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## Features of the low-temperature conductivity of organometallic perovskite films with the introduction of graphene oxide particles into them

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The influence of the introduction of graphene oxide (GO) particles on the low-temperature conductivity of composite films based on organometallic perovskites  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  with GO particles with a concentration of 0–5 wt.% has been studied. It has been established that the introduction of GO particles into ITO/ $\text{CH}_3\text{NH}_3\text{PbBr}_3$ :GO/ITO/glass films manifests itself in a decrease in the activation energy of the temperature dependence of the conductance. A sharp increase by 5–6 orders of magnitude of the resistance of the films at temperatures below 150 K was found. It is assumed that in the studied  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ :GO systems at  $T > 150$  K, the hopping mechanism of transport predominates, associated with the capture and accumulation of charge carriers in GO particles, and the increase in resistance at  $T < 150$  K may be due to the structural phase transition characteristic of organometallic perovskites in this temperature range.

**Keywords:** organometallic perovskites, graphene oxide, electrical conductivity, low-temperature transport.

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### 1. Introduction

Organometallic halide perovskites have been the subject of intensive research in recent years due to the high efficiency of solar cells, LEDs and other structures based on them [1], since they combine the advantages of inorganic and organic materials, which makes them promising for use in various flexible electronic devices [2]. The mechanisms of charge carrier transport in various organometallic perovskites have previously been studied quite intensively [3–6]. The low-temperature dependences of the resistivity of such films were obtained, which demonstrated a significant hysteresis during thermal cycling, which, in particular, was explained by the influence of structural phase transitions in such materials. As shown earlier, organometallic halide perovskites have a temperature-dependent crystal structure, in which phase transitions from cubic to tetragonal and further — to orthorhombic phase are observed with decreasing temperature [7]. Such structural phase transitions can affect both the current–voltage characteristics and the temperature dependences of the conductivity (conductance) of organometallic perovskites at corresponding temperatures close to the phase transition temperatures [6]. It was assumed that the transport of charge carriers in organometallic perovskites is due to the high mobility of ionic defects, such as halide vacancies, and is implemented both through grain boundaries and inside grains [8]. At the same time, low-temperature electronic properties and the fundamental mechanism responsible for the transfer of charge carriers, including the effect of phase transitions on them, in composites of organometallic halide

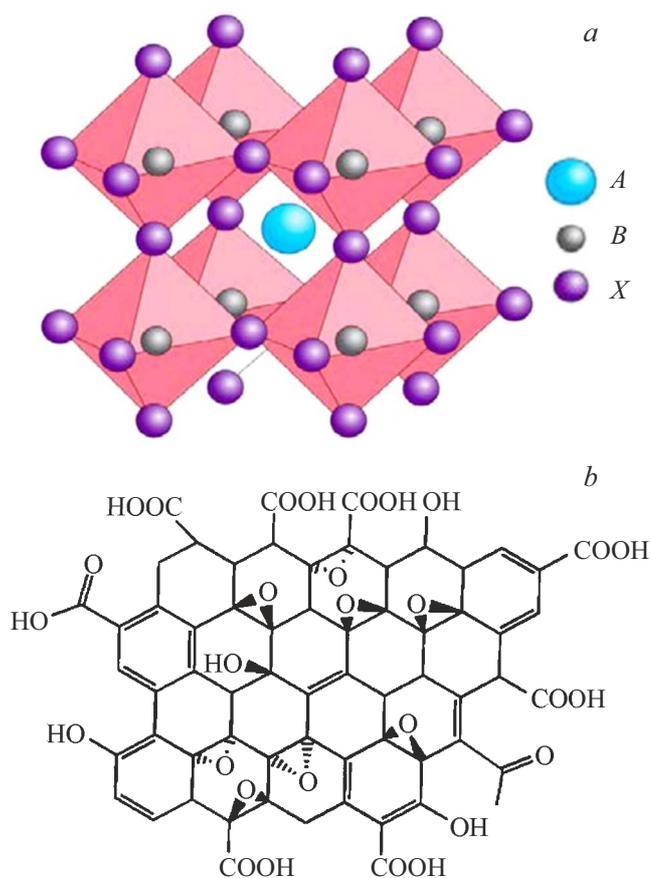
perovskites with graphene derivatives — graphene oxide (GO), have not yet been studied in detail.

