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Gas-sensing properties of nanostructured CeO₂-xZrO₂ thin films obtained by the sol-gel method

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Abstract: With the use of sol-gel technology and heat-treatment at a temperature of 500°C, we obtained CeO_2 -xZrO₂ (where x = 0, 5, 10, 20, 30, 50 mol%) powders and thin films that are promising for oxygen detection. A phase composition of the samples was studied using XRD and Raman spectroscopy. It was shown that under these synthesis conditions, both for powders and films, an increase in the content of zirconium dioxide from 0 to 50 mol% entailed the formation of solid solutions with a fluorite crystal lattice in the structure of cerium dioxide. For CeO_2 -xZrO₂ thin films (where $x = 0 \div 30$ mol%), gas-sensing properties were studied: we identified a resistive response to oxygen in a wide range of concentrations (0.4-20%) at a low operating temperature of 400°C, and studied the effect of moisture on the signal obtained while detecting O_2 . Upon increase of humidity from 0 to 100% resistance and response to oxygen values decrease, and from 75% and larger humidity a significant worsening of kinetic properties occurs, such as response time and recovery time. Selectivity to analyte gases such as H₂, CO, CH₄, NO₂ was studied. The best selectivity to oxygen was displayed by the film containing 20% ZrO₂, while the film with 10% ZrO₂ demonstrated the worst selectivity. Using Raman spectroscopy it was shown that, after studies in a gas-air mixture containing not more than 1% of reducing gases, the nanomaterial surface contained oxygen superoxides and peroxides that were not removed, even after subsequent heat treatment in air at 500°C.

Keywords: sol-gel technology; ceria; zirconia; gas sensor; thin films; Raman spectroscopy

1. Introduction

Resistive oxygen sensors have become increasingly important in the last decade, due to such advantages as lower operating temperature, fast response time, high value of the obtained signal, and small size compared to other types of oxygen sensors. Qualitative and quantitative control of the oxygen content of a gaseous atmosphere is necessary in many branches of human activity and technological processes.

Detecting oxygen with receptor nanomaterials in resistive-type sensors is possible due to defects (oxygen vacancies) in the crystal structure of a nanomaterial [1]. The most popular materials, with a large number of defects and oxygen vacancies, include TiO₂, ZrO₂-Y₂O₃, CeO₂, SrTiO₃ and Nb₂O₅; the latter two are less common, primarily because of their high operating detection temperatures [2-5].

Cerium dioxide is an n-type semiconductor with a fluorite-type structure that allows gas-phase oxygen to integrate into the crystal lattice at elevated temperatures so that one can observe a resistive response [4,6]. Thick and thin films of cerium dioxide have been long and successfully used to detect oxygen at sufficiently high temperatures (> $600^{\circ}C$) [2,4,7–11]. The use of more complex systems, with titanium dioxide or yttrium oxide, for example, can reduce the operating detection temperature [12,13]. In addition to being used as a receptor material for oxygen, CeO₂ is successfully used to detect a wide group of analyte gases (NO₂, CO, NH₃ and many others) [14–21], being used as well as a moisture sensor [22–25], due to its semiconductor properties. Among the main problems with the use of cerium dioxide, as with any other semiconductor, when detecting an analyte gas, are low selectivity and the strong effect of humidity on the obtained signal. These problems can be solved by the modification of cerium dioxide with various dopants [16,18,19,21].

Solid solutions of CeO₂-ZrO₂, in addition to their widespread use as SOFC components [26–29], are also used to produce receptor materials to detect oxygen [30–33] and other analyte gases [34–36]. The introduction of a Zr^{4+} cation, having a smaller cationic radius than Ce⁴⁺, into the crystal structure of ceria increases electrical conductivity and the number of oxygen vacancies [37], thereby increasing sensitivity to oxygen.

When detecting gases, thin-film technology has several advantages over thick-film technology [38, 39]; in particular, it provides the opportunity to significantly miniaturize the sensors [40]. Ceria thin films can be produced using various gas-phase and solution methods: physical and chemical vapour deposition, magnetron sputtering, radio-frequency

deposition, atomic layer deposition, electrochemical deposition [40 41–46], as well as solgel technology [13,16,23,47,48] and others [49,50]. It is known that the sol-gel method is convenient (not employing an expensive and complicated equipment) for obtaining 2Dnanomaterials of complex composition, including solid solutions [19,51,52], which constitutes its advantage over the gas-phase methods. And it is also promising for obtaining ink for high-resolution ink-jet printing [53], which would allow to simplify the process of scaling during production of miniature sensors based on various oxide systems, which would result from crystallization of xerogel films.

The aim of this work was to obtain nanostructured CeO_2 -ZrO₂ thin films by the solgel method, to study their microstructure and phase composition, as well as their sensitivity, selectivity in detecting oxygen and the effect of moisture on the obtained signal.

