

РАБОТА ВЫХОДА ЭЛЕКТРОНА ТРИИОДИДОВ ЛАНТАНОИДОВ

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Энтальпии десорбции ассоциированных ионов трииодидов лантаноидов LnI_4^- и $Ln_2I_7^-$ ($Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, \text{ and } Lu$) и энтальпии сублимации молекул LnI_3 были найдены при помощи масс-спектрометрического подхода с использованием ячейки Кнудсена. Эти данные были использованы для расчета эффективных значений работы выхода электрона ϕ_e для поликристаллических образцов трииодидов лантаноидов LnI_3 , что было сделано впервые. Методика расчета была основана на изучении термодинамического равновесия с кристаллом LnI_3 внутри эффузионной ячейки Кнудсена. Полученные величины для различных лантаноидов имеют весьма близкие значения. Они лежат в интервале от 2,4 эВ до 4,4 эВ со средним значением для всего ряда равным $\phi_e = 3,2 \pm 0,3$ эВ. Эта величина близка к величине работы выхода электрона у трибромидов лантаноидов, изученных авторами ранее. В пределах установленных погрешностей нельзя говорить о проявлении двойной периодичности для величин работы выхода электрона в ряду лантаноидов. Полученные результаты находятся в количественном согласии с теоретическим расчетом ширины запрещенной зоны для трииодидов лантаноидов (работа выхода электрона должна быть больше или равна полуширине запрещенной зоны). Сравнение величин ϕ_e с другими классами соединений лантаноидов, таких как оксиды, гексабориды и металлы лантаноидов показало относительно высокую способность к эмиссии электронов, уступающую лишь щелочным и щелочно-земельным металлам.

Ключевые слова: работа выхода электрона, иодиды, лантаноиды, термодинамика, масс-спектрометрия Кнудсена

ELECTRON WORK FUNCTION OF LANTHANIDE TRIIODIDES

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Desorption enthalpies of LnI_4^- and $Ln_2I_7^-$ associative ions ($Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, \text{ and } Lu$) and the enthalpy of sublimation of LnI_3 molecules were determined by Knudsen effusion mass spectrometric technique. These data were used to calculate the effective values of electron work function ϕ_e of polycrystalline samples of lanthanide triiodides LnI_3 for the

first time. The calculation methodology is based on the study of thermochemical cycles, which include atoms, molecules, ions, and electrons being in thermodynamic equilibrium with the LnI_3 crystal inside the effusion cell. The values obtained for different lanthanides turned out to be close. They lie in the range of about 2.4 – 4.4 eV with an average value in the series: $\varphi_e = 3.2 \pm 0.3$ eV. The latter value is close to those for previously studied lanthanide tribromides. No secondary periodicity of φ_e was found within the calculated errors along the lanthanide series. The results obtained are in quantitative agreement with the theoretical calculation of the values of the band gap of lanthanide triiodides. Comparison of φ_e with other classes of lanthanide compounds such as oxides, hexaborides, and lanthanide metals shows relatively high electron emission ability yielding only to alkali and alkali-earth metals.

Key words: electron work function, lanthanides, iodides, thermodynamics, Knudsen effusion mass spectrometry

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INTRODUCTION

Fast development of modern branches of electronics such as spintronics, laser technologies and electrooptics needs a deep knowledge of electronic structure, which defines in particular the luminescence properties of materials [1]. The key factor in understanding of electronic structure is investigation of emission properties of compounds. Among them the electron work function φ_e is one of the most important. It characterizes the minimum energy required to extract an electron from the surface of a solid [2]. From different classes of materials used in microelectronics the lanthanide halides, and especially iodides, are in the focus of attention of scientists all over the world. This interest is caused by specific peculiarities of lanthanide compounds expressed in a wide variety of properties and possibility of their tuning by selection of desired lanthanide atom, dopant etc.

Nowadays lanthanide iodides have found an extensive range of applications in various areas, such for catalytic processes in organic synthesis [3], production of powerful magnets [4], solar cells [5], laser host crystals [6], transparent ceramics [7], and phosphors [8], biomedical applications for the determination of cellular activity [9], in magnetic resonance imaging [10], scintillators for detection of ionizing radiation [11, 12], pyroprocessing of spent nuclear fuel, and many others [13, 14].

The information on electron work function of lanthanide iodides is absent in literature. Recently we reported the preliminary results of experimental determination of the φ_e value for LnI_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$) [15]. This paper is a continuation of the started work for all other stable lanthanide triiodides. The data

from [15] were revised here because of new experimental measurements obtained and a unified approach used for the thermodynamic functions selection.