In this article, we study the effect of introducing GO particles on the low-temperature conductivity of composite films based on  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  with GO concentration of 0–5 wt.%. It has been established that introduction of GO particles into Ag/ $\text{CH}_3\text{NH}_3\text{PbBr}_3$ :GO/ITO/glass films manifests itself in a decrease in the activation energy of the temperature dependence of the conductance ( $G(T) = 1/R(T)$ , where  $R$  is the resistance). The transport mechanism in the studied structures associated with the capture and accumulation of charge carriers in GO particles, as well as the possible influence on the mechanism of transport of structural phase transitions in perovskites at low temperatures are discussed.

### 2. Research targets and methods

Powders of organometallic perovskites  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  (also designated as MAPbBr<sub>3</sub>, band gap width  $E_g = 2.3$  eV) purchased from Xi'an Polymer Light Technology Corp. and used without further processing were used. Another component of the composites was particles of graphene oxide (GO) synthesized at AkKoLab LLC and used without additional processing. The chemical structures of organometallic perovskite  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ , as well as graphene oxide [9] are shown in Fig. 1, *a, b*.

The  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ :GO films studied in this article were prepared by depositing the appropriate solutions on glass substrates with conducting layers of indium-tin oxide (ITO) 5 mm wide, spaced 200  $\mu\text{m}$ .  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  powder was



**Figure 1.** Structures of organometallic perovskite  $A^+BX^-$ , where  $A^+ = \text{CH}_3\text{NH}_3$ ,  $B = \text{Pb}$ ,  $X^- = \text{Br}_3$  (a), graphene oxide [9] (b).

dissolved in DMA — N,N-Dimethylacetamide, then the solution was stirred for 10 min on ultrasonic mixer Bandelin Sonopuls HD 2070 ( $f \sim 20$  kHz). The resulting solutions were deposited on substrates with ITO contacts by drop-casting, after which they were dried at a temperature of  $100^\circ\text{C}$  for 20 min in an inert box. The film thickness was  $2\text{--}3\ \mu\text{m}$ . Prior to measurements, the samples were stored in MB vacuum desiccator „SANPLATEC Corp.“

