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Investigation of Electronic Conductivity in PbI$_2$:Hf Single Crystals

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A study of the electron-hole conductivity in PbI$_2$ single crystals doped with Hf (0.2 wt %) was conducted using the Wagner polarization cell method. The influence of the Hf alloying admixture (0.2 mass%) on the nature and parameters of lead diiodide's electronic conductivity has been analyzed.

Basing on the received current-potential dependences, p-type conductivity of a single crystal PbI$_2$:Hf was established. The hole conductivity values (σ_p^o) were determined in the studied temperature range allowing to construct temperature dependence. The σ_p^o value for single crystal PbI$_2$:Hf increased responsively to increasing temperature. For PbI$_2$ and PbI$_2$:Hf, a comparative analysis of the electron-hole conductivity was carried out. This investigation allowed determining the activation energy σ_p^o reduction from 0.47 eV to 0.32 eV due to hafnium doping. Consequently, the presence of Hf admixture in PbI$_2$ crystals causes new impurity acceptor levels located at a distance of 0.64 eV from the upper limit of the valence zone.

Keywords: a single crystal, lead diiodide (PbI$_2$), conductivity, polarization cell.

Introduction

Lead diiodide (PbI$_2$) crystals belong to a class of ionic semiconductors with a small fraction of the electron-hole conductivity component. These compounds can be applied in medical devices, as sensitive elements of detection devices, including ionizing radiation detectors, and others. [1-11]. Thus, the electrophysical parameters of these crystals as well as information on the energy levels structure in the forbidden zone are important. Despite the increased scientific interest in PbI$_2$, its electrophysical properties have not been studied sufficiently. In particular, the nature of charge carriers in PbI$_2$ remains questioning, since the literature gives contradictory data on the nature and parameters of electrical conductivity. This phenomenon can be explained by differences in experimental methods [12-15].

Also poorly studied in this field are doped PbI$_2$ single crystals (impurities Ho, Gd, Er, Yb, Ce, Tb, Tm, Al, Co, Mn) whose studies are limited to the measurement of electrical conductivity or electrical resistivity [16-18]. At the same time, these crystals lack data on the type and magnitude of the non-basic charge carriers and their fraction of the total electrical conductivity. Note that the results of this type of research are not only of scientific interest but may also have practical implications. Promising in this direction may be doping of transition metals.

The purpose of this work was to investigate the effect of the Hf dopant on the nature and magnitude of the electron-hole component of the conductivity of PbI$_2$ single crystals.

I. Methodic of experiment

The PbI$_2$:Hf single crystals grown in quartz ampoules according to the modified Bridgman-Stokbarger method [19-20] became the object of the study. Doping was conducted adding a corresponding mass percentage of Hf into the mixture before synthesis. The samples, 0.5 – 2 mm thick and 10 mm in diameter, were scraped from monocrystalline ingots perpendicularly to the crystallographic axis c. PbI$_2$ samples with Hf content of 0.2 % by mass were used for the study, since it was found that at this concentration, hafnium enters homogeneously in the crystalline lattice of lead diode.

The electron-hole conductivity component was

investigated by the Wagner polarization cell method [21], which is related to the methods of solid-state electrochemistry, and compared with similar results obtained in [22] for impure PbI$_2$ single crystals. Wagner's polarization cell method [21] is based on blocking the processes of ion discharge on an inert electrode. The polarization cell consists of the test specimen (PbI$_2$: Hf), which plays the role of a solid electrolyte, and two electrodes: the first is inverse to the electrolyte, and the second is an indifferent electrode (graphite):

$$(-) \, Pb \, | \, PbI_2:Hf \, | \, C \, (+), \tag{1}$$
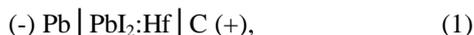
If the external potential U with the sign (+) on the inert electrode, which is smaller than the decomposing potential of PbI$_2$ to Pb and I$_2$ (U$_{dec}$=0.9 V), is applied to the cell (1), then the electrolysis of PbI$_2$ will not occur. In this case, the chemical activity of the components Pb and I$_2$ on the inert (blocking) electrode will depend on the external potential applied to the element, but not on the electrode's chemical composition. If the potential U is applied, then the partial pressure of iodine on the blocking electrode will be equal to one on the right side of the formation element:

$$Pb \, | \, PbI_2:Hf \, | \, I_{2 \, (г)}, \, (C)., \tag{2}$$
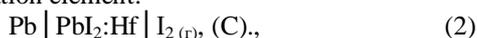
On the blocking electrode, the lead activity will be the same as on the right side of the concentration element:

$$(К) \, Pb \, | \, PbI_2:Hf \, | \, Pb \, (A), \tag{3}$$
$$\overset{\circ}{\alpha_{Pb}} \qquad \alpha_{Pb} < \overset{\circ}{\alpha_{Pb}}$$
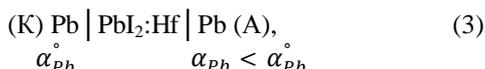
where $\overset{\circ}{\alpha_{Pb}}$ – lead activity in PbI$_2$, that is in equilibrium with lead.

