

**MICROSTRUCTURE CHARACTERISTICS
OF SOME POLYCRYSTALLINE OXIDE COMPOUNDS PREPARED
BY SOL-GEL-SELFCOMBUSTION WAY
FOR GAS SENSOR APPLICATIONS**

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According to sol-gel-selfcombustion method, the reacting substances are metal nitrates and ammonium hydroxide, the coprecipitation takes place into a colloidal medium and the reaction for ferrite synthesis is a quick combustion. By such a method and using an adequate heat treatment we have successfully prepared fine grained spinel ferrites and M-type hexaferrites. Structural characteristics of the heat treated samples by X-ray diffraction and SEM were studied. It was shown that small particle sizes, of about 100 nm, can be obtained. The experimental results have proved that the present method is an effective procedure to elaborate fine, chemically homogeneous and pure ferrite powders at a lower temperature than that of the conventional mixed-oxide method.

Key words: oxide powders, sol-gel-selfcombustion, X-ray diffraction, SEM, microstructure.

1. INTRODUCTION

There are some applications of ferrites which require materials with strict control of homogeneity and submicron granulation. The classical way of preparing ceramic oxide compounds (ferrites) in which the oxides or carbonates of semiconductor components are mixed and annealed at high temperatures ($> 1200^{\circ}\text{C}$) has some inherent disadvantages such as production of chemically inhomogeneous coarse powders as a consequence of high sintering temperature or introduction of impurities during ball milling. To avoid such events, various chemistry-based synthesis methods have been proposed [1–4]: glass crystallization method, sol-gel technique, co-precipitation method, hydrothermal synthesis, micro emulsion synthesis, organometallic precursor method to obtain ceramic products with superior microstructures.

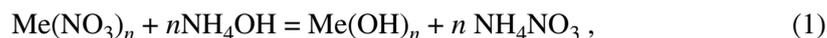
In the present work, sol-gel-selfcombustion (SGS) technology is applied to prepare homogeneous and submicron sized powder of the oxide compounds. The reason for the combination of sol-gel technique and selfcombustion has been to use the heat generated by an exothermic combustion reaction to supply the high

temperature needed for sintering oxide ceramics, thus allowing a low-cost preparing method. The main feature of SGS method is the intimate mixing of constituent ions so that the nucleation and crystallization can occur at relatively low temperatures. SGS method has a number advantages over classic ceramic method (physical mixture of oxides) such as homogeneous mixing, accurate stoichiometry control (no filtering step is required) and it is suitable for the production reactive powders using short processing times. Also, using self-combustion an external heat source is absent, the thermal energy for synthesis reaction of the ceramic compound is provided by a fast exothermic reaction and the final product is a finely divided powder. The powders obtained by sol-gel-selfcombustion are characterized by molecular scale homogeneity, ultrafine granulation, enhanced reactivity (lower heat treatment temperatures) and nanosized grains which can be controlled by subsequent heat treatments.

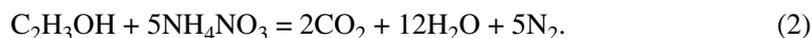
We have applied this method for processing of fine-grained spinel [5] or hexagonal [6] ferrites. The necessary materials are easy to obtain and the preparation technique is relatively simple and with low energy cost.

2. EXPERIMENTAL

In sol-gel-selfcombustion process, the analytical pure grade metal nitrates were weighted according to the desired composition and dissolved in distilled water (10% concentration). An aqueous solution of 10% polyvinyl alcohol was used to make a colloidal solution. A small amount of NH_4OH solution (25% concentration) was dropwise to adjust pH value to about 8. By coprecipitation, a sol of metal hydroxides and ammonium nitrate occurs according to the reaction



where Me is metal ion and n is its valence. By mixing with a magnetic stirrer for 5–10 minutes it was obtained a viscous gel which was dried at 100°C for 12 hours. The dried gel was ignited in a corner with a heated surface and an exothermic reaction takes place between polyvinyl alcohol and ammonium nitrate according to



(The equation is written for one monomer molecule, vinyl alcohol). Once ignited, sufficient heat is generated to propagate the reaction through the whole material. The combustion front spontaneously propagates and all the gel is burnt out. After the completion of the exothermic reaction a loose powder is obtained containing very fine crystallites due to rapid heating and cooling by the passage of the combustion wave from the point of ignition through the solid material.

