

**SYNTHESIS AND CHARACTERIZATION OF SIMPLE, MIXED AND IN MIXTURE
WITH SiO₂ NANOCRYSTALLINE OXIDE COMPOUNDS FROM
METAL NITRATES AND POLYOLS**

PhD Thesis – Summary

to obtain the scientific title of Doctor Chemist at
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The methods used for the synthesis of materials are different, each method providing certain performance characteristics to the resulting product. The obtaining of oxide materials by unconventional synthesis methods has become a requirement without which the evolution of the technologies to obtain these types of materials could not take place.

Each time a product with certain properties is expected, it starts from the synthesis of the desired powder. The state of the reactants is one of the most important factors which affects the evolution of chemical reactions.

The aim of the thesis consist of the synthesis and characterization of oxidic compounds based on Fe, Zn, Mg and Al by the carboxylate precursor method, as well as the study of thermal behavior of these oxide systems in mixture with SiO₂ by the decomposition of metal carboxylates in hybrid silica gels.

The studied compounds were simple oxides Fe₂O₃, ZnO, MgO and Al₂O₃ and mixed oxides ZnO·Al₂O₃ and MgO·Al₂O₃ obtained from metal Fe (VIII-b), Zn (Group II-b), Mg (Group II-a) and Al (group III-a) carboxylate.

The purposed objectives were:

- Synthesis and characterization of γ -Fe₂O₃ from Fe(NO₃)₃·9H₂O and polyethylene glycol (PEG);
- Synthesis and characterization of simple oxides from Zn(II), Mg(II) and Al(III) carboxylate precursors obtained from nitrates and 1,3-propanediol (1,3-PD);
- Synthesis and characterization of mixed oxides from Zn(II) and Al(III), respectively Mg(II) and Al(III) carboxylates mixture;
- Study of the SiO₂ influence on the synthesis of simple and mixed oxides in hybrid silica gels, obtained from carboxylate compounds;
- Study of the electrical properties of ZnO, ZnAl₂O₄ and MgAl₂O₄ nanopowders obtained from carboxylate decomposition method.

The subject of the thesis is part of the current trends in scientific research and brings an important contribution to the study of the synthesis methods and characterization of nanocrystalline oxidic compounds. The synthesis process of oxidic nanomaterials is an original method by which oxidic powders are obtained with nanometric size at relatively low temperatures and with a practical yield of 100 %.

Their characterization was accomplished by modern investigation techniques, used constantly during the experimental studies.

Chapter 1. The current state of research

The first chapter of the thesis presents a comprehensive literature study on the current level of the research in the studied field. An important part of this chapter is the well-documented critical study on the obtaining methods of simple, mixed oxides and systems in mixture with SiO₂.

To obtain nanocrystalline oxidic materials, conventional methods based on the annealing of mechanical mixtures of oxides or salts [1] and unconventional synthesis methods [2-4] are used.

Over time, many specific methods have been developed to provide good control over the homogeneity, purity and particle size, to be more environmentally friendly (lower energy consumption), and the temperatures for obtaining the reaction products to be lower compared to the conventional methods [5, 6].

In this chapter, aspects regarding the simple oxidic systems (Fe₂O₃, ZnO, MgO, Al₂O₃), the spinels (ZnAl₂O₄, MgAl₂O₄), as well as the systems in mixture with SiO₂ were presented. It has been described the synthesis methods used to obtain organic-inorganic hybrid gels, the involved processes and the factors that influence the formation of silica gels.

At the same time, it was detailed presented the original methods used for the synthesis of carboxylate precursors, generators of simple oxidic systems, mixed and embedded in SiO₂ matrix.

A bibliographic study was made on the properties and applications of these materials as well as on the characterization methods that are appropriate for the study of materials.

Chapter 2. The synthesis of simple oxides from Fe(III), Zn(II), Mg(II) și Al(III) carboxylate precursors

In this chapter, it was presented the characterization of simple oxides (Fe₂O₃, ZnO, MgO and Al₂O₃) from metal carboxylate obtained by the redox reaction between metal nitrates and diols (1,3-propanediol and polyethylene glycol).

The method consisted of the 1,3-propanediol oxidation by nitrate ion from metal nitrates (Fe(NO₃)₃·9H₂O, Zn(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O) to the carboxylate dianion.

In the thesis, it was used for the first time in synthesis, the polymer-type diol, polyethylene glycol (PEG) and it was investigated if it can act as a reducing agent on the transition ion Fe(III), much studied in the reaction with diols with shorter chain, when obvious results were obtained for the formation of carboxylate compounds.

The polymer has also been used in the synthesis of nanoparticles by the polyol method, where PEG was solvent and reducing agent [7]. Nam et al. [8] and Popa et al. [9] reported the reducing and stabilizing role of PEG in the synthesis of silver nanoparticles.

