Research Article

Thermal Emission Parameters of Equimolar Compounds of Alkaline Earth Oxides and Rare-Earth Metals

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ABSTRACT

The article is devoted to the study of thermal emission parameters in the oxide compounds of equimolar composition developed on the basis of alkaline earth oxides and rare earth metals RLn_2O_4 (where R - Sr or Ca, Ln - Y, Yb, Sc). The results of compound basic parameters calculation analysis are presented, which allow to determine the values of crystal energy values, revealing the patterns of their electrical and physical property changes in a wide temperature range which are of interest at the practical study of the considered oxides.

The possibility of basic provisions application concerning the statistics of electrons in semiconductors is substantiated theoretically and confirmed experimentally for the calculation of energy performance in the oxide compounds of complex composition. The possibility of simplified relation use for the calculation of the electron output work is shown with the use of its temperature coefficient. The calculated and experimental values of the temperature coefficient concerning the operation of electron output depending on the concentration of the emission centers in oxides at a wide temperature range.

Key words: oxide, composition, compound, alkaline earth metal, rare earth metal, properties, calculation, dependence, vacancies, heating, energy, analysis, operation, electron.

1.INTRODUCTION

The resistance to oxidative environments, thermodynamic, electrical, thermal and other properties of simple high-temperature oxide compounds conditioned their wide application in various fields of science and technology. The differences in physical and chemical properties of individual metal oxides provokes a high expert interest to compounds synthesized on the basis of

different nature metals, in particular alkaline earth and rare earth metal oxides forming the chemical compounds of SrO - Ln_2O_3 and CaO - Ln_2O_3 system the existence of which was previously reported [1, 2]. The variety of metal oxide unique properties is enriched at the development of complex compounds synthesized on their basis, and therefore combining the features characteristic of constituent components.

The systematic studies of SrO - Ln_2O_3 and CaO - Ln_2O_3 state diagrams showed [3, 4] that all lanthanides of the yttrium group of rare earth metals, including yttrium and scandium, form the compounds $SrLn_2O_4$ and $CaLn_2O_4$ with the formation temperatures ranging from 1650 K to 1823 K and various melting temperature which depends on the component composition and varies from 2363 K to 2410 K.

The studies of binary compound conductivity based on alkaline-earth oxides and rare earth metals and performed in the air at a wide temperature range revealed two types of conduction (hole and electron one), passing from one into another with the changes of heating temperature and oxygen pressure [5-7]. It was found [7], that the change of conductivity type at high temperature heating of RLn_2O_4 oxides causes the formation of anionic vacancies in the oxygen sublattice of oxides with the formation of a semiconductor structure with the electronic conductivity type, preserving at a crystal cooling. The thermodynamic analysis of crystal disordering processes at the heating of oxides allowed to find the ratios relating the thermodynamic parameters of anionic defect formation with the electron energy value localized near pointed defects of compound oxygen sublattice, and to display these values on the energy diagram often used at the consideration of the simplest semiconductor materials [9-11].

The ratios found in the course of research allow us to determine the conditions of oxygen vacancy formation and the values of a number of energy indicators concerning RLn_2O_4 crystals and to establish their relation with the thermodynamic

parameters characterizing the surface properties of considered oxide compounds and the processes occurring on it at the contact with other substances.

Currently the study of thermal emission oxide compound parameters RLn_2O_4 did not take its rightful place in the expert studies. The existing data (mainly in the field of electron output operation measurement) do not differ by finesse and are contradictory ones. In order to expand the data about the thermodynamic properties of binary compounds synthesized on the basis of alkaline earth and rare earth metal oxides, the authors tried to complement experimentally the available data on the major electrophysical parameters of oxides by the information on thermal emission characteristics and to substantiate the possibility of application for the research of core statistic ratios of electrons in semiconductors within a wide temperature range.

Methods. For experimental studies equimolar compounds $SrLn_2O_4$ (Ln - Y, Yb, Sc) and $CaLn_2O_4$ (Ln - Y, Yb) were synthesized by direct combined precipitation method of alkaline earth and rare earth metal cations from the mixture of their chloride aqueous solutions in the appropriate proportions with the aqueous solutions ammonium oxalate at a continuous stirring of a reaction mixture. The deposited product precipitate was codeposited, separated from the liquid phase and dried in the air. Compacts were pressed from the dry mixture after the grinding to finely dispersed state pressed.