During the combustion reaction, the metal hydroxides convert into metal oxides via the reaction



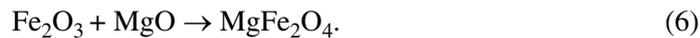
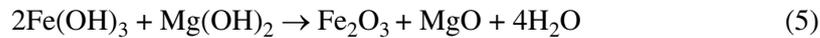
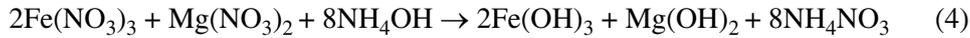
and the synthesis (fusion) between oxides begins to form the hexagonal or spinel structure. The rapidly moving combustion front, the high temperature and extremely high heating rate are the some attractive features of the self-combustion reaction. After quick combustion, the finely dispersed powder is calcined at 450–500°C in air, for one hour, to eliminate the residual organic compounds.

Small sizes, under 50 nm, of the crystallites synthesized during selfcombustion reaction, can be attributed to: a) too short reaction time, b) too low formation temperature or c) oxygen deficiency during selfcombustion.

Then, the calcined powder was compacted and heat treated in an electric furnace at different temperatures for various times to achieve a complete crystallization and controlled growth of the crystallites. The compacts were introduced into furnace after desired annealing temperature was attained.

In Fig. 1 is exemplified the flow diagram for preparing process by sol-gel-selfcombustion and subsequent heat treatment of MgFe_2O_4 ferrite.

The reactions which take place to prepare MgFe_2O_4 can be schematized as follows:



Solid state fusion of MgO with Fe_2O_3 , that is the nucleation and crystallization of MgFe_2O_4 , begins during selfcombustion reaction. After calcination at 450°C the powder was uniaxially pressed in a stainless steel dies in a pellet shape. The pellets were heat treated at 1100°C for 4 hours. The mass and dimensions of the heat treated compacts were measured to determine the bulk density d (density = mass/volume) and porosity p , by the formula

$$p = 1 - \frac{d}{d_x}, \quad (7)$$

where d_x is the theoretical density [7]

$$d_x = \frac{8M}{N \cdot a^3}. \quad (8)$$

Here, M is the molecular weight, N is the Avogadro's number and a is the lattice constant derived from XRD data. The phase composition of the heat treated