EXPERIMENTAL

Apparatus. A single-focusing magnetic sector type mass spectrometer MI1201 modified for Knudsen cell effusion studies (KEMS) was used. The combined ion source allowed to analyze both neutral and charged vapor species under electron ionization (EI) and thermal ion emission (TE) modes, respectively. Detailed description of the apparatus and experimental procedure can be found elsewhere [15–18].

Samples. Eleven thermally stable lanthanide triiodides LnI_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Lu}$) were selected as the objects under study. Pm compounds are radioactive. Samarium, europium, and ytterbium triiodides decompose into diiodides while heating. Sample synthesis and purity control were described elsewhere [19–24].

Calculation method. The method used in this work for calculation of φ_e is based on analysis of thermochemical cycles including atoms, molecules, ions, and electrons desorbing from the crystal surface under thermodynamic equilibrium condition. The electron work function in this case is interpreted as electron desorption enthalpy, i.e. quantity of heat liberated at transition of electron from the crystal to the vacuum. The detailed description of the method can be found in [15]. The first application of KEMS to determine the electron work function was realized by the authors [25]. Registration in saturated vapor in the TE mode of positive and negative ions of the same type made it possible to calculate φ_e for KOH and CsOH hydroxides based on the Sakha-Langmuir equation. Later, this approach was modified by the au-

thors [25-27] and successfully tested on crystals of alkali halides [26, 27] and lanthanide tribromides [28]. In the latter work it was shown that in the TE mode the associative ions LnX_4^- and Ln_2X_7^- (X is halogen) are typical for lanthanide trihalides.

Thermochemical cycles for LnI_4^- and Ln_2I_7^- anions are shown in Fig. 1a and 1b, respectively. According to the Hess law φ_e can be derived from the given cycles by following equations:

$$\varphi_e = \Delta_{\text{des}}H^\circ(\text{LnI}_4^-) - 1/4D(\text{LnI}_3) - 5/4\Delta_sH^\circ(\text{LnI}_3) - EA(\text{I}) + \Delta_{\text{diss}}H^\circ(\text{LnI}_4^-), \quad (1)$$

$$\varphi_e = \Delta_{\text{des}}H^\circ(\text{Ln}_2\text{I}_7^-) - 1/4D(\text{LnI}_3) - 9/4\Delta_sH^\circ(\text{LnI}_3) - EA(\text{I}) + \Delta_{\text{diss}}H^\circ(\text{Ln}_2\text{I}_7^-). \quad (2)$$

where φ_e is the electron work function; $\Delta_sH^\circ(\text{LnI}_3)$ and $D(\text{LnI}_3)$ the sublimation enthalpy and atomization enthalpy of LnI_3 molecule, respectively; $EA(\text{I})$ the electron affinity of iodine atom; $\Delta_{\text{des}}H^\circ(\text{LnI}_4^-)$ and $\Delta_{\text{des}}H^\circ(\text{Ln}_2\text{I}_7^-)$ the desorption enthalpies of the LnI_4^- and Ln_2I_7^- anions, respectively; $\Delta_{\text{diss}}H^\circ(\text{LnI}_4^-)$ and $\Delta_{\text{diss}}H^\circ(\text{Ln}_2\text{I}_7^-)$ the dissociation enthalpies corresponding to reactions:

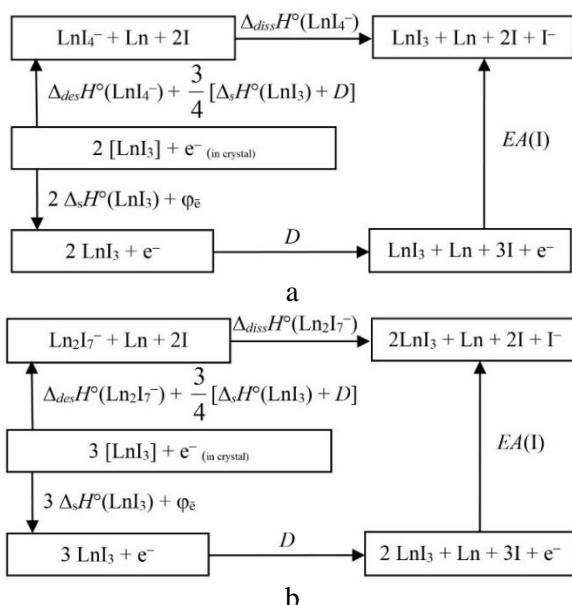
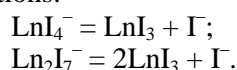


