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Co-based magnetic nanostructured material for high frequency applications

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Abstract. The RF circuits are difficult to be miniaturized without compromises concerning the technical performances. The inductors and antennas are the major constraints for systems miniaturization, due to the lack of magnetic materials with adequate high frequency properties. The paper presents novel Co-based magnetic nanostructured materials, with improved characteristics which recommend them as potential candidates for transformers and inductors in electronic components: higher level for saturation magnetisation and electric resistivity in comparison with commercial ferrites. The magnetic nanocomposites are prepared by sol-gel route and consist on Co magnetic nanocrystallites, arranged in a crystalline matrix (silicates, for example). The main physical characteristics of the Co/SiO₂ nanopowders are developed after appropriate calcination and annealing, being dependent on the SiO₂ amount and on the thermal treatment parameters: saturation magnetisation $M_s = 81.7 - 130.4$ emu/g, coercivity $H_C = 21.7 - 26.9$ kA/m (273 - 338 Oe) and increased resistivities for the sintered samples, due to the presence of the SiO₂ layers.

1. Introduction

The RF technologies limit the current wireless systems in their size, efficiency, range of communication, and last but not least, their cost. The RF circuits are difficult to miniaturize without compromises concerning the technical performances. The inductors and antennas are the major constraints for systems miniaturization, due to the lack of magnetic materials with adequate high frequency characteristics [1].

The applications of soft magnetic materials in AC electronic and electrical devices require the use of soft magnetic core materials with high values for the magnetisation at saturation, Curie temperature, initial permeability, and low levels of hysteresis, dielectric and eddy current losses. Among all the magnetic materials, the metallic alloys have the best soft magnetic properties, but their main disadvantage is the low resistivity (ca $10^{-6} \Omega \cdot \text{cm}$). This level of resistivity is unacceptably, due to the high eddy current loss for frequency more than 100 kHz.



Having high resistivity, the ferrite cores are preferred to be used for parts which operate in high frequency applications. But, compared with the metallic magnetic alloys, the ferrites have some disadvantages: low levels for saturation magnetisation, initial permeability and Curie temperature.

Many works are devoted to the embedding of the metallic nanoparticles into the insulating matrix based on Al_2O_3 [2-4] and SiO_2 [5], for example. In the case of metallic/ceramic composites, where the metallic magnetic phase (with micrometric sizes) is embedded in a nonmagnetic insulator matrix, these materials possess greatly enhanced resistivity, but poor soft magnetic properties, due to the damaging, through demagnetising effect, of the magnetic properties, caused by the presence of the insulating component, which deteriorate the magnetic properties.

Hence, the conventional metal powder materials possess significantly lower permeability than of the corresponding metals or metallic alloys, as bulk. In addition, although the overall resistivity of the powder material is greatly increased, the resistivity of each metallic particle is still low, because the eddy currents produced within the particles constitute a problem for the frequency around 1 MHz.

In the case of the same system, but at the nanometric scale, the exchange interaction which leads to magnetic ordering within a grain, also extends out to neighbouring environments (through spin polarization or the superexchange interaction mechanism) with a characteristic distance called exchange length, which is in the nanometer range [6, 7]. For a conventional powder material, the exchange coupling effect exists only in the interface region of the particles and has essentially no visible effect.

When the particle-particle separation is reduced, the intergrain exchange interaction may take place in a large volume of each particle, tending to align the magnetic moments of neighbouring particles and, in this situation, the exchange coupling plays a significant role to determine the magnetic structure of the system, under which, the material will possess a variety of properties different from the large grained material.

In the nanocomposites with the magnetic particle - particle separation significantly less than the exchange coupling length, the exchange coupling phenomenon acts on the entire volume of the particles. So, each particle exerts exchange interactions from surrounding particles with different magnetic moment orientations, resulting to the cancellation of the magnetic anisotropy for each individual particle [6]. This is the reason why the permeability of such an exchange-coupled nanocomposite can be much higher than the permeability of the large grain material [8]. The core-shell type structures, constituted by magnetic core and oxide layer offer the premises to enhance the magnetic performance and to improve the behaviour in operating conditions for these materials [9-11].

