Influence of structure of Fe₂O₃−In₂O₃ nanocomposites on the sensitivity of thin-film sensors on their base

Dzmitry Kotsikau a,*, Maria Ivanovskaya b

a Belarusian State University, 14 Leningradskaya, 220030 Minsk, Belarus
b Research Institute for Physical-Chemical Problems of the Belarusian State University, 14 Leningradskaya, 220030 Minsk, Belarus

HIGHLIGHTS
- Gas-sensing Fe₂O₃−In₂O₃ composites were prepared by inorganic sol−gel approach.
- Structure of Fe₂O₃−In₂O₃ composites are strongly dependent on synthesis conditions.
- Sensitivity of Fe₂O₃−In₂O₃ thin films were correlated with their structural features.
- Condition optimal for the detection of NO₂, O₃ and C₂H₅OH has been revealed.
- Thin films based on γ-Fe₂O₃ phase demonstrate a high response to NO₂.

ABSTRACT
Thin-film sensing layers based on Fe₂O₃−In₂O₃ nanocomposites with different component ratio and structural features were synthesized by inorganic modification of sol−gel method. The phase composition and morphology of the composites as a function of the synthesis conditions were studied by X-ray diffraction, transmission electron microscopy, electron diffraction, differential scanning calorimetry, electron paramagnetic resonance and infrared spectroscopy. The gas-sensing parameters the Fe₂O₃−In₂O₃ composites were correlated with their structure. The synthesis conditions resulting in the formation in the Fe₂O₃−In₂O₃ composites of metastable γ-Fe₂O₃ phase, which is characterized by an enhanced activity in adsorption and catalysis as compared to α-Fe₂O₃ oxide, were revealed. An improved sensitivity of γ-Fe₂O₃ based composites to different gases was shown. The chemical and structural compositions of Fe₂O₃−In₂O₃ thin-film sensing layers and operating temperatures optimal for the detection of O₃, NO₂ and C₂H₅OH were proposed.

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1. Introduction
Materials based on Fe₂O₃−In₂O₃ mixed oxides in a form of films, powders, ceramics and In₂O₃/Fe₂O₃/In₂O₃ multi-layers are considered to be very promising candidates for gas sensors, optoelectronics and spintronics [1−9]. Most of the reported studies of the Fe₂O₃−In₂O₃ system for gas-sensing applications deal with the composite materials in which iron oxide has a phase structure of α-Fe₂O₃ [4,5,7,8,10]. Due to recent advances in spintronics, materials representing magnetic clusters incorporated into a semiconducting matrix is of great interest [6]. For example, a ferromagnetic behavior of Fe³⁺-doped In₂O₃ oxide were studied over the past five years [3,6,9,11]. In these mixed materials, In₂O₃ oxide is a predominating phase while α-Fe₂O₃ oxide is a magnetic dopant. Depending on the component ratio and the synthesis conditions, the Fe₂O₃−In₂O₃ composites could consist of either two phases (C−In₂O₃ and α-Fe₂O₃) or single C−In₂−xFeₓO₃ phase, which is a substitutional solid solution with x ≤ 0.4 [11]. A high mutual solubility of α-Fe₂O₃ and C−In₂O₃ oxides was achieved by thermal treatment of co-precipitated hydroxides of Fe³⁺ and In³⁺ [12] or by mechanical activation of the corresponding oxides [13,14]. However, there is a lack of information on the stability of the solid solutions formed.

In contrast, the properties of Fe₂O₃−In₂O₃ composites with a high content of Fe₂O₃ are poorly studied [15,16]. Materials based on α-Fe₂O₃ oxide doped with single- and double-charged metal cations were characterized in [17,18] as humidity sensors. The
formation of a ferrite structure is possible in such composites. There are contradictory data about the formation and stabilization of chemical compounds of $\alpha$-$Fe_2O_3$ with triple-charged metal cations including In$^{3+}$ [19]. There are no strict evidences whether In$_2$FeO$_3$, InFe$_2$O$_4$ and InFe$_3$O$_4$ composites are individual compounds or solid solutions based on metastable phases of indium oxides like monoclinic $M$-In$_2$O$_3$ and rhombohedral $R$-In$_2$O$_3$ [19–21]. It was shown in [22] that the presence of Fe$^{3+}$ ions in indium oxide promotes the formation of $R$-In$_2$O$_3$ at low temperature. The emergence of this phase is unwanted for gas-sensing applications due to its lower conductivity and adsorption activity as compared to $C$-In$_2$O$_3$.