These compacts were annealed in an alundum crucible in the air at the temperature of 1500 K - 1550 K, and to room temperature after cooling, they were subjected to repeated compression into tablets at the pressure of 4000 kg/cm2 for a final heat treatment, during which $SrLn_2O_4$ or $CaLn_2O_4$ compound synthesis was completed. In order to preserve stoichiometric composition oxides were placed in the powder of a similar composition, were heated in sealed molybdenum ampoules at 1950 - 1980 K for 20-25 minutes. After completion of the sintering process, the oxides

were cooled together with the furnace. The synthesized compounds were identified by chemical and diffractometric methods, were pulverized and applied to the surface of experimental lamp cathodes with a special diode type design for the thermionic emission current measurements at different values of ambient gas temperature and pressure.

In order to determine the thermal emission parameters of materials the thermionic theoretical emission equation was used during the study of solid materials (including semiconductors):

$$j = A_o T^2 \exp\left(-\frac{\varphi_T}{kT}\right)$$

(1).

where j – emission current density; $A_o = 120{,}4$ A cm^2/grad^{-2} – emission universal constant; T – surface temperature; φ_T – real output operation; k - Boltzmann's constant.

Main part. The most informative parameter is the thermal emission output operation (φ_T), which is composed of Fermi energy in semiconductors, counted down from the conduction area (μ_T), the inner operation of an output and the affinity energy of a crystal surface affinity to an electron, often referred to as an output external work (ψ_o). The total value of the electron output operation (output work) is determined by the following equation (Figure 1):

$$\varphi_T = \psi_o + \mu_T.$$

(2)

Thus, the values of an input real work describe the state the surface (ψ_o) and volume (μ_T) state, the surface and volumetric properties of semiconductor materials and are often used in absorption studies and electrical physical processes occurring in the layer of crystals. When the results of experimental studies are presented the true output work is determined as follows:

$$\varphi_T = \varphi_o + \alpha T,$$

(3)

where $\alpha = d\varphi_T / dT$ is the temperature ratio of an output operation.

At T values lower than the formation temperature of anionic vacancies the conductivity activation energy and the internal work of oxide output characterizing the volumetric properties of semiconductor compounds at a relatively high concentration of emission centers are determined by the following value

$$\mu_T = \mu_o + \alpha T,$$

(4)

where $\mu_o = \varphi_o - \psi_o$.

In other cases, other equations are used α of which changes by the function of temperature and the semiconductor emission center concentration and the selection of ratios for the calculation of temperature coefficient concerning the operation of complex oxides requires additional studies.
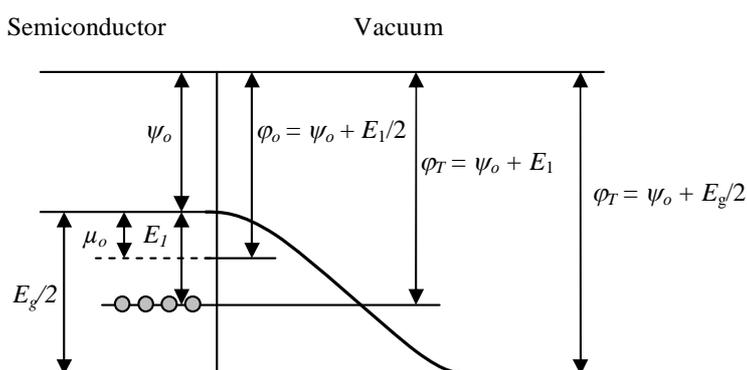
Figure 1. The scheme of electron local level arrangement in the semiconductors with the electronic type of conductivity.

In order to calculate the real work of electron output the equation (2) was applied, in which the determination of the temperature dependence nature φ_T and the determination of values α were based on the main provisions of the electron statistics in semiconductors, according to which the values of the temperature coefficient concerning the inner operation of an output may be determined from the following equation

$$\mu_{\mathrm{T}} = 2\mu_{\mathrm{o}} - kT\ln\frac{1}{2}\left[\sqrt{1 + \frac{2\exp(2\mu_{\mathrm{o}}/kT)N_d h^3}{2(2\pi mkT)^{\frac{3}{2}}}} - 1\right]$$
(5)