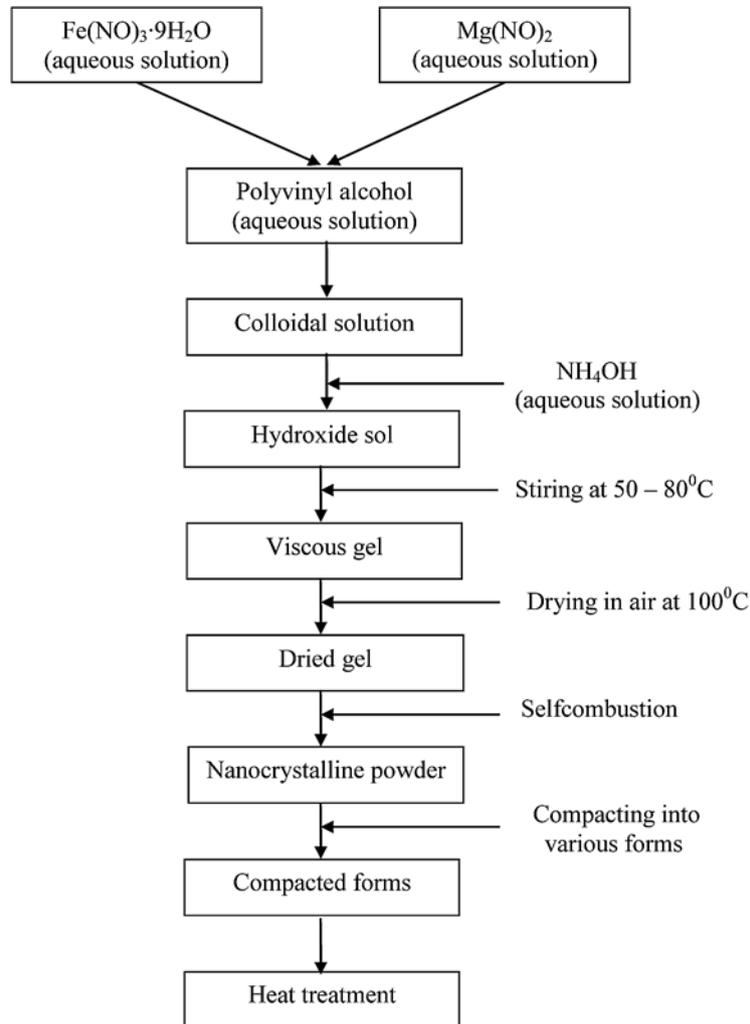


Fig. 1 – Schematic diagram of the preparation of the MgFe_2O_4 ferrite by sol-gel-selfcombustion (SGS) method.

specimens was identified by the standard X-ray diffraction (XRD), using DRON-2 type diffractometer and $\text{CuK}\alpha$ radiation. A number of microstructure studies have been performed by scanning electron microscopy (SEM). The average grain size D_m was determined by the linear-intercept technique [8] from SEM micrographs on the fracture surfaces. The specific surface area (surface area of particles per unit mass) was calculated using the equation [9, 10]

$$A = \frac{s}{v \cdot d} = \frac{6}{d \cdot D_m}, \quad (9)$$

where s and v are the particle surface and volume, respectively, d is the bulk density and D_m is average grain size. The number 6 is the shape factor. (It is assumed that all the particles have the same size and the same shape).

3. RESULTS AND DISCUSSION

3.1. XRD ANALYSIS

Fig. 2 shows X-ray diffractograms of three spinel ferrites, MgFe_2O_4 , $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ and $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Mo}_{0.02}\text{Fe}_{1.98}\text{O}_4$ prepared by SGS and heat treated at 1100°C for 4 hours. By X-ray diffraction it was evidenced the spinel phase as major phase and the presence of foreign phases, nonidentified in the samples containing Sn and Mo. The XRD lines belonging to the spinel structure are presented with Miller indices. The occurrence of the second phase suggests a solubility limit of Sn^{4+} ions in the spinel lattice due to its large radius (0.083 nm) [11]. It is known that the degree of replacement of the host cations by the other ions in the host lattice depends on the cation radius of the substituent [12]. The lattice parameters of the doped Mg-ferrites listed in Table 1 do not differ so much from that of the undoped Mg-ferrite.

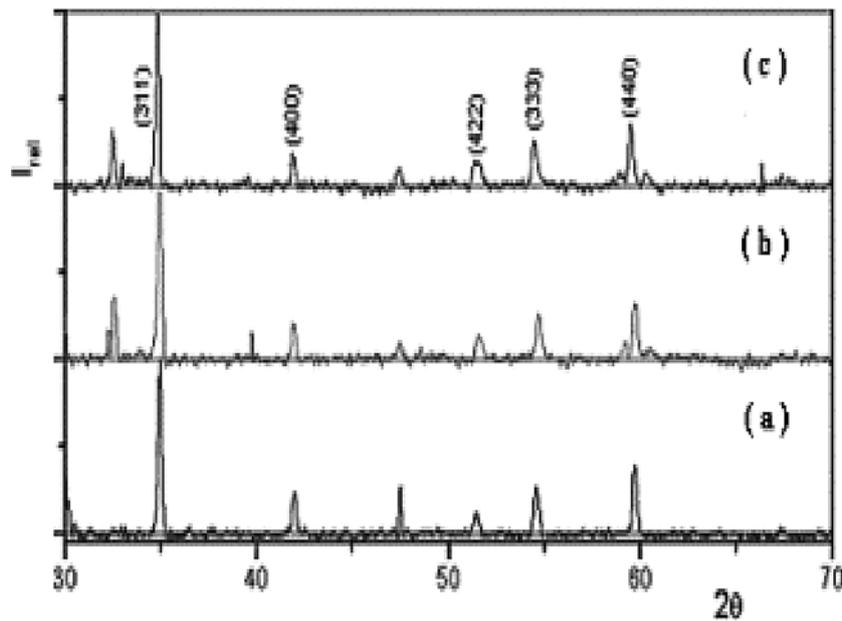


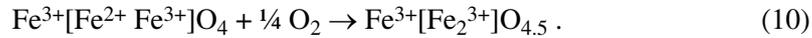
Fig. 2 – XRD patterns for: (a) MgFe_2O_4 , (b) $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ and (c) $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Mo}_{0.02}\text{Fe}_{1.98}\text{O}_4$ ferrites after heat treatment at 1100°C for 4 hours.