In the performed studies, the role of PEG in the mixture with Fe(NO₃)₃·9H₂O, respectively in mixture with Fe(III) carboxylate, obtained from the redox reaction between 1,3-propanediol and Fe(III) nitrate was pursued.

In PEG-Fe(NO₃)₃·9H₂O system, PEG:Fe(NO₃)₃·9H₂O mixtures in different molar ratios (0.10, 0.25, 0.5, 0.75) were synthesized and were subjected to thermal analysis.

It has been found that in mixture with PEG, anhydrous Fe(NO₃)₃ stabilizes in the temperature range 130-200 °C, its decomposition occurring at higher temperatures when PEG also begins to decompose. The reducing atmosphere (CO and NO_x resulting from the decomposition of PEG and Fe(NO₃)₃) favored the formation and stabilization of Fe₂O₃ at low temperatures.

It is known that by thermal decomposition of Fe(NO₃)₃·9H₂O into air, another

polymorphic form of iron oxide, α -Fe₂O₃, is obtained up to 500 °C [10]. From our studies we concluded that a minimum molar ratio of PEG-nitrate iron of 0.25:100 is required to obtain γ -Fe₂O₃ at 300 °C as single phase with a diameter of 7.5 nm and to create a suitable reducing environment during the decomposition of PEG.

From the magnetic measurements it was found that the magnetic properties of γ -Fe₂O₃ nanoparticles can be controlled by the molar ratio PEG-iron nitrate and by the temperature of the thermal treatment.

In the case of Fe(III) carboxylate-PEG synthesis, the spinel phase γ -Fe₂O₃ was also formed at 300 °C as single phase. PEG has been found to act as a stabilizing agent, limiting the agglomeration of γ -Fe₂O₃ nanoparticles.

Fe(III) carboxylate precursor was obtained at 90 °C after the redox reaction between iron nitrate and 1,3-propanediol directly in mixture with PEG. During the synthesis procedure, due to the physico-chemical properties of the PEG in mixture with Fe(III) carboxylate, γ -Fe₂O₃ formed at the same time as the thermal degradation of the polymer.

It has been noticed that with the increase in the amount of PEG, it occurred the reduction of agglomeration and the prevention of nanoparticle growth.

It was further investigated if Zn, Mg, Al nitrates react with 1,3-propanediol by a redox reaction, compared to the transition metal ions leading to the carboxylate compounds.

The redox reaction between zinc nitrate and 1,3-propanediol occurred at ~120 °C with an exothermic effect on DTA curve and mass loss on TG curve. The strong exothermic effect of the redox reaction led to the decomposition of a part of the formed carboxylate, the product being a mixture of zinc carboxylate and zinc oxide, which is also confirmed by FTIR spectroscopy [11].

By annealing this mixture at 400 °C, ZnO nanoparticles resulted with a lower mean crystallite size (33.8 nm) than those obtained from zinc nitrate decomposition (94.8 nm).

The redox reaction between Mg(NO₃)₂·6H₂O and 1,3-PD took place energetically at 150 °C, generating Mg(II) carboxylate, a part of it decomposing as an expanded powder.

By thermal analysis and FTIR spectroscopy the presence of carboxylate and magnesium oxide in mixture [12] was evidenced.

The RX diffractograms showed that the crystalline phase MgO was obtained starting from 300 °C. The mean crystallite size increased from 8.6 nm to 29.8 nm with increasing annealing temperature.

By thermal analysis, the evolution of redox reaction between Al(NO₃)₃·9H₂O and 1,3-PD was confirmed. The temperature at which the redox reaction starts is influenced by the acidity of the metal aquation. The Al³⁺ cation is more acidic than the Zn²⁺ cation (pK_a [Al(H₂O)₆]³⁺ = 4.85; pK_a [Zn(H₂O)₆]²⁺ = 9.60) and the redox reaction took place at lower temperature, with less exothermic effect.

It has been established as synthesis temperature of Al(III) carboxylate the temperature 140 °C.

The FTIR spectra confirmed the formation of the metal carboxylate by recording bands corresponding to asymmetric vibration $\nu_{as}(\text{COO}^-)$ and symmetric $\nu_s(\text{COO}^-)$ [13].

The XRD analysis evidenced the appearance of the weakly crystallized γ -Al₂O₃ phase at 800 °C, at 1000 °C taking place the transition of γ -Al₂O₃ phase to the well-crystallized α -Al₂O₃ phase. At 1200 °C, this transition was complete, and the α -Al₂O₃ phase was identified as single phase with a mean crystallite size of ~48 nm.

