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Formation Of Anionic Vacancies Of Oxygen By High-Temperature Heating Of Compounds On The Basis Of Oxides Of Alkaline-Earth And Rare-Earth Metals Of Equimolar Composition In The Air Environment.

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ABSTRACT

The paper is dedicated to analysis of compounds on the basis of oxides of alkaline-earth and rare-earth metals of equimolar composition in the air environment. The perspectiveness of application of these compounds featuring high melting temperature and resistance to the action of oxygen in different areas is investigated. The material concerning production thereof from the source components of the rare-earth metal oxides, calcium carbonates and strontium taken in appropriate proportions is presented. The equimolar compounds under consideration are synthesized using the method of the direct codeposition of cations of the alkaline-earth and rare-earth elements from the aqueous mixture of chloride in relevant ratio with the aqueous solutions of oxalate ammonium by continuous mixing of the reaction mixture with the use of a magnetic stirrer. The paper considers the operations, temperature and timing parameters of synthesis of equimolar compounds. The non-monotonicity of change of the temperature dependence of electrical conductivity in the air environment of compounds was detected. The observed regularities are associated with formation of anionic vacancies in the crystalline volume and diffusion of the oxygen atoms to the surface with further evaporation in the form of molecules. The attempt of calculation of the main thermodynamic functions of anionic vacancies formed in equimolar compounds RLn_2O_4 is made. The presented equations allow calculating the thermodynamic parameters of formation of anionic vacancies in the crystals of oxide compounds at the fixed values of the oxide temperature and oxygen pressure in the environment with the use of the data about the relevant values contained in the reference literature. The values of concentration of the oxygen defects at the air pressure of 1 atmosphere and minimum temperature of formation of anionic vacancies of the RLn_2O_4 compounds are provided. The schematic layout of the energy levels of RLn_2O_4 oxides is shown. The dependence of conductivity and energy of formation of anionic vacancies on the oxide temperature was identified.

Keywords: oxide, composition, compound, alkaline-earth metal, rare-earth metal, properties, calculation, vacancies, heating, energy, analysis.

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INTRODUCTION

The perspectiveness of analysis of oxides of alkaline-earth and rare-earth metals featuring high melting temperature and resistant to the action of oxygen in different areas of application attract attention of the specialists. Significant difference of physical- chemical properties of oxides of alkaline-earth and rare-earth metals points at the perspectiveness of application of compounds occupying the intermediate position between these types of compounds that may be represented by solid solutions and chemical combinations in the systems $\text{SrO-Ln}_2\text{O}_3$ and $\text{CaO-Ln}_2\text{O}_3$ the existence of which was established [1, 2].

As the result of systematic analysis of the phase diagrams of systems $\text{SrO-Ln}_2\text{O}_3$ and $\text{CaO-Ln}_2\text{O}_3$ specified in [3, 4] it was found 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 temperature of formation from 1550 K to 1823 K and high levels of the melting temperature rising from 2363 K to 2510 K.

PROCEDURE

The synthesis of compounds in the systems $\text{SrO-Ln}_2\text{O}_3$ and $\text{CaO-Ln}_2\text{O}_3$ was performed with the use of the ceramic method by which the source components were the oxides of rare-earth metals, calcium carbonates and strontium taken in appropriate proportions. The samples for analysis were prepared by means of baking of the mechanical mixture in the solid phase at the temperature 1523 K during 20 hours with further hardening. In order to maintain the stoichiometry of compounds baking of the samples took place in the hermetically sealed molybdenum crucibles. The thermal stability of samples varied depending on the composition of compounds by reduction the temperature from the melting point to 1523 K in $\text{CaO-Ln}_2\text{O}_3$ oxides and to 473 K in the SrLn_2O_4 oxides. The detected differences in the temperature of stability of oxide compounds introduce uncertainty in the results of analysis of the material properties and substantiate the purposefulness of further investigation of the processes of formation and changes of the electrical-physical and thermodynamic parameters of the oxide compounds SrLn_2O_4 and CaLn_2O_4 under conditions of high-temperature heating.