Fig 1. Thermochemical cycles for LnI_4^- (a) and Ln_2I_7^- (b) anions desorbing from LnI_3 crystal

Рис. 1. Термохимические циклы для анионов LnI_4^- (a) и Ln_2I_7^- (b), десорбирующихся с поверхности кристалла LnI_3

RESULTS AND DISCUSSION

The electron work function values φ_e were obtained from the thermodynamic quantities experimentally determined for the LnI_3 molecules in EI mode and for the associative LnI_4^- and Ln_2I_7^- ions in TE mode. Desorption enthalpies were found in the framework of

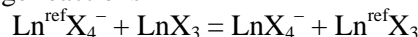
approach of the second law of thermodynamics from the slopes of temperature dependencies of ion currents measured in this work in TE mode (Table 1). The sublimation enthalpies of LnI_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Lu}$) were taken from [19-24]. The electron affinity of iodine $EA(\text{I}, 298.15 \text{ K}) = 301.797 \text{ kJ}\cdot\text{mol}^{-1}$ as well as the formation enthalpies of the gaseous iodine $\Delta_f H^\circ(\text{I}, 298.15 \text{ K}) = 106.76 \text{ kJ}\cdot\text{mol}^{-1}$ and lanthanide atoms $\Delta_f H^\circ(\text{Ln}, 298.15 \text{ K})$ ($\text{Ln} = \text{La}$ (430); Ce (417.07); Nd (355.81); Pr (327.13); Gd (398.51); Tb (386.06); Dy (285.25); Ho (300.19); Er (313.83); Tm (232.76); and Lu (427.86)) $\text{kJ}\cdot\text{mol}^{-1}$ needed for atomization energy determination were taken from the IVTANTHERMO database [29].

In the present study we revise the data from the previous paper [15] according to procedure of determination of formation enthalpies of ions described in recent paper [30]. This procedure allows to reduce the errors in thermochemical values caused by selection of standard. Here we need bring a brief explanation.

The determination by KEMS of the formation enthalpies of LnX_4^- ions incoming in $\Delta_{\text{diss}}H^\circ$ is complicated by the problem of non-equilibrium halogen anions X^- forming in the outer surface of the Knudsen cell thus precluding the direct study of the hetero-phase reaction



To overcome this problem the ion-molecular exchange reactions



were studied.

The reliable $\Delta_f H^\circ(\text{LnX}_4^-)$ value was obtained for LaBr_3 in [31]. Since PrI_3 was chronologically first studied for triiodides [21], it was selected as a standard in Ref. [15] using a consecutive transition $\text{LaBr}_3 - \text{PrBr}_3 - \text{PrI}_3$ in investigating of exchange reaction. However, this two-step transition is relatively long and leads to accumulation of errors. On the other hand, praseodymium has a set of low-lying excited electronic levels impeding precise determination of thermodynamic functions and additionally increasing errors in the $\Delta_f H^\circ$ values. Therefore, to minimize the errors, the better standard LaI_3 was applied recently [30] and the revised formation enthalpies for LnI_4^- ions were used in this work.

Thermodynamic functions $\Phi^\circ(T)$ and $H^\circ(T) - H^\circ(0)$ used in this work were taken from [30] or computed in the "rigid rotator - harmonic oscillator" approximation by StatThermo software [32] with the molecular parameters linearly estimated on the basis of data [33]. The electronic contributions into thermo-

dynamic functions of LnI_4^- were taken equal to those in corresponding LnI_3 [29, 34]. The functions were approximated by polynomials

$$\Phi^\circ(T) = a \ln x + bx^{-2} + cx^{-1} + dx + ex^2 + fx^3, \quad (3)$$

[J mol⁻¹ K⁻¹; $x = 10^{-4} \cdot T/\text{K}$];

$$H^\circ(T) - H^\circ(0) = 10(ax - 2bx^{-1} - c + dx^2 + 2ex^3 + 3fx^4), \quad (4)$$

[kJ mol⁻¹; $x = 10^{-4} \cdot T/\text{K}$].

The coefficients of Eq. (3) and (4) are listed in Table S1 in Supplementary materials (<http://journals.isuct.ru/ctj/article/view/3037/1884>).

