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Effect of the heat treatment of $CH_3NH_3PbI_3$ perovskite on its electrical and photoelectric properties

Dmitriy V. Amasev,*[a] Shamil R. Saitov,[b] Vladislav G. Mikhalevich,[a] Alexey R. Tameev[c] and Andrey G. Kazanskii[b]

[a] *Prokhorov General Physics Institute, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: amoslegkie@gmail.com*
[b] *Department of Physics, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation*

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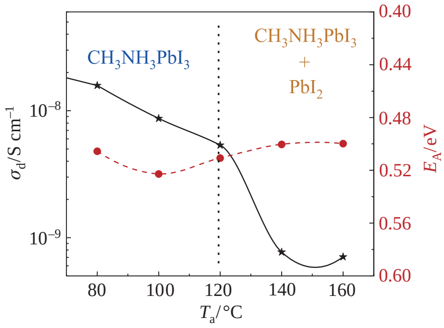
The effect of the annealing of $CH_3NH_3PbI_3$ perovskite on its electrical, photoelectric and optical properties has been estimated. The annealing leads to a two-phase structure consisting of perovskite and lead iodide, whose relative concentrations depend on the annealing temperature. The formation of a PbI_2 phase in a perovskite film upon heating leads to a decrease in the conductivity and photoconductivity of two-phase material, which contradicts the assumption of a decrease in recombination associated with PbI_2, obtained by measuring the parameters of a solar cell.



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Hybrid organometal perovskite based on methylammonium lead iodide $CH_3NH_3PbI_3$ (MAPI) is a promising material for optoelectronics and photovoltaics. The efficiency of solar energy conversion by perovskite elements exceeds 25%.[1] At the same time, research on improving perovskite solar cells continues.[2] However, the stability of the parameters of these solar cells is worse than that in traditional solar cells. The properties of perovskite depend on the preparation conditions.[3] In particular, the PbI_2 phase can also be present in the material upon moderate heating.[4–6] Moreover, the efficiency of perovskite solar cells increased at some PbI_2 concentrations.[7] It was assumed[7,8] that PbI_2 is mainly formed at the grain boundaries of MAPI films, which can be useful for the operation of solar cells leading to a decrease in recombination[7] or an improvement in the processes of charge carrier transfer in the structure of solar cells.[4,8] Thus, the effect of PbI_2 present in a perovskite film on its electrical and photoelectric properties is of great interest, and it was studied in this work.

Microcrystalline $CH_3NH_3PbI_3$ perovskite films with a microcrystal size of ~350 nm and a thickness of 350–400 nm were one-step deposited on a glass substrate using a mixture of PbI_2 and CH_3NH_3I (MAI) in a molar ratio of 1 : 1, which resulted in the formation of an n-type material. Gold contacts in a planar configuration were deposited on the perovskite film surface for electrical and photoelectric measurements. The perovskite film parameters were measured in a vacuum at a residual pressure of 10^{-3} Pa. To form PbI_2 in a perovskite film, we used thermal annealing in a vacuum for 10 min at temperatures T_a from 60 to 160 °C.[5] The dark conductivity σ_d and photoconductivity $\Delta\sigma_{ph} = \sigma_{ph} - \sigma_d$ (where σ_{ph} is the conductivity under illumination) of the perovskite film were measured at room temperature (see Online Supplementary Materials for details).

To control the effect of the annealing temperature on the phase composition of the perovskite film, we measured the spectral dependences of the photoconductivity (normalized to the number of incident quanta N) (Figure 1).

The spectral dependences of the photoconductivity are similar in behavior at $T_a \leqslant 120$ °C. A sharp exponential decrease in the photoconductivity was observed at the photon energies $h\nu < 1.6$ eV, which indicates a band gap of ~1.6 eV corresponding to $CH_3NH_3PbI_3$ in the test films. For $h\nu > 1.6$ eV, the photoconductivity weakly depended on the energy of incident quanta. With increasing T_a to 120 °C, only a slight decrease in the photoconductivity at $h\nu > 1.6$ eV and the formation of a certain feature at $h\nu > 2.25$ eV were observed.

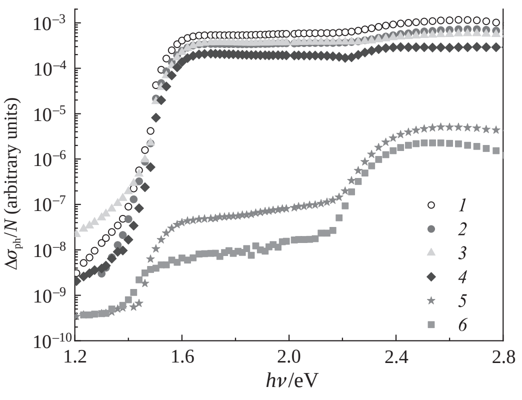

Figure 1 Photoconductivity spectral dependences at room temperature for perovskite films annealed at the temperatures T_a: (*1*) 60, (*2*) 80, (*3*) 100, (*4*) 120, (*5*) 140 and (*6*) 160 °C.