The equimolar compounds under consideration (SrLn_2O_4 , (Ln – Y, Yb, Sc) and CaLn_2O_4 , (Ln – Y, Yb) were synthesized using the method of the direct codeposition of cations of the alkaline-earth and rare-earth elements from the aqueous mixture of chloride in relevant ratio with the aqueous solutions of oxalate ammonium by continuous mixing of the reaction mixture with the use of a magnetic stirrer. The precipitate of the codeposition product was separated from the liquid phase, rinsed and dried in the air during 12 hours at the room temperature. From the dry mix after grinding to a finely-divided state the compacts were pressed at the pressure 25 kg/cm^2 with the diameter of 25 mm, thickness from 2 to 3 mm. The produced compacts were baked in an alundum crucible in the air at the temperature 1500 K - 1550 K during 2 - 2,5 hours and after cooling to the room temperature were subjected to compression into tablets with the diameter 10 mm, thickness 1-2 mm at the pressure 4000 kg/cm^2 for finishing heat treatment during which the synthesis of the compounds SrLn_2O_4 or CaLn_2O_4 was completed. In order to maintain the stoichiometric composition the oxides put in the powder of the similar composition were heated in the leak-proof molybdenum ampules at 1950 - 1980 K during 20-25 minutes. After completion of the sintering process the oxides were cooled down along with the furnace. The synthesized compounds were identified with the use of the chemical and diffractometric methods establishing the formation of equimolar compounds not containing oxides with the pycnometric specific density that is close to the theoretical calculated crystal density.

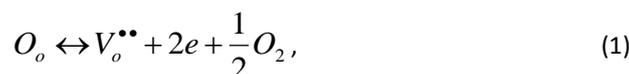
The studies of the temperature dependence of electrical conductivity in the air medium of the RLn_2O_4 compound (where R – Sr, Ca, Ln – Y, Yb, Sc) within the range 500 – 1800 K revealed the non-monotonicity of variance, transition from the p-type of conductivity to the electron one at the oxide temperatures higher than 1500 K and stability of the value of current passing the sample upon application of the DC and AC voltage [5, 6].

We relate the observed regularities to formation of anionic vacancies and diffusion of the oxygen atoms to the surface with further evaporation in the form of molecules. A higher oxygen evaporation rate as compared to the metal atoms assigns the dominating role to the anionic vacancies in formation of the electrical physical properties of oxide compounds and determines the electron conductivity by cooling thereof.

MAIN PART

The attempt of calculation of the main thermodynamic functions of anionic vacancies formed in equimolar compounds is made.

As the analysis of the process of disordering the crystalline structures of oxides being investigated shows the formation of vacancies proceeds according to the reaction [7]



where O_o – oxygen atom at the lattice point; $V_o^{\bullet\bullet}$ - doubly charged anionic vacancy; e - electron.

The law of mass action for (1) is written as follows:

$$\frac{[V_o^{\bullet\bullet}]n^2(\tilde{P}_{O_2})^{\frac{1}{2}}}{[O_o]} = K_r. \quad (2)$$

In the conditions of equilibrium and electrical neutrality of the sample $[V_o^{\bullet\bullet}] = n/2$ where $[V_o^{\bullet\bullet}]$ and n , respectively, the concentration of vacancies and electrons, $[O_o]$ – oxygen atoms at the crystalline lattice point, allow deriving an expression for calculation of changes of the isobaric potential by formation of defects in the oxygen sub-lattice of oxides in the form:

$$\Delta G_{V_o^{\bullet\bullet}} = \frac{1}{3} \left[\Delta G_o^o - \frac{1}{2} \Delta G_{O_2}^o + 2RT \ln 2 + RT \ln (\tilde{P}_{O_2})^{\frac{1}{2}} \right], \quad (3)$$

where ΔG_o^o is the change of isobaric potential of oxygen atoms in the lattice points by formation of O_2 molecules at $P_{O_2} = 1$ atm, $\tilde{P}_{O_2} = \frac{P'_{O_2}}{P_{O_2}}$ - equilibrium pressure of oxygen reduced to 1 atmosphere, R – absolute gas constant.