There is little literature on $Fe_3O_4$–In$_2$O$_3$ composites containing $\gamma$-$Fe_2O_3$ structural modification of iron oxide, which is thermodynamically unstable at temperatures below $-900 \, ^{\circ}C$ [1,2,15]. However, $\gamma$-$Fe_2O_3$ phase was reported to be a promising material for gas sensors [1,2,23,24]. A high sensitivity of thin films of $\gamma$-$Fe_2O_3$ and bilayer films of $\gamma$-$Fe_2O_3$/In$_2$O$_3$ to ozone was shown in [15,24]. The little interest in $\gamma$-$Fe_2O_3$ based materials is possibly caused by a low stability of both $\gamma$-$Fe_2O_3$ phase and Fe$^{3+}$ compounds, which are frequent precursors or intermediates for the preparation of $\gamma$-$Fe_2O_3$ oxide. During the synthesis, the $Fe^{2+/3}$ oxidation process should be strictly controlled to obtain the required $\gamma$-$Fe_2O_3$ structure. The most promising ways to obtain a thermodynamically stable $\gamma$-$Fe_2O_3$ oxide is to control reliably the formation of the primary structure of oxide composite at room temperature. The aim of the work was to reveal the effect of chemical composition and synthesis conditions on the phase structure, grain size and gas-sensing features of the Fe$_2$O$_3$–In$_2$O$_3$ composites prepared by the same method.

2. Material and methods

2.1. Synthesis of oxide composites

The composites were prepared by a modified sol–gel method based on applying aqueous solutions of inorganic precursors [28,29]. This approach allows preparing nanosized metal oxides in forms of colloidal solutions, thin films and powders. The crystallization of the sol–gel derived materials occurs typically at comparatively low temperatures ($300–400 \, ^{\circ}C$) suitable for the stabilization of iron oxide in both $\alpha$-$Fe_2O_3$ and $\gamma$-$Fe_2O_3$ modifications. The main advantage of the approach used in the study is in the formation of the primary structure of oxide composites at room temperature at the stage of the preparation of the corresponding colloidal solutions, and at the stage of their transformation into gel and xerogel states [30]. This allowed us to control reliably the formation of $\gamma$-$Fe_2O_3$ oxide, which is metastable at low temperatures, and to avoid its transformation into $\alpha$-$Fe_2O_3$ modification.

Two series of the In$_2$O$_3$–$Fe_2O_3$ composites were prepared. Series I was prepared by a combined hydrolysis of iron and indium salts with ammonia solution as a base agent, and further transformation of the precipitates into a sol state. Series II was prepared by a separate hydrolysis of indium or iron salts, and a stabilization of individual indium or iron hydroxides/oxides in a sol state. Then the individual sols were mixed together in the required proportions. The two procedures were applied since the mutual influence of indium and iron hydroxides on the structure of the resulting product is more pronounced in the case of the combined precipitation technique rather than under the mixing of the separately prepared hydroxides.

Thermally stimulated transformations of the co-precipitated hydroxides (samples of series I) are hardly predictable, which can lead to a product with unexpected structural features [31]. In order to ensure a homogeneous and nanosized structure of the resulting composite, a reverse order of the precipitation was used. The reverse order means that solutions of metal salts are to be added to an aqueous ammonia solution taken in some excess to maintain a constant $pH$ value ($-11$) of the reaction mixture over the whole duration of the synthesis [31–33]. Under the given experimental conditions, the hydrolysis of all the salts occurs simultaneously, which is especially critical in the case of combined precipitation of Fe(OH)$_2$, Fe(OH)$_3$ and Fe(OH)$_4$ hydroxides. The high $pH$ value ($>10$) prevents the generation of the undesired $R$-In$_2$O$_3$ structure under subsequent thermal treatment of the oxide composite.

To prepare $\gamma$-$Fe_2O_3$–In$_2$O$_3$ and $\alpha$-$Fe_2O_3$–In$_2$O$_3$ composites containing $\gamma$-$Fe_2O_3$ and $\alpha$-$Fe_2O_3$ phases respectively, a number of regularities were taken into account. Namely, the crystallization of In$_2$O$_3$ oxide from a sol–gel derived In(OH)$_3$ hydroxide occurs at $200 \, ^{\circ}C$ [31]. The base hydrolysis of Fe$^{3+}$ salts results in amorphous iron hydroxide [25–27], which transforms into $\alpha$-$Fe_2O_3$ oxide at temperatures higher than $300 \, ^{\circ}C$. The two general approaches to the synthesis of $\gamma$-$Fe_2O_3$ oxide were exploited: i) a base hydrolysis of Fe$^{3+}$ salts with the formation of Fe(OH)$_2$ hydroxide, and its further oxidation with a stream of air or oxygen passed through the suspension at $100 \, ^{\circ}C$ [34]; ii) a combined base hydrolysis of Fe$^{3+}$ and Fe$^{2+}$ salts giving FeO–Fe$_2$O$_3$ intermediate, and its oxidation as described above [35]. The later approach results typically in smaller $\gamma$-$Fe_2O_3$ particles (~10 nm) with a high content of residual OH-groups as compared to the product of Fe(OH)$_2$ oxidation whose grain size is about 40 nm. It worth notice that in composite oxide materials, the thermally stimulated crystallization processes of oxide phases proceed normally under the conditions different from those revealed for individual hydroxides [22,30,31,36,37].