The fundamental requirements for the preparation of the metallic magnetic/insulating nanocomposites used as soft magnetic material are the following [8]: (i) the particle size of the magnetic component should be less than its exchange length. In the case of Co, this exchange length is ~ 30 nm; (ii) the insulating component should be able to provide the exchange interaction between neighbouring magnetic particles. When an inorganic material is chosen as the insulating constituent, it must be in an amorphous state with oxide-like short range ordering [12]; (iii) Another requirement is the smallness of the magnetocrystalline anisotropy for the magnetic particle, in order to benefit from exchange coupling advantage. For example, the Co nanoparticles should have an fcc structure and the hcp crystalline structure Co is not desirable; (iv) The chemical reaction should be complete so as to reduce all of the metal ions in the salt into metal while ensuring the smallness of the particle size. The studies have shown that SiO_2 can deliver an intergrain exchange interaction [13].

Taking into the account the above presented aspects, the Co/ SiO_2 nanocomposites, with Co nanometric particles, having the crystalline structure type fcc, and the SiO_2 as insulator, with amorphous state, and after the completion of the chemical reaction, all these are premises to obtain the soft magnetic, electrically insulated nanomaterials with improved behaviour in high frequency applications.

The paper presents novel Co-based magnetic nanostructured materials, with improved characteristics which recommend them as potential candidates for transformers and inductors in electronic components: higher level for saturation magnetisation and electric resistivity in comparison

with commercial ferrites. The magnetic nanocomposites are prepared by sol-gel route and consist on Co magnetic nanocrystallites, arranged in a crystalline matrix (silicates, for example).

2. Materials and methods

The Co-based soft magnetic, electrically insulated nanopowders were prepared using the sol-gel method. The materials used for the chemical synthesis of Co/SiO₂ nanoparticles were: cobalt(II) chloride hexahydrate - CoCl₂·6H₂O (Chemical Company Iasi), citric acid monohydrate C₆H₈O₇·H₂O (Chimreactiv, Bucharest), ethanol C₂H₆O (96%, Chemicals Company Iasi) and tetraethyl orthosilicate Si(OC₂H₅)₄ – TEOS (Alfa Aesar). The process of preparing Co/SiO₂ nanopowders included several steps:

a) preparation of xerogel: raw materials, less TEOS, were dosed according to the recipe, were homogenized by stirring for a minimum of 6 hours at 60°C. After this, TEOS was added, and the mixture was further stirred for a further 4 hours at room temperature. The resulting xerogel was dried at 80°C, stirring continuously;

b) xerogel calcination was performed in air by maintaining it at 450 to 700°C for 3 hours;

c) reducing oxides in the hydrogen atmosphere by maintaining for 4 hours at 800°C.

The base recipe contained 0.030 moles of CoCl₂·6H₂O, 0.045 moles of C₆H₈O₇·H₂O, to which different amounts of Si(OC₂H₅)₄ were added, according to the molar ratios shown in Table 1, and 300 mL of C₂H₆O. The Si/Co molar ratios used for the Co/SiO₂ nanopowder samples were: 6%; 11%; 14%; 22%; 28%; 30%; 50% and 70%. After the sol-gel synthesis, the resulted xerogels were calcinated at 500°C for 3 hours and annealed in reducing atmosphere for 4 hours at 800°C.

Table 1. The preparation conditions of the Co/SiO₂ nanopowders samples.

Sample code	Material	Si/Co molar ratio (%)
COS 21	Co/SiO ₂	6
COS 2		11
COS 22		14
COS 23		22
COS 24		28
COS 25		30
COS 26		50
COS 27		70

