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SIMULATION OF THE FORMATION AND DISSOCIATION PROCESSES OF SOLID SOLUTION IN CeO₂ - La₂O₃ SYSTEM

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Simulation of the formation and dissociation processes of solid solutions in CeO₂ - La₂O₃ system is carried out. $F \rightarrow F^I$ phase transition in CeO₂ - La₂O₃ system caused by the disordering process of the cerium dioxide structure with small additions of lanthanum oxide is discovered. Mathematical models for the solid solution formation process based on CeO₂ with La₂O₃ additions, which take into account the electronic structure of matter and deviation from stoichiometry of CeO_{2-x}, are developed.

Keywords: CERIUM DIOXIDE, LANTHANUM OXIDE, SOLID SOLUTION, PHASE TRANSITION.

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1. INTRODUCTION

Materials based on CeO₂ with La₂O₃ additions are of a great practical interest due to their electrical conductivity. Thus, for example, CeO₂ - La₂O₃ solid solutions can be used as solid electrolytes for fuel cells, protective refractory coatings, catalyst carriers and others.

There are defects in the cerium oxide structure: anion vacancies which are the elements of this structure; vacancies formed during reduction of the oxide and vacancies formed during dilution of other oxides.

Defects, which are the structure elements, can be combined with impurity atoms and form the defect systems in the form of the donor-acceptor pairs. Accumulation of such defects leads to the changes in polymorphic transformation temperatures, physical properties, solid solution dissociation [1, 2].

2. STATEMENT OF THE PROBLEM

Thermodynamic calculation of solid solutions based on the fluorite structure with structural defects is a complicated process of selection of appropriate models of the solid solution formation, since the solid solution model defines the thermodynamic potential, and thereby, the final result. Calculation of the energy coefficients, which determine the change in the internal energy of the crystal, can not be performed with satisfactory accuracy, and it is reasonable to determine them by comparison with the experiment.

The aim of the present paper is the development of correct models for the solid solution formation process in CeO₂ - La₂O₃ system.

Cerium dioxide (CeO₂) is the structural analogue of ZrO₂, HfO₂, PrO₂. It has the face-centered cubic (fcc-) lattice of the *F*-fluorite type.

Cerium oxide Ce₂O₃ contains 25% of naturally ordered anion vacancies, which are the structure elements, and has the body-centered cubic (bcc-)

lattice of the *C*-pyrochlore type. Ce_2O_3 is the structural analogue of La_2O_3 , Y_2O_3 , Sc_2O_3 , In_2O_3 .

Structures of cerium dioxide and oxide are excellent natural models, which allow to investigate the processes of defect formation and their influence on phase transformations under thermal treatment.

Simulation of the solid solution formation process in the system based on cerium dioxide with additions of lanthanum oxide consists of the following sequential models: 1) the electronic structure model of the electron configuration in atoms and ions of CeO_2 and La_2O_3 ; 2) the mathematical models of the processes of deviation from stoichiometry of La_2O_3 and CeO_2 , which are accompanied by the structure phase transformations at high temperatures in the air medium; 3) the mathematical model of the formation and dissociation processes of solid solutions in CeO_2 - La_2O_3 system in the temperature range of 25-1900°C in the air medium. Consecutive consideration and calculation of these models allows to predict the formation of other oxide systems for obtaining the materials with assigned certain properties.

3. INVESTIGATION RESULTS

3.1 Model of the outer electron configuration in atoms and ions of CeO_2 and La_2O_3

Configurations of oxides during the condensed matter formation from isolated atoms lead to the separation of valence electrons into localized and collective ones. The localized part of valence electrons in a solid is redistributed into the configuration spectrum, and free configurations (half filled and completely filled ones) are the most stable from them.

At room temperature lanthanum oxide exists as $\text{La}(\text{OH})_3$. Lanthanum hydrate is dissolved during the sintering in the air medium that leads to the phase transformations accompanied by the structure changes. At cooling to room temperature the hydration process occurs.