2.2. Structural characterization

The phase composition of the samples was characterized by X-ray diffraction (XRD) analysis. Fine structural features of the Fe$_2$O$_3$–In$_2$O$_3$ composites, which are typically nanosized and poorly crystallized, were revealed by high-resolution transmission electron microscopy (TEM), electron diffraction (ED), differential scanning calorimetry (DSC), infrared spectroscopy (IR), and electron paramagnetic resonance spectroscopy (EPR). The XRD analysis was carried out on a HZC-4A diffractometer by using CuKz radiation. The TEM/ED examinations were performed with a LEOM 906E and a Jeol 4000 EX high-resolution transmission electron microscopes. The DSC analysis was performed on a NETCH STA 449 C instrument. The IR analysis of powdered samples was carried out on an AVATAR FTIR-330 spectrometer supplied with a smart diffuse reflectance accessory. The EPR spectra were recorded on a VARIAN spectrometer with resonance frequency of 9.35 GHz ($\chi$-band), magnetic field modulation of 25 kHz, modulation amplitude of 1–4 G, and microwave power of 5 mW.

2.3. Fabrication and testing of sensors

In order to obtain thin-film sensors, the prepared sols of the Fe$_2$O$_3$–In$_2$O$_3$ composites were deposited by spin-coating onto polycrystalline Al$_2$O$_3$ substrates ($3 \times 3 \times 0.25 \, mm^3$) supplied with Pt interdigitated electrode structure on the front side and Pt-heater on the rear side. The thickness of the thin films was estimated by...
SEM analysis to be about 200 nm. The sensor elements were annealed at 400 °C for 96 h in air. The gas-sensing features of the films to C2H5OH (50 and 100 ppm), NO2 and O3 (0.1 and 0.2 ppm) gases were tested on an 8-channel gas-mixing station with electronic gas flow controllers supplied with a Keithley 2000 multimeter and a computer. A contact electric potential was applied to the interdigitated electrode structure and the current through sensing layers was measured in air (lair) and in air-gas mixtures (lgas). The response (S) of the sensors was calculated as S = lgas/lair or as S = lgas/lair when detecting oxidizing (NO2, O3) and reducing (C2H5OH) gases, respectively. The time that it takes the sensor to be within 10% of the response value it had before the exposure to a gas was taken as the recovery time (trec). The measurements were carried out in a flow chamber (0.2 l) at 0.3 l min⁻¹ flow rate, 20 °C temperature and 30% relative humidity (RH). Since the conductivity of the sensing layers under study is a complex function of their composition, phase structure, grain size and operating temperature, all the measurements were limited to a fixed humidity level. The detailed results on the influence of humidity on the electric conductivity of thin-film layers based on oxide composites are given elsewhere [17,18].

The required concentrations of NO2 and C2H5OH gases were obtained by diluting certified gas mixtures with synthetic air on the ow chamber (0.2 l) at 0.3 l min⁻¹.

3. Results and discussions

3.1. Structural characterization of the composites

The required concentrations of NO2 and C2H5OH gases were obtained by diluting certified gas mixtures with synthetic air on the ow chamber (0.2 l) at 0.3 l min⁻¹.

The structural features of the Fe2O3 composites prepared via the inorganic sol–gel route. All the synthesized samples are nano-sized with the grain size ranging from 2 to 30 nm. There is a clear mutual influence of the components on the formation of the binary composite structure under thermal treatment of the corresponding sols and xerogels (dried gels). An inhibition of the crystallization processes of oxide phases and smaller grain size are typical of the composites as compared to individual iron and indium oxides. According to the ED analysis, the hydrolysis of Fe3⁺ salts (samples 1, 11, 12) always results in α-Fe2O3 structure after thermal treatment of the powders at 300 °C (see Table 1). These samples being heated at temperatures less than 400 °C remain nanosized and X-ray amorphous. The XRD analysis allows registering α-Fe2O3 phase in the powders annealed at 500 °C. A mutual doping of α-Fe2O3 and C-In2O3 oxides was found to take place resulting in substitutional solid solutions. This conclusion follows from the analysis of the lattice constants acquired by the XRD technique for the Fe2O3–In2O3 composites with different component ratios. Thus, the increased constants of α-Fe2O3 phase doped with indium ions (Fe2⁺-InxO3 solid solution, e.g. sample 11, a = 0.505 nm, c = 1.379 nm), and the decreased constant of C-In2O3 phase doped with iron ions (In2⁺-FexO3 solid solution, e.g. sample 12, a = 1.005 nm) as compared to the data for pure α-Fe2O3 (a = 0.504 nm, c = 1.375 nm) and C-In2O3 (a = 1.012 nm) oxides were observed.