By carrying out calculations the equation for determination of concentration of anionic vacancies may be presented as follows:

$$\eta = \left(\frac{1}{4} \right)^{\frac{1}{3}} (\tilde{P}_{O_2})^{-\frac{1}{6}} \exp \left(- \frac{\Delta G_{V_o^{\bullet\bullet}}^o}{RT} \right), \quad (4)$$

Where $\eta = \frac{[V_o^{\bullet\bullet}]}{[O_o]}$ - relative concentration of anionic vacancies being the share of vacant points in the oxide sub-lattice.

At equilibrium when the process of formation of oxygen vacancies is completed ($\Delta G_{V_o^{\bullet\bullet}} = 0$), the values of concentration in the oxide crystalline lattice may be derived from the equation:

$$\frac{\Delta H_{V_o^{\bullet\bullet}}}{T} = \Delta S_{V_o^{\bullet\bullet}}. \quad (5)$$

At that as follows from (2),

$$\Delta H_{V_o^{\cdot\cdot}} = \frac{1}{3} \left[\Delta H_{[O]}^o - \frac{1}{2} \Delta H_{O_2}^o \right], \quad (6)$$

$$\Delta S_{V_o^{\cdot\cdot}} = \frac{1}{3} \left[\Delta S_{[O]}^o - \frac{1}{2} \Delta S_{O_2}^o - 2R \ln 2 + R \ln \left(\tilde{P}_{O_2} \right)^{-\frac{1}{2}} \right], \quad (7)$$

Where $\Delta H_{[O]}^o$ - the change in enthalpy of the free oxygen by formation of an anionic point of the oxide crystalline lattice, $\Delta H_{O_2}^o$ - change in enthalpy by dissociation of the oxygen molecules, $\Delta S_{[O]}^o$ - changes in the oxygen enthalpy by formation of an anionic point of the oxide crystalline lattice, $\Delta S_{O_2}^o$ - change in enthalpy by dissociation of the oxygen molecules. The equations (2) - (7) allow calculating the thermodynamic parameters of formation of anionic vacancies in the oxide compounds crystals at the fixed values of the oxide temperature and oxygen pressure in the environment with the use of the data about the relevant values contained in the reference literature [7, 8]. The results of calculation of thermo-dynamic parameters of formation of anionic vacancies in the oxide being considered under conditions of the temperature dependence of conductivity are presented in the Table 1.

Table 1: The values $\Delta H_{V_o^{\cdot\cdot}}$, $\Delta S_{V_o^{\cdot\cdot}}$ of concentration of oxygen defects at the air pressure of 1 atmosphere and minimal temperature of formation of anionic vacancies of the RLn_2O_4 compounds.

Compound	$\Delta H_{V_o^{\cdot\cdot}}$, kcal/mol	$\Delta S_{V_o^{\cdot\cdot}}$, kcal/mol degree	P_{O_2} , atm	$\lg \eta$	T , K	Note
CaScO ₄	67,0	49,4	0,2	- 9	1550	The oxygen pressure specified in the table corresponds to the content thereof in the air
		45,8		- 8,21	1660	
CaY ₂ O ₂	71,0	49,5	0,2	- 9	1550	
		48,3		- 8,7	1600	
CaYb ₂ O ₄	64,8	47,9	0,2	- 9	1550	
		44,39		- 8,24	1600	
SrSc ₂ O ₄	66,5	49,4	0,2	- 9	1550	
		45,4		- 8,5	1600	
SrY ₂ O ₄	70,0	49,9	0,2	- 9	1550	
		47,6		- 8,5	1600	
SrYb ₂ O ₄	67,0	49,4	0,2	- 9	1550	
		46,2		- 8,2	1600	

The relative concentration of anionic defects in the compound lattice at equilibrium is derived from the values $\Delta S_{V_o^{\cdot\cdot}}$ at the known value of vibrational entropy (ΔS_V) with the use of the proportion:

$$\Delta S_{V_o^{\cdot\cdot}} = \Delta S_V + \Delta S_c, \quad (8)$$

Where ΔS_c - configurable component determined as $\Delta S_c = -R \ln \eta$.