$\text{Ce}(\text{OH})_3$ does not exist in the cerium oxide structure. Cerium can give two electrons with the formation of *f*-configuration that leads to Ce^{4+} valence and CeO_2 formation in the air medium [3, 4]. Under certain conditions such approach allows to reveal the anomalies of electron concentration, calculate them and explain the processes like ion and electron conductivity in matters.

3.2 Mathematical models of the processes of deviation from stoichiometry in lanthanum oxides and cerium dioxide

According to the data of [4] in $\text{La}(\text{OH})_3$ samples the dissolution and the bcc-phase formation of the *C*-lanthanum oxide type was observed under heating. At further heating this phase is transformed to the monoclinic modification of the *B*-type, which at 800°C in the air medium and at 500°C in the vacuum is transformed to the hexagonal modification of the *A*-type. Hexagonal structure of lanthanum oxide exists in the temperature range of 900-1900°C and has a tendency to the texture formation.

Microstructure of lanthanum oxide samples is represented in Fig. 1a.

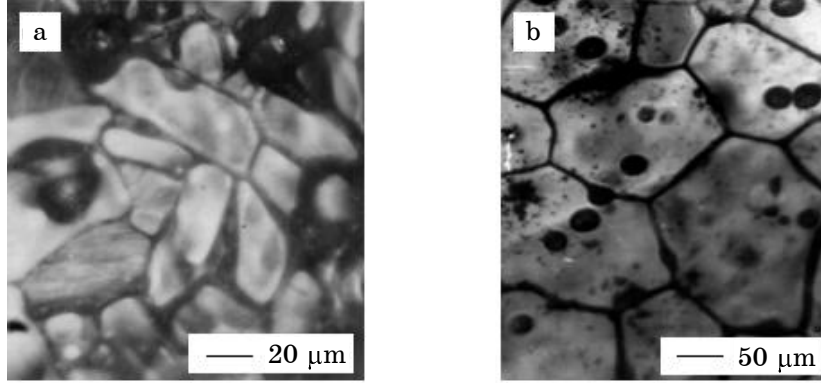
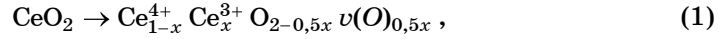


Fig. 1 – Microstructure of the samples: A - La_2O_3 (a) and $\text{CeO}_2 + 5\% \text{La}_2\text{O}_3$ (b) after sintering in the air medium at 1750°C

The reduction processes and phase transformations in cerium dioxide connected with the changes in defect concentrations, which control the phase transformation processes, are calculated in [5, 6].

Formation of anion vacancies in CeO_2 structure and their concentration growth leads to the change in the elementary cell parameter of the structure depending on the sintering temperature of cerium dioxide samples and is performed in accordance with the following model of deviation from stoichiometry:



where $\nu(\text{O})$ are the anion vacancies.

Lattice parameter of the fluorite phase of the stoichiometric composition is defined by the correlation

$$a_0 = \frac{4}{\sqrt{3}} (r_K + r_A), \quad (2)$$

where r_k is the ionic radius of the cation; r_A is the ionic radius the oxygen.

Lattice parameter of the non-stoichiometric composition of cerium dioxide is determined by relation

$$a = \frac{4}{\sqrt{3}} [(1-x)r_{\text{Ce}^{4+}} + xr_{\text{Ce}^{3+}} + (1-x)r_{\text{O}^{2-}} + \frac{x}{4}r_{\nu(\text{O})}], \quad (3)$$

where $r_{\nu(\text{O})}$ is the anion vacancy radius; x is the anion vacancy concentrations. Difference between (2) and (3) is equal to

$$a - a_0 = \frac{4}{\sqrt{3}} [x(r_{\text{Ce}^{3+}} - r_{\text{Ce}^{4+}}) + \frac{x}{4}(r_{\nu(\text{O})} - r_{\text{O}^{2-}})]. \quad (4)$$

Correlation (4) determines changes in the lattice parameter of the $F\text{-CeO}_{2-x}$ phase type.