At Fe:In = 1:1 molar ratio, the major phase occurred in the Fe2O3–In2O3 nanocomposites is cubic indium oxide (C-In2O3) with the a lattice constant decreased comparing to the pure indium oxide (samples 2, 4, 6, 8, 10, 12). In the mentioned samples, α-Fe2O3 phase is X-ray amorphous but it was registered by the ED method. The formation of metastable indium oxide phases like M-In2O3 and R-In2O3 or indium ferrite phases was not revealed by using the diffraction techniques.

The combined hydrolysis of Fe3⁺ and In3⁺ salts does not lead to the formation of γ-Fe2O3 structure. A thermal treatment of the co-precipitated In(OH)3 and Fe(OH)2 hydroxides results in α-Fe2O3 oxide. Under the given synthesis conditions, the presence of In3⁺ ions inhibits the crystallization of γ-Fe2O3 phase. In contrast, the stabilization of γ-Fe2O3 structure is observed under heating the mixtures of the separately prepared hydroxides: Fe(OH)2 + In(OH)3 or FeO4 + NH3 + In(OH)3 (samples 7–10). The γ-Fe2O3 → α-Fe2O3 phase transition registered for the mixed composites by DSC technique shifts towards higher temperatures (485–500 °C) as compared to pure γ-Fe2O3 oxide (−450 °C). The γ-Fe2O3 is the predominant phase in samples 7 and 9, which have Fe:In = 9:1 ratio. According to the Mössbauer spectroscopy studies undertaken in [1,15], the solubility of In3⁺ ions in spinel-type γ-Fe2O3 with the formation of solid solution is lower than in α-Fe2O3 phase.

Sample 5 synthesized by the combined hydrolysis of Fe3⁺, Fe2⁺ and In3⁺ salts is characterized by a complex structure and morphology. According to the TEM and ED data, the composite consists of three phases — anisotropic particles with tetragonal Q-γ-Fe2O3 lattice (JCPDS 25-1402), spherical particles with cubic C-γ-Fe2O3 lattice (JCPDS 39-1346), and spherical particles of rhombohedral α-Fe2O3 phase (JCPDS 33-0664) doped with In³⁺ ions (In³⁺-α-Fe2O3 substitutional solid solution).

The IR spectra given in Fig. 2 also indicate the formation of Q-γ-Fe2O3 phase in sample 5. The Q-γ-Fe2O3 and C-γ-Fe2O3 structures can be distinguished using IR-spectroscopy by the position of an absorption band attributed to γ(Fe-O) vibration, which is the most sensitive to [FeO4]: [Fe2O3] ratio [38]. The maximum intensity of γ(Fe-O) band in the IR spectrum of sample 5 was registered at 548 cm⁻¹. This value corresponds to the [FeO4]:[Fe2O3] ratio typical of Q-γ-Fe2O3 structure. In the spectra of the samples 7 and 9 containing C-γ-Fe2O3 phase, the mentioned absorption band was found at 560–570 cm⁻¹. The anisotropy of the obtained Q-γ-Fe2O3