2. Materials and Equipment

The synthesis of metal acetylacetonates was carried out using $\text{ZrOCl}_2 \ 8\text{H}_2\text{O}$ (cp), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (cp) and $\text{C}_5\text{H}_8\text{O}_2$ acetylacetone (pure) caused by the introduction of a 5% aqueous solution of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (hp) into the solution of these reagents. The identification of compounds was carried out using IR spectroscopy, XRD and combined DTA/DSC/TGA.

The synthesis of $[M(O_2C_5H_7)_x({}^iOC_5H_{11})_y]$ (M = Zr⁴⁺ and Ce³⁺) complexes was carried out by heat treatment of a solution of zirconium and cerium acetylacetonates in isoamyl alcohol ${}^iC_5H_{11}O_2$ (AR) in a round-bottom flask under reflux on a sand bath until the degree of substitution of chelating ligands for OR groups was about 50%, as monitored with a UV-Vis spectrophotometer SF-56. The dynamic viscosity of the resulting solutions determined with a Brookfield rotational viscometer Fungilab Smart L (100 rpm shift speed, L2 spindle, temperature $22 \pm 2^{\circ}C$) was about 7 cP.

Films of the solution of heteroligand precursors were applied to the surface of polycrystalline Al_2O_3 substrates (roughness $R_a \sim 0.4 \ \mu m$) with platinum interdigital electrodes and a microheater on the reverse side, using a dip-coating method with an extraction rate of 1 mm/s [54-56]. An aliquot was taken from the same precursor solutions in order to study the process for obtaining CeO₂-xZrO₂ nanopowders (where x = 0, 5, 10, 20, 30, 50 mol%).

After completion of solvent removal processes, precursor hydrolysis due to air moisture and polycondensation in the solution volume and in the film, the samples were heat-treated in air at 500°C for 1 hour. The second layer of oxide films with the indicated formulas was applied in a similar manner.

The electronic (UV) spectra of precursor solutions were recorded after dilution of precursor solutions with propanol (> 99%) to a concentration of $4 \cdot 10^{-4}$ mol/L (cell thickness is 1 mm), using a UV-Vis spectrophotometer SF-56.

The transmittance IR spectra of heteroligand complex solutions were recorded using a Fourier IR spectrometer InfraLUM FT-08.

The analysis of the thermal behaviour of the xerogel was carried out using a combined DSC/DTA/TG analyzer SDT-Q600 (TAInstruments) in Al_2O_3 crucibles in an air stream (250 ml/min), at a heating rate of 10°/min.

The X-ray patterns of the surface of oxide powders and films were recorded on a D8 Advance (Bruker) X-ray diffractometer in the 20 range of 5°-80°, with a resolution of 0.02° when the signal was accumulated at a point for 0.3 s, and in the interval of 27°-33° with the accumulation time at a point for 2.0 s.

Raman spectra were recorded using the NT-MDT NTEGRA Spectra spectrometer; a laser with a wavelength of 473 nm was used. For powders: lens 100x 0.28 NA, pinhole: 50 μ m, monochromator grating 1800/500 [mm⁻¹/nm], sample intensity ~ 8 mW, diameter of the focused laser beam on the sample surface: ~ 30-50 μ m. For thin films: lens 100x 0.9 NA, pinhole: 100 μ m, monochromator grating 1800/500 [mm⁻¹/nm], sample intensity ~ 8 mW, diameter of the focused laser beam on the sample surface: ~ 30-50 μ m.

The morphology of oxide films was studied using a three-beam workstation NVision 40 (Carl Zeiss). equipped with an EDX Oxford Instruments attachment for energy dispersive analysis.

Gas-sensing properties were measured using a specialized precision system. The gas medium was created in a quartz cell using two Bronkhorst gas flow controllers with a maximum flow rate of 100 and 200 ml/min. The generated gas flow stability was \pm 0.5 ml/min. The sensor element temperature was monitored with a platinum microheater. The obtained 2D nanomaterials were studied for sensitivity to various analyte gases: O₂, H₂, CH₄, CO and NO₂. When detecting oxygen, the baseline was recorded in argon, and in the case of other analytes, in synthetic air. The resistance of the oxide films was measured with a digital multimeter Fluke 8846A (6.5 Digit Precision Multimeter) with an upper limit of 1 G Ω .

The responses to oxygen and NO₂ were calculated using the formula:

 $S_1 = R_{gas}/R_0$

where R_{gas} – the oxide film resistance in the medium with a specified concentration of O_2 or NO_2 ; R_0 – the oxide film resistance in argon (for detecting O_2) or synthetic air (for detecting NO_2).