Chapter 3. The synthesis of mixed oxides from Zn(II) and Al(III), respectively Mg(II) and Al(III) carboxylates mixture

In this chapter the results regarding the obtaining and characterization of the mixed oxides ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$ - spinel ZnAl_2O_4 and $\text{MgO} \cdot \text{Al}_2\text{O}_3$ - spinel MgAl_2O_4) from Zn(II)-Al(III) and Mg(II)-Al(III) carboxylate mixture precursors are presented.

The method of complex combinations decomposition also allows the obtaining of Zn(II) and Al(III) carboxylate mixtures, respectively Mg(II) and Al(III) starting from metal nitrate and 1,3-propanediol.

The metal nitrates of Zn(II) and Al(III) were solubilized in distilled water, to the obtained solution adding HNO_3 conc. and 1,3-PD more than 25% over the stoichiometry of the redox reaction between NO_3^- and 1,3-PD. The mixture was controlled heated in the oven when the redox reactions between Zn(II) and Al(III) nitrates and 1,3-PD started at $\sim 100^\circ\text{C}$ with a massive release of nitrogen oxides (exothermic reaction).

The heating was continued up to 140°C when the redox reaction with the formation of Zn(II) and Al(III) carboxylates mixture took place with a cumulative effect of Zn(II) carboxylate (120°C) and Al(III) (110°C) formation, resulting in a poor exothermic and wide effect.

The FTIR spectra confirmed the formation of the Zn(II) and Al(III) carboxylates mixture by the presence of symmetric $\nu_s(\text{COO}^-)$ vibration bands at 1384 cm^{-1} and asymmetric vibration $\nu_{as}(\text{COO}^-)$ at 1610 cm^{-1} .

The mixture of zinc oxide (ZnO) and aluminum oxide (Al_2O_3), resulting from the annealing of the Zn(II) and Al(III) carboxylates mixture at 400°C was amorphous with a poor tendency to crystallize in the range $25 = 25\text{-}30^\circ$. This showed that the nucleation of ZnAl_2O_4 occurred in accordance with FTIR data.

At 600°C , the XRD spectrum showed characteristic lines of the well-crystallized ZnAl_2O_4 spinel with a mean crystallite size of 14 nm.

The average particle size determined from TEM (24.8 nm) was close to the average crystallite size value calculated from XRD and lower than reported in the literature at 1000°C ($\sim 60\text{ nm}$) [15].

By a similar procedure, Mg(II) and Al(III) carboxylates mixture was obtained.

The mixture of metal nitrates ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and 1,3-PD was subjected to controlled heating in the oven. After the evaporation of water ($\sim 90^\circ\text{C}$), the redox reaction started vigorously with a massive release of gaseous compounds (NO_x) at $\sim 150^\circ\text{C}$ and the formation of a mixture of carboxylates and metal oxides.

By thermal treatments, it has been evidenced that MgO began to crystallize at 300°C , Al_2O_3 at 800°C , and in mixture the spinel MgAl_2O_4 crystallized at 700°C .

By solid state reaction between MgO and polymorph alumina, spinel formation begins at temperatures above 600°C [16]. Due to the high reactivity of $\gamma\text{-Al}_2\text{O}_3$ and MgO and their intimate mixing, the nucleation of the spinel started at lower temperatures (500°C) and the complete conversion of precursors to MgAl_2O_4 was reached by annealing at 700°C .

Data from XRD and FTIR analysis confirmed the formation of the nanocrystalline spinel structure of MgAl_2O_4 .

By the decomposition of carboxylate combinations method, MgAl_2O_4 nanoparticles were obtained at a low temperature, with a yield of 100 %.

From TEM analysis it was found that the powders annealed at 700°C show the presence of irregular, agglomerated particles with an average diameter of 6.6 nm which is comparable to the size of the crystallites calculated from XRD analysis. At 1000°C , it was observed that the mean particle size is greater than the crystallite size calculated from XRD analysis (11.2 nm) due to the particle agglomeration tendency of the non-irregular nanocrystalline MgAl_2O_4 .

Chapter 4. The influence of SiO₂ on the synthesis of simple oxides (ZnO, MgO, Al₂O₃) in hybrid silica gels, obtained from carboxylate compounds

This chapter includes an original study on the formation of carboxylate combinations in the pores of hybrid gels TEOS-1,3-PD (modified sol-gel method) and characterization of the annealing products obtained in binary systems ZnO-SiO₂, MgO-SiO₂, Al₂O₃-SiO₂.

The originality and particularity of the modified sol-gel method compared to other sol-gel synthesis procedures [17,18] consists in the fact that the metal carboxylate precursor, generator of oxidic system is directly obtained in the pores of silica gel by the redox reaction between the two reactants, metal nitrate-diol, depending on thermal treatment.

In the thesis, nitrates Zn(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O were used, where the metal ions have a lower complexing capacity and it was observed the redox reaction of them with 1,3-PD, with the formation of Zn(II), Mg(II) and Al(III) carboxylates in the pores of hybrid silica gel.