Table 1

<table>
<thead>
<tr>
<th>No</th>
<th>Precursors</th>
<th>Fe/In mol. ratio</th>
<th>Phase composition*</th>
<th>Grain size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series I (combined hydrolysis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Fe³⁺, In³⁺</td>
<td>9:1</td>
<td>α-Fe2O3</td>
<td>2–4</td>
</tr>
<tr>
<td>2</td>
<td>In(OH)3, Fe2O3</td>
<td>1:1</td>
<td>C-In2O3</td>
<td>5–8</td>
</tr>
<tr>
<td>3</td>
<td>Fe²⁺, In³⁺</td>
<td>9:1</td>
<td>α-Fe2O3</td>
<td>3–6</td>
</tr>
<tr>
<td>4</td>
<td>In(OH)3, C-In2O3</td>
<td>1:1</td>
<td>α-Fe2O3</td>
<td>5–8</td>
</tr>
<tr>
<td>5</td>
<td>Fe³⁺, Fe³⁺, In³⁺</td>
<td>9:1</td>
<td>Q-γ-Fe2O3</td>
<td>10 × 30</td>
</tr>
<tr>
<td>6</td>
<td>In(OH)3, Fe2O3</td>
<td>1:1</td>
<td>C-In2O3</td>
<td>2–4</td>
</tr>
<tr>
<td>Series II (mixing separately prepared sols)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>In(OH)3, Fe2O3</td>
<td>9:1</td>
<td>C-γ-Fe2O3</td>
<td>4–5</td>
</tr>
<tr>
<td>8</td>
<td>In(OH)3, Fe(OH)2</td>
<td>1:1</td>
<td>C-γ-Fe2O3</td>
<td>5–8</td>
</tr>
<tr>
<td>9</td>
<td>In(OH)3, Fe(OH)2</td>
<td>9:1</td>
<td>C-γ-Fe2O3</td>
<td>8–10</td>
</tr>
<tr>
<td>10</td>
<td>In(OH)3, Fe(OH)2</td>
<td>1:1</td>
<td>C-In2O3</td>
<td>5–6</td>
</tr>
<tr>
<td>11</td>
<td>In(OH)3, Fe(OH)2</td>
<td>9:1</td>
<td>α-Fe2O3</td>
<td>3–8</td>
</tr>
<tr>
<td>12</td>
<td>In(OH)3, Fe2O3</td>
<td>1:1</td>
<td>α-Fe2O3</td>
<td>3–6</td>
</tr>
</tbody>
</table>

* The phases denoted here as α-Fe2O3 and C-In2O3 are actually substitutional solid solutions α-Fe2O3-InxO3 and C-In2O3-FeyO3, respectively.
grains is evoked by the ordering of cation vacancies [39]. As a rule, a highly dispersed $C$-$\gamma$-$\text{Fe}_2\text{O}_3$ phase with $\text{Fe}^{3+}$ cations randomly distributed over the tetra- and octahedral positions of the spinel crystal lattice forms at low temperature [25,40]. The stabilization of the tetragonal structure is not typical at low temperatures. Needle-shape $Q$-$\gamma$-$\text{Fe}_2\text{O}_3$ particles with the ordered distribution of $\text{Fe}^{3+}$ ions and the cation vacancies might be prepared by a high-temperature decomposition of $\alpha$-$\text{FeOOH}$ powder [41]. The formation of $Q$-$\gamma$-$\text{Fe}_2\text{O}_3$ phase in sample 5 at low temperature can be caused by the effect of $\text{In}^{3+}$ ions on the crystallization of iron oxide starting from the product of the combined hydrolysis of $\text{Fe}^{2+}$, $\text{Fe}^{3+}$ and $\text{In}^{3+}$ salts. There is literature reporting the formation of $Q$-$\gamma$-$\text{Fe}_2\text{O}_3$ phase at low temperature in the presence of some modifiers like $\text{Sn}^{4+}$ ions [42], and a partial reduction of iron oxide to $\text{Fe}_2\text{O}_{2.97}$ composition [43].

It follows from the XRD data that the phase composition of the samples under study remains unchanged within the annealing temperature range of 300–400 °C. As determined by DSC-TG and XRD methods, noticeable structural transformations proceed in the samples at temperatures higher than 450 °C.

First, the $\gamma$-$\text{Fe}_2\text{O}_3 \rightarrow \alpha$-$\text{Fe}_2\text{O}_3$ phase transition occurs at 455–550 °C depending on the sample composition. Then, both $\text{Fe}_2\text{O}_{2.97}$-$\text{In}_x\text{O}_3$ and $\text{In}_x\text{Fe}_2\text{O}_3$ solid solutions decompose to give separate iron oxide and indium oxide phases. In the most thermally stable composites, the phase separation occurs at 800 °C. Note that all the $\text{Fe}_2\text{O}_3$-$\text{In}_2\text{O}_3$ samples studied here being annealed at 800 °C consist of $\alpha$-$\text{Fe}_2\text{O}_3$ and $C$-$\text{In}_2\text{O}_3$ oxides. Therefore, a thermal treatment of the $\text{Fe}_2\text{O}_3$-$\text{In}_2\text{O}_3$ sensing layers at 400 °C for 96 h is expected to be sufficient to ensure the stability of their phase composition and morphology at the sensor operation temperatures used in this study (≤300 °C). The gas-sensing features were proved to be stable during a long-term operation of the sensors. This confirms indirectly the assumption that their structural features remain unchanged.