The responses to H₂, CH₄ and CO were calculated using the formula:

$$S_2 = R_{air}/R_{gas}$$

(2)

(1)

where R_{air} – the oxide film resistance in air; R_{gas} – the oxide film resistance in a gas-air mixture with a specified analyte concentration.

3. Results and Discussion

3.1 Synthesis of Hydrolytically Active Heteroligand Precursors

The synthesized $[Zr(C_5H_7O_2)_4]$ and $[Ce(C_5H_7O_2)_3]$ complexes were dissolved in isoamyl alcohol; the ratio of metals in the solution corresponded to those in the target CeO_2 -xZrO₂ oxides (where x = 0, 5, 10, 20, 30, 50 mol%). Furthermore, according to the previously described procedure [54-56], a partial destructive substitution of acetylacetonate ligands for alkoxy moieties was carried out by heat treatment of the solution in a roundbottomed flask, under reflux at a boiling temperature (131 ± 2°C) to form $[M(O_2C_5H_7)_x(^iOC_5H_{11})]$ (M = Zr⁴⁺ and Ce³⁺) heteroligand complexes. The degree of substitution of chelating ligands for alkoxy moieties was monitored by electron (UV) and IR spectroscopy. In the IR spectra of the resulting solutions, double absorption bands related to the vibrations of carbonyl functional groups of the by-products (acetone and ester) appeared in the area of 1700-1750 cm⁻¹ in the course of heat treatment. However, characteristic absorption bands associated with the vibrations of coordinated β -diketonate ligands remained with a maxima at 1518-1530 cm⁻¹ (bathochromic shift with increasing cerium content) and at 1616-1593 cm⁻¹ (hypsochromic shift).

The decrease in the absorption band intensity of the coordinated acetylacetonate group in the UV spectra with a maximum at ~ 285 nm made it possible to estimate the degree of ligand substitution in $[M(O_2C_5H_7)_x({}^iOC_5H_{11})]$ (M = Zr⁴⁺ and Ce³⁺) complexes, which was ~ 50%.

3.2 Obtaining Nanostructured CeO₂-xZrO₂ Thin Films

Thin films of precursor solutions were applied to the surface of polycrystalline Al_2O_3 substrates with platinum interdigital electrodes and a microheater, using a dip-

coating method with an extraction rate of 1 mm/s. In the volume of thin films, due to air moisture, the self-assembly and hydrolysis processes were initiated during polycondensation, forming a coherent dispersion system. After that, the samples were subjected to staged drying in the range of 22-50°C, which resulted in the completion of the gel syneresis process and the formation of xerogel coatings.

After the formation of xerogel films, the samples were heat treated in air in order to crystallize oxide coatings. Based on the TGA/DSC powder analysis data, optimal conditions (500°C with an exposure to air for 1 hour) were chosen.

A phase composition of the obtained nanomaterials was studied by X-ray phase analysis (XRD) and Raman scattering spectroscopy. Since polycrystalline alumina (with an average roughness of 0.4 μ m) was used as a substrate material for depositing 2D nanomaterials, the study of the phase composition of thin films by X-ray diffraction was difficult, due to weak reflections of thin-film nanomaterials on the substrate background. To study the phase composition over a wider 2 Θ range, under the conditions described, powders of the appropriate composition were obtained from precursor solutions. The crystallization conditions were identical to those for 2D nanomaterials – heat treatment in air at 500°C for 1 hour.

Fig. 1 (a) shows the X-ray patterns of CeO_2 -xZrO₂ powders (where x = 0, 5, 10, 20, 30, 50 mol%). By a set of characteristic reflexes, we can infer that the individual cerium dioxide crystallized in a cubic fluorite-type lattice [57,58].

Using the full-profile analysis, we calculated the crystal lattice parameters for powders of all compositions (Table 1): the lattice parameter a (Å), the cell volume V (Å³) and the crystallite size (L, nm) that decreased with increasing ZrO_2 content. As can be seen from Fig. 2, the dependence of the parameter *a* of CeO₂-xZrO₂ powders is linear, which indicates the fulfilment of Vegard's law and the formation of solid solutions with a fluorite structure.

For thin films, the X-ray patterns recorded in the angular range of $2\Theta = 27-31^{\circ}$ (where the most intense reflex (111) is located) with a long signal accumulation time at the point are shown in Fig. 1 (b). Similar to powders, we can speak of a monotonic broadening of the reflex (111) as ZrO_2 increased in the system, which indicated the formation of solid CeO_2 -x ZrO_2 solutions in the film structure. However, it should be noted that the reflex intensity for thin films with x > 5÷10 was so reduced that it was impossible to quantify its position and make correct conclusions. Therefore, the phase composition of the obtained films was determined using Raman spectroscopy.

