



Charge carrier chemistry in methylammonium lead iodide

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ABSTRACT

Both electronic and ionic transport properties are key issues in the performance of perovskite solar cells. In order to understand the electrical behavior of organic-inorganic halide perovskites, and the possibilities to influence them, the elucidation of their equilibrium charge carrier chemistry as a function of stoichiometry and dopant concentration is a necessary and fundamental prerequisite. We provide here insight into the point defect chemistry of methylammonium lead iodide, whereby the decisive carriers are identified and their concentrations discussed as a function of stoichiometry (iodine partial pressure) and dopant content (oxygen partial pressure or Na addition). The experimental results indicate how ionic conductivity, which can be attributed to iodine vacancies, and electronic conductivity, which can be attributed to electron holes (or conduction electrons under reducing conditions), can be significantly and systematically altered by such treatments. Experimental results are discussed in the context of simple defect chemical models.

1. Introduction

The discovery of the extraordinary performance of methylammonium lead halides (in particular of the iodide, here abbreviated as MAPbI₃) as photo-absorbers in all-solid-state dye-sensitized solar cells has led to intensive worldwide activities [1,2]. Since then, the electronic properties of these materials, that are of unquestionable importance for the solar function, have been extensively explored [3–5], while their ionic conductivity has been investigated only recently in a systematic manner [6–8]. These experiments, in agreement with some recent reports, show iodine to be very mobile [9–15]. As far as iodine defects are concerned, despite some computational studies [5,16] having reported low formation energies for interstitial defects, major emphasis should be given to vacancies (Schottky defect pairs) [17], due to the ease of formation that such defects commonly have in the dense perovskite structure. Mobility of the methylammonium cation has also been referred to in studies applying illumination and high bias and focusing on surface effects [15,18,19]. In agreement with NMR [8] and electrochemical [6] studies published earlier, as well as theoretical modeling [9], the effects of iodine partial pressure on the ionic conductivity (shown below) clearly indicate that methylammonium vacancies cannot be the predominant charge carrier shouldering the bulk conduction process at least under dark conditions. All this is not surprising and conforms with the well-known result that similar

compounds such as CsPbBr₃, CsPbCl₃, KMnCl₃ [20] and MAGeCl₃ [21,22] are all halide conductors with comparable absolute values for conductivity and activation energies [6,20–22]. Independently of its nature, such a mixed ionic-electronic conductivity leads to bulk stoichiometry polarization whenever the perovskite is electrically biased while sandwiched between neighboring phases which are blocking for the ions, as it is the case in solar cell devices. This effect provides a straightforward explanation for the long time/low frequency “anomalies” reported in devices under operation, such as high “dielectric constant” [23] and hysteresis in *i*-*V* sweep experiments [24]. The bulk nature of these polarization phenomena has been supported by several studies, which reported on the formation of *p*-*i*-*n* junctions under load seizing the entire sample [18,19,25]. In contrast, other works discussing the consequence of ion conductivity in halide perovskites considered only the occurrence of a space charge polarization at the contacts [14,26–28]. While this process will surely also occur [29,30] - and may be relevant for charge carrier separation - space charge relaxation times are typically much smaller owing to the smaller capacitances involved and cannot explain the low frequency anomalies, at least not in thicker films [6,7]. Furthermore, ion transport is a crucial issue as far as the degradation kinetics of these rather unstable materials is concerned. The aim of the present paper is to elucidate the charge carrier chemistry (point defect chemistry) in methylammonium lead iodide, where this does not only address the nature of the point

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defects involved but also their dependence on the degrees of freedom (such as temperature, stoichiometry, impurity and doping content). Through purposeful tuning of these degrees of freedom we will show that both ionic and electronic conductivities, respectively attributed to iodine vacancies and electron holes, can be severely modified. Here we want to stress once again that these considerations refer to equilibrium conditions and hence to the situation in the dark.

2. Results and discussion

A mixed conductor can exchange matter with the surrounding gas phase, therefore its charge carrier concentrations (and thus electronic and ionic transport properties) will depend not only on the temperature, but also on the outer partial pressure of every exchangeable component. Furthermore, its charge carrier chemistry is crucially influenced by impurities or dopants, if these concentrations are on the order of magnitude of the majority carriers. The impact of these parameters is not only critical for a detailed understanding of the material properties, but also reveals suitable adjusting screws to tune the electrical transport properties. To be precise, for a dilute, simple charge carrier chemistry one can show that the equilibrium concentration of any electronic and ionic charge carrier (j) can be given as

$$c_j(T, P_k, C) = \alpha_j \left(\prod_r K_r^{\gamma_j} (T) \right) C^{M_j} \left(\prod_k P_k^{N_{kj}} \right) \quad (1)$$

where the P_k 's are the partial pressures of the reversibly exchangeable components ($k = I_2, O_2, \text{etc.}$), T is temperature and C is the effective dopant concentration [31,32]. The parameters α, γ, M, N are simple rational numbers and follow from solving the defect-chemical mass action problem [33,34]. These numbers change if the nature of the majority carriers changes and are hence characteristic for the specific defect regimes (highlighted by different capital letters in the defect diagrams of Figs. 1 and 2). Eq. (1) predicts an exponential T -