In order to interpret the physical value obtained by the calculations of $\alpha = d\varphi_T/dT$ from (5), they used universal approximations simplifying the expression (5), according to which the temperature dependence of Fermi energy in the "low" temperature zone, when

$$\exp\left(\frac{\Delta E}{kT}\right) >> \frac{2(2\pi mkT)^{\frac{3}{2}}}{N_d h^3}$$
and "high"

temperatures, in which

$$\exp\left(\frac{\Delta E}{kT}\right) << \frac{2(2\pi mkT)^{\frac{3}{2}}}{N_d h^3}, \text{ is determined by the}$$

following equations, respectively [8]:

$$\mu_{\mathrm{T}} = \frac{\Delta E_1}{2} + kT\ln\left[\frac{N_d h^3}{2(2\pi mkT)^{\frac{3}{2}}}\right]^{\frac{1}{2}},$$
(5a)

and

$$\mu_{\mathrm{T}} = kT\ln\left[\frac{N_d h^3}{2(2\pi mkT)^{\frac{3}{2}}}\right]^{\frac{1}{2}},$$
(5в)

in which $\frac{\Delta E_1}{2} = \mu_{\mathrm{o}}$ - the position of Fermi level relative to the conduction zone bottom at T = 0 K (Figure 1); N_d - the concentration of donor centers (anion vacancies); T - the semiconductor

temperature; h - Planck's constant; m - the electron rest mass; k - Boltzmann's constant.

The weak dependence of the factors standing under the logarithm sign in (5), (5a) and (5b) from T admits the linear extrapolation μ_T from the temperature and $\Delta\varphi_T/\Delta T \approx d\varphi_T/dT$ from the logarithm of anion vacancy concentration. At the calculations of α the temperature values under the logarithm sign were taken as equal to the average values from the respective interval of its changes. Within the specified approximations the values of Fermi energy, measured from the bottom of the conduction zone, and the operation of an output can be found in the areas of "low" and "high" temperatures, from the following equations, respectively:

$$\mu_T \approx \mu_o + \alpha\,\Delta T, \qquad \mu_T = \alpha\,\Delta T,$$
(6).

$$\varphi_T \approx \psi_o + \mu_o + \alpha\,\Delta T, \qquad \varphi_T \approx \psi_o + \alpha\,\Delta T.$$
(7).

The equations (6) and (7) at the fixed values of N_d, ψ_o and the semiconductor temperature allow to calculate the activation energy concerning the transition of electrons into the conduction zone and to create an opportunity for the experimental verification of relations.

The values the real electron output work in the entire temperature range is determined by the sum of its external (ψ_o) and internal component. If the inner operation of an output depends on the concentration of emission centers and the crystal temperature, then the values ψ_o characterize the potential energy of electrons in the semiconductor lattice and there is every reason to believe that $\psi_o=$ const at the consideration an output true work dependence on temperature during the theoretical and experimental studies of oxide compounds. Thus, the answer to the question on the nature of an output operation temperature dependence and the values of considered compounds may be given on the basis of semiconductor theory.

The calculation results of the specified energy parameters concerning the considered compounds

and their experimental values, determined by the authors are presented in Table 1. The top line of the table shows the calculated values, the bottom line shows experimental values.

Table 1. The energy parameters of semiconductor compounds RLn_2O_4 at T = 0 K.

№ i/n	Oxide	E_g, эВ	ψ_o, эВ	E_V, эВ	μ_o, эВ	φ_o, эВ	E_a, эВ
1	CaY_2O_4	6,0	0,9	2,0	1,0	1,9	
		5,9±0,2	1,1±0,2	1,8±0,2	0,9±0,1	2,0±0,2	1,8
2	$CaSc_2O_4$	5,9	0,95	2,1	1,05	2,0	
		6,0±0,2	0,9±0,2	2,0±0,2	0,9±0,1	1,8±0,2	1,8
3	$CaYb_2O_4$	5,7	0,95	1,86	0,93	1,88	
		5,6±0,2	1,0±0,2	1,7±0,2	1,0±0,1	2,0±0,2	1,6
4	SrY_2O_4	6,0	0,9	2,14	1,07	1,97	
		6,1±0,2	0,8±0,2	1,9±0,1	0,9±0,1	1,7±0,2	1,6
5	$SrSe_2O_4$	6,1	0,85	1,7	0,85	1,7	
		5,8±0,2	0,7±0,2	1,8±0,2	0,9±0,1	1,6±0,2	1,7
6	$SrYb_2O_4$	5,7	1,1	1,81	0,90	2,0	
		5,8±0,2	0,8±0,2	1,6±0,2	0,8±0,1	1,8±0,2	2,0

The prohibited zone width was determined from the following equation [7]:

$$Eg = 2(Es - b), \quad (8)$$

where $Es = Eat /$ equiv; b – constant, equal to 2,7; Eat – atomization energy; equiv – the equivalent is taken equal to the number of atoms in a compound molecule of the compound multiplied by their valence.