Fig. 3 (a) shows the Raman spectra of CeO₂-xZrO₂ powders (where x = 0, 5, 10, 20, 30, 50 mol%). The spectrum of individual cerium dioxide contains 4 modes: the most intense F_{2g} (455 cm⁻¹), related to the fluorite phase, and three less intense, at 250, 600 and 1165 cm⁻¹, which are a second-order transverse acoustic mode (2TA), a defect-induced mode (D) and a second-order longitudinal optical mode (2LO), respectively [59,60]. As the content of zirconium dioxide increased in the crystal structure, the same set of bands was observed. The F_{2g} mode of the fluorite phase (455 cm⁻¹) differed in the greatest intensity, but it broadened simultaneously with an increase in the D mode intensity (600 cm⁻¹) as ZrO₂ content increased. These changes indicate the formation of a more defective structure due to a large number of oxygen vacancies in the crystal lattice as a result of the cationic substitution of cerium for zirconium [31,32,37]. The obtained Raman spectra data are in good agreement with XRD (Fig. 2a) and confirm that solid solutions with a fluorite structure were formed.

The Raman spectra of CeO₂-xZrO₂ thin films (Fig. 3b), similar to those of powders, contain four intense characteristic modes of the cerium dioxide phase. In addition, six bands related to the α -Al₂O₃ substrate with a crystal structure of corundum can be observed [61,62]: five E_g modes at 380, 431, 450, 578 and 751 cm⁻¹, and one A_{1g} mode at 419 cm⁻¹. According to the obtained set of characteristic bands, it can be stated that solid CeO₂-xZrO₂ solutions with a fluorite-type structure were deposited on a polycrystalline α -Al₂O₃ substrate. Similar to powders, the F_{2g} mode (455 cm⁻¹) broadened and the D mode (600 cm⁻¹) became more intense as the zirconia content increased, so the argument that a more defective lattice is formed with increasing ZrO₂ in the crystal structure is also applicable to thin films.

The microstructure and morphology of the obtained CeO₂-xZrO₂ films were studied using scanning electron microscopy (SEM). The films formed a continuous dense coating on polycrystalline Al₂O₃ sensors; as can be seen from Fig. 4a, they evenly coated the substrate grains. Fig. 4b-d presents the micrographs of CeO₂-xZrO₂ (x=0-50 mol %) CeO₂, CeO₂-20% ZrO₂ and CeO₂-50% ZrO₂ films. As can be seen, the films were lowporous, and the average particle size for individual CeO₂ was about 40-55 nm and decreased with increasing content of ZrO₂, (for CeO₂-50% ZrO₂, it is 30-40 nm). The micrographs also show that there were breaks of CeO₂-xZrO₂ films at the grain boundaries of the Al₂O₃ substrate, that were probably formed due to the high roughness of the substrate (R_a = 400 nm). A micrograph of the cleaved substrate with a coating (Fig. 5) made it possible to estimate the thickness of the obtained oxide film: depending on the substrate microstructure, it was 45-65 nm.

3.3 Gas-Sensing Properties

3.3.1 Sensitivity to Oxygen

The mechanism for detecting oxygen with cerium dioxide has been well studied, and refers to the defect type. In the crystal structure of CeO₂, as well as some of its solid solutions, for example, with zirconia or yttrium oxide, there are different types of defects. Oxygen vacancies $V_0^{\bullet\bullet}$ can be formed as a result of reactions by reduction of Ce⁴⁺ to Ce³⁺ at the lattice site [2,31]:

$$Ce_{Ce}^{x} + O_{o}^{x} \equiv \rightleftharpoons V_{o}^{\bullet \bullet} + 2Ce_{Ce} + \frac{1}{2}O_{2}$$

$$2O_{o}^{x} \equiv \rightleftharpoons 2V_{o}^{\bullet \bullet} + 4e^{-} + O_{2}$$
(3),
(4)

The reactions (3) – (4) are at equilibrium, so they will proceed most intensely in the forward direction in an inert medium, where there will be a decrease in resistance due to saturation of the conduction band by additional electrons. When the concentration of oxygen is increased, the equilibrium in the reactions (3) – (4) will shift in the opposite direction, as a result of which there will be an opposite effect: an increase in resistance. As a rule, the resistance (R) or the response (S) depends logarithmically on the oxygen concentration or its partial pressure (i.e. R ~ $\log(P_{O2})^{1/n}$), where *n* lies in the range from 4 to 7, depending on the charge carriers' nature [1].

