



Unlocking the hidden potential: exploring the fascinating properties of CoFe₂O₄@SiO₂ nanocomposites driven by annealing

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► To cite this version:

A. Bajorek, A. Czempik, Fabien Grasset, S. Auguste, M. Dulski, et al.. Unlocking the hidden potential: exploring the fascinating properties of CoFe₂O₄@SiO₂ nanocomposites driven by annealing. *Journal of Magnetism and Magnetic Materials*, 2025, 636, pp.173670. <10.1016/j.jmmm.2025.173670>. <hal-05390166>

HAL Id: hal-05390166

<https://hal.science/hal-05390166v1>

Submitted on 1 Dec 2025

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Journal of Magnetism and Magnetic Materials

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--Manuscript Draft--

Manuscript Number:	MAGMA-D-25-01527
Article Type:	Full Length Article
Section/Category:	
Keywords:	Spinel nanoferrites; Nanoparticles; Co-precipitation; Microstructure; magnetic properties; Crystal and electronic structure
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Opposed Reviewers:	

Unlocking the hidden potential: exploring the fascinating properties of CoFe₂O₄@SiO₂ nanocomposites driven by annealing

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Abstract

A study of the influence of multistage annealing on the properties of CoFe₂O₄@SiO₂ (CFO@SiO₂) core-shell nanoparticles synthesized by co-precipitation followed by microemulsion is discussed. The cubic inverse spinel ferrite crystal structure with Fe³⁺ and Co²⁺ cation distribution in the A-tetrahedral and B-octahedral sites is confirmed in all analyzed nanocomposites. The structural characterization revealed the subtle temperature-driven CFO core crystallization to about 13 nm. Concurrently, the silica shell exhibits stability regardless of the sample processing. The interplay between larger multi-domain CFO and smaller superparamagnetic (SPM) CFO single-domains is confirmed by the performance of magnetic properties and *Mössbauer* spectrometry. The spin-canting phenomenon on the CFO surface magnetic dead layer (MDL) is exposed by employing the *Yafet-Kittel* model. The X-ray photoemission (XPS) and absorption spectroscopy (XAS) studies confirmed the complex nature of the Fe and Co states. The Fe³⁺ and Co²⁺ distribution in the crystal lattice is verified by XPS and XAS spectra. The Si-O-Ni/Fe intermixing on the CFO / SiO₂ interface is validated by the core-level line analysis, proving the existence of a disordered layer MDL on the CFO surface.

Keywords

Spinel nanoferrites, Nanoparticles, Co-precipitation, Microstructure, Magnetic properties, Crystal and electronic structure

1. Introduction

The novel development of targeted drug delivery systems for magnetic hyperthermia has recently focused on various spinel ferrites [1-3]. Among a vast class of such materials, one of the most studied is CoFe_2O_4 (CFO) [4-17], which additionally demonstrates wide potential applications, including high-density storage devices, microwave absorption, magneto-optic recording medium or ferrofluids. The applications are driven by magnetic properties such as large magnetocrystalline anisotropy, high coercivity, high Curie temperature (T_C), moderate saturation magnetization and good chemical and surface stability. The optimization of magnetic performance can be achieved by the selection of synthesis methods, which allows the control of the cations distribution between A-tetrahedral and B-octahedral sites in the $(\text{Co}_{\delta}\text{Fe}_{1-\delta})^{\text{A}}[\text{Co}_{1-\delta}\text{Fe}_{1+\delta}]^{\text{B}}\text{O}_4$ crystal lattice. So far, adopted popular synthesis approaches are focused on sol-gel, hydrothermal, combustion, polyacrylamide gel route, co-precipitation, microemulsion, citrate, ball-milling and solvothermal [1-17]. Further calcination procedures allow controlling the CFO crystallite size as directly reflected on the nanoparticles (NPs) magnetic performance.

One of the first attempts to synthesize CoFe_2O_4 (CFO) nanoparticles was made by *Grigorova et al.* [12], who produced powders with a size between 4.3 nm – 46.5 nm by a co-precipitation followed by calcination at several annealing temperatures (T_A) up to 700°C. The authors revealed the existence of the layer of NPs surface with about 10 Å thickness, which, as discussed, did not affect the magnetism. A cubic type of magnetocrystalline anisotropy with the higher coercivity (H_C) of 14.1 kOe at 5K was found for the smallest nanoparticles in contrary to the largest remanence (M_R) of 47.5 emu/g for the largest particles, namely annealed at the highest T_A . As proved, the largest NPs exhibit multiaxial anisotropy. The superparamagnetic (SPM) behaviour was shown at room temperature regardless of the nanoparticle sizes between 4.3 nm – 46.5 nm. The cation distribution based on the Mössbauer study was estimated as $(\text{Co}_{0.5}\text{Fe}_{0.95})^{\text{A}}[\text{Co}_{0.95}\text{Fe}_{1.05}]^{\text{B}}\text{O}_4$, pointing to the distribution of divalent cobalt at the tetrahedral site and trivalent iron at tetrahedral and octahedral sites.

In the following years, many research teams focused on spinel ferrite nanomaterials, including CFO, due to their promising application properties [1-17]. For example, *Penchal Reddy et al.* [5] analyzed mesoporous CoFe_2O_4 nanospheres with tuneable diameters 120-180 nm prepared by hydrothermal method. The complementary analysis proved the divalent cobalt

and trivalent iron oxidation states. The high surface area and excellent magnetic properties were revealed with 50.19 emu/g saturation magnetization and 136 Oe of coercivity, which is a bit lower than for the bulk parent material ($M_S = 80$ emu/g and $H_C = 150$ Oe) [12], probably due to the spin canting effect on the particles' surface. *Naseri et al.* [6], during the synthesis process, utilized a capping agent of poly(vinylpyrrolidone) (PVP) to prevent CoFe_2O_4 nanoparticles from agglomeration. The subsequent thermal treatment stabilized the crystal structure with particle size 14 ± 8 nm ($T_A = 723\text{K}$) to 34 ± 5 nm ($T_A = 873\text{K}$). As demonstrated, the nanoparticles, regardless of thermal treatment, follow the ferromagnetic behaviour with increased saturation magnetization and coercivity of $M_S=9.84$ emu/g and $H_C=823$ Oe for $T_A = 723\text{K}$ to $M_S = 23.47$ emu/g and $H_C = 1163$ Oe for $T_A = 873\text{K}$. The elevated parameters are forced by the domain structure and critical domain size, and anisotropy changes are driven by annealing. The four different synthesis methods were adopted by *Abraime et al.* [13], who used co-precipitation (SG), sol-gel (SG), sol-gel autocombustion (SGA) and microemulsion (ME). In all cases, the synthesized NPs were annealed at two temperatures, $T_A = 400$ and 600°C . The crystallite size and magnetic properties are susceptible to the used synthesis type. Thus, the largest NPs of about 18 – 25 nm were found for SG and SGA methods, which obviously point to the highest M_S values. The estimation of $(BH)_{\text{max}}$ for SG and SGA reactions was additionally improved by annealing.

Thus, the CoFe_2O_4 oxide exhibits larger anisotropy than other known ferrites, and the anisotropy constant depends on the Co content. Hence, the magnetic properties of CFO-based nanoparticles can be additionally tailored by controlling their size and composition. Moreover, the well-established synthesis process and detailed physicochemical characterization enable the CFO nanoparticles to be further modified prior to targeted applications, including biological applications considering drug delivery systems or hyperthermal therapy. However, for medical applications, the most important properties of any magnetic materials are, among others, non-toxicity and biocompatibility, combined with stability in physiological environments and high-level accumulation in the target tissues. Therefore, for such an application, it is desirable to coat the magnetic nanoparticles with a nontoxic, biologically compatible and non-magnetic material [3, 21, 22]. Due to the proven toxicity of Co-based materials [23], the encapsulation process of nanoparticles can be justified. The silica was so far one of the most efficient materials used as a shell, which ensures well-dispersed and homogeneous ultrafine NPs with narrow particle size distribution, prevents NPs aggregation, and stabilises the magnetic core phase, protecting it from unwanted interactions. In addition, the reasonably low cost, high thermal stability, low cytotoxicity and good chemical inertness of the NP's surface, allowing for its further

functionalization, make SiO₂ a promising inorganic matrix in magnetic composite nanosystems. The stabilizing role of silica is especially coveted in the heat treatment process, where it reinforces the metallic core from excessive modification over annealing, which is usually a key factor in enhancing and tailoring the magnetic core properties.

Bearing in mind the excellent properties of CFO nanoparticles, they are a promising candidate to be encapsulated by SiO₂ prior to further functionalization. So far, several research groups made an attempt to optimize the physicochemical properties of CFO@SiO₂ composites. The effect of interparticle interactions on the magnetic behaviour of cobalt ferrite nanoparticles was investigated in a CoFe₂O₄/SiO₂ nanocomposite with 50 wt % of magnetic phase was analyzed by *Peddis et al.* [24]. The irreversible magnetic behaviour in the zero field cooling-field cooling (ZFC-FC) magnetization was manifested. The study shows that the $M_{ZFC}(T)$ maximum is due to the coexistence of two different magnetic behaviours, namely the collective magnetic ordering, but mainly rather to a superparamagnetic transition of a fraction of small nanoparticles. Thus, the 2 nm to 35 nm particle size distribution determines the composite magnetic performance. The population with a small particle size of about 3.2 nm average size is responsible for the low-temperature ZFC maximum at $T_{max} = 28$ K, also confirmed by the other magnetic studies. The population with a large particle size of about 10 nm average size determines the high-temperature ZFC-FC irreversibility behaviour due to strong interparticle interactions that induce a spin-glass-like ordering of nanoparticle magnetic moments.

As found by *Ychianagi et al.* [25], the synthesis of CFO in the SiO₂ matrix by wet-chemistry method followed by annealing at $T_A = 873 - 1123$ K promotes particle growth from 2.2 nm to 4.9 nm. The CFO cores are within the regime of single domains with spin fluctuating with thermal energy at the blocking temperature T_B , which is increased from 154 K to 312 K with the crystallization process. The wet impregnation route was adopted by *Parma et al.* [26], who used mesoporous silica as a support matrix for CFO. Such pores play a role in nanocomposite-controlled growth of embedded NPs achieving 3 nm sized distributed in 20-60 nm amorphous SiO₂. The blocking process was noted below $T_B = 177$ K with a slight hysteresis at room temperature ($H_C = 5$ mT). The divalent cobalt in the octahedral lattice site is a source of CFO high anisotropy. Considerable anisotropy in cobalt-based nanocomposites is dependent on several factors: (i) particle size, (ii) cobalt content, (iii) cobalt inversion degree in the spinel lattice, (iv) chemical state of iron and (v) the magnetic order and disordered magnetic structure of NPs surface. In the considered small-sized CFO, the surface defect dominates the overall sample anisotropy.

The hollow microcapsules made of silica-coated CFO made by co-precipitation followed by the sol-gel method were tested by *Lyubutin et al.* [27]. Additionally, the Poly(MMA-co-MAA) was used as a core template and was entirely removed by annealing at 450°C. The hollow CFO/SiO₂ size was tuned by heat treatment from 300 to 900°C. As found, the inversion degree in the spinel lattice is linked to the annealing process, but its average value is close to the bulk CFO. The magnetic structure changes over the annealing process were clearly noted from low-temperature antiferromagnetic (AFM) to high-temperature ferromagnetic (FM) with increased magnetization. The small-sized CFO did not reveal SPM behaviour but the transit to the paramagnetic state by the so-called jump-like first-order magnetic transition (JMT) as for isolated materials. The effect of annealing in the range of 700-900°C was also verified by *Omelyanchuk et al.* [28], who employed the sol-gel auto-combustion type of synthesis. Such an annealing range is reflected in the 2.5 – 6.6 nm-sized CFO particles, and such a distribution affects the blocking process with T_B between 18-29 K. Nonetheless, a size distribution is noted in the magnetic properties with evident irreversibility temperature as a blocking effect for larger particles with maximum anisotropy. As manifested, the slight crystallization process reduced the effective anisotropy constantly where the surface disorder ceases to play a dominant role as for smaller NPs. Thus, a core structure with cation distribution and spin canting behaviour affects the magnetocrystalline anisotropy. Therefore, the overall anisotropy solidifies the core and the size distribution, which can be controlled by heat treatment. *Katayanagi et al.* [29] utilized the wet chemistry method to fabricate Co_{1-x}Mg_xFe₂O₄ of about 4.5 nm sized embedded in a SiO₂ matrix. The further functionalization by thiol groups enabled the NPs to bind to maleimide proteins as expected theranostic agents. The nanoparticles are single domains with SPM behaviour. As was found, the increase of Mg content, which is an advantageous element for MR signalling, reduces the saturation magnetization. A variety of CFO-based nanomaterials in silica matrix produced mainly by sol-gel method were tested by *Dippong et al.* [30-33]. The applied heat treatment, usually in the range of 400 -1200°C for 4 h or 6 h, allows to determine the crystallization process versus annealing temperature and to find optimal conditions for synthesis for single-phase nanoparticles with narrow size distribution. As seen [31, 33], the crystallization process started above 800°C, leading to particle growth from about 3 nm to around 13 nm. Such an effect is directly linked to coercivity and magnetization rise, meaning that the low crystallinity influenced the low saturation magnetization. The estimated particle size spherical and shape is usually below the SPM limit. In addition, the spin disorder at the surface was revealed. The applied concentration CFO and

SiO₂ ratio is adopted as 40%:60%. The MnFe₂O₄ doped with divalent cobalt stabilizes the spinel phase, improving structural and morphological properties. The reduction of crystallite and particle size from 45 nm to 15 nm over doping influenced the drop in porosity. Moreover, the samples change colours over doping, and as claimed by the authors such, an effect can be suitable as pigment for ceramic tiles. The percentage content of silica in xCoFe₂O₄/(100-x)SiO₂ composite with x = 10, 30, 50, 70 and 90 [31] fabricated by sol-gel method, followed by annealing in 1100°C revealed the single spinel ferrite structure for all samples. The magnetic CFO nanoparticles have spherical shapes and sizes in the 6–35 nm range. The saturation magnetization and coercivity expressed a linear dependence on the mean crystallite size. In addition, M_s increases with the increase of CFO concentration in the silica matrix. As demonstrated by Mössbauer studies, Fe³⁺ and Co²⁺ occupy tetrahedral and octahedral sites. The overall performed analyses pointed out that nanocomposite with x = 30 % manifests promising advantages in thermo-drug delivery and hyperthermia applications as the wasp-waist shape of the hysteresis curve gives better heating efficiency than conventional superparamagnetic systems. Furthermore, x = 50, 70 and 90 % nanocomposites are considered as promising candidates for high-frequency recording materials due to their high coercivity and moderate magnetization. The percentage modification of SiO₂ content from $\delta = 0$ to 100% in doped (Co_{0.6}Mn_{0.4}Fe₂O₄) _{δ} SiO_{2(100- δ)} nanocomposites [32] is reflected in the crystallite and particles change from 2 nm to 74 nm with the raise of ferrite content in the nanocomposite. Additionally, the magnetism is tuned in a two-fold way, once by changing the ferrite content and twice by selecting the annealing temperature. Thus, the M_s and anisotropy constant increase with T_A and the raise in ferrite size.