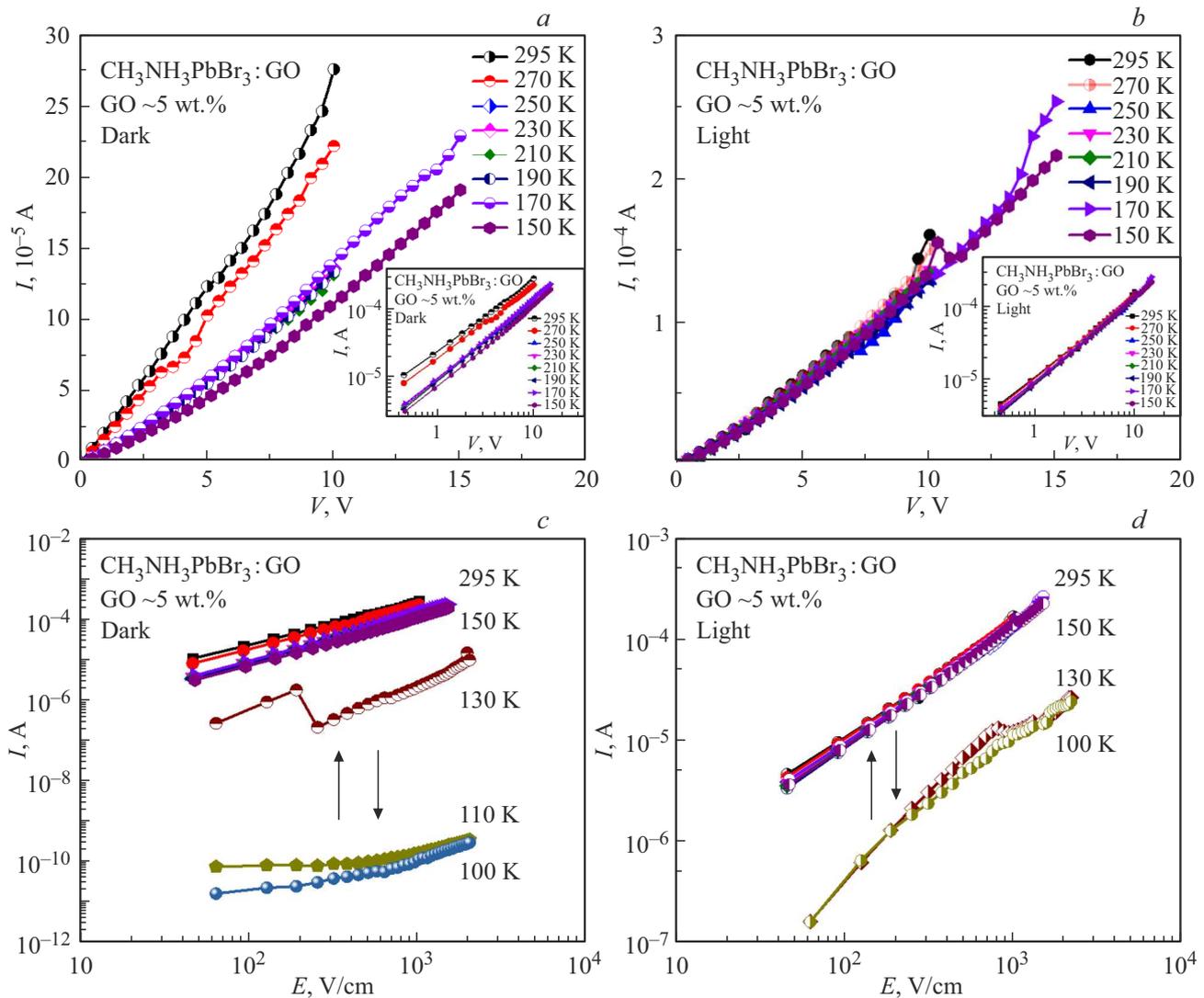
The current-voltage characteristics (I-Vs) of the samples were measured in planar geometry using a two-probe scheme in the temperature range  $290\text{--}77$  K in the dark and under illumination with a sunlight simulator with a wavelength of  $300\text{--}700$  nm using nitrogen ( $\text{N}_2$ ) optCRYO198 optical cryostat with temperature stabilization function and automated measuring setup based on Keithley 6487 picoammeter. The voltage on the electrodes varied from  $-20$  to  $+20$  V with a variable step. Contacts to ITO electrodes were made with silver wire using carbon and silver pastes (SPI).

### 3. Results and discussion

Typical I-Vs of  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  (GO  $\sim 5$  wt.%) films in linear and double logarithmic scales at temperatures of