Table 1

The lattice parameter values of some spinel and hexagonal ferrites derived from XRD analysis

Sample	Lattice parameters [nm]
MgFe ₂ O ₄	0.8354
Mg _{0.9} Sn _{0.1} Fe ₂ O ₄	0.8352
Mg _{0.9} Sn _{0.1} Mo _{0.02} Fe _{1.98} O ₄	0.8382
SrFe ₁₂ O ₁₉	a = 0.5875; c = 2.3042
Sr Er _{0.2} Fe _{11.8} O ₁₉	a = 0.5876; c = 2.3045
Sr Er _{0.5} Fe _{11.5} O ₁₉	a = 0.5879; c = 2.3061

Fig. 3 shows X-ray diffraction pattern of SrFe_{11.8}Er_{0.2}O₁₉ hexaferrite powder heat treated at 900°C for 40 minutes. For comparison, XRD pattern of pure Sr hexaferrite is also given (thin line). The diffraction pattern (solid line) proves that the sample has been formed in M-type hexagonal structure. Main peaks of hexaferrite phase are clearly seen in the diffraction pattern. Well-defined sharp peaks indicate the good crystalline quality of this sample. It can also observe peaks of α -Fe₂O₃ phase, as second phase. One suppose that during the heat treatment, magnetite oxidizes and converts in very stable nonmagnetic hematite, α -Fe₂O₃, according to reaction



There is also trace of Er₂O₃, that suggests a partial incorporation of Er ions in the hexagonal structure. We remind that Er ions prefer octahedral sites in the

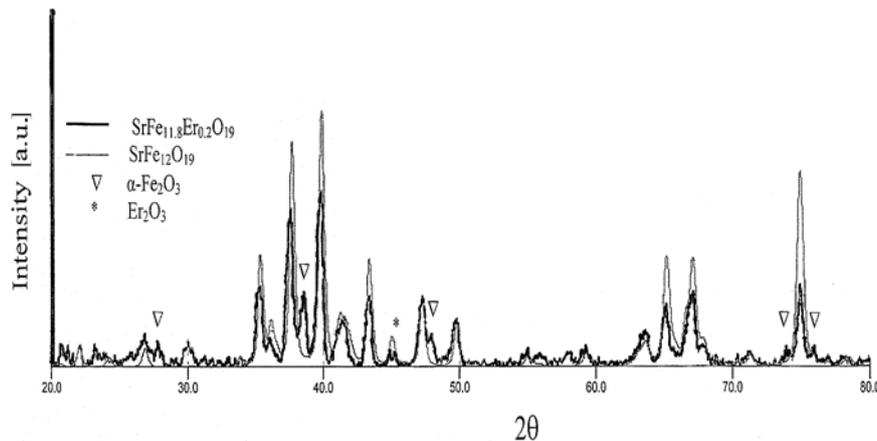


Fig. 3 – XRD pattern for Sr Er_{0.2}Fe_{11.8}O₁₉ hexaferrite after heat treatment at 900°C for 40 minutes.

spinel block of hexaferrite structure. It is also possible that some Er^{3+} ions form a weak magnetic compound, ortoferrite ErFeO_3 , in a small amount, undetectable.

In Table 1 are given the lattice parameters of the Er doped Sr hexaferrites treated at 900°C for 40 minutes resulted from X-Ray analysis. One can see that the lattice parameters slightly increase with Er content, being larger than those of pure Sr ferrite, $a = 0.58751$ nm and $c = 2.3042$ nm. The shrinkage of the crystal lattice cannot be expected because of large radius of Er ion (0.103 nm) as compared to that of Fe^{3+} ion (0.069 nm) [11]. This result is a prove of partial solubility of Er ions in the spinel block of the M-type hexagonal structure. However, the solubility limit of Er^{3+} ions in hexagonal lattice is not known yet. By analogy with Ca^{2+} ions we can say that Er^{3+} ion has an acceptable solubility in the spinel block resulting in increasing the lattice parameters as clarified in XRD analysis. Thus, the heat treatment of the powders obtained by sol-gel-combustion was beneficial in order to eliminate some secondary phases, Fe_3O_4 , FeO , SrFe_2O_4 , present in the as combusted powder and to crystallize the hard magnetic hexaferrite.