The thermal decomposition synthesis method was adopted by *Daboin et al.* [34], who additionally functionalized CFO with PVP, cetyl trimethyl ammonium bromide and polyethylene glycol (PEG) as a dispersing agent and modified the surface by SiO₂. As expected, the type of dispersing agent used affected the structure and magnetic properties. Thus, the surface effects are critical in determining the structural and magnetic performance. Therefore, the control of the surface effect can tune the magnetic properties at the nanoscale. So, the size can be modified from 6 nm (CFO) to 65 nm (CFO/PEG/SiO₂), which is reflected in the drop of saturation magnetization from 65.9 emu/g to 0.16 emu/g and coercivity from 200 Oe to 6 Oe for CFO and CFO/PEG/SiO₂ nanomaterials respectively. In other words, the surface anisotropy determines the overall anisotropy and becomes smaller, with the coating influencing the coercivity. The CFO/SiO₂ composites were also tested by *Yakob et al.* [35] as materials for the photodegradation of methylene blue. The smaller optical band compared to pure CFO was

1 explained as smaller surface defects and larger particle size influencing the efficiency of the
2 photodegradation process. The authors expected the application as nanocatalyst and
3 nanoabsorbers prospective materials for organic pollutants. *Blanco – Gutierrez et al.* [36]
4 utilized the solvothermal method to synthesize $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanoparticles with a 30/70 %
5 ratio. The particle size 2 - 17 nm was tuned by annealing at $T_A = 500 - 1000^\circ\text{C}$ of different times
6 12 - 96 h. As manifested, the CFO samples are characterized by high anisotropy values, while
7 the silica matrix avoids all kinds of particle interactions that modify the magnetic behaviour. In
8 this way, in 2 – 5 nm embedded Co-based nanoferrites, the almost constant H_C value indicates
9 that interactions between surface spins of different particles are absent for this particle size
10 range. Furthermore, it was observed that the coupled-moment carrier proportion remains almost
11 invariable regardless of the presence of the silica matrix, according to the nonmagnetic layer
12 3.2 Å thickness. The blocking temperature is raised with the particle size, which is an effect of
13 the surface-to-volume ratio.

23 The Mn-substituted CoFe_2O_4 nanoparticles dispersed in a SiO_2 matrix ($\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4/\text{SiO}_2$) were synthesized by a sol-gel method by *Hua et al.* [37]. The lattice constant
24 increased with increasing Mn^{2+} content because of the substitution of divalent cobalt ions with
25 a small ionic radius of divalent manganese ions due to a larger ionic manganese radius, which
26 in spinel lattice mitigates to the B site. The average crystallite size increased with increasing
27 annealing temperature selected by the authors in the $700 - 1110^\circ\text{C}$ range. The optimal T_A
28 temperature was found above 700°C , where the samples exhibit pure cubic spinel structure. As
29 manifested, the saturation magnetization, coercivity and hyperfine fields increase with
30 increasing manganese up to $x \leq 0.2$, and the subsequent decrease of mentioned parameters is
31 attributed to the cations distribution. A similar increase in magnetic performance was also noted
32 with the rise of T_A where the sample transfers from the mixed state of superparamagnetic and
33 magnetic order to the completely magnetic order associated with the migration of Mn^{2+} ions
34 from the tetrahedral A sites to octahedral B sites. The increase of the hyperfine field was
35 explained as a replacement for lower magnetic moment Co^{2+} by Mn^{2+} with larger magnetic
36 moment, while the as a spin canting effect.

51 The sol-gel auto-combustion method was utilized by *Jummaa et al.* [38] to fabricate
52 CFO/ SiO_2 ferrite nanocomposites with variable content of $\text{SiO}_2 = 0, 20, 40, 60\%$. The impact
53 of heat treatment (up to $T_A = 700^\circ\text{C}$) was also analyzed versus the percentage of ferrite. Thus,
54 depending on the calcination temperature, the CFO crystallite size changes from (33.46 - 46.50
55 nm) and hopping length from (3.625 - 3.614 Å), whereas depending on the SiO_2 mixing ratio,
56

crystallite size changes from (46.50 - 49.05 nm) and hopping length from (3.627 - 3.628 Å). The performed magnetic analysis revealed that samples displayed ferrimagnetic behaviour at various calcination temperatures and SiO₂ mixing ratios. At $T_A = 700^\circ\text{C}$ the maximum saturation magnetization (M_s) value was found to be 70.335 emu/g. The analyzed dielectric factors decreased with frequency due to electron hopping between Fe²⁺ and ferric Fe³⁺ ions.

Besides potential drug delivery systems, the Co-based ferrites combined with silica matrix can be tested for other applications. *Racik et al.* [39] utilized the sol-gel method to produce the magnetic CoFe₂O₄/SiO₂, potentially applied as supercapacitors. The synthesized material was found to be polydispersed with a nearly hexagonal plate-like shape of nanoparticles having around 50 nm in size. Silica matrix reduced magnetism to $M_s = 11.84$ emu/g and $H_C = 74.25$ Oe. The specific capacitance of tested composites is 316.14 F/g, significantly higher than their single counterparts. What is more, CoFe₂O₄/SiO₂ exhibits 95.4 % retention capacitance at a current density of 1 A/g after 5000 cycles. Such a hybrid electrode has an unusual synergistic effect, which increases electron transfer efficiency. Thus, the samples attribute the inherent electrocatalytic activity as a result of the efficient engineering at the interface between the two CoFe₂O₄ and SiO₂ phases. Such parameters enable the cost-effective composite to be used as potential electrode materials for high-performance energy storage devices.

Considering the perspective applications of CFO@SiO₂ nanocomposites, our paper fits into the trend of fundamental research focused on spinel ferrites-based nanoparticles embedded into biocompatible silica shells. Thus, the current paper aims to annealing - driven the structural, microstructural and magnetic evolution of the CoFe₂O₄@SiO₂ core-shell composite. To achieve this goal, we have utilized a complementary multi-technique analysis. The deepened studies of the electronic structure by photoemission spectroscopy and using the synchrotron radiation for absorption spectroscopy correlated with structural microstructural and magnetic properties is the key novelty part of presented data compared to other research for CoFe₂O₄@SiO₂ nanomaterials. The clear evidence of the Si-O-Ni/Fe intermixing on the interface between CFO and SiO₂ nanoparticles was confirmed by electronic structure analysis employing X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) by synchrotron radiation.

2. Experimental Section

2.1. Synthesis

The core-shell $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ ($\text{CFO}@\text{SiO}_2$) nanoparticles were synthesized two-fold by microemulsion preceded by a co-precipitation process. Thus, the CFO nanoparticles were first synthesized by co-precipitation from metallic salts, which were weighed in a 1:2 molar ratio according to the stoichiometric formula. A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (291.03 g/mol, 5.821(1)g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($M = 270.3$ g/mol, 10.812(1)g) with purity higher than 99%, from Aldrich, were prepared in 60 ml distilled water. This solution was poured as quickly as possible under vigorous stirring to the hot alkaline solution (90°C) of NaOH (300 ml to 1.33 mol/l) and subsequently stirred for 90 minutes and cooled down to the ambient temperature. The CFO powder was washed by using diluted HNO_3 aqueous solution (100 ml, 10%vol HNO_3 65%) for 15', followed by the addition of acetone before centrifugation (8000 rpm, 10', 10°C) and finally dispersed in distilled water (80 ml). Then the $\text{CFO}@\text{SiO}_2$ nanocomposite was synthesized based on our previous results on functional silica prepared by the microemulsion process [40-44] using high-purity heptane, surfactant Polyoxyethylene(4)lauryl ether (Brij™30-27.4 mL), TEOS (4 mL) from Aldrich and ammonia 28% (2.5 mL) from Merck laboratory.

Afterwards, the synthesized as-received core-shell samples were annealed in furnace Elite TSH15/50/180-2416CG at selected temperatures $T_A = 200, 400, 500, 600, 700, 800^\circ\text{C}$ at the ambient atmosphere. First, powdered as-received samples were placed directly into a ceramic vessel and inserted in the furnace. They were heated from the room to a set temperature with a $10^\circ\text{C}/\text{min}$ slope. The maximum set temperature remained stable for 2 hours. Afterwards, the annealing process was turned off, and the samples were slowly cooled in the oven.

2.2. Characterization

The crystal structure of synthesized $\text{CFO}@\text{SiO}_2$ composites was revealed using the X-ray Powder Diffraction (XRPD) method employing the Empyrean PANalytical diffractometer (Malvern Instruments, Malvern, UK). The Co X-ray source ($K_{\alpha 1}$ of $1.1789 \text{ \AA}$) was selected to avoid the X-ray fluorescence. The Bragg-Brentano geometry θ - 2θ in the 2θ range of $10^\circ - 100^\circ$ with a step of 0.067° was set up. To determine the size of the diffraction coherent domain and strain, a calibration sample LaB_6 was used. The XRD patterns were processed and analyzed in the HighScore software (Version 4.9) [45].

The Scanning Transmission Electron Microscopy (STEM) studies with Jeol JEM 2100 HR were performed for as-received samples and those annealed at $T_A = 600^\circ\text{C}$ and 800°C . The resolution of the STEM option was 1 nm, the applied accelerating voltage was 200 kV, and an energy-dispersive (EDS) detector was an Oxford X-Max 80T silicon drift detector (SDD). The

1 Jeol BF/HAADF (Bright Field / High Angle Annular Dark Field) detectors were used. The
2 sample annealed at $T_A = 400^\circ\text{C}$ was studied with Transmission Electron Microscopy (TEM)
3 using Jeol JEM 3010 with high-resolution mode (HRTEM). The applied accelerating voltage
4 was 300 kV, and the EDS detector was EDAX SSD EDS Elite-T. Both apparatuses were
5 equipped with an LaB_6 electron source with a line resolution of 1.4 Å and point resolution of
6 2.3 Å and 1.7 Å for the first and second mentioned apparatus, respectively. Before the
7 measurement, the powdered sample was suspended in ethanol and placed in the ultrasonic
8 washer for 5 minutes or 10 minutes (for the first and second apparatus, respectively) to fracture
9 agglomerates. Next, a few drops of the suspension were placed on the carbon-coated Cu grid
10 (300 mesh for the first and second apparatus). As usual, TEM and HRTEM images were
11 recorded for multiple regions of interest (ROI).
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20 The structural characterization of cobalt ferrite cores encapsulated with silica shells, along
21 with composites sintered at 200, 400, 600, and 800°C , was performed using a WITec confocal
22 Raman microscope (CRM alpha 300R). A solid-state laser with a wavelength of 457 nm was
23 coupled to the microscope through a single-mode optical fibre (50 µm diameter) and focused
24 onto the sample using an Olympus MPLAN air objective (50x/0.76 NA). Scattered light was
25 collected through a multi-mode optical fiber (50 µm diameter). Calibration of the spectrometer
26 monochromator, equipped with a 600 lines/mm grating, was validated prior to measurements
27 using a silicon standard (520.7 cm^{-1}).
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35 Raman spectra were acquired ten times independently, with each acquisition consisting of
36 20 scans at an integration time of 20 seconds per scan and a spectral resolution of 3 cm^{-1} . Post-
37 processing steps, including cosmic ray removal and baseline correction, were carried out using
38 WITec Project Five Plus software. Advanced spectral analysis using Gauss-Lorentz band fitting
39 was performed with the Grams 9.2 software package to extract critical parameters such as peak
40 position, area, and full width at half maximum (FWHM) for the vibrational features of the
41 cobalt ferrite core and silica shell. This analysis provided valuable insights into the structural
42 evolution of the materials, highlighting the influence of the silica shell and the overlapping of
43 vibrational bands with cobalt ferrite as a function of sintering temperature.
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51 All X-ray Photoemission Spectroscopy (XPS) results were obtained at room
52 temperature by the use of PHI 5700/600 (Physical Electronics Inc., Eden Prairie, MN, USA)
53 spectrometer equipped with monochromatic X-ray source $\text{Al K}\alpha$ (1486.6 eV). The sample was
54 fixed into the sample holder by double-coated conductive carbon tape and subsequently stored
55 under an ultra-high vacuum for a week. Next, the XPS measurement was performed in two
56 consecutive steps. In the first one, the as-prepared material was studied directly after its storage.
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1 Afterwards, the same specimen was sputtered by an Ar^+ ion beam for 30 min with an energy
2 beam of 1.5 keV prior to measurement in the main chamber. All the XPS spectra obtained were
3 calibrated using the C1s peak (BE = 284.8 eV) as carbon peak as a reference to charge
4 correction. All spectra measured were processed in the MultiPak 9.8 software. The selected
5 XPS core level lines were analyzed after Ar^+ treatment for 30 min and deconvoluted by the
6 Gauss-Lorentz function and Shirley background type. The overall XPS analysis was done for
7 three selected samples, namely as-received annealed at $T_A = 400$ and 800°C .
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10 The electronic structure was also measured at the National Synchrotron Radiation
11 Centre SOLARIS [46] using the PHELIX and PIRX beamlines [47] at room temperature. In
12 PHELIX, the radiation source is based on an elliptically polarizing undulator (EPU), APPLE II
13 type, with permanent magnets. The photon energy range is between 50-1500 eV. The X-ray
14 absorption (XAS) spectra were acquired in a Total Electron Yield (TEY) mode. Prior to XAS
15 analysis, all samples were prepared similarly; a small amount of powder was stuck in a flux-
16 style holder by a double-coated carbon tape. Additionally, the XAS data was acquired by a
17 PIRX beamline with a bending magnetic radiation source with photon energy 100–2000 eV. In
18 this case, the XAS spectra were obtained in two detection modes, total electron yield (TEY)
19 and partial fluorescence yield (PFY), which differ in the sampling depth. The beam size
20 (FWHM) at the sample was $160\ \mu\text{m} \times 40\ \mu\text{m}$ (h x v). Photon energy calibration was done on a
21 reference sample of Fe_2O_3 , stored under UHV conditions. The peak at Fe L3 edge of 708.30 eV
22 was used as the reference standard, which was determined with the accuracy of ± 20 meV.
23 Spectra acquired by PHELIX and PIRX beamlines were normalized to the simultaneously
24 measured current of the last optical element (mirror) of the beamline before the measurement
25 chamber. Afterwards, all acquired XAS spectra by PHELIX and PIRX beamlines were analyzed
26 and processed by PyMca 5.9.2 software.
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29 The magnetic properties were determined using the wide-range Physical Property
30 Measurements System (PPMS) (Quantum Design Inc., San Diego, CA, USA). The thermal
31 dependence of DC magnetization was collected in the zero-field-cooled (ZFC) and the field-
32 cooled (FC) modes at the external field of 100 Oe in the temperature range from 5 to 350 K,
33 while the isothermal magnetic curves $M(H)$ were recorded at 5 K, 100 K, and 300 K.
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36 Mössbauer spectrometry (MS) measurements were carried out to investigate the
37 dependence of the annealing process on the magnetic order, cation distribution and hyperfine
38 structure of iron atoms in the sample. The spectra were collected with standard transmission
39 geometry using a ^{57}Co source in a Rh matrix and a constant acceleration spectrometer at room
40 temperature (approximately 300 K) and liquid nitrogen temperature (77 K). Regular (on
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average once-a-week) calibration was performed using a pure α -Fe sample. The hyperfine parameters were refined by using the MOSFIT program [48].