$295\text{--}150$  K, measured in the dark are shown in Fig. 2, a and in the inset to Fig. 2, a respectively. It follows from Fig. 2, a that the I-Vs characteristics of the  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films in the dark demonstrate the temperature dependence characteristic of semiconductor materials (the current decreases with increasing temperature), while the I-Vs characteristics are actually linear both at  $295$  K, and at lower temperatures up to  $150$  K. As shown in the inset to Fig. 2, a, at all temperatures in the filed range up to  $500$  V/cm, the I-Vs characteristic slopes follow the law  $I(V) = V^m$ , where the exponent  $m$  varies from  $1.04$  ( $295$  K) to  $1.22$  ( $150$  K), which indicates the ohmic nature of the conduction in such composite films in the dark in the temperature range  $295\text{--}150$  K. When the samples were illuminated by a sunlight simulator with a wavelength in the range of  $300\text{--}700$  nm, a slight increase in current was observed, while the I-Vs characteristics had a weak nonlinear character, as shown in Fig. 2, b, which indicates that the  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films remained in the ohmic regime under illumination, in which the current follows the power law  $I(V) = V^m$ , where  $m$  varies from  $1.2$  ( $295$  K) to  $1.16$  (at  $150$  K), i.e. close to  $m \sim 1$ . In this case, under illumination, a very weak temperature dependence of the I-Vs was observed in the temperature range  $295\text{--}150$  K, which was accompanied by weak photoconductivity in the  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films in the visible spectral range. So for  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  samples with content GO  $\sim 2.5$  and  $5$  wt.% conduction values at  $295$  K increased from  $2.58 \cdot 10^{-5}$  S/cm and  $5.49 \cdot 10^{-3}$  S/cm in the dark to  $3.04 \cdot 10^{-5}$  S/cm and  $5.95 \cdot 10^{-3}$  S/cm under illumination, i.e. by  $18$  and  $8\%$ , respectively. As the temperature decreases below  $150$  K, in the  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  (GO  $\sim 2.5$ ;  $5$  wt.%) films a reversible jump-like decrease in the current through the sample was found, both in the dark (by  $5\text{--}6$  orders) and under illumination (by  $1$  order), as shown in Fig. 2, c, d. In this case, the I-Vs characteristics of such films in the dark at  $T < 150$  K become nonlinear in fields up to  $2000$  V/cm, and the conduction values in the dark decrease from  $2.54 \cdot 10^{-3}$  S/cm at  $150$  K to  $2.5 \cdot 10^{-9}$  S/cm at  $110$  K. It should be noted that I-Vs behavior at temperatures  $T < 150$  K observed in the  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  (GO  $\sim 2.5$ ;  $5$  wt.%) films differs from the I-Vs observed earlier in similar materials at  $295$  K with the effect of resistive switching, when the current, on the contrary, increased abruptly when offset of  $\sim 0.1\text{--}0.2$  V was applied [10].

As shown in Fig. 3, the character of the I-Vs characteristics and field dependences of the current of  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  films without GO particles has a more complex form, than that of  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$ , both in the dark and under simulated sunlight. As follows from Fig. 3, the current in such samples is much lower (by  $5$  orders of magnitude) than in films doped with GO particles, and the dependence  $I(V) = V^m$  has two slope with a characteristic inflection point at electric field strength of  $E \sim 300$  V/cm, where  $m \sim 1.0\text{--}1.1$  (at  $T = 295\text{--}150$  K) at  $E = 0\text{--}300$  V/cm, and at  $E > 300$  V/cm the slope  $m$  increases to  $\sim 3.2\text{--}3.8$ . A similar character of the



**Figure 2.** I-Vs of  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  (GO  $\sim 5$  wt.%) films in linear and double logarithmic (insets) scales at various temperatures measured in the dark (a, c) and under sunlight simulator (b, d); c, d are dependences of the current on the electric field strength in the temperature range 295–100 K for the same sample in a double logarithmic scale.

dependence  $I(E)$  was observed at 295 K in  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  films at their illumination, ( $I(V) = V^m$ ,  $m \sim 1.1$  in fields up to 300 V/cm and  $m \sim 2.8$  at  $E = 0\text{--}300$  V/cm), while, in contrast to the  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films, a noticeable photosensitivity of such samples was observed (Fig. 3). Generally, this behavior of the  $I(E)$  dependences at different temperatures in  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  films resembles behavior characteristic of the mechanism of currents limited by the space charge, although the exponent in this case should be somewhat lower than that observed for the samples we studied [11].