3.2. ELECTRON MICROSCOPY CHARACTERIZATION

The microstructure and morphology have an important role in determining the magnetic and electric transport properties and these were examined by a high resolution scanning electron microscope. SEM images are shown in Figs. 4 and 5,

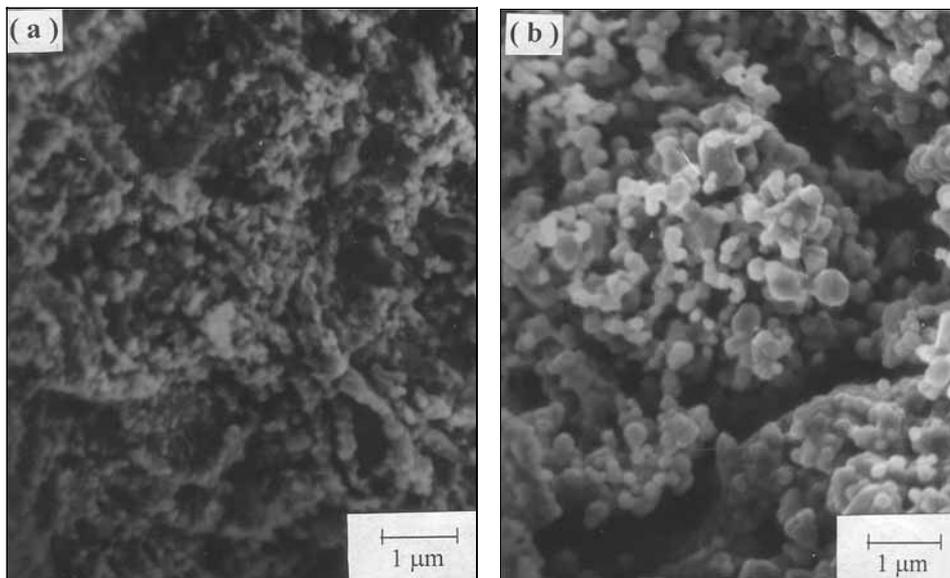


Fig. 4 – SEM images of spinel ferrites: (a) $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$, (b) $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_{1.98}\text{Mo}_{0.02}\text{O}_4$ prepared by sol-gel-selfcombustion and heat treated at 1100°C for 4 hours.