Fig. 1. The XRD patterns of the $\text{Fe}_2\text{O}_3$–$\text{In}_2\text{O}_3$ (9:1) composites prepared by different routes as a function of the annealing temperature (1–300 °C; 2–400 °C; 3–500 °C; 4–800 °C): a – sample 5; b – sample 7; c – sample 1; d – sample 11.
and pure oxides annealed at 400 °C is seen that sample 5, which differ from the other samples, demonstrated a low response to the oxidizing gases. Whereas all the mentioned sensors have negligible signals at maximum responses to these gases lay in the range of 70 ppm.

3.2. Gas-sensing properties

All the studied Fe₂O₃-In₂O₃ thin-film sensors demonstrate lack of sensitivity to CH₄ and CO. This makes them promising candidates for the development of sensors selective to other gases, in particular, to C₂H₅OH, NO₂ and O₃.

3.2.1. Sensitivity to oxidizing gases

The studied γ-Fe₂O₃-In₂O₃ thin films (samples 7–10) demonstrate a high sensitivity to O₃ and NO₂ at low operating temperatures. Their maximum responses to these gases lay in the range of 70–135 °C, whereas all the mentioned sensors have negligible signals at 250–300 °C. Samples 1, 3 and 11 based on α-Fe₂O₃ oxide display low response to the oxidizing gases.

The maximum response values and the optimal operating temperatures to detect NO₂ ambient with In₂O₃ and Fe₂O₃-In₂O₃ sensors are compared together in Table 2. From the reported data it is seen that sample 5, which differ from the other γ-Fe₂O₃ based composites in structural composition, is the most sensitive to NO₂ gas.

Among the studied composite materials, one can mark out two sensors (samples 5 and 9) whose sensitivity to O₃ and NO₂ are considerably distinct in different temperature ranges as visually demonstrated by a diagram in Fig. 3.

The response values are given at concentrations higher than the threshold levels. At 70–100 °C, sample 5 shows a sensitivity maximum to NO₂ and no response to O₃. Its sensitivity maximum to O₃ is shifted to 150 °C when the signal to NO₂ is low. In contrast, sample 9 is highly sensitive to O₃ and non-sensitive NO₂ at 100 °C. The indicated variety in the behavior of composites 5 and 9 are evidently caused by the distinctions in their phase composition and grain size (Table 1).

The sensing features of thin-film materials to a certain gas are hardly predictable. Specifically, the sensitivity of thin-film oxide sensors to O₃ and NO₂ is known to depend on many variables like chemical composition, crystalline structure and grain size of sensing layers [1,15,24,44,45]. Both nanosized state and highly defective structure of metal oxides prepared by sol–gel approach cause their enhanced response to oxidizing gases such as O₃ and NO₂. Based on the data obtained in this study and available from literature, one can suggest a possible reason for the sensing behavior of samples 5 and 9 described above. Their unequal sensitivity to the oxidizing gases might be explained both by distinctions in the microstructure of the Fe₂O₃-In₂O₃ composites and by unequal adsorption affinity of NO₂ and O₃ molecules to porous metal oxides [45,46].

The sensitivity to NO₂ and O₃ depends on the balance of the adsorption and reaction ability of an oxide surface [44–48]. Composite materials containing both effective adsorption centers, and highly conductive microcrystals and grain boundaries provide an enhanced sensor sensitivity.

The adsorption mechanism of the electrical conductivity change

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**Table 2**
The phase composition and the gas-sensing features of the samples to NO₂ (0.5 ppm).

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Phase composition</th>
<th>T, °C</th>
<th>S, r.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>In₂O₃ [22]</td>
<td>C-In₂O₃</td>
<td>100</td>
<td>30</td>
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<tr>
<td></td>
<td></td>
<td>135</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>Q-γ-Fe₂O₃, C-γ-Fe₂O₃, α-Fe₂O₃-In₂O₃</td>
<td>70</td>
<td>50</td>
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<td>100</td>
<td>75</td>
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<tr>
<td>7</td>
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<td>65</td>
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<td>8</td>
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<td>α-Fe₂O₃, C-In₂O₃</td>
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</tr>
</tbody>
</table>

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**Fig. 3.** The response of the Fe₂O₃-In₂O₃ (9:1) sensors to NO₂ and O₃ as a function of the composite microstructure at different operating temperatures.