Due to the absence of data about the ΔS_V values the η values were determined by the authors based on the results of analysis of temperature dependence of the oxide work function within the temperature range 1500 – 1800 K, previously hardened at $T = 1450 - 1500$ K in the conditions preceding the oxide transition to the electron conductivity.

The practicability of such approach is determined by the approximate equation ΔS_c and entropy of formation of electrons filling the local energy levels in a crystal and not containing ΔS_v .

$$\Delta S'_e = \Delta S_c + R \ln 2, \quad (9).$$

Which follows from the definition of η , the condition of electrical neutrality and dependence of the Fermi energy on the donor concentration (in our case – point defects at the lattice points) at the fixed temperature values.

The analysis of the results of measurement of the work function showed that location of the Fermi level in the oxide samples heated within the specified temperature range corresponds to the self-conductivity domain and is located at the middle of the band gap (Figure 1 a). At the same time the η value takes the values $10^{-9.3} - 10^{-9}$ corresponding to concentration of anionic vacancies of $5 \cdot 10^{12} - 10^{13} \text{ cm}^{-3}$. According to the estimates, the change of vibrational entropy of compounds by formation of vacancies takes depending on the oxide composition the values 6 – 8 kcal / mole degree.

The heating of oxides at the temperature exceeding 1500 K, as follows from the Table 1, results in changing of η and the growth of electron concentration within the conductivity area as compared to the values corresponding to the area of self-conductivity and the transition thereof from the p-type of conductivity to the electron one which can be observed experimentally at the temperature exceeding 1500 K. At the same time, as can be seen from (4), the reduced concentration of anionic vacancies is a slightly varying function of the partial pressure of oxygen contained in the gas medium as compared to the temperature. The results of calculations with the use of (2) and (4) shown that the increase of η by one order at the constant temperature is achieved by reduction of the oxygen partial pressure in the gas mixture by six orders whereas the same result is achieved by increase in the oxide temperature by 200 K at the unchanged values of the oxygen pressure.

The results of design of thermodynamic characteristics and temperature dependence of the oxide work function show that the compounds being considered at the temperature exceeding 1500 K are transformed into semiconductors with the electron conductivity the role of donors in which is assigned to the oxygen vacancies with enthalpy of formation amounting to 65 - 71 kcal / mole depending on the composition.

By substituting according to the conditions of electric neutrality of samples the vacancy concentration through the electron concentration in (2) we find equations for calculation of all thermodynamic functions of formation of electrons that occupy the local levels of the oxide semiconductors:

$$\Delta G_e = \frac{1}{3} \left[\Delta G_o^o - \frac{1}{2} \Delta G_{O_2}^o - RT \ln 2 + RT \ln \left(\tilde{P}_{O_2} \right)^{\frac{1}{2}} \right], \quad (10).$$

$$\Delta H_e = \frac{1}{3} \left[\Delta H_o^o - \frac{1}{2} \Delta H_{O_2}^o \right], \quad (11).$$

$$\Delta S_e = \frac{1}{3} \left[\Delta S_o^o - \frac{1}{2} \Delta S_{O_2}^o - 2R \ln 2 + R \ln \left(\tilde{P}_{O_2} \right)^{\frac{1}{2}} \right], \quad (12).$$

Where ΔG_e , ΔH_e , ΔS_e - changes in the isobaric potential, enthalpy, entropy of the electron formation at the local levels.

It can be seen from the correlation (6) and (11), (7) and (12) that

$$\Delta H_{V_o^{\bullet\bullet}} = \Delta H_e \text{ и } \Delta S_{V_o^{\bullet\bullet}} = \Delta S_e + \frac{R}{3} \ln 2. \quad (13)$$

The correlations (13) substantiate the possibility of designing the layout diagram of the energy bands and electron levels used by analysis of electric-physical properties of semiconducting materials [9-11]. The simplest energy diagram of arrangement of the energy levels of RLn_2O_4 oxide electrons in the state of inherent and electron conductivity at $T = 0 \text{ K}$ that have been previously heated at $T = 1450 \text{ K}$ a) and $T = 1550 \text{ K}$ b) is presented in the Figure 1.