The lead activity near the blocking electrode in this concentration element can be determined based on the equation:

$$U = U_K - U_A = \frac{RT}{2F} \ln \frac{\overset{\circ}{\alpha_{Pb}}}{\alpha_{Pb}},$$

thus:

$$\alpha_{Pb} = \overset{\circ}{\alpha_{Pb}} \cdot e^{-\frac{2UF}{RT}}. \tag{4}$$

If one applies the polarization potential U to the element (1), migration of ionic defects, the main current carriers, will begin.

At an initial moment, the current in the sample is determined by the drift of ionic defects, electrons, and holes. Ions Pb^{2+} will start moving to the cathode polarization cell, vacancies of lead cations - in the opposite direction. However, the electrochemical decomposition of PbI$_2$ and the formation of Pb^{2+} ions near the anode do not occur when U < U$_{dec}$. Thus, ions migration will gradually decrease. Such ions

displacement will create a counteracting electric field and concentration gradients of current-carrying ionic defects along the sample's thickness. As a result, the electric field in the crystal will be eliminated, and the voltage drop will occur at the interface between the PbI$_2 \, | \, C$ phases. After electric polarization, there will be no oscillatory current of either electrons or ions. The gradient of lead activity on the sample's thickness will determine the corresponding gradient of the electron or electron-hole concentrations, that will cause diffusion electron (hole) current through the crystal.

According to Fick's law, the diffusion flow of electrons (holes) will be:

$$J_e = -D_e \frac{dn_e}{dx}, \tag{5}$$

where: J_e – diffusion electrons current; D_e – coefficient of electrons' diffusion; $\frac{dn_e}{dx}$ – gradient of electron concentration.

Under equilibrium condition J_e=const and assuming that D_e=const for the sample's thickness, formula (5) can be rewritten as:

$$J_e = D_e \cdot \frac{\overset{\circ}{n_e} - n_e}{L} = \frac{D_e \overset{\circ}{n_e}}{L} \left(1 - \frac{n_e}{\overset{\circ}{n_e}} \right), \tag{6}$$

where: $\overset{\circ}{n_e}$ і n_e – electron concentration in the left and right parts of the element (1); L – the sample's thickness.

Taking into account that (в PbI$_2$) + e (in PbI$_2$), electron concentration n$_e$ should change proportionally to $\overset{1/2}{\alpha_{Pb}}$, thus:

$$\frac{n_e}{\overset{\circ}{n_e}} = \left(\frac{\alpha_{Pb}}{\overset{\circ}{\alpha_{Pb}}} \right)^{\frac{1}{2}}. \tag{7}$$

After calculations in the equations (4) – (7):

$$J_e = \frac{D_e \cdot n_e}{L} \left(1 - exp \left(-\frac{UF}{RT} \right) \right). \tag{8}$$

Taking into account that $I_e = e \cdot J_e$ and the Nernst-Finsten ratio for electron mobility is $D_e = RT \frac{\mu_e}{F}$, diffusion electrons current can be expressed as:

$$I_e = \frac{\overset{\circ}{n_e} \cdot e \cdot \mu_e \cdot RT}{LF} \left(1 - exp \left(-\frac{UF}{RT} \right) \right), \tag{9}$$

or

$$I_e = \frac{RT}{LF} \cdot \overset{\circ}{\sigma_e} \left(1 - exp \left(-\frac{UF}{RT} \right) \right), \tag{10}$$

where: $\overset{\circ}{\sigma_e} = \overset{\circ}{n_e} \cdot e \cdot \mu_e$ – electron conductivity of PbI$_2$, that is in equilibrium with lead; e – the electron charge; μ_e – mobility of electrons.

The total stationary diffusion current passing through the PbI$_2$ crystal can be expressed as the sum of the electron I$_e$ and the hole I$_p$ currents:

$$I = I_e + I_p = \frac{RTS}{LF} \left(\overset{\circ}{\sigma_e} \left(1 - exp \left(-\frac{UF}{RT} \right) \right) + \sigma_p \left(exp \left(\frac{UF}{RT} \right) - 1 \right) \right), \tag{11}$$

where: R – universal gas constant, 8.3144 J·mol^{-1}·K^{-1}; T – absolute temperature; S – the area of the sample's cross-section; F – Faraday constant, 96485 C mol^{-1}; L – sample thickness; U – applied voltage; s_e^o і s_p^o – electron and hole electrical conductivity PbI$_2$, that is in

equilibrium with lead.