The external output work was calculated from the series comprising the transfer of oxygen ion from the lattice into the environment, the separation of two electrons from it with an oxygen atom development, and an oxygen atom return into a crystal. The ratio for the calculation of ψ_o may be written as follows:

$$\psi_o = 3 \, \Delta H_e - 7{,}8, \quad (9)$$

where $\Delta H_e = \Delta H_{V_o^{\cdot\cdot}}$; 7,8 - electron enthalpy occupying donor level and, accordingly, the affinity of oxygen atom energy to two electrons, expressed in electron volts.

The set of energy parameters listed in Table 1, and the equations (5) - (9) provide an opportunity to conduct the evaluations of the electrical physical properties of considered oxide compounds in a wide temperature range without the experimental studies.

The correctness of this approach to the definition of the oxide energy parameters by the authors was tested by the experimental studies of thermionic properties held in the diode structure lamps, evacuating up to to 10^{-5} - 10^{-9} atm, when cathodes are heated with applied oxide coatings up to 1500 - 1800 K, under the conditions promoting the formation of anionic vacancies. In the studies the measuring temperature varied in the range of 1000 - 1450 K, and the concentration of vacancies made 10^{13} - 10^{16} cm^{-3}.

The energy parameters of semiconductors were determined from Richardson graphs designed in the coordinates lg (j/T^2) and 5040 / T according to the results of thermal emission saturation current measurements density within a specified temperature range.

During the study of thermionic properties for RLn_2O_4 oxides in a wide temperature range a break is experienced, characteristic for oxide semiconductor compounds [4], which separate Richardson's straight lines, built in the areas of "low" and "high" temperatures.

The values of the output operation obtained from the slope of the inclining of straight lines in each of the areas are very different from the value φ_T, calculated from (1). As [4] showed, the observed differences in the magnitude of an output operation are conditioned by temperature dependence peculiarities of Fermi energy in semiconductors at the consideration of which the value φ_o at "low" temperatures is calculated as follows:

$$\varphi_{O_1} = (\psi_o + \frac{E_1}{2}) - 0{,}75kT_1$$

(10),

and at «high» temperatures it is calculated as follows:

$$\varphi_{O_2} = \psi_o - 1{,}5kT_2$$

(11),

where φ_{O_1} and φ_{O_2} is the oxide output operation, determined from the inclination of Richardson's straight lines in the areas of "low" and "high" temperatures, respectively, T_1 and T_2 – average values T in the respective areas of thermal emission measurements.

At the same time, at a marked transfer of electrons from the valent area into the conduction area, observed at high temperatures or at the process of anion vacancy development (T less than 1500 K) which has not started yet.

$$\mu_T = -\frac{E_g}{2} + kT\text{lln}\left(\frac{m_p}{m_n}\right),$$

(12)

$$\varphi_{O_3} = \psi_o + \frac{E_g}{2},$$

(13),

where m_p and m_n – the effective masses of holes and electrons, respectively.

Thus, the development of Richardson's graphs throughout the whole temperature range provides the opportunity to carry out an experimental validation of the calculated energy parameters correctness concerning the oxide compounds of RLn_2O_4 equimolar composition.

The comparison of calculated and experimental values indicates a satisfactory agreement between the compared values and the possibility of the equations (5) - (13) use at the studies of the electrical properties concerning the considered oxide compounds.

CaY_2O_4 output operation values at different temperatures, found experimentally are presented in the form of dots on Figure 2. The experimental points correspond to the average values of the measurement series.

An absolute error at a confident probability of 0.95 does not exceed 0.2 eV. The data for other RLn_2O_4 oxides have similar values and their deviations are determined by the energy of point defect formation. As can be seen from Figure 2, the temperature dependence of an output operation has a linear character in accordance with (7) and (8).