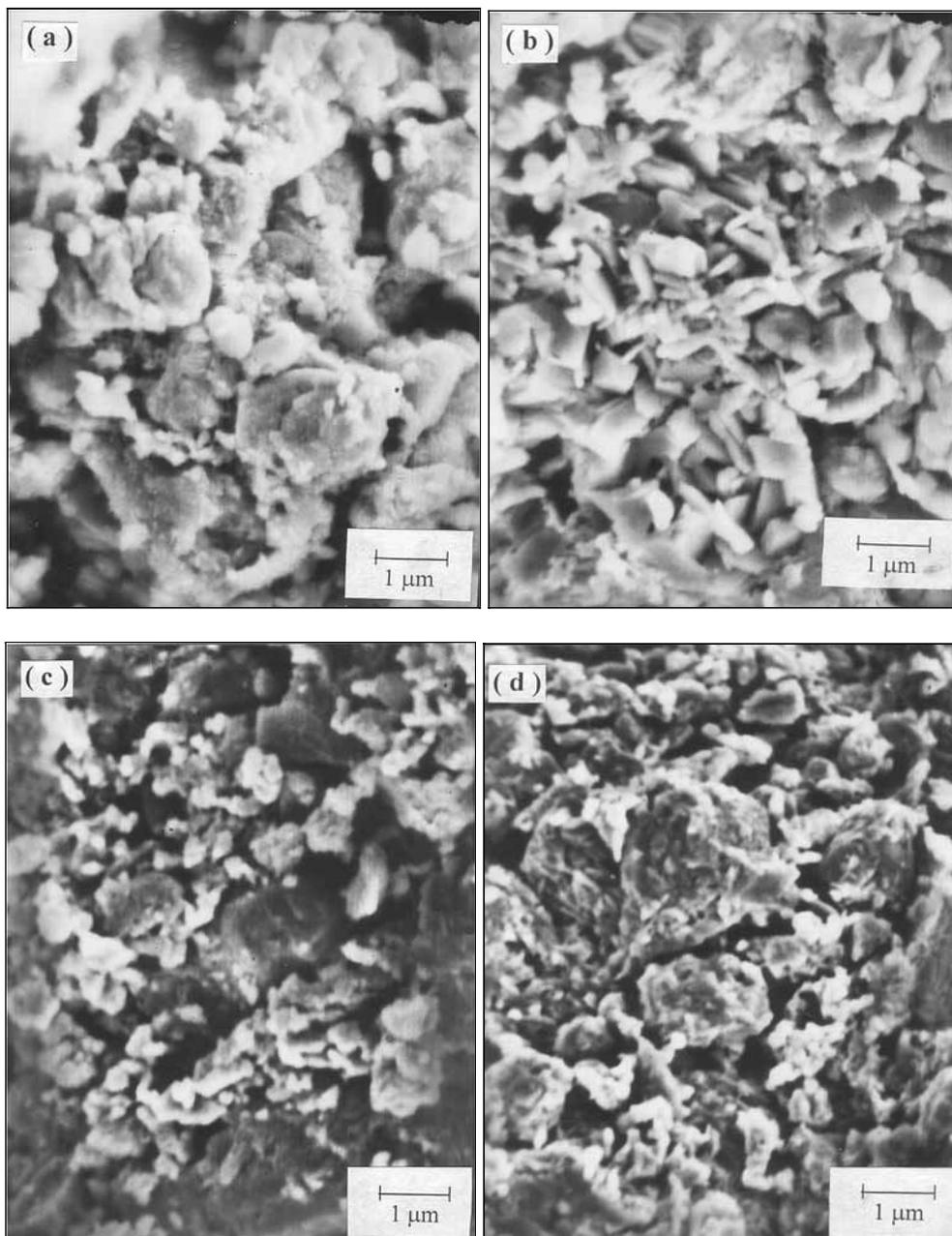


Fig. 5 – SEM images of hexaferrites prepared by sol-gel-selfcombustion: SrLa_{0.2}Fe_{11.8}O₁₉ after heat treatment at (a) 800°C for 40 minutes, (b) 1000°C for 40 minutes; SrEr_{0.2}Fe_{11.8}O₁₉ after heat treatment at 900°C for: (c) 10 minutes, (d) 160 minutes.

for some spinel ferrites and hexaferrites. Each ferrite is characterized by porous structure and submicron grains. The porosity is entirely intergranular, the pores are interconnected to form pore channels. Since the pores are channeled and do not have well defined shape, it is difficult to give a particular dimension of the pores.

In the spinel ferrites (Fig. 4) one can observe submicron grains, an uniform grain size distribution and the absence of the grain agglomerates.

SEM images given in Fig. 5a–d of hexagonal ferrites reveal remarkable changes in the microstructure, regarding grain size, porosity and the particle distribution by changing the heat treatment conditions (time and temperature). In the samples treated at 800°C (Fig. 5a) one can see the formation of multigrain agglomerations consisted of very small discrete crystallites (0.1–0.2 μm). It is recognized that the extremely fine powders show a strong tendency to formation of aggregates and/or agglomerates [13]. When the treatment temperature increased at 1000°C, a radical change in the microstructure takes place: individual particle size increases to about 0.8 μm and the lamellae structure appears (Fig. 5b), attesting a better crystallinity of the hexagonal phase. This result can also indicate that the sintering mechanism (grain growth) is a combined grain boundary and surface diffusion rather than volume diffusion. It is well known that the surface diffusion mechanism has a low activation energy [14] and that the sintering rate by surface-diffusion is faster than that by volume diffusion [15].