As noted in Chapter 2, the formation and isolation of Zn(II), Mg(II) and Al(III) carboxylates following the redox reaction is difficult to pursue, as compared to the transition metal carboxylates.

In the case of studied systems, the conditions for the solubilization of metal nitrates in distilled water and ethanol by magnetic stirring were determined. The required amount of 1,3-PD, concentrated nitric acid and ethanolic solution of TEOS were added and stirring was continued for one hour. The clear solution was allowed to jelly, and after a while a gel was obtained. The gel was dried at 40 °C, then milled and treated in the oven at 60-70 °C for 4 hours, whereby, by milling, was obtained a powder in the pores of which was found the nitrates and diol mixture.

By controlled heating in the range 100-140 °C, the redox reaction takes place depending on the nature of the metal nitrate, with formation of the carboxylate which is isolated and stabilized in the pores of the hybrid silica gel.

Thermal analysis and FTIR evidenced the formation of the carboxylate precursor. Thermal analysis showed that in the temperature range 300-450 °C the decomposition of carboxylate precursors takes place in the pores of the gel, with the formation of simple or mixed metal oxides.

By suitable thermal treatments, the influence of SiO₂ on the formation of simple oxidic compounds (ZnO, MgO, Al₂O₃) or mixed (ZnO·Al₂O₃, MgO·Al₂O₃) was pursued.

Three TEOS-Zn(NO₃)₂·6H₂O gels with different compositions (molar ratio ZnO:SiO₂ 1:4, 1:1 and 4:1) were prepared according to the synthesis procedure.

The powders obtained at 70 and 140 °C were characterized by thermal analysis and FTIR.

By thermal analysis of ZnO:SiO₂ gel with molar ratio 1:1 dried at 70 °C and then heated to 140 °C (when the redox reaction occurred), the DTA curve of the gel at 70 °C had an intense exothermic effect at 130 °C with mass loss on the TG curve. This corresponds to the redox reaction between zinc nitrate and 1,3-propanediol to form the complex combination dispersed in the pores of the gel.

The evolution of the TG and DTA curves of the thermally treated gel at 140 °C showed a broad endothermic effect in the temperature range 50-200 °C, assigned to water elimination and polycondensation of the silica gel.

In the range 250-450 °C, a broad exothermic effect with a peak at 368 °C was recorded, with significant mass loss, corresponding to the combustion of the organic ligand from the Zn(II) complex combination embedded in the pores of the silica gel. A similar thermal behavior was observed for Z14 gels (ZnO:SiO₂ molar ratio 1:4) and Z41 (ZnO:SiO₂ molar ratio 4:1).

The FTIR spectra of the three gels dried at 70 °C showed the characteristic bands of the silica gel. In addition to the bands of the silica matrix, the FTIR spectra of the gels heated to 140 °C, after the redox reaction occurred, recorded the bands characteristic to the carboxylate at 1300-1400 cm^{-1} corresponding to the symmetrical vibration $\nu_s(\text{COO}^-)$ and at 1500-1600 cm^{-1} , corresponding to asymmetric vibration $\nu_{as}(\text{COO}^-)$ [14].

The formation of Zn(II) carboxylate in the pores of the gels was confirmed and the temperature 140 °C was set as temperature for the carboxylate synthesis.

By annealing the gel Z14 (ZnO:SiO₂ molar ratio 1:4) it was found that the powder was weakly crystallized at 800 and 1000 °C, the diffractograms identifying two phases, α -Zn₂SiO₄ (willemite) with rhombohedral structure and β -Zn₂SiO₄ (heated hemimorphite) with orthorhombic structure.

It has been established that Zn₂SiO₄ begins to form at 700 °C by the reaction between ZnO and SiO₂ [19], and at 960 °C the phase β -Zn₂SiO₄ transforms to α -Zn₂SiO₄ [20].

The presence of β -Zn₂SiO₄ in the sample annealed at 1000 °C indicates that the hemimorphite was not completely transformed to the more stable phase, α -Zn₂SiO₄, being probably stabilized by dispersing and embedding in the silica matrix.

For the sample Z11, at 1000 °C, only the well-crystallized single-phase α -Zn₂SiO₄ is present, because the β -Zn₂SiO₄ phase has been transformed to willemite.

The transformation of the β -Zn₂SiO₄ phase into α -Zn₂SiO₄ was influenced by the lower SiO₂ content in the powder, which allowed greater phase mobility in the silica matrix pores.

XRD spectra of the gel Z41 annealed at 400 and 600 °C showed the diffraction peaks of the single phase, well-crystallized ZnO phase (found in excess to the stoichiometric amount required for the formation of Zn₂SiO₄) with nanoparticles size of ~9 nm.