3. Results and discussion

3.1. Crystal structure

The XRPD studies of CFO@SiO₂ composites, contrary to previously analyzed NFO@SiO₂ [41], indicate crystal structure for all measured samples, even in as-received form, as presented in Fig.1a. The crystal structure was refined in the HighScore Plus software, and the refined data are placed in Table Ia. The structure was assumed as a mixed spinel structure with a cations distribution in A-tetrahedral and B-octahedral sites as (Co_{0.36}Fe_{0.64})^A[Co_{0.64}Fe_{1.36}]^BO₄, and the occupancy was not refined during the Rietveld refinement procedure. In Fig.1b, the selected refined XRPD patterns are depicted. Please note that the hump of amorphous silica was included in the background to isolate the peaks originating from the CFO phase. Then, the position and profile of individual peaks were determined, and the appropriate phase was matched from the database Cobalt Diiron(III) Oxide CoFe₂O₄ - ICSD:109044). It should be noted that the value of the area of peaks located on the hump may be underestimated. However, the method was sufficient for determining and comparing the parameters mentioned in this work.

The prominent diffraction peaks can be indexed by the cubic CFO structure with the space group $Fd\bar{3}m$, lattice parameter $a = 8.3940$ Å and X-ray density 5.27 g/cm³ (ICSD:109044). In addition, the amorphous SiO₂ phase is also visible as broad peaks, as in the case of NFO@SiO₂. There is no trace of silica crystallization over the annealing process, meaning that SiO₂ remains stable and amorphous. The variation of the lattice parameter of spinel ferrite structure versus annealing temperature a (T_A) shows non-linear dependence (see Table Ia). The estimates a values indeed suggest the existence of inverse spinel ferrite CFO structure, although for middle annealing stages ($T_A = 200^\circ\text{C}$, 400°C and 500°C), the calculated values are lower compared to the literature. The calculated crystallite size and lattice strain showed the opposite trends. So, the crystallite size $d_{cryst}^{Rietveld}$ is raised with annealing temperature from 12.3 ± 1.2 nm (as-received) to 16.6 ± 0.9 nm ($T_A = 800^\circ\text{C}$), which enhances the crystallization process, whereas the strain tends to decrease. Such an effect may indicate the relaxation of the crystalline phase. A similar tendency for CFO@SiO₂ was observed by Lyubutin *et al.* [27], who found a CFO size from 2.2 to 10.2 nm in the temperature range from 300 to 900°C. Such a crystallization process driven by annealing was also observed, e.g. by Dippong *et al.* [30-33] and Hua *et al.* [37]. Moreover, the crystallization of CFO is not only

manifested in CFO@SiO₂ composites but also in pure annealed CFO [4-17]. However, in such a scenario, the grain growth is more intensive under the same applied temperatures, e.g. 46.5 nm $T_A=700^\circ\text{C}$ observed by *Grigorova et al.* [12], 25.4 nm sized CFO noted by *Abraime et al.* [13] for sol-gel auto-combustion (SGA) NPs annealed at $T_A = 600^\circ\text{C}$ or significant growth from 9 to 61 nm under $T_A = 300\text{-}900^\circ\text{C}$ annealing range observed by *Pal Singh et al.* [15]. Thus, it seems that for CFO@SiO₂ core-shell nanostructures, the protective role of silica prevents an excessive crystallization process, which is significant in the magnetic interactions between encapsulated nanoparticles.

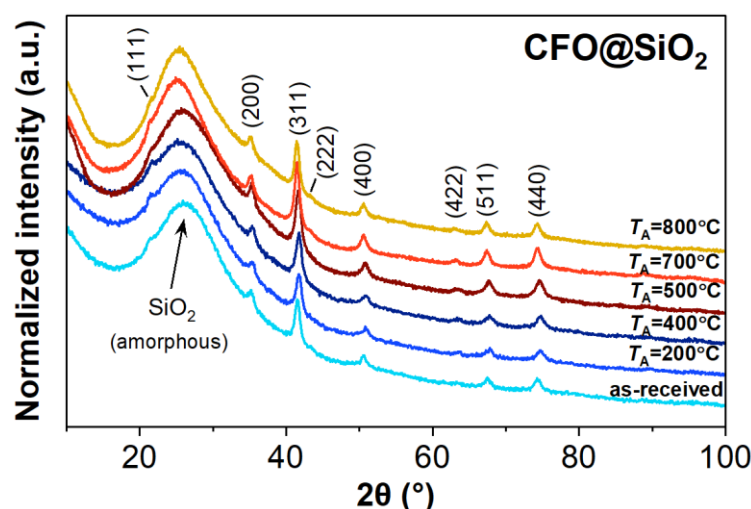


Fig.1a. The evolution of XRPD patterns for CFO@SiO₂ versus annealing temperature T_A .

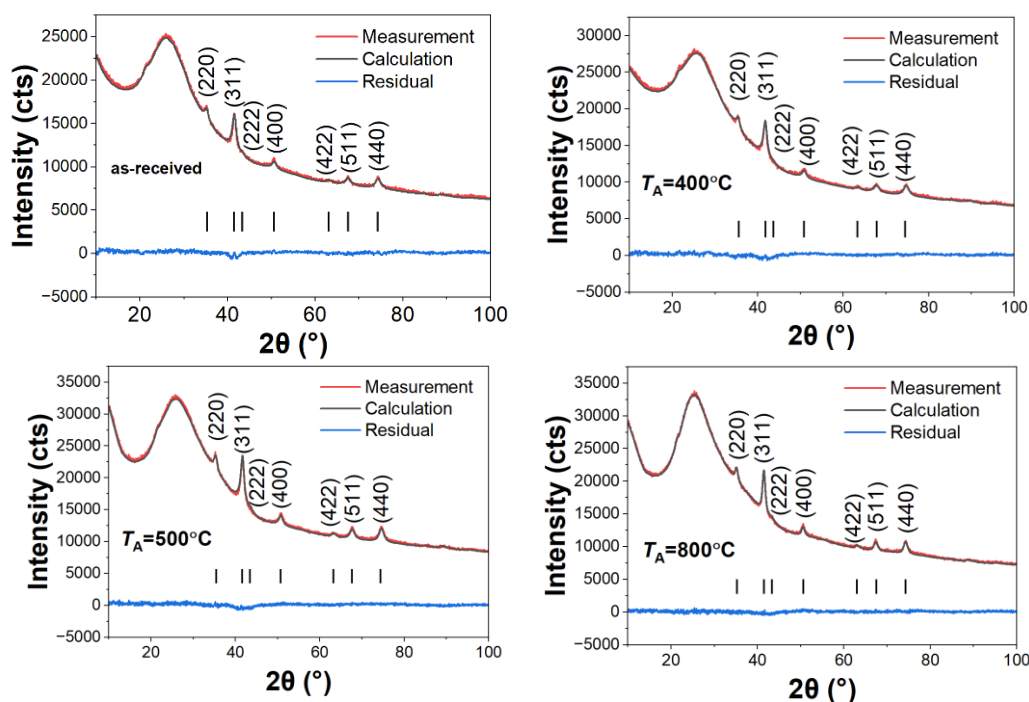


Fig.1b. Exemplary results of Rietveld refinement for CFO@SiO₂ sample as received and annealed at $T_A=400, 500$ and 800°C .

The calculated specific surface area (S) was estimated considering the values obtained from the Rietveld refinement $d_{cryst}^{Rietveld}$ and ρ_{X-ray} based on equation:

$$S = \frac{6}{d_{cryst}^{Rietveld} \times \rho_{X-ray}} \quad (1)$$

The analysis of the obtained data, which is placed in Table Ia, exhibits slight modifications of specific surfaces with the annealing temperature. Nonetheless, a decreasing trend with T_A can be noticed. A similar effect was found by *Caldeira et al.* [9], who revealed the drop of such parameter estimated by the BET method in the annealing range 550-750°C from 19 m²/g to 5 m²/g in relation to the annealing time in specific T_A .

Table Ia. Refined crystal structure parameters for the CFO@SiO₂ samples.

Phase CoFe ₂ O ₄ cubic $Fd\bar{3}m$		Wyck	x	y	z	B _{iso}	Occ.
	O1	32e	0.249	0.249	0.249	0.5	1
	FE1	16c	0	0	0	0.5	0.68
	CO1	16c	0	0	0	0.5	0.32
	FE2	8b	0.375	0.375	0.375	0.5	0.64
	CO2	8b	0.375	0.375	0.375	0.5	0.36
Analyzed samples	as-received	Annealed at T_A (°C)					
		200	400	500	700	800	
Lattice parameter a (Å)	8.3909 ±0.004	8.3528 ±0.0028	8.3559 ±0.0026	8.3640 ±0.0012	8.3880 ±0.0009	8.3899 ±0.0014	
Volume of the unit cell V (Å ³)	590.78 ±0.7	582.78 ±0.59	583.42 ±0.53	585.11 ±0.26	590.16 ±0.19	590.56 ±0.29	
Crystallite size $d_{cryst}^{Rietveld}$ (nm)	12.3 ±1.2	11.6 ±1.0	12.2 ±1.0	13.2 ±0.6	14.5 ±0.5	16.6 ±0.9	
Strain ε (%)	0.62 ±0.08	0.53 ±0.08	0.53 ±0.07	0.45 ±0.04	0.29 ±0.03	0.37 ±0.04	
X-ray density ρ (g/cm ³)	5.28	5.35	5.34	5.33	5.28	5.28	
Specific surface area S (m ² /g)	92 ± 9	97 ± 8	92 ± 8	85 ± 4	78 ± 3	68 ± 4	
R_{Bragg} factor (%)	1.03	1.5	1.25	1.47	0.61	0.87	

The amorphous SiO₂ structure present in all analyzed samples obfuscates the structural information of the spinel ferrite phase. Therefore, in further analysis of CFO nanoparticles encapsulated in SiO₂ shells the Nelson-Riley extrapolation was adopted, first to determine the lattice parameter a corresponding to (hkl) planes for cubic lattice,

$$a = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2} \quad (2)$$

where λ is the wavelength Co-K α :1789 Å, the Nelson-Riley function $F(\theta)$ was used [16, 50] instead of the angle θ :

$$F(\theta) = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \quad (3)$$

From the error-minimized lattice constant, a , the X-ray density was estimated as:

$$\rho = \frac{8M_w}{Na^3} \quad (4)$$

where M_w the molecular weight of CoFe_2O_4 (234.6208 g/mol) and N is the Avogadro constant ($6.022 \times 10^{23}/\text{mol}$). The obtained lattice parameter values were subsequently employed in further calculations and discussions.

To determine the crystallite size, we have employed three models based on XRPD line profiling. First, we selected the (311) peak as the dominant one in the CFO crystal structure. During the adopted line profiling procedure, we used the Co K incident line doublet and the Pseudo-Voigt line shape function, which was weighted by parameters. The refined FWHM and 2θ values were subsequently employed to determine the crystallite size using the Scherrer formula:

$$d_{cryst}^{Scherrer} = \frac{K\lambda}{\beta_{hkl}\cos\theta} \quad (5)$$

where to calculate the $d_{cryst}^{Scherrer}$ value of CFO, the incident X-ray wavelength λ (here the Co K_α line), the Scherrer constant $K \approx 0.89$ for spherical particles and the total β_{hkl} full width at half-maximum (FWHM) containing the measured full width at half maximum β and $\beta_{inst} = 0.08504$ is the instrumental broadening determined using LaB_6 calibration sample as:

$$\beta_{hkl}^2 = \beta^2 + \beta_{inst}^2 \quad (6)$$

For comparison, as the second model, we selected the Williamson-Hall (WH) approach, which was adopted to estimate the associated microstrain. The effective crystallite size d_{cryst}^{WH} and the intrinsic strain ϵ_{WH} were calculated using a modified WH method known as the uniform deformation model (UDM) [16]. Based on UDM, the crystal structure imperfections lead to microstrains, and the strain-induced peak broadening of XRPD can be expressed as:

$$\beta_{hkl} = 4\epsilon \tan \theta_{hkl} \quad (7)$$

As a consequence the peak broadening resulting from the size and strain is described as:

$$\beta_{hkl}\cos\theta_{hkl} = \frac{k\lambda}{d_{cryst}^{WH}} + 4\epsilon_{WH} \sin \theta_{hkl} \quad (8)$$

The plots of $\beta_{hkl}\cos\theta_{hkl}$ versus $\sin \theta_{hkl}$ should be approximated by a straight line, where the slope and intercept of the linear fit give an estimation of microstrain ϵ_{WH} and crystallite size d_{cryst}^{WH} , respectively. The exemplary WH method approximation is shown in Fig.2. All the values of crystallite size are compared in Table Ib. As one may notice, the different methods lead to slightly different crystallite size values. Those from Rietveld refinement are comparable to the applied Scherrer equation, while the Williamson-Hall approach may give more insight into crystal structure imperfections, noted especially for smaller diffraction angles [51, 52]. If

the WH model does not have a satisfactory linear approximation to solve such problems for spinel ferrites, the size-strain (SSP) model is successfully employed [53], enhancing the lower-angle reflections.

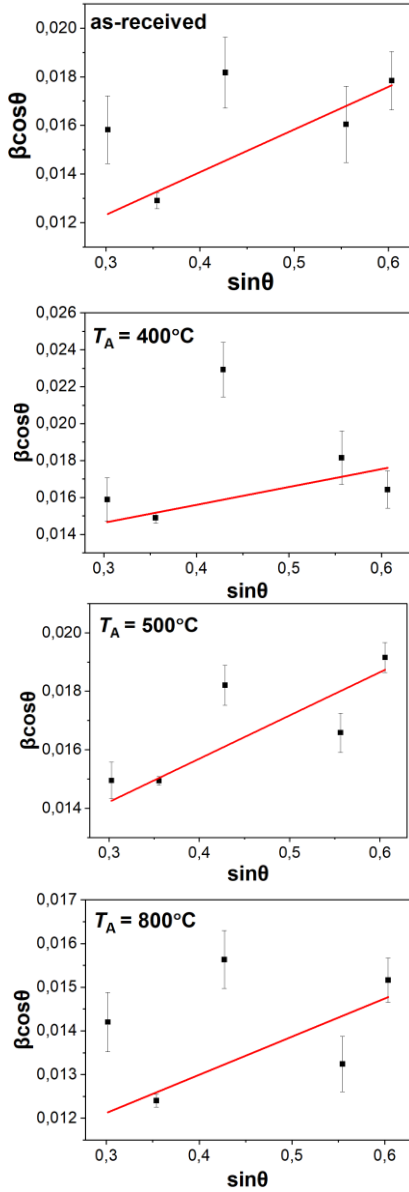


Fig.2. The application of the WH model for selected CFO@SiO₂ core-shell composites.