SEM images of $\text{SrEr}_{0.2}\text{Fe}_{11.8}\text{O}_{19}$ compound treated at 900°C when the treatment time changes from 10 and 160 minutes are given in Fig. 5 (c and d). The microstructure of the sample heat treated for 10 minutes (Fig. 5c), consists of fine particles, of about 0.1–0.2 μm and high porosity. When the heat treatment time increases from 10 to 160 minutes agglomerates with large diameters, up to 4–5 μm , appear, but, the grain growth was insignificantly.

The structural parameters of some ferrites prepared by the described method and which were investigated by us as gas sensor are summarized in Table 2. Such microstructures marked by high specific surface area and porosity

Table 2

Structural parameters of some ferrites prepared by sol-gel-selfcombustion

Sample	Sinterization		Average grain size D_m [nm]	Bulk density [g/cm ³]	Porosity [%]	Specific surface area [m ² /g]
	Temperature [°C]	Time [min]				
NiFe_2O_4	1000	30	200	3.5	35.2	8.6
ZnFe_2O_4	1000	30	100	2.7	48.4	22.2
$\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Mo}_{0.02}\text{Fe}_{1.98}\text{O}_4$	1100	240	270	2.7	48.5	8.2
$\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$	1100	240	100	2.5	51.6	23.8
$\text{MgMn}_{0.02}\text{Fe}_{1.8}\text{O}_4$	1000	20	100	2.18	54.0	27.2
$\text{SrLa}_{0.2}\text{Fe}_{1.8}\text{O}_4$	800	40	200	2.22	42.0	13.5

contribute to improve the gas sensitivity of the ferrites. As can see in Fig. 6 the gas sensitivity of $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ ferrite can exceed 70–80% at optimum working temperature of 370°C. Therefore, the sol-gel-selfcombustion can be a promising method for preparing ferrites for gas sensor application.

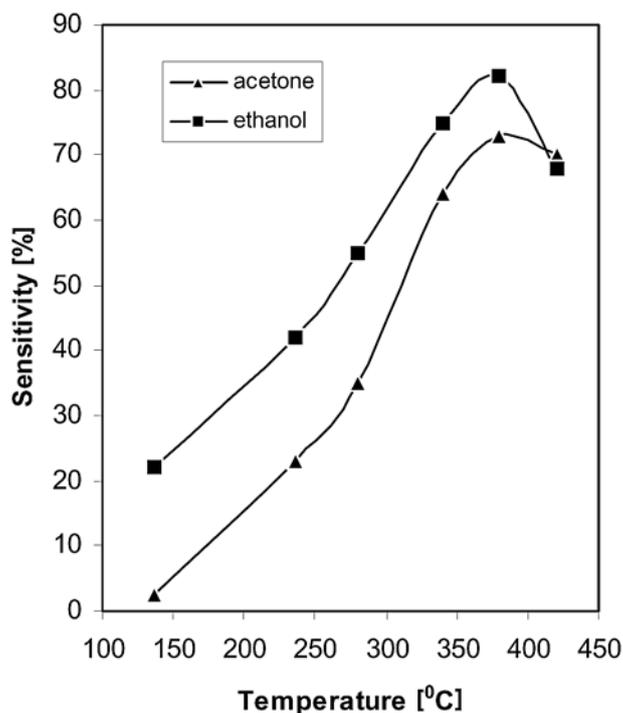


Fig. 6 – Sensitivity *versus* operating temperature for the $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ ferrite to acetone and ethanol gases.

4. CONCLUSIONS

Finely dispersed powders of the oxide compounds (ferrites) were produced by sol-gel-selfcombustion processing. In this method metal nitrates were used as raw materials and the coprecipitation takes place into a colloidal medium. The formation process of the ferrite powder is an exothermic solid-state reaction (combustion synthesis). The structure and morphology of the heat treated samples were investigated by XRD and SEM. The obtained results show that by suitable heat treatment of the combusted powder it is possible to control the structural characteristics, porosity, grain size and specific surface area which can influence the electrical properties of ferrites in various atmospheres. The grain sizes of the formed ferrites were $< 0.3 \mu\text{m}$, that is much smaller than these obtained by classical method. Hence, the sol-gel-selfcombustion procedure is promising for producing fine-grained ferrites.

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