At 800 and 1000 °C, in addition to the ZnO phase peaks, the XRD spectra recorded the diffraction peaks of the well-crystallized α -Zn₂SiO₄ phase.

It was found that the β -Zn₂SiO₄ phase was formed only for the Z14 and Z11 samples in which the ZnO:SiO₂ molar ratio was less than the stoichiometric ratio of 2:1 [20].

Whatever the composition of mixtures was, ZnO formed in the pores of the silica gels, reacting with SiO₂ at 800 °C to form the zinc silicate.

TEM microscopy revealed the morphology of annealed Z41 powder at 600 and 800 °C and confirmed the results obtained from XRD analysis.

At 600 °C, the Z41 powder consisted in ZnO nanoparticles smaller than 10 nm, well dispersed in the amorphous silica matrix.

The images of Z41 sample annealed at 800 °C showed that ZnO and Zn₂SiO₄ nanoparticles are dispersed in the amorphous silica matrix and the SAED diffraction rings have proved the polycrystalline nature of the sample.

Through the proposed synthesis method, nanomaterials and nanocomposites have been obtained which, depending on the final composition, have controlled properties and can be used in various application domains.

The synthesis procedure of the MgO-SiO₂ system was similar to the ZnO-SiO₂ system.

A mixture of 50% MgO-50% SiO₂ (mass percent) was synthesized. The gel obtained and dried at 60 °C was subjected to thermal analysis, with a strong exothermic effect at 150 °C on DTA curve, assigned to the redox reaction between Mg(NO₃)₂·6H₂O and 1,3-propanediol in the pores of the gel to form Mg(II) carboxylate.

Unlike the synthesis without TEOS, in this case, the redox reaction could be controlled. The nitrate and diol are dispersed in the hybrid gel, and silica takes up most of the heat generated by the redox reaction. Therefore, once formed the carboxylate, it does not decompose to MgO. Thus, Mg(II) carboxylate can be synthesized in the pores of gel at 150 °C.

The FTIR spectra of the synthesized compound at 150 °C showed the characteristic bands of asymmetric $\nu_{as}(\text{COO}^-)$ and symmetric $\nu_s(\text{COO}^-)$ carboxylate group. The band at

1383 cm^{-1} overlaps with the NO_3^- vibration, indicating that NO_3^- was not consumed totally in the redox reaction [14].

The sample heated to 150 °C was annealed in the temperature range 600-1200 °C. The diffractograms of the annealed gel at 600 and 700 °C showed the amorphous character of the samples, with a tendency to crystallize and interact with MgO (obtained from the decomposition of the carboxylate) with SiO_2 from the matrix (nucleation).

From 800 °C, the formation of well-crystallized phases, enstatite (MgSiO_3) and forsterite (Mg_2SiO_4) was evidenced. The two phases maintain up to 1200 °C.

The formation of MgSiO_3 and Mg_2SiO_4 in the MgO- SiO_2 system can be explained by the higher reactivity of MgO resulting from the carboxylate decomposition compared to SiO_2 . MgO is consumed as long as it remains unreacted in the mixture. In a first stage, MgO reacts with SiO_2 to form enstatite MgSiO_3 . Due to its high reactivity, unreacted MgO, and not SiO_2 , reacts further with the formed enstatite, resulting forsterite Mg_2SiO_4 . After MgO is consumed, Mg_2SiO_4 reacts with SiO_2 , resulting MgSiO_3 [21, 22].

The presence in the XRD spectra only of forsterite and enstatite indicated that precursors are sufficiently homogeneous for Mg_2SiO_4 , MgSiO_3 , MgO and SiO_2 to coexist and completely react one with another.

According to the procedure, similar to the synthesis of Zn and Mg gels, the Al_2O_3 - SiO_2 gel (50% Al_2O_3 -50% SiO_2 mass percent) was also obtained.

It was found from the experimental data in Chapter 2 that the redox reaction in the bulk synthesis is energetic, Al(III) carboxylate being difficult to isolate.

The redox reaction in the silica gel could be controlled, since Al(III) nitrate and 1,3-propanediol are dispersed on a molecular scale in the hybrid gel. Thus, Al(III) carboxylate embedded in the pores of the gel could be synthesized at 150 °C.

The evolution of the thermoanalytical curves of the gel heated to 150 °C showed a mass loss up to 140 °C, assigned to the polycondensation of the silica matrix with the removal of volatile compounds. The decomposition of the carboxylate with mass loss in the temperature range 300-450 °C was evidenced on the DTA curve by the exothermic effect with maximum at 383 °C.

The presence of the complex combination in the heated gel at 150 °C was also evidenced by FTIR spectroscopy, recording the vibrations of the carboxylate group $\nu_{\text{as}}(\text{COO}^-)$ in the range 1600-1700 cm^{-1} and of the carboxylate group $\nu_{\text{s}}(\text{COO}^-)$ in the range 1300-1400 cm^{-1} [14].