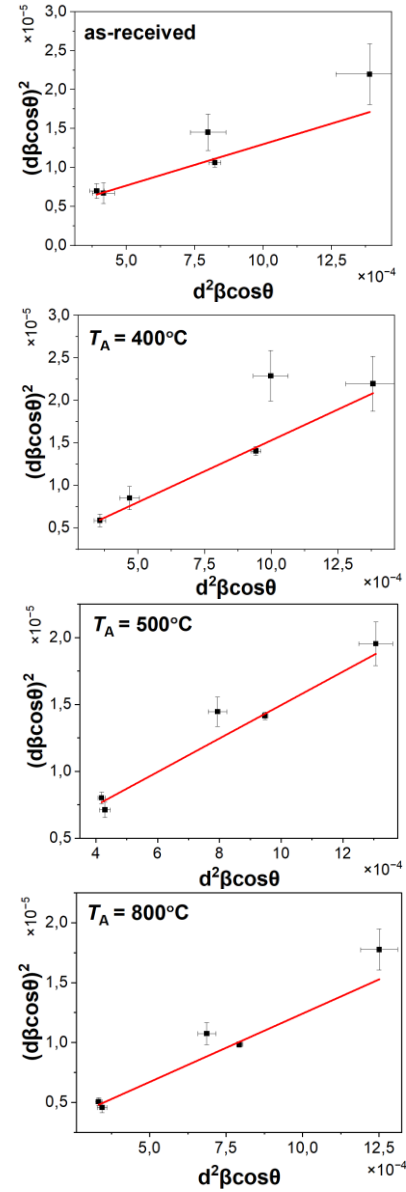


Fig.3. The application of the SSP model for selected CFO@SiO₂ core-shell composites.

According to the SSP model, the total XRD peaks broadening is defined as follows:

$$(\beta_{hkl} \cos \theta_{hkl})^2 = \frac{k\lambda}{d_{cryst}^{SSP}} (\beta_{hkl} \cos \theta_{hkl}) + \frac{\varepsilon_{SSP}}{4} \quad (9)$$

Thus from linear approximation plots by SSP model shown exemplary in Fig.3 the d_{cryst}^{SSP} and ε_{SSP} can be determined. The obtained values are in good agreement with previously utilized models. The comparison between crystallite size versus annealing temperature estimated by all models is depicted in Fig.4. As seen, all the methods show a similar trend with a slight increase

in d_{cryst} driven by annealing. However, it should be emphasized that for $T_A = 400^\circ\text{C}$, the estimated value exhibits a minimum, which is in correlation with other crystal structure parameters. Probably at this annealing stage, there is a mixture of small and larger crystallites that leads to non-uniform microstructural performance.

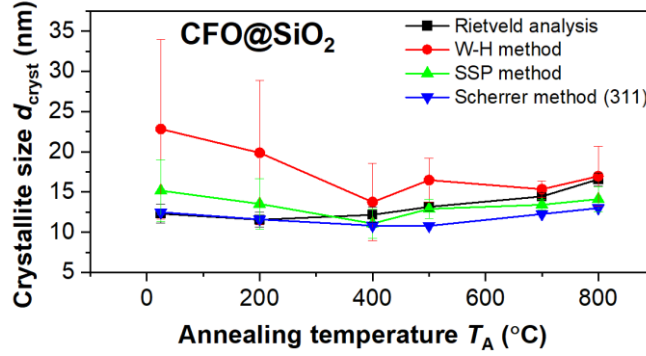


Fig.4. The comparison of the d_{cryst} values versus T_A obtained by Rietveld analysis, Scherrer method, Williamson-Hall (WH) and size strain (SSP) models.

The cation distribution can be obtained from the error-minimized lattice parameter by applying the Nelson-Riley extrapolation. The distribution of cations in the A-tetrahedral and B-octahedral sites in a CFO spinel structure can be expressed as:

$$(Co_{\delta}Fe_{\delta-1})^A[Co_{1-\delta}Fe_{1+\delta}]^BO_4 \quad (10)$$

where δ is a constant which decides the inversion parameter or degree of inversion $(1-\delta)$ in the mixed spinel ferrite structure, where cations (Co^{2+} and Fe^{3+}) in nanoparticles are randomly distributed between the A and B sites with the inversion parameter having values dependent on the applied synthesis type [18, 54]. As known for ideal cases δ is zero for inverse spinels and one for normal spinels, which is not the case for CFO nanoparticles. Thus, the mean crystal radii for the A and B sites are denoted by:

$$\begin{aligned} r_A &= \delta r_{Co} + (1 - \delta)r_{Fe} \\ r_B &= 1/2[(1 - \delta)r_{Co} + (1 + \delta)r_{Fe}] \end{aligned} \quad (11)$$

The crystal radii of appropriate ions in A and B sites are tabularized by *Shannon* [55] and in the current calculations are equal: at A site $r_{Co^{2+}}^A = 0.72 \text{ \AA}$ and $r_{Fe^{3+}}^A = 0.63 \text{ \AA}$, while at B site respectively, $r_{Co^{2+}}^B = 0.885 \text{ \AA}$ and $r_{Fe^{3+}}^B = 0.69 \text{ \AA}$, respectively. Therefore the average ionic radii per molecule at the tetrahedral (r_A) and octahedral (r_B) sites and can be estimated from the experimental value of the lattice constant by:

$$\begin{aligned} r_A &= a\sqrt{3}(u - 0.25) - R_0^A \\ r_B &= a\left(\frac{5}{8} - u\right) - R_0^B \end{aligned} \quad (12)$$

where R_o is the crystal radius of the oxygen ion equals 1.24 Å for A and 1.26 Å for B site, respectively, [16, 55] and a is the error-minimized lattice constant from Nelson-Riley approximation. The positional anion parameter, u , for nanocrystalline CFO spinels, is reported to be equal to 0.381 [16, 55]. Considering the above-mentioned (11) and (12) equations, the inversion parameter was calculated versus sample processing, and subsequently, the cation distribution in tetrahedral and octahedral sites was estimated (see Table Ib). As noted the cation distribution is different regarding the stage of sample processing. Thus, the inversion parameter δ is slightly modified over annealing. As known, the cation distribution is strictly related to the synthesis type. *Lyubutin et al.* [27] noted the change of δ from 0.62 to 0.76 in the T_A range from 300 to 900°C. Similar increase was estimated by *Hunpratub et al.* [20] for pure CFO synthesized by co-precipitation method at various pH from 9 to 14. In this case the inversion parameter was found in the range of 0.25 to 0.31. The migration of Fe^{3+} and Co^{2+} between sites in the crystal lattice is linked to the particle size and the highest migration of divalent cobalt from B to A site was found for pH = 11. The effect of increasing Fe^{3+} at the A site with simultaneous decrease in B site tuned by annealing from 300°C to 900°C was also observed by *Pal Singh et al.* [15] tested cation distribution in CFO by spectroscopic methods. Based on spectroscopic analyses it was found that the Co^{2+} occupancy at the A site is reduced with increased crystallite size. Thus in our case, the δ is reduced from 0.37 for as-received samples to 0.39 for $T_A=400^\circ\text{C}$ followed by further slight increase. Indeed, as manifested the reduced Co^{2+} occupancy at A sites is linked to the crystallites size raise (see Tables Ia and Ib) and further stabilization or crystallites size small growth seems to be also linked to the cations distribution. Similarly, the Fe^{3+} distribution in A site is raised to 0.71 in the temperature range $T_A= 200 - 400^\circ\text{C}$.

Table Ib. Crystal structure parameters were determined based on line profiling and using the Nelson-Riley extrapolation for the CFO@SiO₂ samples.

Annealing temperature T_A (°C)	Lattice parameter a (Å)	Density ρ (g/cm ³)	Crystallite size			Strain		Inversion parameter		Cations distribution
			$d_{Scherrer}^{cryst}$ (nm)	d_{cryst}^{WH} (nm)	d_{cryst}^{SSP} (nm)	ϵ_{WH} (%)	ϵ_{SSP} (%)	δ	$1-\delta$	
as-received	8.388 ± 0.006	5.2805 ± 0.0012	12.5 ± 0.4	23 ± 12	15.2 ± 4.0	0.44 ± 0.23	0.31 ± 0.26	0.37	0.63	$(Co_{0.37}Fe_{0.63})^A[Co_{0.63}Fe_{1.37}]^B O_4$
200	8.355 ± 0.003	5.3437 ± 0.0007	11.6 ± 0.3	20 ± 9	13.5 ± 4.0	0.43 ± 0.24	0.30 ± 0.28	0.29	0.71	$(Co_{0.29}Fe_{0.71})^A[Co_{0.71}Fe_{1.29}]^B O_4$
400	8.355 ± 0.003	5.3438 ± 0.0006	10.8 ± 0.3	14 ± 5	11.1 ± 1.9	0.24 ± 0.27	0.17 ± 0.50	0.29	0.71	$(Co_{0.29}Fe_{0.71})^A[Co_{0.71}Fe_{1.29}]^B O_4$
500	8.361 ± 0.003	5.3335 ± 0.0007	10.8 ± 0.2	16 ± 3	12.9 ± 1.3	0.37 ± 0.11	0.31 ± 0.12	0.30	0.70	$(Co_{0.30}Fe_{0.70})^A[Co_{0.70}Fe_{1.30}]^B O_4$
700	8.387 ± 0.002	5.2837 ± 0.0003	12.3 ± 0.2	15 ± 2	13.4 ± 0.7	0.19 ± 0.05	0.20 ± 0.08	0.37	0.63	$(Co_{0.37}Fe_{0.63})^A[Co_{0.63}Fe_{1.37}]^B O_4$
800	8.388 ± 0.004	5.2803 ± 0.0007	13.0 ± 0.2	17 ± 4	14.1 ± 1.6	0.22 ± 0.14	0.20 ± 0.17	0.37	0.63	$(Co_{0.37}Fe_{0.63})^A[Co_{0.63}Fe_{1.37}]^B O_4$

Based on the estimated lattice parameters, the hopping lengths L_{A-A} and L_{B-B} describing the distance between the magnetic ions in the A and B sites, can be calculated using the following formula [16, 56-59]:

$$L_{A-A} = a\sqrt{3}/4 \text{ and } L_{B-B} = a\sqrt{2}/4 \quad (13)$$

Further, the tetrahedral and octahedral bond length (L_{AX} and L_{BX}), tetrahedral edge (L_{AXE}), and shared and unshared octahedral edges (L_{BXE} and L_{BXEU}), can be calculated by the set of the following equations using $u = 0.381$ and the error-minimized lattice constant from Nelson-Riley approximation:

$$\begin{aligned} L_{AX} &= a\sqrt{3}/(u - 1/4) \\ L_{BX} &= a \left[3u^2 - \left(\frac{11}{4}\right)u + \left(\frac{43}{64}\right) \right]^{1/2} \\ L_{AXE} &= a\sqrt{2}/(2u - 1/2) \\ L_{BXE} &= a\sqrt{2}/(1 - 2u) \\ L_{BXEU} &= a \left[4u^2 - 3u + \left(\frac{11}{16}\right) \right]^{1/2} \end{aligned} \quad (14)$$

The values of L_{A-A} are higher than those of L_{B-B} , which can be explained by a less effective covalent bonding in the A site than in the B site. This tendency is preserved in all studied composites. By analyzing the hopping lengths, bond, and other estimated parameters as a function of annealing temperatures, we can deduce that such values are slightly reduced during heat treatment up to $T_A = 400^\circ\text{C}$, probably due to modifications in the distribution of cations in the two crystallographic sites.

Table Ic. Inter-ionic distances determined based on Nelson-Riley extrapolation for the CFO@SiO₂ samples.

Annealing temperature T_A (°C)	Tetrahedral hopping length L_{A-A} (Å)	Octahedral hopping length L_{B-B} (Å)	Tetrahedral bond length L_{AX} (Å)	Octahedral bond length L_{BX} (Å)	Tetrahedral edge L_{AXE} (Å)	Octahedral shared edge L_{BXE} (Å)	Octahedral unshared edge L_{BXEU} (Å)
as-received	3.63226	2.96573	1.90331	2.04799	3.10808	2.82337	2.96744
200	3.61790	2.95400	1.89578	2.03990	3.09580	2.81221	2.95570
400	3.61787	2.95398	1.89576	2.03988	3.09577	2.81219	2.95568
500	3.62020	2.95588	1.89699	2.04119	3.09776	2.81400	2.95758
700	3.63153	2.96513	1.90292	2.04758	3.10746	2.82281	2.96684
800	3.63232	2.96578	1.90334	2.04803	3.10813	2.82342	2.96748

3.2. TEM

The TEM micrographs for as-received and annealed samples reveal the typical core-shell structure. All particles are well dispersed and separated from each other, compared to

NFO@SiO₂ [41]. However, there are evident differences in the CFO core morphology comparing as-received and annealed samples. In the case of as-received nanoparticles, it is clear that CFO cores are formed of many crystallites distributed in silica shells. The acquired selected area electron diffraction (SAED) pattern reveals the amorphous structure of silica, as it was for NFO samples [31, 41], but there are also visible slight spots corresponding to (311), (400), (422), (511), (440), (620) and (731) planes of CFO (see Fig.5b). The HRTEM analysis revealed individual particles with CFO cores encapsulated inside a silica matrix. The distribution of CFO is not homogeneous, and one may notice smaller and larger nanoparticles with irregular shapes (see Figs.5c-d). The size of the visible single particle is around 47 per 41 nm with a cluster composed of two CFO cores of 22.4 per 11.1 nm sized. The performed FFT analysis on the selected CFO core marked by the green rectangle in Fig.5d shows several spots with the estimated interplanar distance d_{hkl} of about 4.4 Å resembles the (111) lattice plane. The measured local EDS from two regions indicates (see Fig.5f) the structure of CFO, silica, and additional elements: Cu, C, and Na, which come from the copper grid, surface impurity, and synthesis residuals, respectively. The examples of chemical composition maps (see Fig.5g) indicate the presence of CFO cores encapsulated within SiO₂, also proved by the line profile depicted in Fig.5h. However, as can be seen, not all shells are filled with CFO, which is also consistent with the TEM bright-field images. The size of nanoparticles estimated from the line profile is comparable to those previously shown in TEM images.