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**Fig. 4.** The EPR spectra of sample 5: 1 – initial; 2 – after exposure to NO₂-air mixture at 120 °C.
was shown earlier to be dominating for metal oxides (in particular, In2O3) when exposed to NO2 acceptor-type molecules at 100–150 °C [44,45]. Below 150 °C, NO2 gas remains in a molecular (not reduced) form, which was confirmed by the EPR characterization of the samples studied here (Fig. 4). Thus, a weak triplet signal typical of NO2 radicals (average g-factor is 2.003) is registered in the spectrum of sample 5 after its exposure to NO2 at 120 °C (spectrum 2). The signal is unambiguously attributed to NO2 species due to the hyperfine splitting with a constant $A = 5.9$ mT (spectrum 2) arisen form $^{14}$N nuclei (nuclear spin is 1). However, the desorption of NO2 molecules from the oxide surface proceeds slowly at low temperatures, which could result in a slow dynamics of sensors. Two intensive lines found in both EPR spectra are attributed to Fe3+In2O3 solid solution and [FeIIIO$_x$]$_n$ oxide state.

Molecules of NO2 can get deep inside highly porous materials [46]. Their decomposition proceeds at the whole oxide surface including inner pores. A meso- and macro-porous structure required for an effective adsorption of NO2 molecules is likely typical of sample 5 consisting of grains, which differ substantially in phase composition, grain size and morphology. The obtained results correlate with the literature data reported a high sensitivity to NO2 of oxide materials modified with meso- and macro-porous SnO2 and In2O3 oxides [49–51]. However, the desorption of NO2 molecules and the products of their transformation is slow at low temperatures [45], which causes a long relaxation time of sensors. As it is seen from Fig. 5, the response and recovery times $t_{\text{resp}}$/$t_{\text{rec}}$ are 55/850 s for the detection of 0.5 ppm of NO2 at 70 °C (sample 5). The relaxation times could be greatly reduced by applying increased working temperatures (130–150 °C), at which the response values of the Fe2O3–In2O3 sensors to NO2 are still high. The $t_{\text{resp}}$/$t_{\text{rec}}$ times measured at 130 and 150 °C are 30/220 s and 25/200 s, respectively.

In contrast to NO2, the detection of O3 proceeds through the adsorption of oxygen atoms instead of ozone molecules whose decomposition ($\text{O}_3 \rightarrow \text{O}_2 + \text{O}$) occurs in a gas phase at 70 °C. This prevents the adsorption of O3 molecules and their heterogeneous decomposition at an oxide surface [47]. Due to a high chemical reactivity, the generated oxygen atoms are unable to pass inside a porous oxide structure [46]. A low-temperature mode of O3 detection (100–170 °C) is typical of sensors based on In2O3 and γ-Fe2O3 due to acceptable dynamic parameters [1,24,44,45]. The $t_{\text{resp}}$/$t_{\text{rec}}$ times measured for sample 9 are 40/200 s when detecting 0.1 ppm of O3 at 100 °C (Fig. 6). The less sensitive samples demonstrate significantly slower values ($t_{\text{res}} = 40 \div 100$ s,

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The crystalline structure of oxides appear to be a predominating factor for O₃ detection processes. An effective detection of O₃ is known to proceed on sensing layers based on metastable γ-Fe₂O₃ oxide. Their advanced sensitivity to O₃ is related to a high adsorption ability of spinel-type γ-Fe₂O₃, a fast adsorption-desorption of O₂ [44,45], and an easiness and reversibility of Fe³⁺ + e⁻ ↔ Fe²⁺ transition [24]. C-γ-Fe₂O₃ phase predominates over C-In₂O₃ in sample 9, which causes its increased selectivity to O₃. Note that thin film layers based on C-In₂O₃ also have a high sensitivity to O₃ and NO₂ at 100–150 °C [44,51]; however, they are characterized by lack of selectivity.

3.2.2. Sensitivity to ethanol

All studied Fe₂O₃–In₂O₃ composites are sensitive to C₂H₅OH vapors (50 ppm) at 250–350 °C with a maximum response at 300 °C. As it was noted above, no response to O₃ and NO₂ is typical of the sensors in this temperature range. However, the response to ethanol varies for different samples as a function of their composition and microstructure. As it follows from Figs. 7 and 8, the composites with an equal C-γ-Fe₂O₃ and C-In₂O₃ content are the most sensitive to ethanol vapors.

The mechanism of ethanol detection with complex metaloxide layers, in particular, with Fe₂O₃–In₂O₃ materials, is discussed in [2,48,52]. It is considered as a multi-stage process including the stages of reduction-oxidation and acid–base interactions of ethanol molecules on an oxide surface. The detection of deuterium marked ethanol (C₂D₅OD) with SnO₂ sensors allowed revealing a variety of products generated as a result of the decomposition of this molecule [48].