Additional oxygen vacancies can be formed if metal cations with a lower oxidation state or a smaller cationic radius are introduced into the crystal structure [63]. The oxidation state of zirconium is equal to that of cerium (+IV), but the cationic radius is less: 1.75 (Zr^{4+}) vs. 2.04 Å (Ce⁴⁺) [64], which allows the formation of additional oxygen vacancies in accordance with equations [37]:

$$\operatorname{CeO}_{2} = \rightleftharpoons \operatorname{Ce}_{Zr}^{x} + 2\operatorname{V}_{0}^{\bullet \bullet} + 2\operatorname{O}_{i}^{''}$$
(5)

$$2\operatorname{Ce}_{Zr}^{A} + \operatorname{O}_{0}^{A} \equiv \stackrel{\sim}{\rightleftharpoons} 2\operatorname{Ce}_{Zr} + \operatorname{V}_{0}^{\bullet\bullet} + \frac{1}{2}\operatorname{O}_{2}$$

$$(6)$$

The authors of [37] argued that, at high dopant concentrations, it is possible to form associates $(Ce_{Zr} V_0^{\bullet \bullet})^{\bullet}$ that can also participate in the mechanism of oxygen detection.

The obtained CeO₂-xZrO₂ thin films (where x = 0, 5, 10, 20, 30 mol%) showed a sufficiently high reproducible response to oxygen over a wide range of concentrations (0.4-20%) at an operating temperature of 400°C (Table 2 and Fig. 6). At lower operating temperatures, the baseline resistance (in an Ar medium) was above 1 GΩ, so the response

could not be recorded. With an increase in the operating temperature to 450°C, there was a significant decrease in the response magnitude to the level approaching base line drift, and in the stability of the obtained signal. The CeO₂-xZrO₂ film (where x = 50 mol%) showed a high value of baseline resistance (>1 GΩ), even at a temperature of 400°C, and the response could not be measured.

The detection of oxygen for films of all compositions was carried out according to reaction (4), which proceeded in the opposite direction and was characterized by the introduction of oxygen from the gas phase into the oxygen vacancies of the crystal lattice. Fig. 6 shows the dependence of the response R_{O2}/R_{Ar} on the oxygen concentration in a gas mixture. It is seen that the response magnitude is a logarithmic function of O₂ concentration, which is typical for resistive semiconductor receptor materials [1,11,65]. For individual CeO₂, the response R_{O2}/R_{Ar} increased from 1.26 to 2.31 (Table 2), with an increase in the oxygen content from 0.4 to 20%.

The greatest response magnitude over the entire range of oxygen concentrations was observed for a composition containing 10% ZrO₂, where R_{O2}/R_{Ar} increased from 1.49 to 2.89 (Table 2), with an increase in oxygen from 0.4 to 20%. The introduction of Zr⁴⁺ to the crystal structure promoted the formation of more oxygen vacancies ($V_0^{\bullet\bullet}$) due to the reactions (5) - (6); the latter is a limiting one. The further increase in zirconia content did not lead to an increase in the response value, but contributed to the retardation of reactions (3), because Zr⁴⁺ (with a stable oxidation state) replaced Ce⁴⁺ in the lattice sites that could react to form Ce³⁺. As a result, we see a decrease in the response magnitude when oxygen is added, as can be seen from Fig. 6. For CeO₂-20mol% ZrO₂ films, the response R/R₀ changed from 1.37 to 2.37 (Table 2), with an increase in oxygen from 0.4 to 20%.

Fig. 7 presents the experimental data on the sensitivity of CeO_2 -xZrO₂ thin films (where x = 0, 10, 20 mol%) to oxygen in a wide range of concentrations (0.4-20%). As can be seen, the signal quickly reached a constant value and went to a stable mode when oxygen was added. The response and recovery time did not depend on the composition of the obtained solid solutions, and changed only when the oxygen concentration increased from 0.4 to 20% (Table 3).

3.3.2 The Effect of Humidity on the Obtained Signal

The effect of humidity on the signal obtained when detecting oxygen was studied (Fig. S1). Fig. 8 shows the dependence of reproducibility of the resistance (a) and the response R_{02}/R_{Ar} (b) of a CeO₂-xZrO₂ thin film (where x = 20 mol%) when detecting 5%

 O_2 at 0, 25, 50, 75, 100% humidity. The data were well reproduced for all humidity values in a gas medium – the signal returned to the same resistance values, and its value remained unchanged when oxygen was added to the specified concentration. With an increase in humidity from 0 to 100%, there was a consistent decrease in film resistance, both in argon and in the presence of oxygen. At 0% humidity for a CeO₂-xZrO₂ film (where x = 20 mol%), the baseline was at 230 MOhm, and the response R/R₀ to 5% O₂ was 1.74. With an increase in humidity up to 25%, the baseline fell to 205 MOhm, and the response R_{O2}/R_{Ar} – to 1.51. An increase in humidity up to 50% resulted in a slight decrease in the baseline resistance to 200 MOhm; this was not the case for the response R_{O2}/R_{Ar}, which dropped to 1.42. A further increase in humidity to 75 and 100% reduced the baseline resistance to 170 and 130 MOhm, respectively, and the response value slightly decreased, to 1.37 and 1.39, respectively. These phenomena when detecting oxygen with different moisture contents in a gas medium were observed for all CeO₂-xZrO₂ films (where x = 0, 5, 10, 20, 30 mol%) and were a consequence of a change in the defect nanomaterial structure when the composition of a gas atmosphere was changed.