The values of an outpt operation calculated using (7) and (8) in which α is determined by the derivative function (5) and (6) according to the temperature are represented by straight lines on Figure 2, revealing one-to-one correspondence of an output operation temperature coefficient concerning anionic vacancy concentrations at which it becomes possible to quantify the content of emission centers according to the value of α or to find α at given N_d.

The concentration values corresponding to the values φ_T on the figure 2, were determined from the graphs, developed in the coordinates α and N_d.
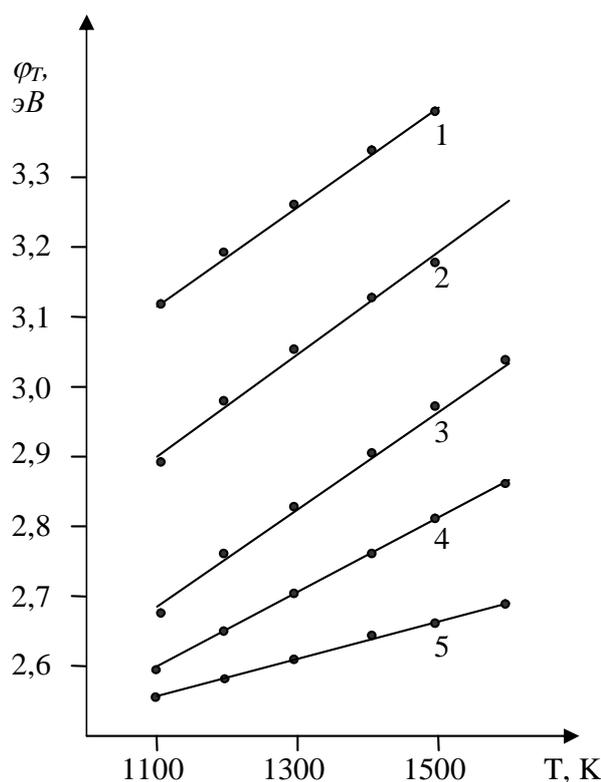
Figure 2. Temperature dependence of $CaLn_2O_4$ electron output operation:
1. $N_d = 10^{13}$ cm^{-3}, $\alpha = 5{,}5 \cdot 10^{-4}$ eV / grad;
2. $N_d = 5 \cdot 10^{14}$ cm^{-3}, $\alpha = 5 \cdot 10^{-4}$ eV / grad;
3. $N_d = 3 \cdot 10^{15}$ cm^{-3}, $\alpha = 3{,}3 \cdot 10^{-4}$ eV / grad;
4. $N_d = 5 \cdot 10^{15}$ cm^{-3}, $\alpha = 3 \cdot 10^{-4}$ eV / grad;
5. $N_d = 7 \cdot 10^{15}$ cm^{-3}, $\alpha = 2{,}3 \cdot 10^{-4}$ eV / grad;

The temperature dependence study concerning oxide output operation within the intrinsic conductivity showed that with the temperature increase in the range of 1100 - 1500 K the value φ_T decreases, indicating the narrowing of the prohibited zone width (E_g) and the approximation of the crystal Fermi energy (Figure 1) to the donor level. The temperature coefficient of the output operation with a negative sign makes (5-6) 10^{-4} eV/grad. At that, according to the studies of thermionic parameters, the Fermi level of oxides containing the defects of biographical origin at T greater than 1550 K, falls below the local electron levels and the difference between the Fermi level positions is reduced to 0.2 eV in a high-temperature heating. At a further increase of

temperature up to 1750 - 1800 K the transfer of electrons from the filled zone into the conductivity zone becomes evident and the crystals are transferred into the state of own conductivity at which the semiconductor properties cease to appear.

SUMMARY
The conducted complex of studies expands the representations about the electrophysical properties of RLn_2O_4 oxides, complementing them by thermionic parameters and ratios which allow to evaluate their values, confirmed by experimental data. Although the matches of compared values were good, the accuracy of results requires further clarifications. Firstly, the high sensitivity of an output temperature coefficient to the concentration changes of anion vacancies may guarantee the reproducibility of its assessments results up to one order and justifies the use of the averaged N_d values during the calculation of physical value parameters. Secondly, they used thermodynamic parameters

that are listed in the reference literature during the calculations, often without the indication of their determination error and greatly differing from each other. For these reasons, their average values were taken during calculations, which differed from the individual values by 5 - 10%. Nevertheless, the results of the performed complex research concerning the thermionic properties of RLn_2O_4 oxides are of great interest to various experts.

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