For the qualitative identification of the crystallographic phases involved in the magnetization processes, respectively for calculating the parameters of the crystalline lattice and the crystallite dimensions, the X-ray diffraction technique was used. The X-ray diffractograms have been recorded by means of D8 Discover diffractometer, equipped with X-ray tube with Co anode ($\lambda = 1,78897 \text{ \AA}$), 1D Lynx-Eye detector, configured in Bragg-Brentano geometry with an angular increment of 0.04°, sampling time of 1s/step. Qualitative identification was performed using the ICDD PDF2 Release 2014 database after instrument error correction. After preparation, the Co/SiO₂ nanopowders with different SiO₂ amounts have been magnetic characterised by vibrating sample magnetometry (VSM). The magnetic measurements of the nanopowders samples were performed using a magnetometer Lakeshore 7300 type, at room temperature, the applied magnetic field being ca. 9 kOe (715 kA/m). In order to estimate the electrical properties, the Co/SiO₂ nanopowders were compacted and then sintered in argon atmosphere at 1300°C, for 1 hour. The measurement of the samples volume resistivity was performed using the High resistance meter (model 4339B, from Agilent), with the following technical characteristics: resistance measuring range: 1 k Ω - 10¹⁸ Ω ; accuracy: $\pm 0.6 \%$; voltage range: 0 - 1000

V, d.c.; current intensity range: 100 pA - 100 mA. The measurement conditions for all samples were: $F_p = 5$ kgf; $U = 500$ V and $I = 500$ μ A.

3. Results and discussions

By analyzing the diffraction spectra it was possible to determine relevant information regarding the constituents of the elaborated materials (their nature and their crystalline structure, the lattice parameters), as well as the data regarding the particle size of cobalt. The results of the structural investigations, analyzed from the point of view of the influence of the SiO_2 content and the size of the nanoparticles of cobalt, are presented below.

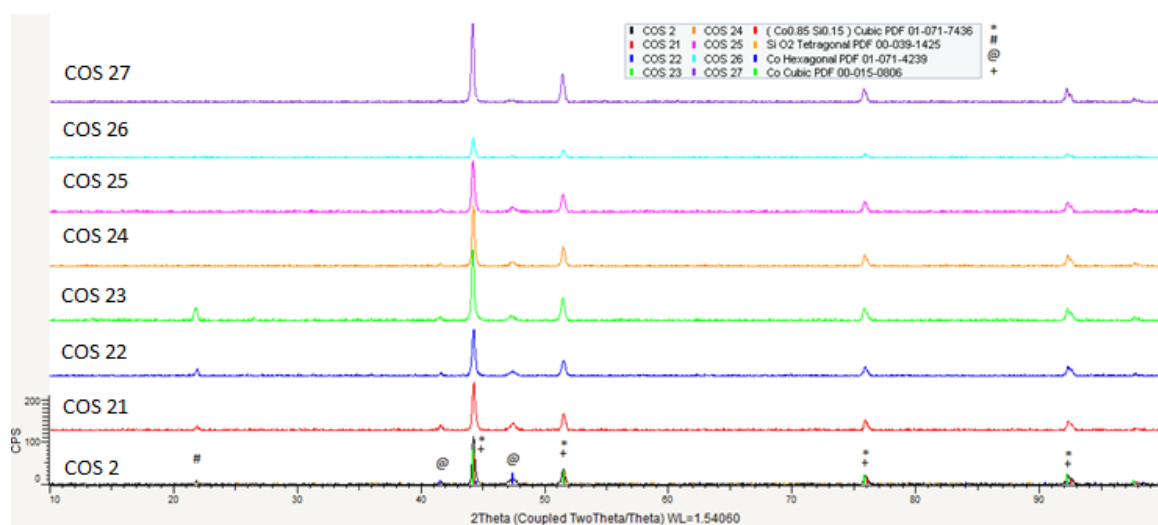


Figure 1. X-ray diffractograms of Co/SiO₂ nanopowders with different Si/Co molar ratios (see Table 1), after calcination for 3 hours at 500°C and reducing at 800°C for 4 hours.

Figure 1 shows the diffractograms of Co/SiO₂ nanopowders prepared with different Si/Co molar ratios: 6%; 11%; 14%; 22%; 28%; 30%; 50%; 70%, the encoding of samples being the same as shown in Table 1. From Figure 1 we can find the presence of fcc type crystalline structure for cobalt in all samples, the most intense peaks being at $2\theta = 44^\circ$. The intensity of these peaks increases as the Si/Co molar ratio increases. The exception is the COS 26 sample, with a molar ratio Si/Co = 50%, for which the corresponding peak intensity of $2\theta = 44^\circ$ has a much lower level, indicating a weaker cobalt crystallization during the chemical synthesis step of the Co/SiO₂ nanoparticles. Along with fcc cobalt, the compound $\text{Co}_{0.85}\text{Si}_{0.15}$ can also appear, crystallized in a cubic system, but its presence can be doubtful because of parameters very similar to those of fcc cobalt, which can lead to confusion.