In an inert argon medium, the H_2O molecules from the gas phase begin to interact with defects of the oxide nanomaterial after sorption onto its surface [66]:

$$\frac{1}{2} H_2 O_{ads} + O_o^x = \rightleftharpoons HO_o^{\bullet} + e^- + \frac{1}{4} O_{2gas}$$
(7)

The consequence of this reaction will be a decrease in the oxide film resistance due to additional electron saturation.

The authors of [67] also stated that the reactions are possible:

$$H_{2}O_{ads} + V_{o}^{\bullet\bullet} = \rightleftharpoons O_{o}^{x} + 2H^{\bullet}$$

$$H^{\bullet} + O_{o}^{x} = \rightleftharpoons HO_{o}^{\bullet}$$
(8)
(9)

When adding oxygen, usually the reaction (4) will occur, which will lead to an increase in resistance (Fig. 8); the increase in humidity resulted in a decrease in the response value, as can be seen from Fig. 8 and Fig. 9. For CeO₂, as for TiO₂, the response magnitude and kinetic characteristics (response time and recovery time) depended on the number of oxygen vacancies involved in the mechanism of O₂ detection during the reaction (4). Water molecules that interacted with O_0^x and $V_0^{\bullet\bullet}$ defects and quantitatively decreased them, thereby inhibiting the reaction (4). Consequently, we saw a decrease in the response magnitude with increasing humidity in a gas medium. The water sorbed on the surface interferes with the sorption of oxygen and makes it difficult to incorporate it into oxygen vacancies.

Fig. 9 shows the changes in kinetic characteristics (response time and recovery time) when detecting 5% O_2 in the context of increasing humidity from 0 to 100% for a CeO_2 -xZrO₂ thin film (where x = 20 mol%). In a dry medium, the response time and the recovery time were low enough when adding 5% O_2 : t₉₀ values were 25 and 53 sec, respectively. The increase in humidity to 25 and 50% slightly affected the kinetic characteristics in a negative way, in contrast to the response magnitude. The greatest response time and recovery time were observed at 75% humidity – t₉₀ values were 293 and 484 sec, and at 100% humidity they were 223 and 351 sec, respectively. The obtained nonmonotonic dependence of the sensing properties of nanomaterials on humidity warrants further study. In general, the deterioration of the kinetic characteristics with increasing humidity mainly occurred due to the fact that water molecules can be chemically bonded to metal cations [67] located on the nanomaterial surface, to prevent sorption of oxygen molecules, and so the form of dynamic response curve with increase in humidity started to be more and more bell-shaped.

3.3.3 Selectivity

As is known, the semiconductor properties of cerium dioxide make it possible to detect a wide variety of analyte gases. The mechanism of their detection is classical and consists of the oxidation or reduction of analyte gases with sorbed oxygen ions (O_2^- , O^- , O^{2-}) on the surface of a semiconductor [15,16,18,20].

To study the selectivity of CeO₂-xZrO₂ thin films (where x = 0, 5, 10, 20, 30 mol%), we additionally measured the response to the most practically significant gaseous analytes: 1% H₂, 1% CH₄, 0,01% (100 ppm) CO and 0,01% (100 ppm) NO₂ (Fig. 10). It can be seen that sensitivity to any given analyte gas depends strongly on the chemical composition of the oxide films. Thus, individual CeO₂, in addition to the response to oxygen, showed a relatively high response (R_{air}/R_{gas}=1.32) to 1% H₂; the response did not exceed 1.10 for other analyte gases. With a slight ZrO₂ doping (5 mol%), the response to hydrogen decreased to 1.11, the sensitivity to CH₄ and NO₂ almost completely disappeared, and the response to CO increased to 1.14. A further introduction of zirconia (10 mol%) into the structure significantly increased the response R_{gas}/R_{air} to 0,01% 100 ppm NO₂ to 1.43. In general, we should note that the film of this composition showed the worst selectivity, although it had the best sensitivity to O₂. A CeO₂-xZrO₂ thin film (where x = 20 mol%) showed the best selectivity to oxygen; the responses to other analyte gases did not exceed 1.05. A further increase in the ZrO₂ content (30 mol%) in the crystal

structure made it possible to establish the greatest response to 1% H₂, which was 1.45; the responses to CH₄ and CO did not exceed 1.10; the response to 0,01% $\frac{100 \text{ ppm}}{100 \text{ ppm}}$ NO₂ could not be measured, since the resistance in a gaseous analyte medium exceeded 1 GΩ.