Table 1

Experimental data on temperature dependencies of ion currents of associative ions over lanthanide triiodides in the form $\ln(I \cdot T^{0.5})$ vs $1000/T$, where I is ion current (arb. un.) and T temperature (K)

Таблица 1. Экспериментальные данные по температурным зависимостям ионных токов ассоциативных ионов трииодидов лантаноидов в виде $\ln(I \cdot T^{0.5})$ vs $1000/T$, где I – ионный ток и T – температура (K)

1000/T	LnI_4^-	Ln_2I_7^-	1000/T	LnI_4^-	Ln_2I_7^-	1000/T	LnI_4^-	Ln_2I_7^-	1000/T	LnI_4^-	Ln_2I_7^-
LaI₃			PrI₃			TbI₃			1.127	-17.64	-22.71
1.023	-15.14	-19.73	1.058	12.11	8.05	1.083	-13.73	-18.59	ErI₃		
1.023	-15.36	-19.82	1.070	11.70	7.65	1.083	-13.98	-18.97	1.065	-16.27	-20.74
1.061	-17.46	-21.71	1.097	10.47	5.93	1.112	-14.94	-20.32	1.018	-14.83	-18.79
1.061	-17.31	-21.76	1.061	11.92	7.76	1.168	-16.82	-22.57	1.049	-15.62	-19.83
1.092	-19.17	-23.63	1.044	12.37	8.48	1.239	-19.78		1.086	-17.01	-21.45
1.092	-18.98	-23.53	1.024	13.03	9.24	1.321	-23.04		1.136	-18.61	
1.136	-21.27		1.033	12.73	8.94	1.284	-21.74		1.171	-19.87	
1.137	-21.37		1.049	12.33	8.34	1.200	-18.61		1.117	-18.04	
1.081	-17.77	-22.48	1.001	13.75	10.32	1.144	-16.42	-21.96	1.054	-15.85	-20.20
1.081	-17.80	-22.23	0.971	14.42	11.59	1.093	-13.99	-19.09	1.000	-14.10	-17.77
1.055	-16.49	-21.23	0.954	15.02	12.46	1.050	-12.43	-16.94	1.034	-15.15	-19.41
1.054	-16.49	-21.10	0.990	13.86	10.89	1.112	-14.38	-19.45	TmI₃		
1.041	-15.89	-20.46	1.014	13.13	9.82	DyI₃			1.228	-20.72	
1.041	-15.95	-20.59	1.113	9.89	5.51	1.012	-16.25	-20.51	1.182	-18.58	-24.68
1.010	-14.76	-19.45	1.066	11.65	7.47	1.030	-17.07	-21.67	1.137	-16.86	-22.54
1.010	-14.91	-19.27	1.039	12.43	8.57	1.030	-16.96	-21.60	1.103	-15.49	-20.93
0.979	-13.89	-17.62	1.006	13.33	9.87	1.067	-18.47	-23.52	1.065	-14.37	-19.57
0.979	-14.08	-17.47	1.052	12.15	7.94	1.067	-18.37	-23.38	1.061	-14.02	-19.17
CeI₃			1.103	9.92	5.34	1.103	-19.81		1.086	-15.02	-20.50
1.067	-12.14	-17.85	1.074	11.34	7.04	1.071	-18.10	-23.26	1.116	-16.16	-21.95
1.090	-12.92	-18.97	1.028	12.88	8.96	1.029	-16.76	-21.22	1.152	-17.65	-23.65
1.138	-14.75	-21.31	1.014	13.25	9.71	0.984	-15.52	-19.29	1.196	-19.67	
1.188	-16.60	-23.62	NdI₃			0.984	-15.80	-19.38	LuI₃		
1.252	-18.94		1.074	-15.34	-19.79	0.994	-16.22	-19.95	1.062	-17.04	-22.15
1.328	-22.77		1.127	-17.20	-22.11	0.994	-16.42	-20.16	1.114	-18.96	-24.59
1.284	-20.89		1.176	-18.68		1.031	-17.21	-21.88	1.088	-17.98	-23.34
1.221	-17.66		1.153	-17.93		1.073	-18.68	-23.74	1.049	-16.60	-21.45
1.152	-14.83	-21.64	1.095	-16.13	-20.64	1.124	-20.62		1.067	-17.26	-22.29
1.160	-14.72	-21.74	1.058	-14.76	-18.87	HoI₃			1.105	-17.95	-23.66
1.113	-12.79	-19.12	1.031	-13.84	-17.75	1.070	-16.62	-21.21	1.126	-19.02	-25.01
1.073	-11.31	-17.16	1.010	-13.16	-16.86	1.099	-17.69	-21.83	1.155	-20.06	
1.027		-14.86	GdI₃			1.041	-15.26	-19.35	1.143	-19.65	
1.042	-10.32	-15.68	1.061	-23.05	-16.60	1.003	-14.11	-17.72	1.163	-20.34	
1.082	-11.82	-17.72	1.061	-22.95		1.024	-14.42	-18.35	1.182	-21.03	
1.121	-13.37	-19.72	1.041	-21.93	-15.93	1.015	-13.52	-17.71	1.224	-22.54	
1.183	-15.74	-22.83	1.019	-20.65	-14.98	0.989	-13.73	-17.43	1.258	-23.87	
1.252	-18.38		1.036	-21.75	-15.70	1.024	-14.66	-18.56	1.209	-22.14	
1.290	-20.26		1.026	-20.64	-15.09	1.070	-15.79	-20.22	1.244	-23.45	
1.340	-22.89		1.014	-20.09	-14.56	1.117	-17.48	-22.30	1.198	-21.76	
1.314	-22.19		1.005	-19.33	-14.12	1.093	-16.68	-21.14	1.108	-18.42	-24.20
1.285	-20.45		0.991	-17.52	-12.36	1.054	-15.28	-19.63	1.072	-17.13	-22.48
			0.976	-16.68	-12.45	1.007	-14.24	-18.06	1.032	-15.95	-20.79
			0.968	-16.44	-11.98	1.030	-14.73	-18.55	1.034	-15.95	-20.81