The peaks observed in this diffractograms, illustrated in Figure 1, are sharp, well defined and very intense, indicating that the resulting cobalt is very pure and with pronounced crystallinity. On certain diffractograms, for example those of samples with molar ratios Si/Co = 6%; 11%; 14%; 22% (COS 21, COS 22 and COS 23 samples), appears a low intensity peak, corresponding to SiO₂, at $2\theta = 22^\circ$. The absence of this peak in the other diffraction spectra of the samples is determined either by the fact that SiO₂ is in the amorphous state or the crystallites dimensions are extremely small. In this case, its presence can not be highlighted by X-ray diffraction, but only through subsequent TEM investigations. These investigations will prove not only its formation, but will allow also the determination of the SiO₂ layer thickness, for the different Si/Co molar ratios.

As previously mentioned, the diffraction lines presented by the Co/SiO₂ nanopowder samples provide clear evidence of cobalt formation with fcc cubic structure. The calculated XRD parameters, such as the lattice constant a and the average size of the crystalline grains D , are shown in Table 2. It

compares the crystalline dimensions and lattice parameters of Co/SiO₂ nanopowders, calcinated at different temperatures and synthesized with different Si/Co molar ratios.

Table 2. The crystallite average sizes and lattice parameter for the Co/SiO₂ nanopowders, with various Si/Co molar ratios, after calcination and annealing, according to processing conditions from Table 1.

Sample code	2 θ position (°)	Interplanar distance, d (Å)	Lattice parameter, a (Å)	Crystallite average size, D (Å)
COS 21	44.261	2.04478	3.542	323.6
COS 2	44.238	2.04578	3.543	339.6
COS 22	44.249	2.04530	3.543	318.2
COS 23	44.176	2.04851	3.548	350.4
COS 24	44.220	2.04658	3.545	348.7
COS 25	44.198	2.04755	3.546	330.0
COS 26	44.233	2.04601	3.544	341.6
COS 27	44.162	2.04913	3.549	368.2

In the case of Co/SiO₂ nanopowders with various Si/Co molar ratios, the value of the lattice parameters of the studied samples is in the range $a = 3.543 - 3.549$ Å, values close to those of the theoretical parameter $a_{\text{cor}} = 3.5447$ Å (see Table 2). The average sizes of the cobalt crystallites are in the range of 31.8 - 36.8 nm, which indicates that they do not vary greatly with the SiO₂ content in the investigated samples. A possible explanation for this is the increase in SiO₂ content that acts as a barrier to the growth of the cobalt crystallites sizes during thermal treatments.

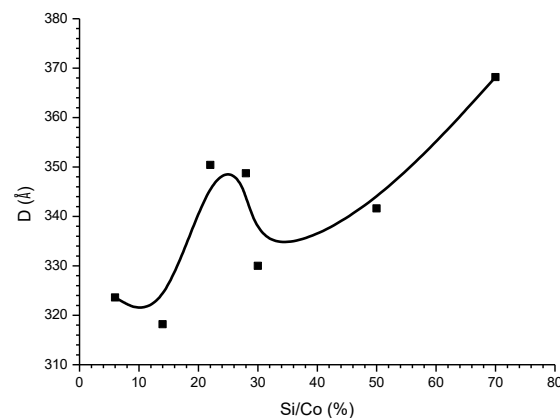


Figure 2. Variation of cobalt average crystallite size on Si/Co molar ratio for Co/SiO₂ nanoparticles.

This variation with Si/Co different molar ratios of the average sizes of cobalt crystallites in Co/SiO₂ nanopowders is illustrated in Figure 2. It can be observed the ascending trend, of Co crystallite sizes increasing with the increase of the Si/Co molar ratio.