3.3.4 Modification of a Chemical Composition of the Surface when Detecting Reducing Gases

After carrying out the experiments to study the gas-sensing properties of CeO_2 xZrO₂ thin films, (studying sensitivity to oxygen, investigating the effect of humidity on the obtained signal, and determining selectivity), we recorded the Raman spectra of sensors of all compositions (Fig. 11).

It has been established that two sufficiently intense bands appeared at 520 and 834 cm^{-1} after the detection of even small concentrations of reducing gases (1% H₂, 1% CH₄, 0,01% 100 ppm CO), in addition to the characteristic 2TA, F_{2g}, D and 2LO modes related to the fluorite phase of individual CeO₂ or its solid solutions with ZrO₂. These modes differed in intensity; the most intense band at 834 cm⁻¹ was observed for a CeO₂ $xZrO_2$ film (where x = 20 mol%). According to the available literature data [68-71], these modes characterize oxygen superoxides and peroxides (O_2^-, O_2^-, O_2^-) , respectively) that are present on the nanomaterial surface. It was noted earlier that the formation of such oxygen forms is possible when powders are heat-treated (400°C or higher) in a reducing gas medium (5% H₂ [60] or CO [69]) diluted with an inert gas (Ar or He) but necessarily containing 10% of oxygen. In our experiment, oxygen superoxides or peroxides were formed on the surface of thin films when detecting much lower concentrations of reducing gases (1% H₂, 1% CH₄, 200 ppm CO) at an operating temperature of 400°C. The H₂ or CO molecules restored Ce^{4+} cations to Ce^{3+} , creating additional oxygen vacancies, and the oxygen formed as a result of the reduction of chemical bonds to Ce⁴⁺, forming superoxide or peroxide groups on the surface [60,68,69]. After heat treatment and partial reduction of the surface layer in the crystal lattice, the O_2^- and O^{2-} groups remained on the nanomaterial surface after cooling down to room temperature, resulting in characteristic bands on the Raman spectra at 520 and 834 cm⁻¹.

To remove the O_2^{-} and O^{2-} groups from the semiconductor surface, the sensor with a deposited film was additionally heat-treated in air at a temperature of 500°C for 1 hour, and then in an argon atmosphere. As can be seen in Fig. 12, calcination in air did not remove the O_2^{-} and O^{2-} groups, since the Raman spectra still retained the modes at 520 and 834 cm⁻¹. Heat treatment in an inert atmosphere led to surface regeneration, which is in

good agreement with the literature data [68], since the Raman spectra contain only modes related to the fluorite cubic phase of CeO_2 -xZrO₂.

Thus, when detecting reducing gases *in-situ*, the formation of oxygen superoxide and peroxide groups on the surface of CeO₂-xZrO₂ films was initiated. The presence of these groups had no effect on sensitivity to H₂, CH₄, CO and NO₂, since the detection mechanism involved the oxidation or reduction of analyte gases with O₂⁻ and O²⁻ oxygen located on the semiconductor surface. In our case, these oxygen forms were retained even at room temperature, although, according to the available literature data, their intensive formation on the semiconductor surface begins at temperatures above 150°C [72]. In our laboratory experiment, the presence of O₂⁻ and O²⁻ groups on the surface did not affect sensitivity to oxygen, since the sensor was pre-heated in an inert medium (Ar) to an operating detection temperature of 400°C.

4. Conclusion

Using $[M(O_2C_5H_7)_x({}^iOC_5H_{11})_y]$ (M = Zr⁴⁺ and Ce³⁺) heteroligand complexes as precursors, we synthesized highly dispersed CeO₂-xZrO₂ oxides (where x = 0, 5, 10, 20, 30, 50 mol%) in the form of nanopowders and thin films using the sol-gel method. Using XRD and Raman spectroscopy, it has been shown that heat treatment of powders and thin films of xerogels at 500°C (1 hr) provoked crystallization of cerium dioxide with a fluorite structure, while an increase in zirconium dioxide content resulted in the formation of solid CeO₂-ZrO₂ solutions based on a specified structure, accompanied by a decrease in the average size of crystallites.

Nanostructured CeO₂-xZrO₂ thin films (x = 0.30 mol%) showed a good reproducible resistive response to oxygen in a wide range of concentrations (0.4-20%) at a relatively low operating temperature of 400°C. It has been established that they have sufficient selectivity to O₂ that depends on the composition of receptor materials; the best selectivity to O₂ was observed for CeO₂-xZrO₂ nanomaterial (where x = 20 mol%).