Change in the lattice parameter of the F -type phase of cerium dioxide during the reduction process can be represented as the limit of one-variable function $\Delta a = f(x)$, $x = f(T)$, T is the sintering temperature.

Oxygen evaporation from the cerium dioxide lattice starts at 1500°C. In the lattice anion vacancies appear and CeO_{2-x} dioxide composition changes. This process can be explained as the variation limit of the lattice parameter subject to the defect concentration (within the single structure) and the sintering temperature of the samples

$$\lim_{T \rightarrow 1500^\circ\text{C}} f(a_0) = \lim_{T \rightarrow 1500^\circ\text{C}} f(a_1) = (a_1 - a_0). \quad (5)$$

This break in function can be considered as the relative one since the F -type structure keeps in a wide temperature range (1500-1800°C) in the air medium [5, 6], and changes in the parameter are very small and equal to 0,0001-0,0005 nm in this range.

Structure of the F -type cerium dioxide is energy efficient only in the presence of totally ordered cation sublattice. Since the electron density distribution over cations is almost uniform, the disorder of cation sublattices occurs at some deviations from stoichiometry (the equivalence of cation positions is lost) and this leads to the $F \rightarrow F^1$ phase transition. The same situation takes place while adding other cations to the cerium dioxide lattice and the temperature of this phase transformation significantly decreases.

The models are calculated using the limit of one-variable function while determining the limit defect concentrations connected with the temperature change. Such approach allows to study the extreme break points of the function, which correspond to the critical points of phase transformations in cerium dioxide. This information gives the possibility to investigate the model of the solid solution formation based on cerium dioxide with lanthanum oxide additions.

3.3 Mathematical models of the formation and dissolution process of solid solutions in $\text{CeO}_2\text{-La}_2\text{O}_3$ system

Samples based on CeO_2 with different concentration additions of La_2O_3 (1-70 mol%), which were previously annealed at 1000°C, were sintered in the temperature range 1000-1900°C with subsequent air cooling. Samples containing the solid solution were not destroyed in the air. Samples containing the solid solution and free lanthanum oxide were destroyed due to the hydration of lanthanum oxide. Microstructure of the single-phase solid solution is represented in Fig. 1b.

Dependence of the lattice parameter of solid solution, which is formed based on F^1 with La_2O_3 additions, is shown in Fig. 2. Increase in the sintering temperature up to 1400°C leads to the single-phase solid solution formation of the fluorite type based on F^1 ; at 1900°C the single-phase region of solid solution reaches 60 mol% of La_2O_3 . These cooled samples are not destroyed in the air at room temperature.

In accordance with the X-ray data we obtained the linear dependence of the lattice parameter of cerium dioxide on the additions of lanthanum oxide. Using this dependence we can assert that in the given system the solid solutions of the substitution-subtraction type are formed.

Formation of the single-phase solid solution based on cerium dioxide with additions of lanthanum oxide passes through the $F \rightarrow F^1$ phase transition, which is observed in the samples of $\text{CeO}_2 + 1\text{-}5 \text{ mol\% } \text{La}_2\text{O}_3$ composition.

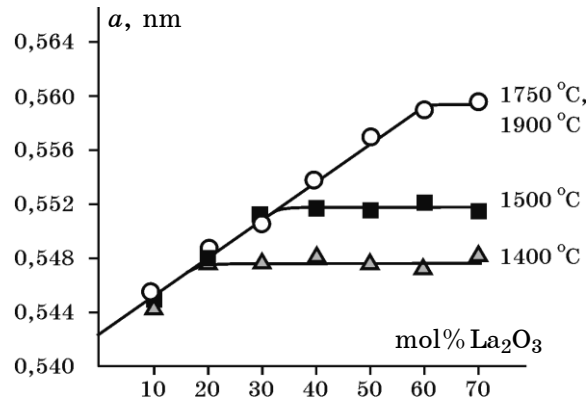


Fig. 2 – Solid solution formation in $\text{CeO}_2 - \text{La}_2\text{O}_3$ system

Appearance of the F^1 -type phase in the mixture with the F -type phase was also observed in the samples sintered at 1000°C . Increase in the sintering temperature up to 1400°C leads to the formation of the single-phase solid solution of the fluorite type based on F^1 .