The materials containing several centers of adsorption and catalysis with close characteristics are the most sensitive to ethanol [53,54]. The Fe₂O₃–In₂O₃ nanocomposites prepared in this paper meet the mentioned requirement. A C-In₂O₃C-γ-Fe₂O₃ phase interface plays a role of an active surface at which the transformation of ethanol proceeds effectively. The occurrence of two type centers of different nature in our composites provides a multi-way pass of ethanol molecule decomposition and complete oxidation of intermediates. A partial reduction of metal ions without changes in the phase composition is possible for some metal oxides. These oxides are effective promoters of an oxidative dehydration of alcohols [2,53,54]. In particular, easily reversible In³⁺ ↔ In²⁺ and Fe³⁺ ↔ Fe²⁺ equilibria, which are not accompanying with any phase transitions, are typical of C-In₂O₃ and C-γ-Fe₂O₃ oxides. The low energy of metal-oxygen bonds in the mentioned oxides promotes an oxidation of the intermediate products in the reaction of ethanol decomposition [54], which leads to the growth of sensor responses. The described type of sensing layers is characterized by acceptable dynamics at 300 °C, which is optimal temperature for ethanol detection. The parameters \( t_{rec} = 1400 \pm 1800 \) s.

The optimal compositions of the samples and the operating conditions to detect different gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>C_{min}, ppm</th>
<th>T, °C</th>
<th>S, r.u.</th>
<th>Fe/In mol. ratio</th>
<th>Major phase</th>
<th>Minor phase</th>
<th>Sample No</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>0.1</td>
<td>100</td>
<td>130</td>
<td>9:1</td>
<td>C-γ-Fe₂O₃</td>
<td>In₂O₃</td>
<td>9</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.5</td>
<td>100</td>
<td>75</td>
<td>9:1</td>
<td>Q-γ-Fe₂O₃</td>
<td>C-γ-Fe₂O₁</td>
<td>5</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>50</td>
<td>300</td>
<td>105</td>
<td>1:1</td>
<td>C-In₂O₃</td>
<td>C-γ-Fe₂O₁</td>
<td>8</td>
</tr>
</tbody>
</table>

Note, that the given regularities are valid for the sol–gel derived Fe₂O₃–In₂O₃ materials with the reported component ratio, phase composition and morphology, and obtained in a form of thin films [31]. Any modifications in the synthesis conditions might result in materials with different properties. The gas-sensing behavior of In₂O₃ and Fe₂O₃ oxides depends on a variety of structural parameters, which are dependent on the preparation conditions. There is literature reporting unequal sensing properties of In₂O₃ oxide prepared in form of films, porous layers, spherical nanoparticles, nanocubes, hollow spheres, nanorods, nanowires, nanotubes, flowers, nanotowers [5].

4. Conclusions

The sol–gel approach based on inorganic metal precursors was used to obtain Fe₂O₃–In₂O₃ (9:1, 1:1) nanocomposites with different microstructure and grain size. The grain size, the chemical and phase composition of the samples were correlated with their gas-sensing parameters. Hetero-junction Fe₂O₃–In₂O₃ nano-composites based on cubic C-In₂O₃ phase, which is active in adsorption of gases, were prepared. The synthesis conditions that result in the formation of metastable cubic C-γ-Fe₂O₃ phase in the Fe₂O₃–In₂O₃ composites were revealed. This phase stabilized in the Fe₂O₃–In₂O₃ thin films was found to be more active in adsorption and catalytic transformations of O₃, NO₂ and C₂H₅OH vapors compared to thermodynamically stable γ-Fe₂O₃ phase. The possibility to stabilize a nanosized In-doped Q-γ-Fe₂O₃ phase with an improved sensitivity to NO₂ was shown. The described variety of structural features of the obtained materials provides the possibility to select oxide composites preferable to detect a required gas ambient. The optimal chemical and structural compositions of the Fe₂O₃–In₂O₃ thin-film sensing layers and operating temperatures were proposed to detect a series of gases – O₃, NO₂ and C₂H₅OH. It was shown that the optimal working temperatures of the proposed sensors are significantly lower than the temperatures inducing phase transformations in the Fe₂O₃–In₂O₃ composites. This provides the long-term stability of their sensing parameters. Note that an optimization of the functional features of the developed materials is still required for their commercial use. In particular, the dynamic parameters and the influence of humidity on the response of the sensors should be considered. For example, some techniques that allow minimizing the humidity effect on the signal are commonly used in commercially available sensors. Satisfactory dynamic parameters of the sensors could be achieved by applying different heating modes of the sensing elements like higher working temperatures and a pulse mode of heating.

References