We studied the influence of humidity on the obtained signal when detecting oxygen: with an increase in humidity, a systematic drop in resistance and response has been observed, and at a high humidity (\geq 75%) the kinetic characteristics (response time and recovery time) deteriorated by 9-11 times.

Selectivity of obtained thin-film nanomaterials to other analyte gass was studied, such as H₂, CO, CH₄, NO₂. Thin film of composition CeO₂- $xZrO_2$ (x= 20 mol. %) possesses the best selectivity, with response to other analyte gases not exceeding 1.05.

Raman spectroscopy showed that oxygen superoxides and peroxides remained on the surface of oxide nanomaterials, after studying the sensitivity of CeO₂-xZrO₂ thin films (x = 0.30 mol%) to small concentrations of reducing gases (1% H₂, 1% CH₄ and 0,01% 200 ppm CO in air) at T = 400°C.

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Captions to Figures

Fig. 1. X-ray patterns of CeO_2 -xZrO₂ powders (a) and thin films (b) (where x = 0, 5, 10, 20, 30, 50 mol%)

Fig. 2. The dependence of the parameter 'a' of a fluorite-type lattice on the ZrO_2 content in CeO_2 -x ZrO_2 powders (where x = 0, 5, 10, 20, 30, 50 mol%)

Fig. 3. Raman spectra of CeO_2 -xZrO₂ powders (a) and thin films (b) (where x = 0, 5, 10, 20, 30, 50 mol%)

Fig. 4. Microstructure of CeO₂-xZrO₂ thin films, where x = 0 (a), 5 (b), 10 (c), 20 (d), 30 (e), 50 (f) mol%.

Fig. 5. Microstructure of the cleavage of Al₂O₃ substrate with CeO₂ film, SEM

Fig. 6. The dependence of the response R_{O2}/R_{Ar} on the oxygen concentration at an operating temperature of 400°C

Fig. 7. Sensitivity of CeO₂-xZrO₂ thin films (where x = 0, 10 20 mol%) to oxygen at an operating temperature of 400°C

Fig. 8. Reproducibility of the signal of CeO_2 -xZrO₂ thin films (where x = 20 mol%) with different moisture content when detecting 5% O₂: change in resistance (a) and response (b)

Fig. 9. Signal change kinetics (R_{O2}/R_{Ar}) of CeO₂-xZrO₂ thin film (where x = 20 mol%) when detecting 5% O₂ at different humidity and an operating temperature of 400°C

Fig. 10. Selectivity of CeO_2 -xZrO₂ thin films (where x = 0, 5, 10, 20, 30 mol%) at an operating temperature of 400°C

Fig. 11. Raman spectra of CeO_2 -xZrO₂ films (where x = 0-50 mol%) after detection of reducing gases

Fig. 12. Raman spectra of CeO_2 -xZrO₂ film (where x = 20 mol%) after the experiment to study the sensitivity to reducing gases and subsequent heat treatments in air and argon

Table 1. I arameters of the crystal fattice of CeO ₂ -X21O ₂ powders							
CeO ₂ -xZrO ₂ , x (mol. %)	a, Å	V, Å ³	L, нм	R _{wp}			
0	5.413(1)	158.60(6)	17.7(7)	7.47			
5	5.403(1)	157.79(9)	13.8(6)	7.25			
10	5.394(1)	156.96(1)	10.5(4)	7.02			
20	5.377(2)	155.50(1)	8.0(4)	7.15			
30	5.367(3)	154.61(2)	6.3(4)	6.76			
50	5.334(3)	151.78(2)	6.4(4)	6.44			

Table 1. Parameters of the crystal lattice of CeO₂-xZrO₂ powders

Table 2. The response R_{O2}/R_{Ar} of CeO₂-xZrO₂ thin films

	Response R ₀₂ /R _{Ar} O ₂ concentration, mol. %					
CeO ₂ -xZrO ₂ , x (mol. %)						
-	0.4	1	5	10	15	20
0	1.26	<mark>1.52</mark>	1.80	2.01	2.18	2.31
5	1.25	1.48	1.80	1.96	2.06	2.12
10	1.49	1.73	2.18	2.47	2.70	2.89
20	1.37	1.56	1.74	2.07	2.24	2.37
30	1.35	1.64	2.05	2.30	2.49	-

Table 3. Response time and recovery time of CeO₂-xZrO₂ thin films

	O ₂ concentration, mol. %						
	0.4	1	5	10	15	20	
Time response, s.	15	22	25	28	37	39	
Time recovery, s.	28	37	53	58	67	72	





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Highlights

- Nanostructured thin films CeO_2 -x ZrO_2 have been synthesized by sol-gel method.
- Powders and films solid solutions with a fluorite structure are formed.
- Thin films showed resistive response to at a low operating temperature of 400°C.
- Superoxide and peroxo-forms of oxygen remain on the surface of the nanomaterial.