attractive potential energy:

$$kT = \frac{e^2}{4\pi\varepsilon\varepsilon_0 r_C} \quad \text{then} \quad r_C = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT}. \tag{1}$$

where e is the elementary charge, ε_0 is the permittivity of the vacuum, ε is the dielectric permittivity of the medium, k is a Boltzman constant and T is the temperature. The formula describing the bimolecular recombination rate constant resulting from a Langevin model is given by an electric field and temperature independent ratio:

$$\gamma = \frac{e\mu}{\varepsilon\varepsilon_0} \tag{2}$$

where μ is the sum of the carrier mobilities.It is worth to point out that the above formula has been derived from the Smoluchowski expression [10] with the assumption that in the long-time limit charge recombination is a process fully controlled by diffusion and without taking into account the influence of external electric field on the motion of charge carriers. In a variety of molecular solids predictions of the Langevin model of recombination are found to be in agreement with experimental data [e.g., 11]. However the observed values of the bimolecular recombination rate constant in low-mobility materials such as some disordered materials [12,13], polymers [14,15], polymers blends [e.g., 16] and dense media of high charge carriers mobilities [e.g., 17] have been found to be much smaller than those calculated by the Langevin equation. These facts show that not in the all cases the Langevin formalism seems to be adequate for the description of the recombination process in molecular solids. Furthermore, the

Langevin formalism does not take into account the electric field effect on the recombination process.

Theoretical studies of the electric field effect on the recombination process are very few [e.g., 18–20]. However, the most of them refer to theoretical and experimental studies of the electric field effect on geminate recombination in molecular medium [e.g., 21,22] based on classical Onsager model [23]. The influence of electric field on the bimolecular recombination in molecular solid state has been taken into account only in a few papers. Based on the time-dependent Onsager model derived by Hong and Noolandi [22], the influence of external electric field on the bimolecular charge carrier recombination in molecular medium has been analysed in papers [19,24]. The effect of an external electric field on diffusion-controlled bulk ion recombination in medium with high values of charge carrier mobility such as gases or molecular liquids, can be also found [e.g. 25,26].

In our analysis, which refers to molecular solids of low mobility, we predict the decrease of the bimolecular recombination rate with increasing electric field. The reason for this result may be explained in the following way: In the absence of an external electric field, charge carriers perform only diffusive motion. In the presence of an external electric field, they perform drift motion in addition to diffusive motion. Since positively and negatively charged carriers drift in opposite directions, the drift motion affects the rate of encounter between them. For high external electric field, the drift motion prevails the diffusive motion therefore it is rather difficult for two oppositely charged particles approach each other to the encounter distance. It means that the cross section for recombination process in low electric field is larger then those for high electric field. Because of this effect, we conclude that the rate of recombination should be reduced in high external electric field conditions.

DETERMINATION OF THE PROBABILITY OF CHARGE CARRIER RECOMBINATION

In the present treatment of the electric field effect on bimolecular recombination, we consider the system consisted of a thin organic material sandwiched between two metal contacts. Our analysis refers to a bipolar device in which electrons and holes can be effectively injected and their radiative recombination results finally in the emission of light. Although, the direct recombination of free charge carriers without involving recombination centres and the indirect recombination through recombination centres exist simultaneously, we assume that the second recombination mechanism is predominant in the system because the density of trapped charge carriers prevails the density of free charge carriers in molecular medium. We consider that charge carriers injected into the material are temporarily captured at recombination centres and form the space charge. Thus, the maximal average value of density of space charge, resulting form space charge limited current (SCLC), that can be stored inside a sample can be represented by the following expression [27]:

$$\langle n_t \rangle \approx \frac{3}{2}\frac{\varepsilon\varepsilon_0 E}{ed}, \tag{3}$$

where E is electric field strength and d is a thickness of a layer.

Charge carriers injected into the sample can be captured at recombination centres and then recombine with carriers of opposite sign at a rate k_r or they can freely move into the sample and finally discharge at the exit contact at a rate of k_t. Hence, the probability that injected carriers recombines is:

$$P_R = \frac{k_r}{k_r + k_t}. \tag{4}$$

The rate of recombination is defined by the recombination time according to the formula:

$$k_r = \frac{1}{\tau_{rec}} \quad \text{where} \quad \tau_{rec} = \frac{1}{\gamma n_t}. \tag{5}$$

In the above equation γ denotes the recombination rate constant and n_t the density of charge carriers trapped at recombination centres.

The rate constant for discharge equals the reciprocal of transit time as follows:

$$k_t = \frac{1}{\tau_t} \quad \text{where} \quad \tau_t = \frac{d}{\mu E}. \tag{6}$$

Inserting the expressions for k_r (Eq. (5)) and k_t (Eq. (6)) into Eq. (4), the probability of charge carrier recombination can be represented by the recombination time to transit time ratio as:

$$P_R = \frac{1}{1 + \tau_{rec}/\tau_t}. \tag{7}$$

From the above formula follows that the value of the recombination probability tends to 1 when $\tau_{rec} \ll \tau_t$, that is for high density of charge carriers trapped at recombination centres, and thick samples made of low-mobility materials, at low electric fields. Inserting into Eq. (7) the average value of density of trapped charge carriers (Eq. (3)) and the Langevin form for the kinetic coefficient of bimolecular recombination (Eq. (2)), yield $P_R = 0.6$ for the probability of charge carrier recombination.