For the Co/SiO₂ studied samples (synthesized by varying the Si/Co molar ratio between 6 and 70%), the recorded hysteresis curves are shown in Figures 3 - 4. The represented curves are corrected for the outer demagnetization factor by the hysteresis loop tracer, a VSM from Lake Shore. Our interest was to characterise the composite as a whole, so that we don't apply the correction for the inner demagnetization factor. From these hysteresis curves the values of the main magnetic

characteristics were extracted and presented in Table 3. From the magnetization curves and from the data presented in Table 3, can be concluded that all the samples show remanence (hysteresis different from zero).

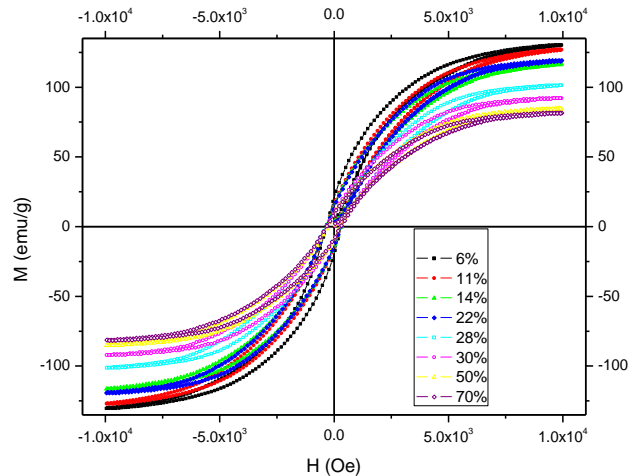


Figure 3. The hysteresis curves of the Co/SiO₂ nanopowders with various molar ratios (according with Table 1), calcinated at 500°C/3 hours and reduced at 800°C/4 hours.

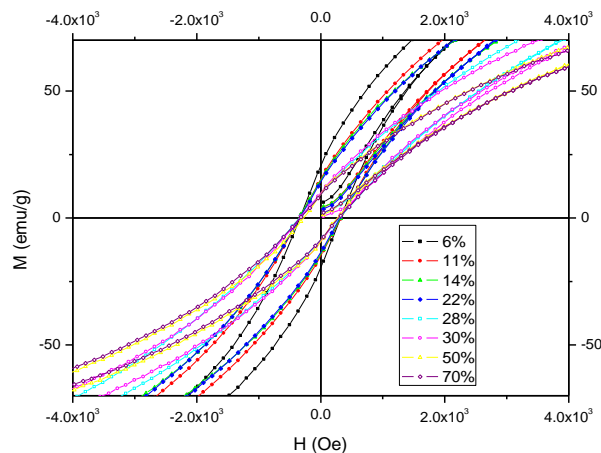


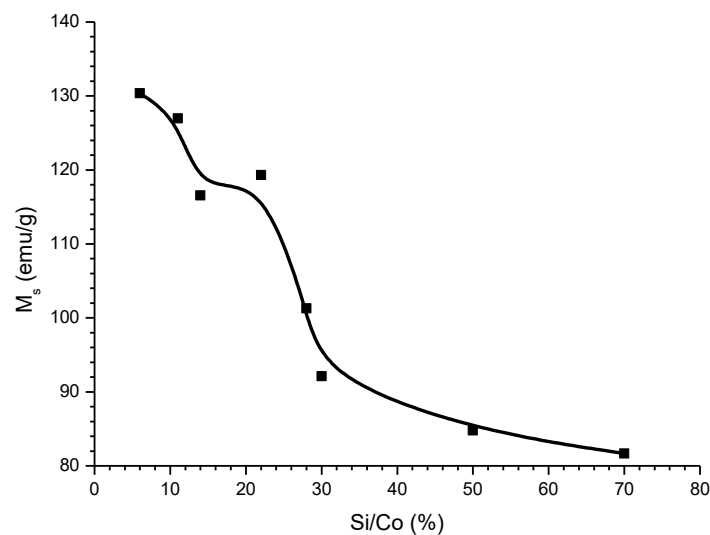
Figure 4. Comparative hysteresis of Co/SiO₂ nanopowders with various molar ratios, calcinated at 500°C/3 hours and reduced at 800°C/4 hours, measured in the range [- 4, 4] kOe.

Figure 5 illustrates the variation of magnetisation at saturation with Si/Co molar ratio for Co/SiO₂ nanopowders. The values of magnetisation at saturation ranged from 81.7 to 130.4 emu/g. It can be seen that the saturation magnetization of the Co/SiO₂ nanopowders varies with the SiO₂ content, its values decreasing as the Si/Co molar ratio increases (see Figure 5).