Analysis of the found φ_e (Table 2, Fig. 2) shows a reasonable agreement of values calculated from the equations (1) and (2), but we give preference to the values obtained by the equation (1) as more precise. One can see that obtained values through the lanthanide series are close to each other within the given errors with the exception for GdI_3 , whose value is apparently somewhat higher. It can be explained by feature of band structure of lanthanide triiodides. Electron work function is linked with other parameters of band structure by following equation [35]

$$\varphi_e = E_g/2 + \chi, \quad (5)$$

where E_g is the band gap and χ is the electron affinity of the crystal. Theoretically calculated band gap values of lanthanide iodides published recently by Rogers et al. [36] can be used for checking our results (Fig. 2). According to (5) $\varphi_e \geq E_g/2$. This expression is fulfilled for all examined compounds except HoI_3 . However, it is known that χ can take a negative value [37]. Here one can see the maximum at GdI_3 agrees well with our data.

Comparison of our results with data from [28] reveals closeness of electron work function values of lanthanide tribromides and triiodides. It indicates that the nature of lanthanide atom is primary factor defining φ_e of lanthanide trihalides.

The calculated average value of electron work function for lanthanide iodides $\varphi_e = 3.2 \pm 0.3$ eV is

quite low and points out high electron emission ability of this class of compounds. Among the compounds used as cathode materials φ_e of lanthanide iodides is a little bit higher than those of LaB_6 (2.8 eV) [40], CeBix® (cerium hexaboride based cathode) (2.65 eV) [38], but lower than those of transition metals carbides (HfC (3.58 eV), NbC (3.53 eV), ZrC (4.0 eV), TaC (4.2 eV), TiC (3.8 eV)) and tungsten (4.55 eV) [39]. At the same time, it is considerably higher than those of alkali and alkali-earth metals (from 1.95 to 2.93 eV) [2] and BaO (~1 eV) [39].

There are no literature data on electron work function of lanthanide iodides. Handbook of Fomenko [39] contains the data on lanthanide oxides. φ_e values of lanthanide metals are given in [41]. However, both these works bring a very scattered data collected from different sources, e.g. the φ_e value for La_2O_3 lies into a range from 2.5 to 4.2 eV thus precluding precise comparison. This fact can be explained by a strong dependence of the φ_e values determined by usual thermoionic or photoelectron methods from structural features (type of face and the type of lattice) whereas in our approach the efficient work function was found. The average value φ_e for lanthanide oxides is about 3.0 eV [39] that is similar to our data for LnI_3 . Recently Wang et al. [41] published theoretical research on lanthanide hexaborides LnB_6 .