The diffractograms of the annealed gel at 800 °C showed the amorphous character of the sample, with a crystallization tendency in the range $2\theta = 20-30^\circ$, assigned to the interaction of the aluminum oxide (amorphous and reactive resulting from the decomposition of the carboxylate) with SiO_2 from the matrix (nucleation).

Compared to bulk synthesis, Al_2O_3 in SiO_2 gel was also formed at 1000 °C when interacted with SiO_2 to form the mullite compound (Al_2SiO_5), crystallized as single phase.

By the method of Al(III) complex combination decomposition directly into the pores of the silica gel, the mullite was obtained as single phase at low temperature and with nanometric size compared to the average size reported in the literature (0,82 μm) [23].

Chapter 5. The influence of SiO_2 on the synthesis of mixed oxides ($\text{ZnO}\cdot\text{Al}_2\text{O}_3$, $\text{MgO}\cdot\text{Al}_2\text{O}_3$) in hybrid silica gels, obtained from carboxylate compounds

In this chapter, the formation of Zn(II)-Al(III) and Mg(II)-Al(III) carboxylates embedded in the pores of the hybrid silica gel were studied. They decompose similar to the undispersed combinations (bulk) at 350 °C with the formation of metal oxides in the pores of the silica matrix. By appropriate thermal treatments ternary systems $\text{ZnO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ are obtained.

The modified sol-gel method is based on the following particularity: in a first step, a part of the diol present in the synthesis mixture (TEOS-metal nitrate-1,3-propanediol) interacts with TEOS and/or its hydrolysis products, when the hybrid silica gel is formed, and a part, which is found along with the metal nitrate solution, molar dispersed in the pores of the gel, will form the complex combinations (Zn(II)-Al(III) and Mg(II)-Al(III) carboxylates) in the pores of the gel, following the redox reaction at ~ 130 °C. Finally, by complex combinations decomposition at ~ 360 °C and suitable thermal treatments, metal oxides embedded in the silica matrix are obtained.

Under this conditions, hybrid gels were synthesized for the composition 25% ZnO-25% Al₂O₃-50% SiO₂ and 25% MgO-25% Al₂O₃-50% SiO₂ (mass percent).

By the thermal analysis of ZnO-Al₂O₃-SiO₂ gel, the evolution of the redox reaction metal nitrate-1,3-PD was pursued, with the formation of Zn(II) and Al(III) complex combinations in the hybrid gel pores and the temperature 130 °C was proposed as the precursor synthesis temperature. FTIR spectrometry revealed the formation of the carboxylates in the pores of the gel [14].

From the XRD spectrum at 800 °C, it was found that the sample was amorphous and at 1000 °C the crystalline phases (zinc aluminate - ZnAl₂O₄) with a mean crystallites size of 13.6 nm and mullite (Al₂SiO₅) with a mean crystallites size of 26.7 nm were identified.

From TEM images of the annealed powder at 1000 °C, small nanoparticles of mullite and gahnite with irregular shapes, embedded in the silica matrix and with a size comparable to that determined by XRD analysis were observed.

The appearance of the two phases is in agreement with the literature, which says that binary compounds (gahnite, mullite and willemite) and no ternary compounds are formed in ZnO-Al₂O₃-SiO₂ ternary system [24].

The thermoanalytical curves of MgO-Al₂O₃-SiO₂ gel showed an exothermic effect at 143 °C assigned to the redox reaction between NO₃⁻ ion and 1,3-PD to form Mg(II) and Al(III) carboxylates mixture in the pores gel.

In the temperature range 300-400 °C a mass loss on the TG curve was recorded, corresponding to the carboxylates mixture decomposition, with the formation of metal oxides in the pores of the gels.

The formation of carboxylates was also evidenced by FTIR analysis.

It was observed that by annealing the sample at 800 °C, it began to crystallize and at 1000° C magnesium and aluminum silicate (MgAl₂Si₄O₁₂) in mixture with η-Al₃O₄ were identified as crystalline phase.

The temperature 1000 °C was insufficient for magnesium-aluminum silicate to polymerize as α-cordierite (indialit-Mg₂Al₄Si₅O₁₈).

At 1200 °C, SiO₂ crystallized as β-quartz (β-SiO₂), and magnesium-aluminum silicate to the polymorph α-cordierite (indialite) and sapphirine (Al₅Mg₃)(Al₄Si₂)O₂₀.

The sapphirine and cordierite are ternary compounds that appear in the diagram phase of MgO-Al₂O₃-SiO₂ system [25]. The appearance of the two phases in the XRD spectrum at 1200 °C is probably due to the insufficient sintering temperature to form the cordierite as main phase.