The most dramatic changes in the spectral dependence and the photoconductivity occurred after film annealing at T_a = 140 °C. The photoconductivity significantly decreased in the entire test spectral range, where the ‘second edge’ of photoconductivity was formed at $h\nu$ > 2.25 eV. These changes were associated with the thermal decomposition of MAPI into PbI_2 and MAI and the formation of lead iodide PbI_2 with a band gap of 2.4 eV in the structure.[8]

Figure 2(*a*) shows the effect of annealing temperature on the photoconductivity at room temperature for photon energies of 1.8 and 2.4 eV. The most significant decrease in the photoconductivity after film annealing at T_a = 160 °C was observed at photon energies of 1.6–2.2 eV corresponding to the generation of nonequilibrium charge carriers in perovskite. This indicates a significant decrease in the fraction of MAPI in the two-phase film formed at this annealing temperature.

On the other hand, as can be seen in Figure 1, despite the increase in the fraction of PbI_2 in the film after its annealing at 160 °C, the photoconductivity decreased at $h\nu$ > 2.4 eV, which corresponds to the generation of nonequilibrium carriers in PbI_2. The photoconductivity measured at $h\nu$ > 1.6 eV in the film annealed at T_a = 160 °C indicated the generation of nonequilibrium charge carriers in both MAPI and PbI_2. At the same time, relative changes in the photoconductivity due to annealing at T_a = 160 °C (photon energies $h\nu$ of 1.6–2.25 and > 2.4 eV) pointed out that the generation and transfer of nonequilibrium charge carriers in these two-phase films mainly occurred in PbI_2. The contribution of $CH_3NH_3PbI_3$ to the photoconductivity can be associated with the close energy positions of the conduction band edges of $CH_3NH_3PbI_3$ and PbI_2.[4] The observed decrease in photoconductivity as a result of annealing in the entire spectral region was apparently associated with a decrease in the mobility and, possibly, in the lifetime of charge carriers in the formed two-phase structure.

The effect of the annealing temperature on the dark conductivity of the films indicated a possible decrease in the drift mobility of charge carriers as a result of the film annealing. Figure 2(*b*) shows the dependences of the dark conductivity at room temperature and the activation energy on the annealing temperature. At $T_a \leqslant$ 120 °C, the conductivity slightly decreased due to the formation of wide-gap PbI_2 at the interfaces of perovskite microcrystals[3] and, accordingly, a decrease in the mobility of charge carriers. As in Figure 2(*a*), a sharp decrease in the dark conductivity after film annealing at 140 °C can be explained by a significant increase in the fraction of PbI_2 in the test material as a result of annealing. The conductivity of the test semiconductor material is determined by the concentration and mobility of charge carriers. As can be seen in Figure 2(*b*), the annealing of perovskite films led to a decrease in the conductivity by more than an order of magnitude. Meanwhile, the activation energy of the conductivity did not change significantly. It is well known that the activation energy of the conductivity of disordered semiconductors is mainly determined by the position of the Fermi level relative to the percolation level of charge carriers, which, in turn, determines the concentration of free charge carriers.[9] The experimental results revealed no significant changes in the activation energy and, accordingly, in the position of the Fermi level relative to the percolation level in the two-phase film formed after annealing. In this case, the annealing-induced decrease in conductivity can be associated with a decrease in the charge carrier mobility in the two-phase material formed as a result of annealing, with the main fraction being lead iodide PbI_2.

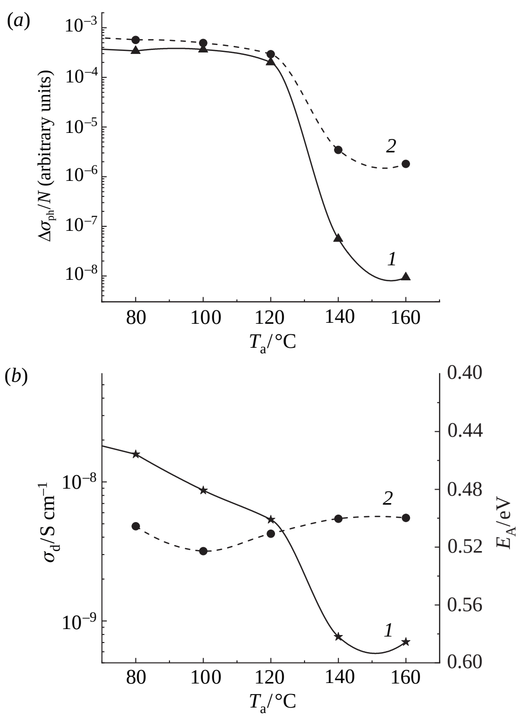

Figure 2 Effects of annealing temperature (*a*) on the photoconductivity at room temperature at photon energies of (*1*) 1.8 and (*2*) 2.4 eV and (*b*) on (*1*) the dark conductivity at room temperature and (*2*) the activation energy.

Thus, we found that the formation of the PbI_2 phase in a perovskite film upon heating leads to a decrease in the photoconductivity of the two-phase material, which contradicts the assumption of a decrease in recombination associated with PbI_2, obtained by measuring the parameters of a solar cell. In addition, as a result of the appropriate heat treatment of a perovskite film, it is possible to create a planar two-phase structure consisting of semiconductor materials with significantly different band gaps.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.07.010.

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