Therefore, according to theoretical analysis, the electron current passing through the cross-section of the sample S can be described as a function of the applied voltage U:

$$I_e = \frac{RTS}{LF} \cdot \sigma_e^\circ \left(1 - exp\left(-\frac{UF}{RT}\right)\right), \qquad (12)$$

while for the hole current

$$I_p = \frac{RTS}{LF} \cdot \sigma_p^\circ \left(exp\left(\frac{UF}{RT}\right) - 1\right) \qquad (13)$$

For voltages higher than 0.15 V, when $\frac{UF}{RT} \gg 1$, the one in the equation (13) can be neglected. Thus, the current dependence on voltage should be of a straight line in the coordinates $lg\frac{ILF}{RTS}$ and $\frac{UF}{2,3RT}$. The tangent angle between this line and the abscissa axis will be 1, while the segment cut from the ordinate axis will be equal to σ_p°.

Electrical characteristics measurements were carried out at a constant current in a specially designed reactor. The measuring cell with the sample and the "sandwich"-form electrodes was placed under the vacuum post VUP-4M. The investigation was carried out in an atmosphere of purified argon at an optimum pressure of argon $P_{Ar} = (0,2-0,9) \times 10^5$ Pa in the temperature range 378-454 К. The characteristics were measured in a direction parallel to the crystal's axis. The electrodes were pressed towards the sample using a spring with an effort of 14-17 kPa. The current (I) passing through the sample PbI$_2$:Hf was registered with a nanovoltampermeter P-341. The constant sample temperature was maintained using a system of thermal regulation based on VRT-3M with an accuracy of ±0.5 K.

When the voltage was applied, the sample PbI$_2$:Hf was polarized in the cell (1) at a constant temperature and graphite electrode potential, that was lower than the expansion potential in PbI$_2$. The measurement was conducted until the value of the current became unchanged in time. After registering this current, the voltage level was changed, causing a jump-like current change. Such polarization cycles were carried out in the range of graphite electrode potentials of 0.15-1.10 V. Thus, current-potential dependencies were recorded in the 378-454 K range aiming to determine the type and magnitude of the electron-hole conductivity component.

II. Results and discussion

Fig. 1 presents current-potential dependencies $lg\left(\frac{ILF}{RTS}\right) = f\left(\frac{UF}{2,3RT}\right)$ for the PbI$_2$ single crystals with 0.2 wt.% Hf. In semi-logarithmic coordinates, the graphs are almost straightforward in the temperature range 378-454 K, that, according to Wagner's theory [21], proves the hole character of the electron-hole conductivity component in PbI$_2$:Hf single crystals. The similar effect was described for pure PbI$_2$ [22]. However, straight lines and the abscissa axis form angle, which tangent is significantly lower than 1 (Table 1). This fact was not fully consistent with the theoretical description of Wagner's equation (13). A similar deviation from the Wagner equation exists in case of current-potential dependences for pure and doped with cadmium copper iodide [23].

The authors [23] explain such a deviation by increase in the electron (hole) conductivity component proportion in comparison with ionic, and partially by ion current shunting during the measurement in the polarization cell. Therefore,
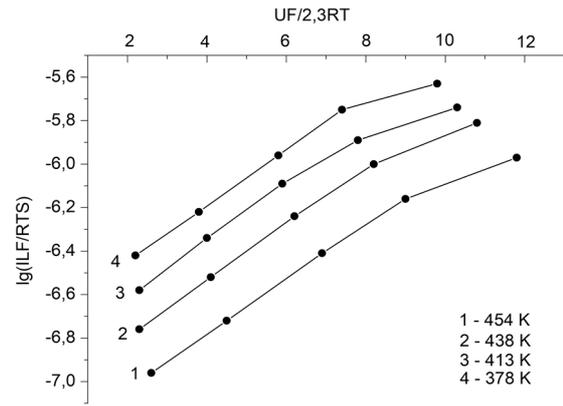
Fig. 1. Current-potential dependences for the polarization cell (-) Pb│PbI$_2$:Hf│C (+).

Table 1

Results of current-potential dependencies analysis

T, K	k	σ_p°, Ohm$^{-1}\times$m^{-1}
378	0.13	6.67×10^{-9}
413	0.13	1.11×10^{-8}
438	0.14	1.97×10^{-8}
454	0.13	2.65×10^{-8}

in this paper the definition of σ_p° was carried out according to the following equation [22]:

$$I_p = \frac{RTS}{LF} \cdot \frac{\sigma_p^\circ}{k}\left(exp\left(\frac{kUF}{RT}\right) - 1\right), \qquad (14)$$

where k – correction factor.

One can assume that the coefficient k characterizes the applied voltage fraction, which creates a chemical potential gradient of ionic current-bearing defects in the sample.

Analysis of the obtained curves shows a deviation from the linear dependence at a voltage close to the decomposing potential of PbI$_2$ (0.9 V). Results of research and calculations for graphs on Fig. 1 are shown in the table. 1.