However, the α-cordierite phase was obtained by annealing at lower temperatures than those reported in the literature [26].

Chapter 6. The electrical properties of some oxidic systems with Zn, Mg and Al

This chapter includes a study of the electrical properties of ZnO, ZnAl₂O₄ and MgAl₂O₄ nanopowders obtained by the decomposition of carboxylates method.

The investigation of the electrical properties of the samples was performed in the

frequency range 20-2 MHz at different temperatures from room temperature to 220 °C.

Stoichiometric zinc oxide has a very high resistivity, but usually contains excess of zinc atoms, affecting the structure of defects, electrical conductivity and piezoelectricity.

Zinc oxide is a semiconductor n-II-IV type with a large band gap (3.3 eV) included in the binary semiconductor group A^{II}B^{VI}.

It has been found that ZnO powder obtained by the annealing of Zn(II) carboxylate at 400 °C has typical behavior of a semiconductor in the temperature range 120-220 °C.

The electrical conductivity increased with the increasing temperature between 27 °C and 40 °C, while between 40 °C and 100 °C it decreased with the increasing temperature, due to the scattering of electrical charge carriers by phonons.

At all temperatures in the region of low frequencies, the imaginary component of electrical permittivity ε'' was higher than the real component ε' , due to the effects of electrical conduction in the sample, but also to the polarization of the electrodes.

It was found that in the case of ZnO obtained by annealing the sample Zn(NO₃)₂·6H₂O-1,3-PD at 600 °C, as in the case of the annealing of the sample at 400 °C, the frequency and temperature dependencies of electrical conductivity showed that at each of the 11 temperature values, the real part of complex electrical conductivity follows a Jonscher type law [27].

The semiconductor character of the sample was confirmed, the activation energy having the values $E_a = 0.170$ eV, respectively $E_a = 0.534$ eV, on each of the temperature range 28-140 °C and 160-220 °C.

Using the complex impedance measurements at different temperatures in the range 30-230 °C and at frequencies of the electric field between 20 Hz to 2 MHz, the Nyquist diagrams were presented for MgAl₂O₄ obtained by annealing Mg(II)-Al(III) carboxylates mixture at 1000 °C, 3h.

It has been found that at temperatures between 100 °C and 220 °C, MgAl₂O₄ has a typical semiconductor behavior, which is confirmed by the activation energy of the conduction process at the frequency 150 Hz ($E_a = 0.049$ eV).

Similar to the behavior of ZnO obtained by annealing Zn(II) carboxylate at 400 °C, the electrical conductivity decreased with temperature rise between 40 °C and 60 °C, due to the scattering of electrical charge carriers by phonons.

Since magnesium aluminate is a dielectric material (not a conductive one), we can assume that the high values of the dielectric permittivity components are because the sample is hydrophilic.

This was confirmed by the fact that both the real component ε' and the imaginary component ε'' of the complex dielectric permittivity diminished after the thermal treatment at 230 °C compared to the measurements made before this operation.

It has been demonstrated that the sample is hydrophilic also based on the temperature dependence of the imaginary component of the complex dielectric permittivity, which was correlated with the electrical energy losses in the sample.

It has been shown that ZnAl₂O₄ obtained by annealing Zn(II)-Al(III) carboxylates mixture at 1000 °C has a typical semiconductor behavior at temperatures between 28-40 °C and 120-220 °C, which is confirmed by the activation energy of the conduction process which is $E_a = 0.105$ eV (for the temperature range 28-40 °C) and $E_a = 0.038$ eV (for the temperature range 120-220 °C).

It has been observed that in the low frequency region, the imaginary component of the complex dielectric permittivity ε'' is larger than the real component ε' .

At temperatures above 100 °C, the frequency dependences of complex dielectric permittivity showed that the polarization of the electrodes is no longer present, so it was confirmed that the sample is hydrophilic.

Capitolul 7. General conclusions

The last chapter contains general conclusions of the research results on obtaining simple, mixed oxide and systems in mixture with SiO₂ from metal carboxylates.

It has been investigated if redox reaction NO₃⁻-1,3-propanediol (1,3-PD) occurs with the formation and isolation of carboxylate compounds.

It was found from the FTIR analysis of the synthesized compounds that, regardless of the metal nitrate used, the obtained spectra are similar, showing the characteristic bands $\nu_s(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ of the carboxylate group coordinated to the metal ion.

It was first used for the synthesis of $\gamma\text{-Fe}_2\text{O}_3$ the polymer-type diol, polyethylene glycol (PEG).

In the case of the synthesis Fe(NO₃)₃·9H₂O-PEG, the diffractometry XRD revealed the formation of spinel phase $\gamma\text{-Fe}_2\text{O}_3$ as a single phase at 300 °C for a minimum molar ratio PEG-nitrate iron (III) of 0.25:100.