The variation of coercivity is sinuous, around the value of 300 Oe, depending on the variation of the demagnetizing fields due to the existence of SiO₂ nanoparticles and its displacement in the mass of Co/SiO₂ nanopowders.

Table 3. The main magnetic characteristics (M_s and H_c) of the CoSiO_2 nanopowders samples with different Si/Co molar ratios (according to the Table 1).

Sample code	Material	Si/Co molar ratio (%)	Magnetisation at saturation, M_s (emu/g)	Coercivity, H_c (Oe)
COS 21	Co/SiO ₂	6	130.36	328.8
COS 2		11	126.97	335.3
COS 22		14	116.56	338.5
COS 23		22	119.33	324.8
COS 24		28	101.30	320.9
COS 25		30	92.11	310
COS 26		50	84.78	273.1
COS 27		70	81.66	312.2

**Figure 5.** Variation of magnetisation at saturation with Si/Co molar ratio for the Co/SiO_2 nanopowders.

After the consolidation of nanopowders by sintering in argon, at 1300°C, for 1 hour, the values of the measured densities of consolidated bodies were between 3.48 - 6.85 g/cm³, in close dependence on the SiO_2 content. The values of resistivity measured on sintered samples were of order of $10^{17} \Omega \cdot \text{cm}$, significantly higher than the values of resistivity of soft ferrite and Fe-Si alloy, which are in the range of 100 – 1000 $\mu\Omega \cdot \text{cm}$, respectively 46 – 49 $\mu\Omega \cdot \text{cm}$, depending on the materials class [14, 15].

If we consider the Co/SiO_2 composite as a homogenous material with the above mentioned electrical resistivity, than we conclude that in an a.c magnetic field, commonly reached in electrical machines (of the order of 100 Hz) we cannot have significant power losses, but only hysteresis losses. To the same conclusion we come if we consider the penetration depth:

$$\Delta = (\pi \nu \mu \sigma)^{-1/2} \quad (1)$$

where ν is the frequency of the magnetic field, μ is the absolute permeability of the material with the conductivity σ . If we calculate now δ for the Co with $\mu = 4\pi \cdot 10^{-7} \cdot 250 \text{ H/m}$ and $\sigma = 1.7 \cdot 10^7 \text{ S/m}$ in a field with a normal frequency in electrical machines of $\nu = 100 \text{ Hz}$, we obtain around 0.08 cm, which is around $2.35 \cdot 10^4$ times the average diameter of 34 nm of our particle size, that means that we cannot have any significant energy losses in our particle. In order to have dynamic energy losses (normal

eddy current losses and excess losses) we must have the penetration depth comparable with the particle size, that means, with the assumed values, at frequencies of the order of 30 GHz. We conclude that our composite material has a.c. energy losses comparable with soft ferrites, but at a much more higher saturation magnetization. Our conclusions are in concordance with the results reported in literature on the microwave magnetic properties of the Co/SiO₂ nanocomposites [16,17].

4. Conclusions

The Co-based electrically insulated nanopowders, consisting of Co/SiO₂ nanoparticles, were prepared by chemical synthesis, using a complex process that involves non-aqueous sol-gel technique, calcination and annealing in reducing atmosphere.

The Co/SiO₂ nanoparticles were characterised by the presence of Co crystallites, with fcc crystalline structure and SiO₂ in amorphous state.

The effect of SiO₂ amount on the structural, magnetic and electric properties of Co/SiO₂ nanopowders has been confirmed, the presence of SiO₂ leading on the increase of resistivity for the Co/SiO₂ nanopowders.

Our study shows that the SiO₂ amount strongly influenced the physical properties of the final Co/SiO₂ nanostructured material and this influence can be controlled during the preparation process.

The high level of saturation magnetisation is combined with the low values of coercivity.

The soft magnetic properties, combined with the increased resistivity recommend the Co-based nanostructured materials as candidate for sintered parts operating in high frequency; the future work will approach the magnetic characterisation and the functional evaluation of Co/SiO₂ sintered materials in frequency.

5. References

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