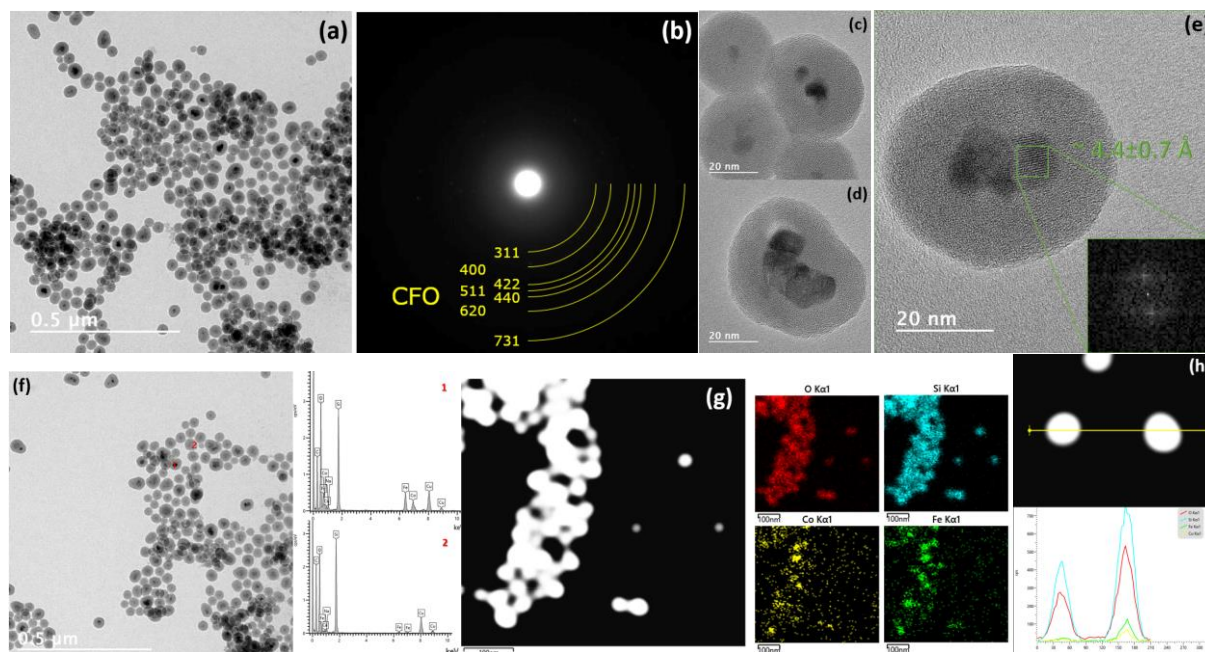


Fig.5. Microstructure of CFO@SiO₂ as-received nanoparticles: (a) bright field (BF) TEM image of agglomerated NPs; (b) SAED pattern; (c-e) HRTEM of individual core-shell nanoparticles with visible CFO cores and SiO₂ shell. The bottom inset in (e) represents an FFT on a marked CFO core; (e) collected local EDS spectra on the right panel acquired from nanoparticles marked on the left panel; (g) EDS chemical maps; and (h) line profiles for selected nanoparticles.

In the case of the sample annealed at $T_A = 600^\circ\text{C}$, the core-shell structure is still preserved (see Fig.6). The particles are distributed inhomogeneously, and some silica shells are fused. By analyzing individual particles in HRTEM images, one may notice multiple CFO and individual crystallites in one silica shell, as evidenced by the as-received sample. The SAED pattern similarly confirms an amorphous silica structure and spots corresponding to the (311), (400), (511), (440) and (622) spinel ferrite crystal planes. The HRTEM image shown in Fig.6e revealed a single particle with an average diameter of about 47 ± 2 nm with one CFO core of an average size of 17 ± 3 nm. The performed FFT analysis resembles a cubic spinel structure with the estimated interplanar d_{hkl} distance equals $4.8 \text{ \AA}$ as for the (111) lattice plane also shown for the as-received sample. The chemical elemental composition maps acquired from the marked region of interest (ROI) depicted in Fig.6f yield two nanoparticles that resemble CFO cores with low EDS signal encapsulated in SiO_2 . The measured overall EDS spectrum (see Fig.6g) confirms the presence of nanocomposite building blocks and synthesis impurities residuals (like e.g. K, Ca, Cl and S) and Cu from the used copper grid.

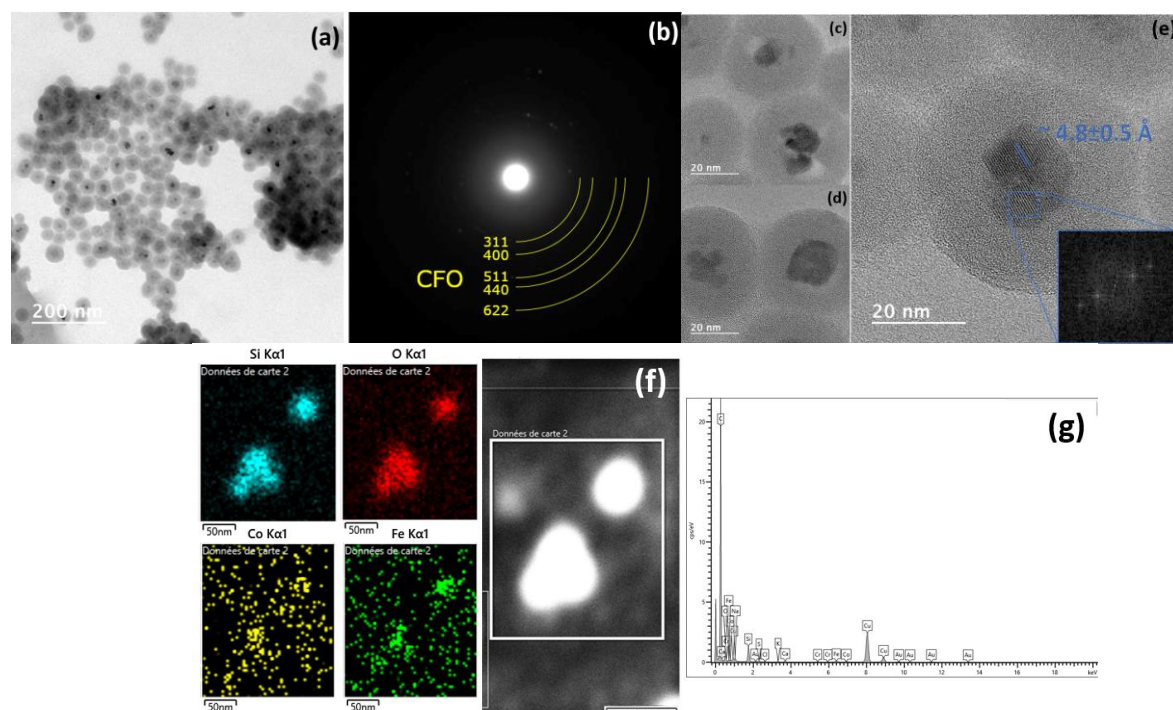


Fig.6. Microstructure of CFO@SiO₂ nanoparticles annealed at $T_A = 600^\circ\text{C}$: (a) bright field (BF) TEM image of agglomerated NPs; (b) SAED pattern; (c-e) HRTEM of individual core-shell nanoparticles with visible CFO cores and SiO₂ shell. The bottom inset in (e) represents an FFT on a marked CFO core; (f) collected local EDS chemical maps on the right panel acquired from nanoparticles marked on the left panel; (g) EDS spectra from the marked region of interest (ROI).

At the last applied annealing stage at $T_A = 800^\circ\text{C}$, the silica seems partially melted. However, the core-shell nanoparticles are separated quite well after easy dissolution in anhydrous ethanol, ultrasonication, and deposition on a copper grid. Notably, the annealing induced the fusing of CFO cores to form slightly bigger crystallites, which is in agreement with

XRD results. Thus, the core crystallization process is gradually driven by the applied staged-annealing procedure. The SAED pattern shows an amorphous structure of silica and the spots corresponding to the (311), (422), (511), (440) and (533) cubic spinel phases. The CFO cores (see Figs.7c-e) are irregularly shaped and distributed like other samples. The average diameter of the silica shell is about 47 nm, confirming the stability of SiO₂ over annealing. The exemplary analysis of the selected CFO core reveals an average size of around 18 ± 2 nm. The estimated d_{hkl} interplanar lattice equals 4.4 Å as for the (111) lattice plane. The FFT analysis performed from the marked ROI confirms the cubic spinel structure of the CFO core. The chemical composition of EDS maps confirms the previous observations. Similarly, the profile lines and EDS spectrum, like in previously discussed results, are consistent with the presence of CFO surrounded by SiO₂, meaning that the structure and distribution of elements did not change significantly over annealing.

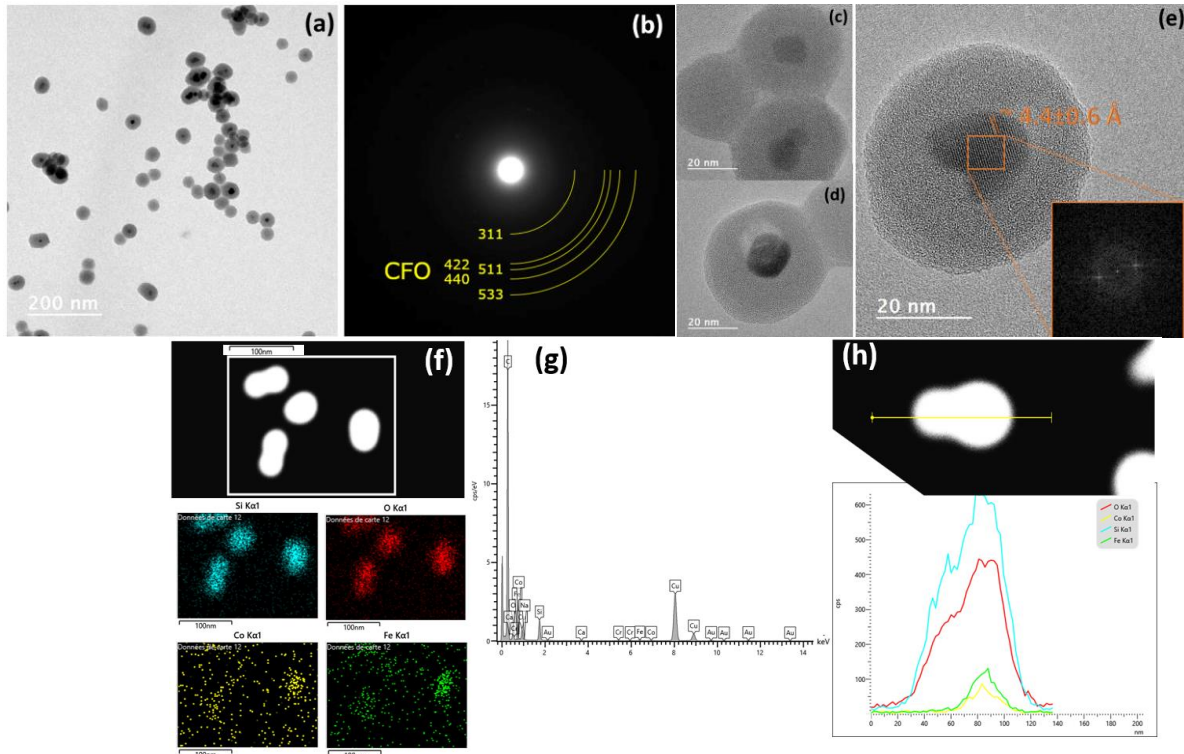


Fig.7. Microstructure of CFO@SiO₂ nanoparticles annealed at $T_A = 800^\circ\text{C}$: (a) bright field (BF) TEM image of agglomerated NPs; (b) SAED pattern; (c-e) HRTEM of individual core-shell nanoparticles with visible CFO cores and SiO₂ shell. The bottom inset in (e) represents an FFT on a marked CFO core; (f) collected local EDS chemical maps from the marked ROI; (g) EDS spectrum; and (h) line profiles for selected nanoparticles.

The particle size distribution (see Fig.8) for all tested specimens was established using ImageJ software based on the distribution of CFO inside silica shells. The histogram statistical distribution analysis was performed on 600 cores, which were distinguishable in HRTEM images. The histogram was fitted with a log-normal distribution function in each case, and the results are tabularized. As revealed, the NPs distribution is quite broad, which is slightly

contrary to the most desirable stable structure. Compared to XRD results, the average particle size d_{TEM} should be greater than d_{XRD} when a crystallographically disordered NPs surface is present [60].

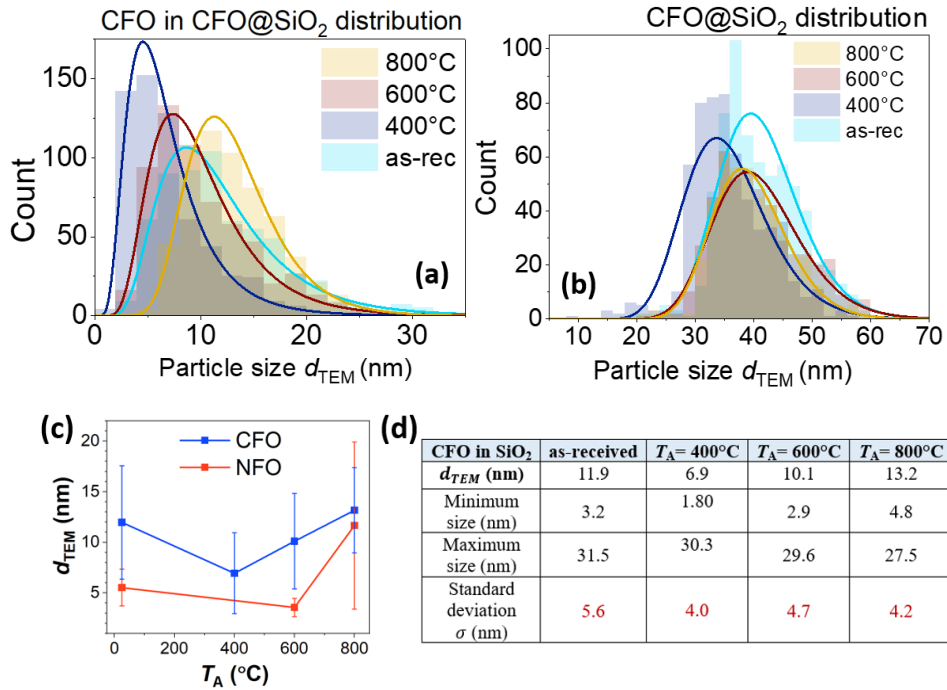


Fig.8. The particle size distribution (PSD) histograms for (a) CFO cores and (b) total (CFO cores plus SiO₂ shells) in the CFO@SiO₂ core-shell composites as-received and annealed at $T_A = 600^\circ\text{C}$, $T_A = 400^\circ\text{C}$, and $T_A = 800^\circ\text{C}$, (c) The comparison between CFO and NFO [41] cores, (d) Tabulated results of fitting histograms by log-normal function.

The average size determined by both methods is comparable to the current analysis. Thus, d_{TEM} varies from 12 ± 0.2 nm (as-received) to 13.2 ± 0.2 nm (annealed at $T_A = 800^\circ\text{C}$). However, one needs to consider the estimated significant size distribution with noticeably different minimum and maximum d_{TEM} values. By following this trend, as found, the minimum detected d_{TEM} is raised from 3.2 nm (as-received) to 4.8 nm (annealed at $T_A = 800^\circ\text{C}$), while the maximum d_{TEM} is reduced from 31.5 nm (as-received) to 27.5 nm (annealed at $T_A = 800^\circ\text{C}$), which signifies the assumed difference between XRD and TEM is fulfilled. Interestingly, the lowest particle size was estimated for $T_A = 400^\circ\text{C}$ (see Fig.8a), which might be an effect of irregular core distribution in the SiO₂ shell, but such a minimum well correlates with cations Co^{2+} distribution at A site, which was found as the lowest for $T_A = 400^\circ\text{C}$. Obviously, the analyzed particle size concerns only CFO cores in CFO@SiO₂ composites. By adding the silica shell diameters, the total d_{TEM} is considerably larger with an average diameter of about more than 40 nm (see Fig.8b). Additionally, the comparison between the estimated average size CFO and previously tested NFO nanoparticles indicates a similar trend (see Fig.8c), but the cores of CFO are noticeably larger, reflected in the magnetic performance of both nanoparticles.