Table 2

Thermochemical data and φ_e of lanthanide iodides
Таблица 2. Термодимические данные и φ_e трийодидов лантаноидов

Molecule	Ion	<i>T</i>	$\Delta_{\text{des}}H^\circ(T)$	$\Delta_s H^\circ(298.15 \text{ K})$	$D^\circ(298.15 \text{ K})$	$\Delta_{\text{diss}}H^\circ(298.15 \text{ K})$	$\varphi_e(\text{LnI}_3)$
		K	kJ·mol ⁻¹				
LaI ₃	LaI ₄ ⁻	950	396±18	305±4	1119±4	257±19	3.4±0.3
	La ₂ I ₇ ⁻	959	419±17			456±44	2.6±0.5
CeI ₃	CeI ₄ ⁻	841	350±8	294±4	1110±5	258±21	3.0±0.2
	Ce ₂ I ₇ ⁻	901	430±18			453±45	2.9±0.5
PrI ₃	PrI ₄ ⁻	962	264±8	293±6	1048±8	256±22	2.4±0.3
	Pr ₂ I ₇ ⁻	962	369±8			467±47	2.7±0.5
NdI ₃	NdI ₄ ⁻	917	278±4	293±3	993±5	274±24	3.0±0.3
	Nd ₂ I ₇ ⁻	938	374±7			492±46	3.4±0.5
GdI ₃	GdI ₄ ⁻	982	448±32	285±5	1058±6	266±22	4.4±0.4
	Gd ₂ I ₇ ⁻	982	621±27			470±45	5.4±0.6
TbI ₃	TbI ₄ ⁻	864	329±7	280±3	1050±4	265±21	3.2±0.2
	Tb ₂ I ₇ ⁻	904	404±29			474±45	3.3±0.6
DyI ₃	DyI ₄ ⁻	960	281±14	280±3	943±4	280±23	3.2±0.3
	Dy ₂ I ₇ ⁻	971	395±14			492±46	3.8±0.5
HoI ₃	HoI ₄ ⁻	951	267±19	281±3	962±4	277±23	3.0±0.3
	Ho ₂ I ₇ ⁻	951	339±16			493±46	3.1±0.5
ErI ₃	ErI ₄ ⁻	932	279±4	278±4	975±5	283±24	3.1±0.3
	Er ₂ I ₇ ⁻	958	352±14			500±46	3.3±0.5
TmI ₃	TmI ₄ ⁻	883	333±9	276±3	897±5	268±21	3.7±0.2
	Tm ₂ I ₇ ⁻	899	378±15			475±45	3.5±0.5
LuI ₃	LuI ₄ ⁻	884	291±5	278±10	1075±10	277±24	2.9±0.3
	Lu ₂ I ₇ ⁻	928	374±12			466±47	2.9±0.5

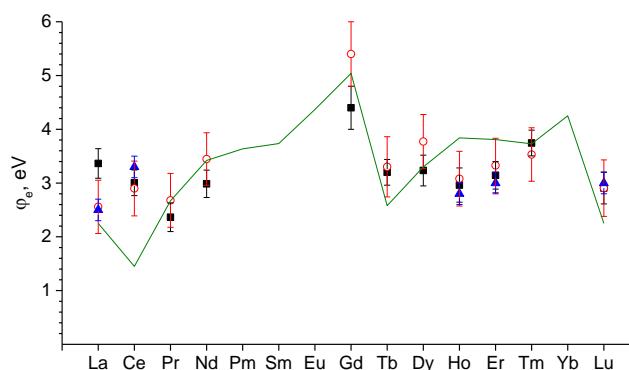


Fig. 2. Electron work function of lanthanide triiodides calculated from the cycles with LnI_4^+ (eqn. (1), filled squares) and Ln_2I_7^- (eqn. (2), open circles). The filled triangles are the ϕ_e values for LnBr_3 from [28]. The line is half of band gap for LnI_3 from [36]
 Рис. 2. Работа выхода электрона трииодидов лантаноидов, рассчитанная из циклов для ионов LnI_4^+ (ур. (1), заполненные квадраты) и Ln_2I_7^- (ур. (2), пустые кружки). Заполненные треугольники соответствуют величинам ϕ_e для LnBr_3 из [28]. Линия указывает на полуширину запрещенной зоны LnI_3 из [36]

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CONCLUSION

Analysis of the electron work function of lanthanide triiodides LnI_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Lu}$) determined by Knudsen effusion mass spectrometry reveals relatively high electron emission ability for this compounds, that can be used for production of various electron sources and vacuum devices. The average ϕ_e value is close to those of lanthanide oxides, hexaborides and pure lanthanide metals. Thus, the emission ability of LnI_3 yields only to those of alkali and alkali-earth metals, but the latter are more hygroscopic and chemically active.

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