$F \rightarrow F^1$ phase transition was studied using two-phase samples sintered at 1300°C . We used samples of $\text{CeO}_2 + (5-15) \text{ mol}\% \text{La}_2\text{O}_3$ composition. Such samples were investigated by the high-temperature X-ray method in the temperature range $25-1400^\circ\text{C}$ in the air medium. While heating, we simultaneously watched out for the changes in the lattice parameters of two phases. With the temperature rise the lines of two phases are shifted uniformly towards small angles up to the temperature of 1300°C , and starting from this temperature only they begin to approach; at the same time redistribution of the line intensity of these phases takes place. Formation of the solid solution based on F^1 structure occurs by the complicated mechanism.

This process can be represented as the second-order phase transition. It is accompanied by the gradual transformation of the cubic ordered F -type structure into the cubic disordered F^1 -type structure, and this structure keeps while cooling to room temperature (Fig. 3).

The same results were obtained using the hardened samples. $F \rightarrow F^1$ phase transformation can be considered as the second-order break in one-variable function depending on the defect concentration, which appear in the structure both during the oxide reduction and the lanthanum oxide dissolution

$$\lim_{T \rightarrow 1400^\circ\text{C}} f(F) = \lim_{T \rightarrow 1400^\circ\text{C}} f(F^1) = a^1 \quad (6)$$

where $a^1 = f(x, y)$; x is the anion vacancy concentration; y is mol.% La_2O_3 in the solution.

$$F = f(a); F^1 = f(a^1).$$

Below 1300°C the coefficients of thermal expansion of two phases for all compositions are almost the same and equal to $11,50 \cdot 10^{-6} \text{C}^{-1}$. Above 1300°C the coefficient of thermal expansion of F^1 -type phase decreases to the value of 10^{-6}C^{-1} .

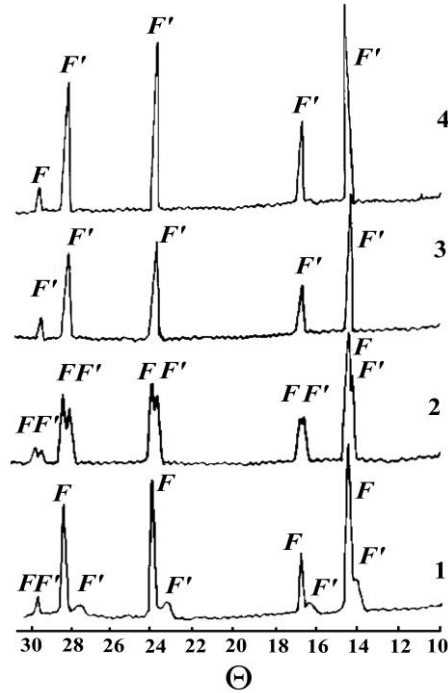
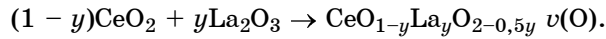
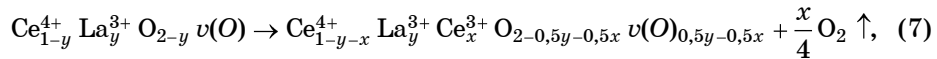


Fig. 3 – X-ray diffraction patterns of the samples with $\text{CeO}_2 + 5 \text{ mol}\% \text{La}_2\text{O}_3$ composition after sintering in the air medium at: 1 – 1000°C; 2 – 1300°C; 3 – 1400°C; 4 – after cooling at 25°C

Mathematical model of the solid solution based on cerium dioxide with lanthanum oxide additions can be represented as the solution of two sublattices



Under deviation from stoichiometry, solid solution additionally contains the anion vacancies and can be represented by the following model:



where y is mol.% of lanthanum oxide addition; x are the defects in oxygen.