ELECTRIC FIELD DEPENDENCE OF THE BIMOLECULAR RECOMBINATION RATE CONSTANT

The aim of our analysis is determination of the electric field dependence of the probability of charge carrier recombination. To solve the problem Eq. (7) and the new formula for the bimolecular recombination rate constant as a function of external electric field described in paper [19] have been used.

The expression of bimolecular recombination rate constant as a function of external electric field is given by:

$$\gamma = \frac{4}{3}\pi r_0^3 \frac{v_0\left(1 - e^{-\frac{eaE}{kT}}\right)}{\sqrt{D^2 + \left[v_0 r_0 (1 - e^{-\frac{eaE}{kT}})\right]^2 - D}} \cdot \frac{\sin h(eEr_0/2kT)}{(eEr_0/2kT)} \frac{1}{\pi^{1/2}}$$
$$\times \int_0^{t\frac{4D}{r_c^2}} \frac{d\eta}{\eta^{3/2}} \exp\left[-\left(\frac{r_0^2}{r_c^2\eta} + \frac{1}{4}\left(\frac{eEr_c}{2kT}\right)^2 \eta\right)\right] \quad (8)$$

where v_0 is thermal velocity of the charge carriers, a is lattice separation distance, E is the electric field intensity, kT is the thermal energy, D is the diffusion coefficient, e is the elementary charge carrier, t is the real time, r_0 is the charge carrier separation distance and r_c is the coulumbic radius.

The above expression has been considered in two physical limited cases: at low ($E \to 0$) and high ($E \to \infty$) electric field. From that analysis analytical approximation for the bimolecular recombination rate constant as a function of electric field intensity (E) has been obtained.

The derived formula for the bimolecular recombination rate constant in low external electric field is similar to that given by Langevin formula (Eq. (2)) but with the factor 2/3:

$$\gamma_{LF} \cong \frac{2}{3}\frac{e\mu}{\varepsilon\varepsilon_0}. \quad (9)$$

The similar formula has been also presented in paper [24].

For higher electric field ($eEa > kT$) the bimolecular recombination rate constant can be expressed as a the function of the charge carrier concentration and external electric field intensity:

$$\gamma_{DHF} \cong \left(\frac{2^4}{3^{7/2}\pi}\right)^{1/3} \frac{v_0(ekT)^{1/2}}{\varepsilon\varepsilon_0} \langle n_t\rangle^{1/6} E^{-3/2}. \tag{10}$$

Based on the above expression it can be noted that the increase of the electric field intensity leads to the decrease of the bimolecular recombination rate constant. However, the opposite effect can be seen for the charge carrier concentration dependence on the bimolecular recombination rate constant.

DETERMINATION OF THE PROBABILITY OF CHARGE CARRIERS RECOMBINATION AS A FUNCTION OF ELECTRIC FIELD

Now we present the results of theoretical investigation on the probability of charge carriers recombination under the influence of external electric field. We take into account the new formulas for the bimolecular recombination rate constant obtained for low (Eq. (9)) and high electric field (Eq. (10)) conditions presented in previous section.

The formula for the probability of charge carrier recombination (Eq. (7)) by substituting into equations determining the transit and recombination times (Eq. (5) and (6)) and the average charge carrier density (Eq. (3)) under SCLC conditions can be rewritten as follows:

$$P_R = \left[1 + \gamma^{-1}\frac{2}{3}\frac{e\mu}{\varepsilon\varepsilon_0}\right]^{-1}. \tag{11}$$

According to the above expression and using the analytical equation determining the bimolecular recombination rate constant for low electric field given by Eq. (9), the value of probability for charge carriers recombination is of $\mathrm{P_R} = 0.5$.

For high electric field, taking into account Eq. (10), the probability for the charge carrier recombination becomes a function of the external electric field intensity and it can be represented as follows:

$$P_R \cong [1 + \alpha E^{1/3}]^{-1}, \tag{12}$$

where

$$\alpha = \left(\frac{\pi^2 e^4 d}{2\varepsilon\varepsilon_0 (kT)^3}\right)^{1/6}.$$

The last expression shows that the increase of the electric field intensity leads to decrease of the probability for charge carrier recombination.

Based on the above expression, the range of external electric field for which the dependence of the recombination probability could appear can be determined from the condition:

$$\alpha E_{HF}^{1/3} > 1. \tag{13}$$

Taking into calculations: kT = 0.025 eV, the molecular medium dielectric constant $\varepsilon = 3.4$ [28] and the thickness of a layer d = 10^{-6} m, from the above expression $E_{HF} > 2.5 \times 10^4$ V/m.

It should be noticed that based on Eq. (8) also another condition must be paid:

$$E_{HF}\, ea > kT. \tag{14}$$

For a = 10 nm based on the above formula we obtain $E_{HF} > 2.5 \times 10^6$ V/m.

From the above considerations follows that for high electric fields with value of intensity larger then about 2.5×10^6 V/m, the electric field dependence of the recombination probability could appear and the value of the electroluminescence efficiency will be decreasing with electric field.

CONCLUSIONS

Based on the new model of electric field dependence on the bimolecular recombination rate constant, the description of the probability for charge carrier recombination is presented. It should be noticed that for low electric field under SCLC conditions, the value of probability is constant and tends to 0.5. Such result is quite similar to that which can be obtained using the classical Langevin formula for the bimolecular recombination rate constant. In molecular materials for high electric fields ($E > 2.5 \times 10^6$ V/m), the derived expression for the recombination probability is a weak function of electric field intensity. Furthermore, it can be seen that the increase of electric field leads to decrease of the probability.

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