In the case of Fe(III)-PEG carboxylate synthesis, the spinel phase $\gamma\text{-Fe}_2\text{O}_3$ was also formed at 300 °C in mixture with fine carbon particles, influencing the magnetic properties of the nanoparticles.

From magnetic measurements it was found that the presence of residual carbon prevents the agglomeration of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles and influences specific saturation magnetization and coercive field, important for possible biomedical applications for the magnetic orientation of drug transport.

ZnO was obtained as a single phase by Zn(II) carboxylate decomposition at 400 °C with a diameter of ~34 nm, much lower compared to ZnO obtained from the decomposition of zinc nitrate (95 nm).

MgO was obtained with a mean crystallite size of ~9 nm at 300 °C as a single phase, lower than that reported in the literature (500 °C).

The XRD analysis revealed the appearance of the $\alpha\text{-Al}_2\text{O}_3$ phase with traces of $\gamma\text{-Al}_2\text{O}_3$ at 1000 °C, and at 1200 °C the complete transition of $\gamma\text{-Al}_2\text{O}_3$ phase to the $\alpha\text{-Al}_2\text{O}_3$ phase took place with the mean crystallites size of ~47 nm.

The formation of Zn(II) and Al(III), Mg(II) and Al(III) carboxylates mixtures was carried out with molecular homogeneity.

In ZnO-Al₂O₃ system, the ZnAl₂O₄ spinel was obtained as single phase with a mean crystallite size of ~14 nm at a lower temperature (600 °C) than that reported in the literature (700 °C).

The MgAl₂O₄ spinel crystallized at 700 °C as a single phase with a nanocrystalline size of 6 nm. The same crystallization temperature of the spinel phase was reported in the literature, but the mean crystallite size was higher (14-30 nm).

The spinels were obtained at relatively low temperatures, 600 °C (ZnAl₂O₄) and 700 °C (MgAl₂O₄), for a 100% yield and small crystallites size.

A novel synthesis of oxidic nanomaterials in hybrid silica gels has been used by combining the sol-gel method with the thermal decomposition of complex carboxylates (modified sol-gel method).

In silica gels, the strong exothermic redox reaction between metal nitrates and diol, with the formation of carboxylate precursors was controlled, due to the presence of SiO₂ in the mixture.

Regardless of the composition of ZnO-SiO₂ mixtures, ZnO was formed in the pores of the silica gels and reacted with SiO₂ at 800 °C to form zinc silicate.

ZnO crystallized as a single phase at 400 and 600 °C only for the mixture with an excess of ZnO (80% ZnO-20% SiO₂).

In the case of MgO-SiO₂ system at 800 °C, the interaction of MgO with SiO₂ took place, forming well-crystallized compounds enstatite (MgSiO₃) and forsterite (Mg₂SiO₄). The formation of the two phases is in agreement with the literature, which shows that during the synthesis of forsterite, it is difficult to avoid the formation of enstatite.

Compared to bulk synthesis, Al₂O₃ in silica gel was also formed at 1000 °C when interacted with SiO₂ to form the mullite compound crystallized as a single phase. The lowest temperature reported in the literature for mullite formation is 1200 °C, when it was obtained in mixture with α -Al₂O₃.

In ZnO-Al₂O₃-SiO₂ system, at 1000 °C, the gahnite ZnAl₂O₄ crystallized as main phase, along with mullite Al₂SiO₅.

The appearance of the two phases is in agreement with the literature, which states that binary compounds (gahnite, mullite and willemite) and no ternary compounds are formed in the ternary system ZnO- Al₂O₃-SiO₂.

In MgO-Al₂O₃-SiO₂ system, ternary compounds such as magnesium and aluminum silicate (MgAl₂Si₄O₁₂), sapphirine (Al₅Mg₃)(Al₄Si₂)O₂₀ and indialite (α -cordierite Mg₂Al₄Si₅O₁₈) were obtained.

The α -cordierite (indialite) phase was obtained by annealing the sample at lower temperatures than those reported in the literature.

The ZnO powder obtained by annealing the Zn(NO₃)₂·6H₂O-1,3-PD sample at 600 °C had the typical behavior of a semiconductor on the temperature range 28-140 °C and 160-220 °C.

Since MgAl₂O₄ is a dielectric material, the high values of the dielectric permittivity components are because the sample is hydrophilic.

At temperatures between 28-40 °C and 120-220 °C, ZnAl₂O₄ obtained by annealing the sample Zn(NO₃)₂·6H₂O-Al(NO₃)₃·9H₂O-1,3-PD at 1000 °C had a typical semiconductor behavior.

The results obtained from the electrical measurements are important data for the future applications of the synthesized materials as thermistors or electric capacitors.

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