Solid solutions of the substitution-subtraction type are formed in the present system. When cerium cations are substituted by trivalent lanthanum cations, one vacancy appears per two substituted cerium cations. Lanthanum cations can not be implanted in non-structural positions due to big difference between the values of ionic radiuses for lanthanum and cerium. Thus, the solutions of the substitution-subtraction type are formed in the given system that provides the linear behavior of the dependence $a(x, y)$ (Fig. 2).

Dissociation of solid solutions was carried out using samples with the composition of 1-50 mol% of lanthanum oxide in the temperature range 1100-1900°C with air exposure during 20-80 hours at temperatures of 1100, 1400, 1600°C and 6 hours at 1900°C. In accordance to this data, solid solutions

both with small and large additions dissociate. Samples with 10 mol% of lanthanum additions in cerium dioxide segregate into phases of F and F^I fluorite type at 1100°C. At 1400-1600°C the cubic phase of C -type in cerium oxide and solid solution based on cerium dioxide of the F -type were observed in the samples with small additions (1-5 mol% of lanthanum oxide) (see Fig. 4).

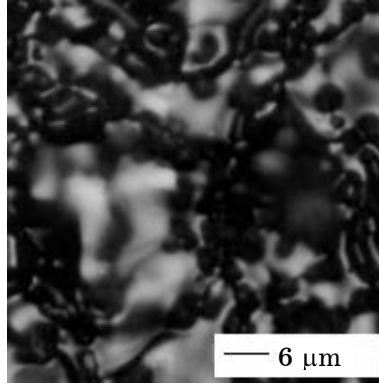


Fig. 4 – Microstructure of the sample with $\text{CeO}_2 + 5 \text{ mol.}\% \text{La}_2\text{O}_3$ composition obtained after isothermal annealing at 1600°C (80 hours) in the air

Phase of C -type in Ce_2O_3 appears on the grain boundaries of solid solution based on cerium dioxide with lanthanum oxide additions. The grain size of the C -phase is equals to 6 μm . Obtained results of the solid solution dissociation in the given system are shown in Fig. 5.

The single-phase solution keeps at 1600°C for samples with 10-50 mol% of lanthanum oxide additions in the solution. At 1900°C samples both with small and large lanthanum oxide concentrations do not dissociate.

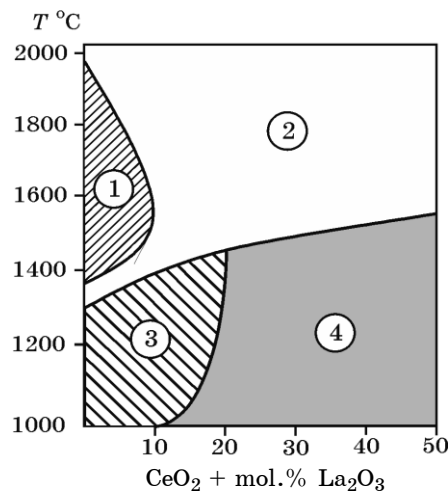


Fig. 5 – Schemes of non-equilibrium dissociation of solid solutions of the fluorite type in $\text{CeO}_2 - \text{La}_2\text{O}_3$ system: 1 – $C + F$ phase, 2 – F^I phase, 3 – $F + F^I$ phase, 4 – $F^I + \text{La}_2\text{O}_3$ phase

4. CONCLUSIONS

It is established that in the given system the solid solution of the substitution-subtraction type is formed. Solid solution formation and dissociation in CeO_2 - La_2O_3 system can be studied using three models. Each model is based on complicated calculations, which take into account the experimental data, that allows to explain the regularities of the formation and dissociation processes of solid solutions based on CeO_2 . Presented mathematical models of the process of deviation from stoichiometry of cerium dioxide, mathematical models of the solid solution formation of the substitution-subtraction type based on cerium dioxide with lanthanum oxide additions explain all structural changes in the investigated samples.

$F \rightarrow F^1$ phase transformation is revealed, and it is connected with the disordering process of the cerium dioxide structure with lanthanum oxide additions. This phase transformation is the second-order structural transition.

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