Based on the I-Vs obtained from their ohmic regime, the dependences of the conductance  $G = 1/R$  of  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  and  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films on the reciprocal temperature,  $G(1000/T)$  in the temperature range 295–150 K shown in Fig. 4 were constructed. As follows from Fig. 4, the  $G(T)$  dependences of the  $\text{CH}_3\text{NH}_3\text{PbBr}_3$

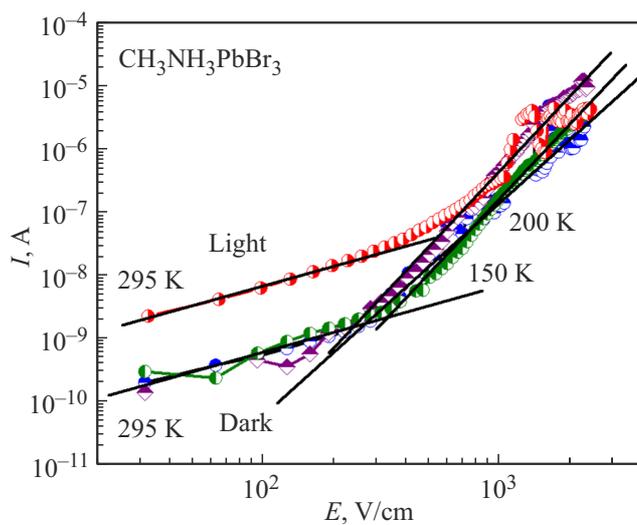
and  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  (GO = 2.5; 5 wt.%) films have a weak activation character and can be described by expression

$$G(T) = G(0) \exp(-Ea/k_B T), \quad (1)$$

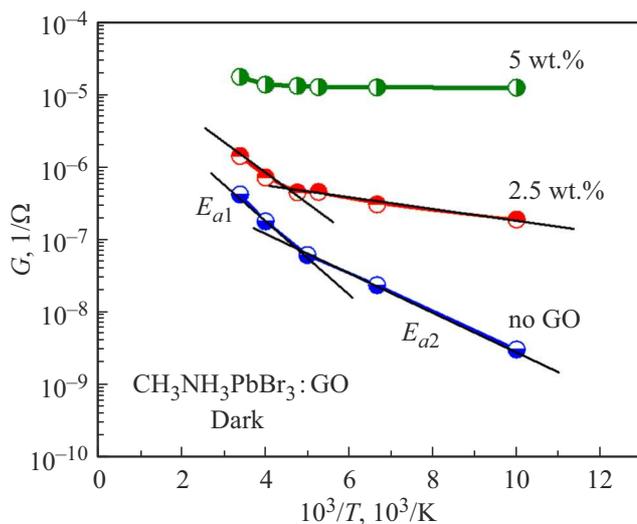
where  $Ea$  is activation energy,  $T$  is temperature,  $k_B$  is Boltzmann constant. The conduction activation energy,  $Ea$ , was determined based on the temperature dependences  $G(T)$  by the formula:

$$Ea \text{ (meV)} = (200 \Delta \lg G(T)) / (\Delta 1000/T), \quad (2)$$

where  $G$  is conductance;  $T$  is temperature. As follows from Fig. 4, typical dependences  $G(T)$  have two activation energies with an inflection point at temperatures  $\sim 200$  K. Thus, at  $T > 200$  K for  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films with concentration GO  $\sim 0; 2.5$  and 5 wt.%,  $Ea = 104; 73$  and 18 meV



**Figure 3.** Dependences of the current on the electric field strength of  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  films in double logarithmic scale at different temperatures (295–150 K), measured in the dark and illuminated by a sunlight simulator at 295 K.