It is noteworthy that the coefficient k is equal to 0.13-0.14 in the studied temperature range. Also, the value of the hole conductivity component σ_p° of the single crystal PbI$_2$:Hf increases correspondently to increasing temperature. This dependence is presented in Fig. 2 (curve 2) in semi-logarithmic coordinates $lg\sigma = f\left(\frac{10^3}{T}\right)$. The temperature dependence graph (2) forms a straight line with a slope that corresponds to the activation energy of the hole conductivity in PbI$_2$:Hf. According to the calculations, the value of this energy is 0.32 ± 0.04 eV. Curve (1) in Fig. 2 describes the temperature dependence of the hole electroconductivity in the pure PbI$_2$, with the activation energy of 0.47 ± 0.05 eV (data from the article [22]).

After a comparison of temperature dependences σ_p° for pure and doped with hafnium PbI$_2$ one may conclude that hafnium doping causes a decrease in the activation
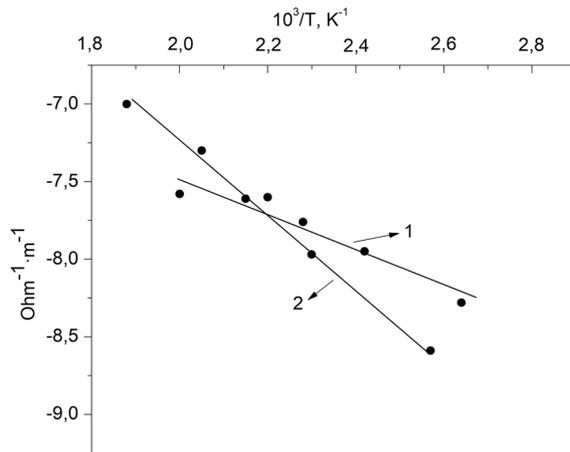
Fig. 2. Temperature dependences of hole electrical conductivity in PbI$_2$ (curve 1) and PbI$_2$:Hf (curve 2).

energy of the hole conductivity from 0.47 ± 0.05 eV to 0.32 ± 0.04 eV. Obtained results indicate the change in the nature of the acceptor impurity levels in the forbidden zone. Adding hafnium in PbI$_2$ during its synthesis causes the formation of new electrically active energy acceptor levels in the forbidden PbI$_2$ zone located at a distance of $0.32 \times 2 = 0.64$ eV from the valence zone's upper limit. The activation energy for the hole conductivity in PbI$_2$:Hf is higher in comparison with the pure crystal. This phenomenon can be explained by an increase in electron holes concentration during the doping of PbI$_2$

crystals with hafnium.

Conclusion

The Wagner polarization cell method was used to investigate the electron-hole conductivity component for PbI$_2$:Hf (0.2 mass% Hf) single crystals. Basing on the analysis of current-potential dependencies, it was found that the PbI$_2$:Hf has a hole conductivity. The temperature dependence σ_p^o was obtained at temperature intervals 378 - 454 K. It allowed determining that doping of PbI$_2$ single crystals with Hafnium leads to a decrease in the activation energy σ_p^o from 0.47 ± 0.05 eV to 0.32 ± 0.04 eV. This indicates the increase in electronic hole concentration in the crystal related to hafnium doping, as well as the formation of new impurity acceptor levels in the forbidden zone of PbI$_2$. These levels are located at distance of 0.64 eV from the upper limit of valence zone. In the future, similar studies are planned for PbI$_2$ crystals doped with impurities of other elements.

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Дослідження електронної провідності монокристалів PbI₂:Hf

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Проведено дослідження електронно-діркової складової провідності монокристалів PbI₂, легованих Hf (0,2 мас. %) з використанням методу поляризаційної комірки Вагнера. Проаналізовано вплив легуючої домішки Hf на характер і параметри електронної провідності дийодиду свинцю.

На основі одержаних струмопотенціальних залежностей встановлено p-тип провідності монокристалу PbI₂:Hf. Визначено величини діркової провідності (σ_p^o) у досліджуваному інтервалі температур, за якими побудовано температурну залежність. Виявлено закономірність збільшення величини σ_p^o монокристалу PbI₂:Hf із підвищенням температури. Проведено порівняльний аналіз результатів дослідження електронно-діркової складової провідності PbI₂ і PbI₂:Hf, з якого встановлено зменшення енергії активації σ_p^o з 0,47 еВ до 0,32 еВ при легуванні гафнієм. Зроблено висновок про виникнення нових домішкових акцепторних рівнів, розташованих на відстані 0,64 еВ від стелі валентної зони, обумовлених наявністю домішки Hf у кристалах PbI₂.

Ключові слова: монокристал, дийодид свинцю (PbI₂), електропровідність, поляризаційна комірка.