3.3. Raman spectroscopy

Raman spectroscopy was utilized to investigate structural modifications in the cobalt ferrite (CFO) core induced by the presence of silica (SiO_2) shell, focusing on the estimation degree of depolymerization, considering silica as well as the degree of inversion, crystallinity, and activation of vibrational confinement effects in the spinel ferrite structure.

The formation of the core-shell structure, consisting of a CFO core, caused a significant overlap of Raman bands from both phases, particularly in the $200 - 600 \text{ cm}^{-1}$ region. As a result, a Voigt fitting procedure has to be applied to disentangle contributions of individual phases to the spectrum, allowing for precise deconvolution of the composite spectra and enabling the identification of vibrational modes of ferrite and silica separately.

Raman analysis adopted a dual perspective, addressing the distinct thermal effects on the silica shell and the ferrite core. This comprehensive approach provided valuable insights into the interfacial interactions and structural evolution within the core-shell system, highlighting the role of the silica shell in modulating the vibrational and crystallographic properties of the CFO core and SiO_2 shell.

A) The analysis of as-received and heat-treated composites from the point of view of silica shell

Raman spectra in $150 - 850 \text{ cm}^{-1}$ region featured a very complex image (Fig. 1) with the lowest-frequency bands ($<350 \text{ cm}^{-1}$) pointing to the silica network deformations and point defects (e.g., E' centres, non-bridging oxygen hole centres (NBOHCs), neutral oxygen-deficient centres, etc.) [61-63] and bands (ω_1) between $350 - 470 \text{ cm}^{-1}$ derived from medium-range order superstructures, including O-bending motions in silica rings ($n=3,4,5,6,\dots$) which depends on the number of oxygen atoms in the ring and the strain within the silica network [64, 65]. Unfortunately, the interpretation of these bands is challenging due to overlapping Raman signals from cobalt ferrite, which can affect defect-related and medium-range-order bands, making analysis ambiguous. In turn, bands of the $700 - 850 \text{ cm}^{-1}$ range (ω_3) correspond to silica defects and Si-O bond breakage due to interactions with cobalt ferrite [66-68].

Analysis of the high-frequency bands (ω_4) located $900 - 1250 \text{ cm}^{-1}$ explains the quality of the three-dimensional silica, allowing the determination of the degree of polymerization and structural ordering within the silica shell. In this region appeared so-called Q^n ($n = 1, 2, 3, 4$, where n refers to non-bridging oxygen) bands corresponding to the concentrations of n -type species and serve as a marker of silica network organization [69-71]. In the as-prepared CFO@ SiO_2 sample appeared five Gaussian bands centred at 918, 943, 976, 1005, and 1023 cm^{-1} linked to Si-O-Si stretching vibrations (Fig.9a), suggesting the formation of substructures

with terminal oxygen atoms [72-74]. Bands at 918 and 943 cm^{-1} originated from Si-OH vibrations, while the band at 976 cm^{-1} is derived from Q^2 units, indicating SiO_4 tetrahedra with two non-bridging oxygen (NBO) atoms. In turn, bands at 1005 and 1023 cm^{-1} pointed to Q^4 units, representing symmetric stretching vibrations in fully bridged SiO_4 tetrahedra [67].

Heat treatment profoundly alters the silica structure. Initially observed, Si-OH groups decrease in intensity during annealing and vanish entirely at $T_A \sim 800^\circ\text{C}$, indicating a complete dehydroxylation process. The Q^2 -related bands increase in intensity with a concurrent broadening (higher FWHM), while Q^4 bands decrease, pointing to enhanced depolymerization. This structural reorganization is likely driven by the interaction between silica and the cobalt ferrite core, which induces the strain and modifies the silica network. These findings highlight the complex interplay between silica network defects, structural organization, and interactions with the cobalt ferrite core in CFO@SiO_2 composites, providing critical insights into their thermal stability and material properties.

B) The analysis of as-received and heat-treated composites from the point of view of the CFO core

Cubic spinel compounds exhibit five Raman-active modes (A_{1g} , E_{1g} , and $3T_{2g}$) associated with divalent ions occupying the tetrahedral sites and trivalent ions occupying the octahedral sites [75, 76]. Variations in ionic radii of the metal ions in CFO influence metal-oxygen bond lengths, leading to structural distortions and splitting of the A_{1g} mode into $A_{1g(1)}$ and $A_{1g(2)}$. These distortions disrupt the theoretically predicted Raman modes, resulting in complex band arrangements, including shifts in position, intensity, and the emergence of additional bands.

Raman spectrum of pure CFO features one E_{1g} and three T_{2g} modes below 600 cm^{-1} [77-79]. In turn, these modes in CFO@SiO_2 samples overlap with the deformational modes of silica, complicating spectral interpretation. Furthermore, the silica effect causes significant spectral distortion and doesn't allow for observation of low-frequency $t_{2g(3)}$ modes near 200 cm^{-1} and bands attributed to quantum size effects around 115 – 120 cm^{-1} [80]. Despite, the Raman spectrum of CFO@SiO_2 revealed typical ferrite E_{1g} (280 – 320 cm^{-1}), $T_{2g(2)}$ (440 – 480 cm^{-1}), and $T_{2g(1)}$ (530 – 570 cm^{-1}) bands originated, respectively from symmetric and antisymmetric bending of oxygen ions in M–O bonds within tetrahedral and octahedral sites [81, 82], wherein their positions and intensities are particle size-sensitive [77]. Hence, a high band complexity suggests the coexistence of CFO particles of varying sizes, which, in correlation with the high intensity and low FWHM of the E_g , $T_{2g(1,2)}$ bands, indicates a microcrystalline structure. A situation slightly changes upon heating with minor E_{1g} and $T_{2g(2)}$ band shifts $\sim 10 \text{ cm}^{-1}$ toward higher frequencies, and $T_{2g(1)}$ about $\sim 5 \text{ cm}^{-1}$ toward lower frequencies. Simultaneously,

significant increases in FWHM rising from 29.5, 39.6, and 20.1 cm⁻¹ in as-received samples to 49.3, 87.5, and 49.3 cm⁻¹, respectively, for samples annealed at 800 °C pointing to the appearance of size-dependent compressive stress [83].

A similar observation was found analyzing the 600–700 cm⁻¹ region with the number and intensity of CFO bands, while well-separated bands correspond to symmetrical A_{1g(2)} stretching modes of Co²⁺–O bonds and A_{1g(1)} stretching of Fe³⁺–O bonds [80]. Encapsulation of CFO by a silica shell results in two double A_{1g} bands at 606/628 and 655/682 cm⁻¹, attributed to Co–O and Fe–O vibrations, respectively (Fig.9a). A notable 20 cm⁻¹ downshift in these bands, compared to other CFO phases [75], resulted in the reduction of crystallinity, internal strain, and smaller particle size. The increasing intensity of A_{1g(1)} bands (FeO₄) and decreasing intensity of A_{1g(2)} bands (CoO₄) with rising temperatures also suggest a redistribution of Co²⁺ and Fe³⁺ ions between tetrahedral and octahedral sites. This redistribution alters the spinel structure, with the A_{1g(2)} mode reflecting local distortions from cation inhomogeneity [84]. In turn, a weak A_{1g*} mode near 711 cm⁻¹, assigned to Fe³⁺ vibrations in incomplete tetrahedral sites of maghemite, diminishes upon heat treatment, and beyond 400 °C, maghemite is no longer detected. Spectral changes are summarized in Table II, highlighting shifts in A_{1g(1,2)} and A_{1g*} modes and corresponding FWHM values for as-received and heat-treated samples.

Table II. Raman phonon modes characteristics in the 600 – 700 cm⁻¹ range.

as-received		200°C		400°C		600°C		800°C	
ν (cm ⁻¹)	FWHM	ν (cm ⁻¹)	FWHM	ν (cm ⁻¹)	FWHM	ν (cm ⁻¹)	FWHM	ν (cm ⁻¹)	FWHM
606.5	43.1	604.9	48.9	609.1	48.2	605.2	47.1	600.1	54.6
628.2	26.7	628.1	34.7	639.8	23.5	634.6	31.7	629.5	31.9
656.5	42.1	658.3	45.7	664.4	51.6	666.7	45.7	669.7	43.3
682.6	30.5	686.8	32.3	694.0	52.0	698.2	46.5	699.1	38.3
711.1	17.2	720.1	23.3	-	-	-	-	-	-

Inversion vs. crystallinity and strain

The mutual relation between the integrated intensity of specific A_{1g(1,2)} components with a degree of cation inversion can be followed by equation 1 [78].

$$x_{Me(A)} = I_{A1g(1)} / [I_{A1g(1)} + S \cdot I_{A1g(2)}] \quad (15)$$

where A_{1g(1,2)} corresponds to the integrated intensity of suitable bands and S equal to 0.58 represents the relative oscillator strength of the Co²⁺–O bonds with respect to the Fe³⁺–O bonds in tetrahedrons [55, 85].

According to theoretical calculations, the inversion parameter, which quantifies the contribution of iron cations occupying tetrahedral sites, was estimated to be 0.83 for larger particles and 0.63 for smaller ones (see Fig.9b). The inversion value for larger particles aligns

well with the literature-reported CFO nanoparticles, which typically exhibit an inversion parameter around 0.8 [79]. It corresponds to Co^{2+} cations predominantly occupying octahedral sites, with Fe^{3+} cations distributed between both octahedral and tetrahedral sites. In contrast, the slightly higher inversion observed in smaller particles suggests tetrahedral occupancy of cobalt ions. Both structures, however, exhibited decoupled oscillations of Co-O_4 and Fe-O_4 tetrahedral sites, indicating local structural distortions.

Interestingly, the as-received sample displayed a relatively high lattice parameter and significant strain ($\sim 0.62\%$), suggesting a high density of point or structural defects and an abundance of surface atoms. These effects may also stem from interactions with silica defects, hydroxyl groups, and dangling bonds, which induce additional deformation in the crystal structure. This strain was further amplified by the coexistence of less ordered nanosized CFO particles and more structurally ordered micro-sized CFO particles, both confined within the silica shell. Heat treatment caused a notable increase in the inversion degree, with smaller particles reaching an inversion parameter of 0.68 at 400°C and larger particles increasing to 0.92. It was accompanied by a reduction in the lattice parameter of approximately $0.04\text{ \AA}$, although strain remained relatively high at $\sim 0.53\%$. These changes reflect the migration of cobalt and iron ions within the crystal lattice, altering occupancy between octahedral and tetrahedral positions. As a result, the ion redistribution altered the crystallographic parameters, resulting in lattice contraction accompanied by a simultaneous increase in crystallite size.

A comprehensive correlation between Raman spectroscopy, TEM, and PXRD data revealed that crystallization was driven by confinement effects imposed by the silica shell, which significantly influenced internal stress. This confinement increased point defects, as evidenced by the broadening of diffraction peaks (increased FWHM). Notably, beyond a certain temperature threshold, an inverse trend was observed, i.e., the inversion parameter declined and stabilized at approximately 0.68 for both smaller and larger particles at higher temperatures (Fig.9b). This decrease strongly correlated with an increase in lattice parameters and morphological changes, including particle growth. These structural changes reduced strain to $\sim 0.37\%$ (see Table Ia), highlighting the intricate interplay between thermal treatment, crystallization dynamics, and structural evolution.

Impact of Crystal Dimensions on Raman Scattering in CFO@SiO₂ Composites

The modification of first-order Raman scattering phonons in spinel ferrites, particularly in CFO@SiO₂ composites, is highly influenced by crystal dimensions. For microscopically sized crystals, phonon vibrations are largely confined near the centre of the Brillouin zone ($q = 0$). However, reducing crystal size disrupts long-range order, enabling phonon scattering with $q \neq 0$.

0. This relaxation of the momentum selection rule gives rise to quantum confinement effects, allowing phonons from regions far from the Brillouin zone centre to contribute to first-order Raman scattering. These effects are observed as broadening of peaks, reduced amplitude of individual modes, and shifts of bands toward lower frequencies, especially in as-received CFO@SiO₂ samples and those annealed at lower temperatures ($T_A = 200^\circ\text{C}$ and 400°C).

The downward shift in the band frequencies further highlights crystalline disorder and the presence of grain boundaries, corroborating the existence of low-dimensional nanomaterials [86]. Notably, a quantum confinement phenomenon of optical phonons has been extensively studied, particularly in materials such as silica spheres [55, 87, 88], silica wires [89], and cobalt ferrites [78, 79]. These studies collectively demonstrate that the relaxation of the momentum selection rule enables significant modifications in phonon behaviour as crystal dimensions decrease. Table 1 underscores the contrasting behaviour between smaller, more defective particles and more prominent, more ordered counterparts, e.g. the Raman shift ($\Delta\omega$) of the $A_{1g(1)}$ mode, directly linked to particle size, was effectively modelled using the bond-polarizability approach. This modelling elucidates the dependence of Raman shifts on the structural and dimensional characteristics of CFO@SiO₂ composites, providing insight into the interplay between crystal size, defects, and vibrational properties:

$$\Delta\omega = \omega(L) - \omega_0 = -A \cdot (a/L)^\gamma \quad (16)$$

where $\omega(L)$ is the Raman frequency for CFO particles of size L , ω_0 is the phonon frequency at the Brillouin zone centre for a perfect microcrystalline crystal, a is the lattice constant, and A and γ refer to the vibrational confinement parameters [55]. The values of A and γ for CFO@SiO₂ composites were determined to be 63.9 cm^{-1} and 11.68 , respectively. The notably high γ value is likely a result of the strongly aspherical shape of the nanostructures and the irregularly distributed variable-sized particles encapsulated within silica spheres. These structural characteristics inhibit further agglomeration and enforce a unique recrystallization process typical of individual core-shell systems. Upon heat treatment, the $A_{1g(1)}$ mode exhibited a broadening of its FWHM for both small and large particles up to $T_A = 400^\circ\text{C}$, followed by a gradual narrowing at higher temperatures ($T_A = 600^\circ\text{C}$ and 800°C). In contrast, the FWHM of $A_{1g(2)}$ modes consistently increased across the entire temperature range. Additionally, the relative intensity ratio of $A_{1g(1)}$ to $A_{1g(2)}$ displayed distinct trends for different particle sizes (Table II). For smaller particles, the $A_{1g(1)}/A_{1g(2)}$ ratio increased from 0.97 (as-received) to 1.07 ($T_A = 400^\circ\text{C}$), then declined to 0.79 upon higher temperatures ($T_A = 800^\circ\text{C}$). The ratio for larger particles evolved from 1.14 (as-received) $\rightarrow 2.21$ ($T_A = 400^\circ\text{C}$) $\rightarrow 1.35$ ($T_A = 800^\circ\text{C}$). These variations confirmed significant cationic redistribution, characterized by the migration

of iron ions to octahedral sites and cobalt ions to tetrahedral sites in different ways considering variable-size particles. This redistribution influences the structural and vibrational properties, causing lattice parameter contraction, defect generation, and enhanced vibrational confinement up to $T_A = 400$ °C. Similar behaviours have been observed in non-silica-encapsulated CFO particles synthesized using alternative methods [77].