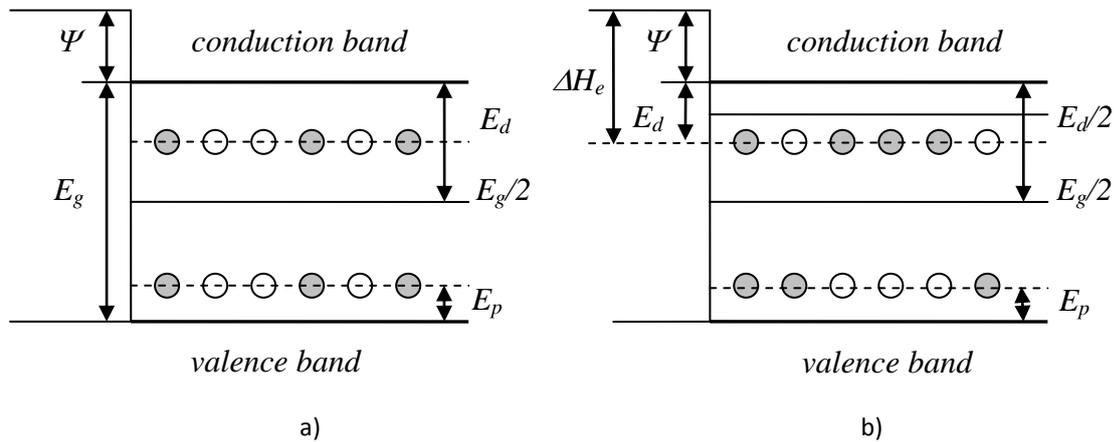


Figure 1: Schematic arrangement of the energy levels of RLn_2O_4 oxides in the state of inherent a) and electron b) conductivity at $T = 0 \text{ K}$.

The shaded circles correspond to the levels occupied by electrons and holes, E_g – band gap energy, ψ – energy of the crystal affinity to an electron (external work function), E_d – local level energy estimated from the conduction band bottom, E_f – Fermi energy estimated from the conduction band bottom, E_p – hole level energy estimated from the top of the valence band.

According to the provisions of the electron statistics in semiconductors the energy of activation of the electron conductivity of oxides being considered is determined by the position of the Fermi level in respect of the conduction band bottom that depends on the donor concentration (oxygen vacancies) and the sample temperature. In the conditions of analysis of the temperature dependence of oxide conductivity (high temperature, air environment and low vacancies concentration) the Fermi level is located lower than the local electron levels (Figure 1b) and the estimated values of the activation energy in this case make 1,9 - 2,0 eV. The experimental values of the activation energy measures at $T = 1550 - 1800 \text{ K}$ and the air pressure of 1 atm varied within the range 1,7 - 1,9 eV, thus, confirming the presented model of the formation processes and the related changes in the magnitude and type of conductivity of the RLn_2O_4 oxides in the high-temperature heating conditions.

SUMMARY

The results of calculations of thermodynamic parameters of the RLn_2O_4 oxide compounds and the coincidence thereof with the experimental values of the energy of conductivity activation showed the possibility of application of the model of vacancies formation in the crystals of simple oxides that can be used by investigation of more complex oxide compounds.

CONCLUSIONS

The deformed thermodynamic analysis of processes of the anionic vacancies formation determined:

- Changes in the conductivity type by heating within the temperature range of 1500 -1800 K;
- The values of enthalpy and entropy of formation of anionic vacancies;

- The values of the energy of activation of the RLn_2O_4 oxides conductivity within the temperature range of 1500 - 1800 K;
- The possibility of application of the energy diagram of arrangement of the local electron levels by analysis of the electric physical properties of complex oxide compounds.

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