dependence via the mass action constants K_r of reaction r , a power law behavior as regards P_k and a power law behavior as regards the doping content C . For the oxide perovskite $A^{II}B^{IV}O_3$ it is well established that, owing to the dense lattice, the major disorder reaction is the partial Schottky reaction leading to AO deficiency and hence to A and O vacancies (V_A'', V_O'') as majority defects. As oxygen vacancies are sufficiently mobile, the decisive partial pressure that can induce stoichiometry variations is the oxygen partial pressure (P_{O_2}). At sufficiently low P_{O_2} , the perovskite is n-type (excess electrons in B orbitals, forming B^{3+}) and at sufficiently high P_{O_2} p-type (holes in oxygen orbitals, yielding O^-), providing the stability limit is not exceeded. Similarly in $MAPbI_3$, valence and conduction bands are formed by I and Pb orbitals respectively [4,5], whereupon at low P_{I_2} , presumably extremely low P_{I_2} , we expect the material to be n-type (excess electrons predominantly in Pb orbitals, forming Pb^+) and at sufficiently high P_{I_2} p-type (holes predominantly in I orbitals, forming I^0). MA-interstitials and Pb-defects may also occur, but can be treated as frozen dopants (entering the C factor of Eq. (1)). Their effect on the defect chemistry can be neglected as long as their concentrations are not in the range of the majority carriers. Moreover, their mobilities are expected to be too low to influence the overall ion transports [9,10]. As mentioned, in $MAPbI_3$ iodine mobility is significant, while the mobility of MA^+ ions appears to be minor but possibly not negligible [6,9,19]. Hence the major control parameter in terms of electric transport is P_{I_2} , together with temperature and dopant content. The latter comprises frozen-in native defects as well as intentional or non-intentional impurities, all summing up (positively or negatively) in C .

Regarding the I_2 effect, this consists in decreasing the iodine deficiency (we ignore here the possible occurrence of I-excess) according to:

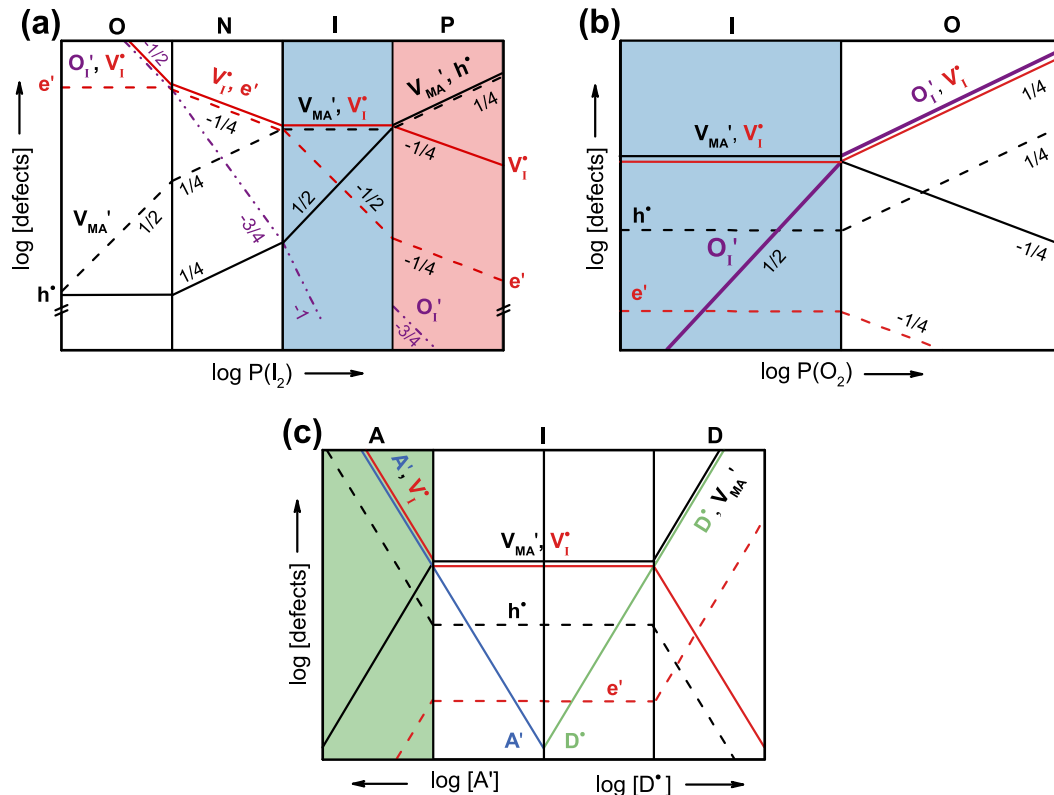
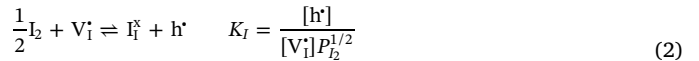


Fig. 1. Kröger-Vink diagrams of undoped $MAPbI_3$ as a function of (a) I_2 , (b) O_2 partial pressures (also given in Ref. [35]), (c) doping content. The capital letters on the abscissas indicate different transport regimes depending on the majority mobile carriers dominating: excess electron holes (P), intrinsic (I), excess electrons (N), oxygen-dominated (O), acceptor doped (A), donor doped (D). The slopes for the various defect concentration are given directly on the figure.

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