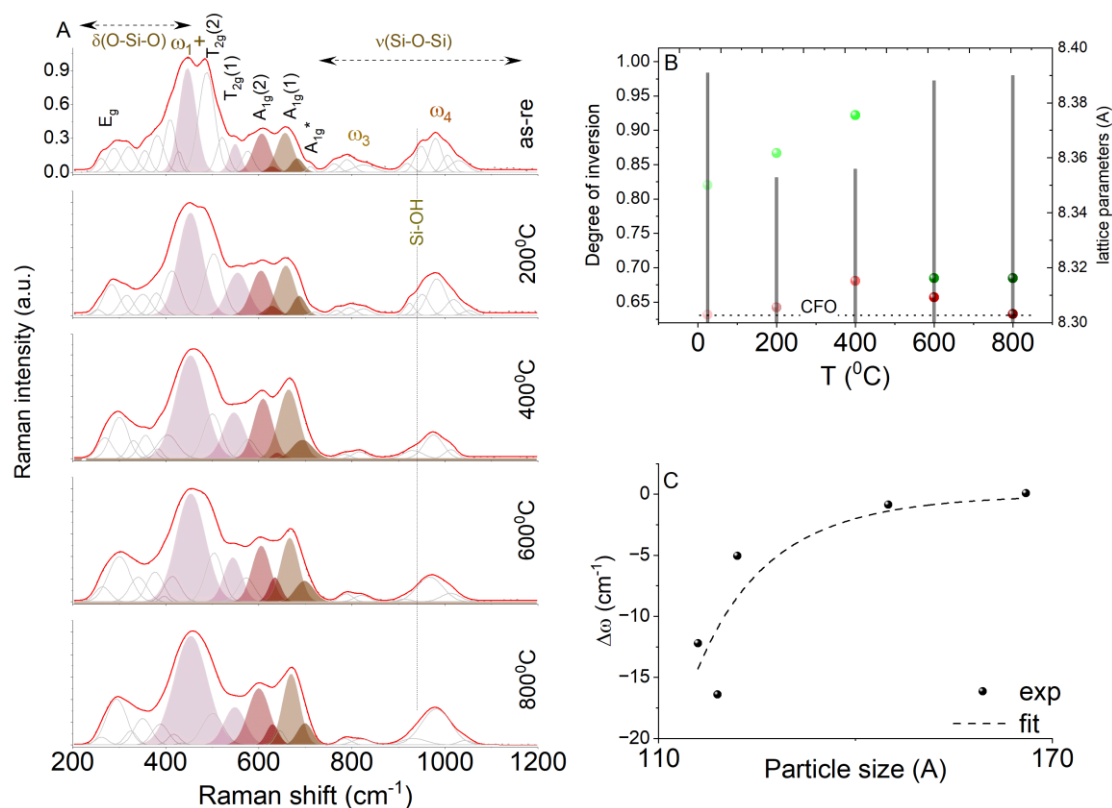


Fig.9. Raman spectra of as-received and heat-treated CFO@SiO₂ composites across the 200–1200 cm⁻¹ range (a). Spectra were fitted using the Gauss function, and characteristic bands of ferrite were color-highlighted. The degree of inversion within tetrahedral sites for smaller (red) and larger (green) particles was correlated with lattice parameter changes (b). The dotted line in B represents the behaviour of CFO nanoparticles without a silica shell, providing a comparative framework. The variation in Raman shift as a function of crystallite size, modelled using the confinement approach, captures the effects of thermal annealing (c).

Interestingly, larger microcrystalline particles transitioned toward an inverted spinel configuration up to $T_A = 400$ °C, reverting to an initial mixed spinel structure upon further heating to $T_A = 800$ °C. This finding is explicitly consistent with XRD cations distribution analysis. Conversely, smaller particles maintained an inverse spinel structure throughout the annealing process. This divergent behaviour underscores the role of particle size in determining the structural evolution of CFO under thermal treatment.

The coexistence of variable-sized particles within silica spheres complicates the correlation of bulk Raman and XRD data with TEM observations. Such complexities may result in over- or underestimation of structural parameters, highlighting the need for advanced fitting procedures and multi-technique analyses to ensure accurate interpretation. Moreover, the

interplay between particle size, cationic redistribution, and silica encapsulation significantly impacts the structural and vibrational properties of CFO@SiO₂ composites. These findings have important implications for their magnetic and other functional applications performance.

3.4. Electronic structure - XPS

Comparison of the valence band (VB) spectra acquired at $h\nu = 1486.6$ eV in the broad binding energy (BE) range is depicted in Fig.10. To compare the VB in the vicinity of the Fermi level (E_F), the normalization was done for the dominated O2s peak located around the binding energy $E_B \approx 25.5 \pm 0.1$ eV. The shape of VB is stable over sample processing, meaning that the dominated silica matrix is just slightly suppressible for feasible modification during the applied heat treatment procedures, which is in contrast to the previously studied NFO@SiO₂ core-shell structures [41]. One may note an evident three features assigned as A, B and C and D. The double peaks denoted as A and B stretched from about 17.7 eV to 3.7 eV originated from strongly hybridized Si3d3s-O2p and Co/Fe(3d) states as already evidenced for various SiO₂ – based layer or oxides [90-92]. The last low-intensity states marked as C between the Fermi level (E_F) and 3.7 eV mainly arise from metallic Co/Fe(3d) states, as observed for pure elements or other Co/Fe compounds [93-96].

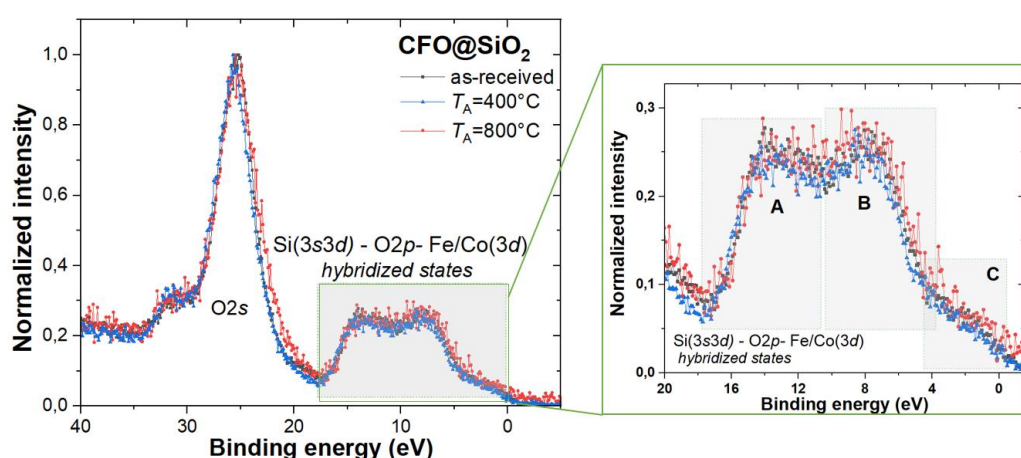


Fig.10. The selected valence bands (VB) for as-received and annealed CFO@SiO₂ nanoparticles.

The comparison between normalized core level spectra for as-received and annealed samples is presented in Figs.11a-b and 13a-b. As demonstrated, the applied annealing procedure does not significantly modify the shape of all detected core-level lines. As visible, the main photoemission broad Co2p lines are generally composed of two spin-orbit (L-S) split peaks, Co2p_{3/2}, which maxes around $E_B \approx 778.4$ eV and Co2p_{1/2} around $E_B \approx 793.3$ eV, respectively. So, the L-S splitting is about $\Delta E \approx 14.9$ eV. The main lines are accompanied by visible broad satellites. Similarly, the Fe2p lines demonstrated the complex doublet lines with two evident maxima at $E_B \approx 710.5$ eV for Fe2p_{3/2} and $E_B \approx 723.6$ eV for Fe2p_{1/2}, respectively, with the spin-

orbit splitting of about $\Delta E \approx 13.1$ eV as noted for various iron oxides and ferrites [4, 5, 7, 9, 14, 39, 41, 97-99]. The complex iron lines confirm the domination of the trivalent state of iron cations within tetrahedral and octahedral sites as in the inverse spinel ferrite lattice. As seen, the Fe2p structure is slightly modified over the annealing process, confirming the stability of ferrite cores.

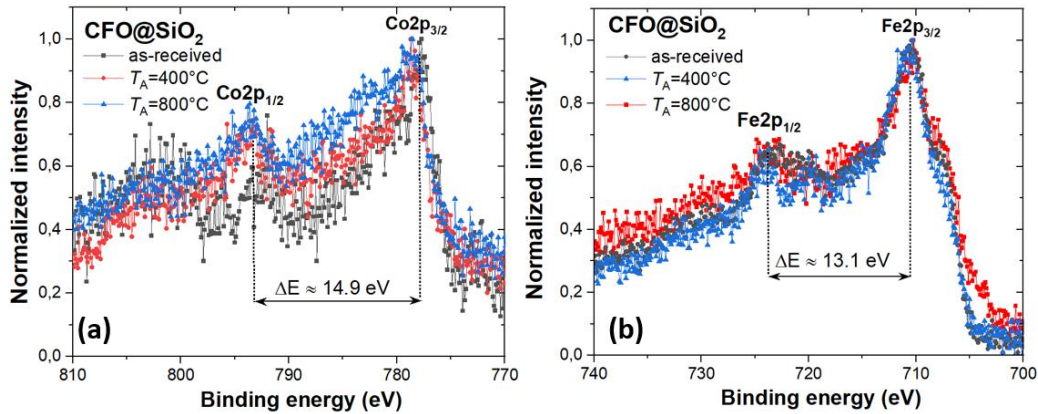


Fig. 11. The comparison between core level lines (a) Co2p and (b) for as-received and annealed CFO@SiO₂ nanoparticles.

A closer look at the comparison between deconvoluted Co2p_{3/2} and overall Fe2p core level lines spectra for as-received and annealed at composites indicated well the complexity of both magnetic components in the sample formula (see Fig. 12a-b). Thus, for Co2p_{3/2}, regardless of the sample type, three species with different percentage contributions are estimated based on the peak area after applying deconvolution (see Table S1 in Supplementary Materials). The first one at about $E_B \approx 777.6 \pm 0.2$ eV and changed percentage from 48.68 % (as-received) to 46.66 % ($T_A = 800^\circ\text{C}$) is assigned to divalent cobalt cations in B-octahedral sites. The second visible at around $E_B \approx 781.1 \pm 0.1$ eV and percentages from 35.78 % (as-received) to 42.95 % ($T_A = 800^\circ\text{C}$) represents Co²⁺ in tetrahedral A-site. The double nature of Co²⁺ is in good agreement with previously tested forms of CoFe₂O₄ compounds [4, 14, 100]. Finally, the low-intensity last one around $E_B \approx 784.8 \pm 0.7$ eV and percentages from 15.54 % (as-received) to 10.39 % ($T_A = 800^\circ\text{C}$) is a shake-up satellite peak being a direct indication of divalent oxidation cobalt state. The noted satellite is an effect of the admixture of oxygen 2p character and leads to two possible final states in the photoemission process:

- (1) $2p^6 3d^7 + h\nu \rightarrow 2p^5 3d^7 + e^-$
- (2) $2p^6 3d^7 + h\nu \rightarrow 2p^5 3d^8 V + e^-$

In this scenario, V denotes an electron vacancy in the 2p band of the neighbouring O²⁻ lattice anions. Due to the intense sensitivity of the charge-transfer process on the overlapping phenomenon between adjacent Co²⁺ and O²⁻ orbital, the satellite to the main photoemission

peak intensity ratio is highly dependent upon the geometry and defect nature of measured specimens [4, 100, 101].

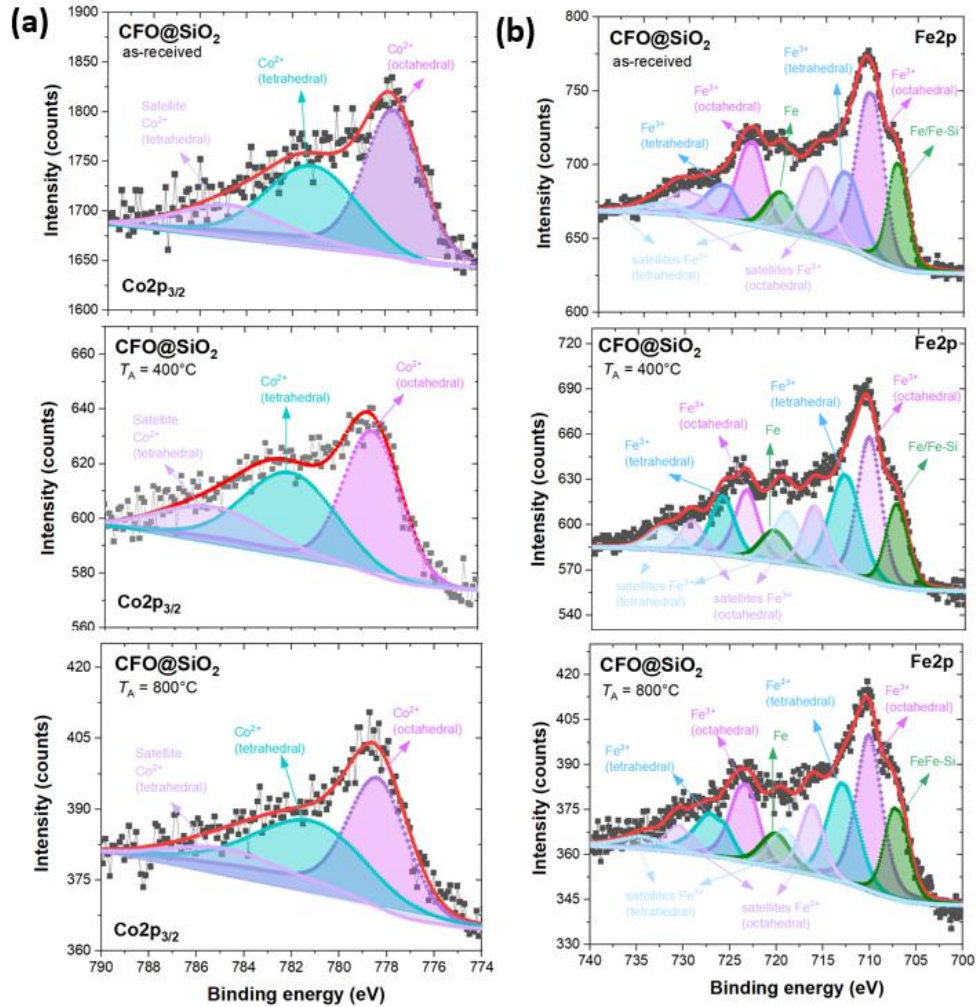


Fig. 12. The comparison between deconvoluted (a) Co₂p (right panel) and (b) Fe₂p (left panel) spectra for CFO@SiO₂ nanoparticles in the as-received and annealed at $T_A = 400$ and 800°C forms.