**Figure 4.** Dependences of conductance on  $1000/T$  for  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films with different GO content: 0; 2.5; 5 wt.%.

are observed respectively. With a decrease in temperature for films with a concentration of GO particles from 0 to 5 wt.%, a decrease in the values of  $E_a$  for the temperature dependences of the conductance is observed, namely,  $E_a = 52.1; 14.3$  and  $2.2$  meV for samples with  $\text{GO} = 0; 2.5; 5$  wt.%, respectively. The obtained values  $E_a$  indicate the energies required for the transfer of charge carriers (electrons and holes) in transport processes at given temperatures.

The presented temperature dependences of I-Vs and  $G(T)$  demonstrate the change in the character of charge carrier transport in  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  and  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$

films as the temperature decreases. As follows from the above results, the dependences  $G(1000/T)$  for the sample without GO have the so-called inflection point at a temperature of 150–200 K, which agrees with the results of our previous studies of the low-temperature dependences of the conduction of perovskite films [6]. As the GO concentration increases, this effect becomes less noticeable: for example, even at 5 wt.% of the GO concentration in the film, the sample demonstrates an extremely weak change in the slope of the dependence  $G(1000/T)$  with decreasing temperature. However, in contrast to  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  films, in  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  ( $\text{GO} = 2.5; 5$  wt.%) films at  $T = 150$  K there is a sharp reversible current drop by 5–6 orders both in the dark and under illumination, as shown in Fig. 2, c, d. It can be assumed that the nature of the dependence  $G(1000/T)$  at relatively high temperatures (above 200 K) with a higher activation energy can be associated with conduction through polaron states. The absence of noticeable photoconductivity and temperature dependence of the I-Vs characteristics upon illumination of  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films may be due to the effect of modifying the initial perovskite by GO particles and excitation of charge carriers above the mobility edge, respectively. At temperatures below 150–200 K, in our opinion, the hopping mechanism of transport associated with the capture and accumulation of charge carriers in GO particles predominates in the studied systems. The reversible sharp decrease in current observed at  $T < 150$  K (an increase in resistance by 5–6 orders of magnitude) and a transition to a lower  $E_a$  in the  $G(1000/T)$  dependence for  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  films can be related to the fact that organometallic perovskites of the  $\text{MAPbX}_3$  family have a temperature-dependent crystal structure, in which, as the temperature decreases, phase transitions from cubic to tetragonal and then to orthorhombic phases are successively observed. The characteristic temperatures  $T_{\text{char}} = 150\text{--}200$  K observed in the samples we studied, correlate with the temperature of the phase structural transition from the tetragonal to the orthorhombic phase in organometallic perovskite films [7]. This allows us to assume that the current jump in the I-Vs characteristic observed by us with decreasing temperature and the transition in the  $G(1000/T)$  dependence from higher to lower activation energy at  $T_{\text{trans}} = 150\text{--}200$  K can also be related to the structural phase transition both in the  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  films and in the  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  samples. It is necessary to further study the influence of the composition and deposition conditions of  $\text{CH}_3\text{NH}_3\text{PbBr}_3:\text{GO}$  films on the effects found, various substrates, and also the influence of materials and geometry of the electrodes.

#### 4. Conclusion

In the article the influence of introduction of GO particles on the low-temperature conduction of composite films based on organometallic perovskites  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  with

GO particles with a concentration of 0–5 wt.% is studied. It has been established that introduction of GO particles into ITO/CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>:GO/ITO/glass films manifests itself in a decrease in the activation energy of the conductance temperature dependence —  $G(1000/T)$  in the presence of an inflection point of this dependence at  $T = 150–200$  K. A sharp reversible increase in film resistance by 5–6 orders at temperatures below 150 K is found. It is assumed that the hopping mechanism of transport associated with the capture and accumulation of charge carriers in GO particles prevails in the studied systems, and the increase in resistance at  $T < 150$  K is possibly due to a structural phase transition characteristic of organometallic perovskites in this temperature range.

### Conflict of interest

The authors declare that they have no conflict of interest.

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