The deconvolution procedure applied to Fe₂p lines exhibits the fine structure of iron doublet, confirming the existence of iron species in several chemical states. The goodness of fit is confirmed by the fitted envelope line good rendering the experimental spectra for each measured sample (see Fig.12b). Thus, as found, each Fe₂p spectrum after deconvolution comprises ten overlapped line components regardless of sample forms. So, there are five species per pair, Fe₂p_{3/2} and Fe₂p_{1/2}, with a low-binding energy component around $E_B \approx 707 \pm 0.5$ eV and $E_B \approx 720 \pm 0.3$ eV. Such a structure can be linked to the overlapped pure metallic Fe states with Fe-Si, more likely mainly Fe₃Si [40, 102] probably formed on the CFO surface as an effect of SiO₂ coating. The other four species are well known and typical of other inverse spinel ferrites, as confirmed by *Biesinger et al.* [97] as for various coordination environments of iron cations in the inverse spinel structure. Thus, one pair of them, the main line at about $E_B \approx 713$

± 0.3 eV with accompanied satellite, can be assigned to Fe^{3+} distributed in the A-tetrahedral crystallographic site. Simultaneously, the other at lower binding energy $E_B \approx 710 \pm 0.3$ eV with a shake-up satellite represents the Fe^{3+} of the B-octahedral sites. By analyzing the percentage contribution from each revealed iron component, one may notice the slight reduction of Fe/Fe-Si states from about 18.23 % (as-received) to 17.76 % ($T_A = 800^\circ\text{C}$), which is around 10 % less than in the case of NFO@SiO₂ composites [41]. Such an effect is linked to the crystallization of silica shell, which in nickel-based samples was more pronounced. Additionally, there is a very slight modification of the $\text{Fe}^{3+}(\text{A})/\text{Fe}^{3+}(\text{B})$ ratio from about 0.69 (as-received) to 0.72 ($T_A = 800^\circ\text{C}$), confirming a good thermal stability of the CFO structure. Thus, the minority changes might originate from a slight iron redistribution in the crystal lattice driven by applied annealing or, in addition, by using an Ar^+ beam, which was essential to explore the CFO core. The complete fitting parameters for $\text{Fe}2p$ are collected in Table S2 in Supplementary Materials.

The comparison between $\text{Si}2p$ and $\text{O}1s$ core level lines for all measured composites displays no significant change in each collected spectrum (see Figs.13a-b). Thus, a further detailed analysis was performed after deconvolution. The fitting of the $\text{Si}2p$ line (see Fig.14a) exhibits four components. The dominated broad states around $E_B \approx 103.3 \pm 0.2$ eV can represent O-Si-O chemical bonds partly overlapped by Si-O-C with an overall percentage area of 78.21 % (as-received) to 77.03 % ($T_A = 800^\circ\text{C}$). The line with the lowest intensity around $E_B \approx 100.3 \pm 2$ eV with 4.44% for an as-received sample and 2.53 % for $T_A = 800^\circ\text{C}$ may indicate a trace of $\text{Fe}3s$ states. The remaining peaks around $E_B \approx 101.7 \pm 0.1$ eV can be assigned to Si-O-Co/Fe covalent bonds reinforced by the contribution of Si-C states around $E_B \approx 104.4 \pm 0.5$ eV indicating Si-OH states, respectively. The $\text{O}1s$ lines after deconvolution similarly indicate four species (see Fig.14b) having binding energies of about 529.5 ± 0.1 eV, 531.2 ± 0.2 eV, 532.8 ± 0.2 eV and 533.6 ± 0.5 eV, respectively. The first one can be recognized as Co/Fe-O states, the second confirmed the overlapped Si-O and C-OH states, the third as the dominant component of all analyzed samples represents the typical Si-O-Si bonds overlapped with Co/Fe-OH states, whereas the last one can be ascribed as overlapped Si-OH chemical states with the adsorbed H₂O. The chemical composition recognized after $\text{Si}2p$ and $\text{O}1s$ deconvolution was already revealed for various nanomaterials based on silica matrix [41, 101, 102], including previously studied NFO@SiO₂ composites [41]. The percentage contribution of all recognized states is slightly varied upon annealing (see Tables S3 and S4 in Supplementary Materials), which can be linked to subtle modification of the silica shell driven by the applied heat treatment procedure.

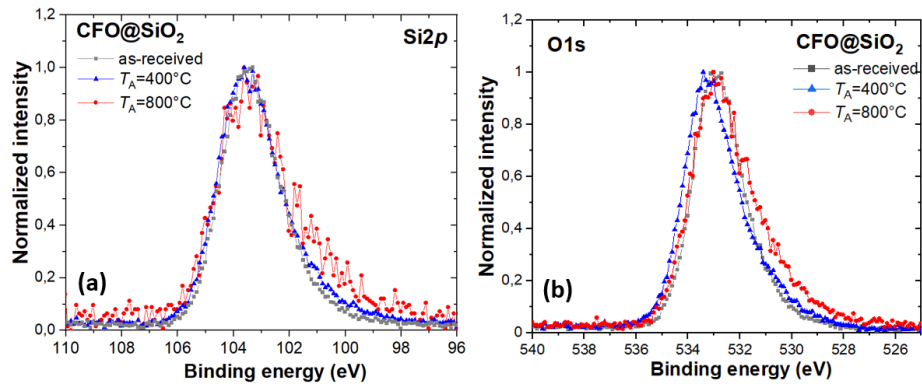


Fig. 13. The comparison between (a) Si2p and (b) O1s core level lines for as-received and annealed CFO@SiO₂ nanoparticles.

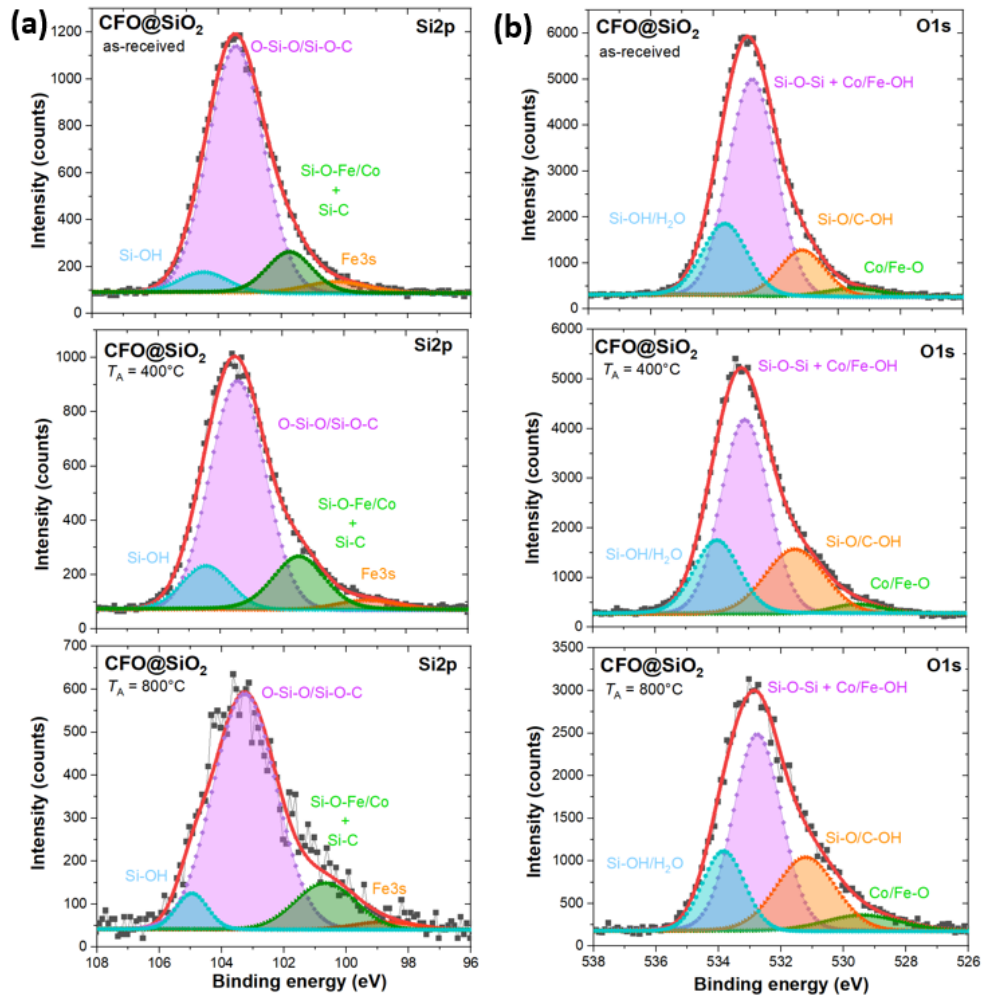


Fig.14. Deconvoluted core level line (a) Si2p (right panel) and (b) O1s (left panel) spectra for CFO@SiO₂ nanoparticles as-received and annealed at $T_A = 400$ and 800°C .

3.6. XAS

The X-ray absorption spectra (XAS) were acquired for the magnetic elements like Co and Fe $L_{2,3}$ - edges to verify cobalt and iron states (see Fig.15a). The XAS method was employed as a sensitive tool to probe the local crystal field environment, giving insight to ionic species in different crystallographic sites. For all materials with transition metal elements, the

determination L-edge XAS envisages the transition from the $2p$ to the $3d$ shell [103, 104]. In this way, the absorption spectra for pure $3d$ metals are consisted of two broad peaks, L_3 and L_2 , related to the width of the $3d$ bands and the spin-orbit interactions. However, in the case of compounds with $3d$ elements like various oxides, the multiplet structure is revealed for each peak L absorption peak as an effect of a mixture of the $2p3d^9$ and $2p3d^{10}\underline{L}$ final state configurations [105, 106]. Thus, the first multiplet component is the product of the $2p$ - $3d$ exchange interaction, while the second one is the band-like character of the ligand hole.

For comparison, all presented XAS spectra have been normalized first to the beam current and second using the XAS normalization function. The presented spectra were acquired in two experimental beams and two different modes, total electron yield (TEY) and particle fluorescence yield (PFY). The first used mode gives insight into several nm depths, while the second is a more bulk technique with a depth of hundreds of nm utilised for problems with charge-discharged samples [107, 108].

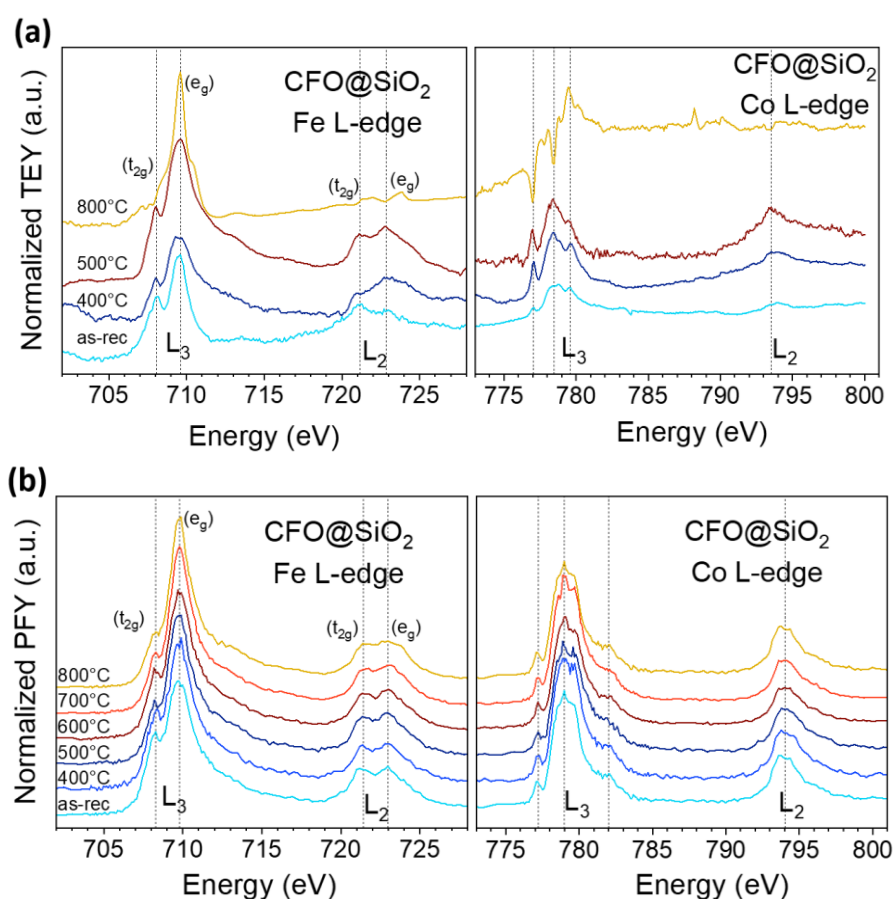


Fig.15. The comparison of XAS spectra in CFO@SiO₂ composites measured on Fe and Co L-edges in (a) TEY and (b) PFY modes.

In our case, the measured XAS spectra for Co and Fe L-edges acquired in TEY and PFY follow the same trend, but PFY spectra provide more accuracy. As one may notice, for both spinel structure elements, two main peaks, L_3 ($2p_{3/2} \rightarrow 3d$ transitions) and L_2 ($2p_{1/2} \rightarrow 3d$

transitions) are present. In the case of Fe L-edge, the L_3 is placed in the photon energies range 706 - 714 eV while L_2 in 718 - 726 eV, respectively. Considering the Co L-edge, the L_3 is in the 775 - 782 eV while L_2 is in the 792 - 797 eV photon energies range. It is worth mentioning that the applied heat treatment did not affect the XAS spectra significantly. The general shape is preserved for Fe and Co L-edge XAS structures. A detailed analysis of both L_3 and L_2 peaks revealed the presence of additional features. Thus, in the case of Fe L_3 - edge XAS spectrum, two distinct maxima at 708.1 (peak A associated with $2p_{3/2} \rightarrow 3d(t_{2g})$ low-spin states) and 709.5 eV (peak B associated with $2p_{3/2} \rightarrow 3d(e_g)$ high-spin states) can be easily distinguished. The same situation is well justified in Co L_3 - edge XAS spectrum, where such maxima are observed at 779.1 (denoted as peak A linked to the t_{2g} low-spin states) and 778.4 eV (denoted as peak B associated with e_g high-spin states). The double structure is an effect of Co^{2+} and Fe^{3+} distribution in A-tetrahedral and B-octahedral sites, consistent with XPS spectra. The apparent double maxima are also well recognized in the case of spinel ferrites thin films [109-112]. Thus, the Co L_3 and L_2 species in L-edge spectra are well reproduced as the experimental and theoretical XAS spectra for a single $CoFe_2O_4$ crystal by Wang *et al.* [113], proving the distribution of divalent cobalt ions in tetrahedral symmetry) and octahedral (D_{3d} symmetry) crystal sites. Moreover, the reproducibility herein presented Co L-edge lines are well justified comparing those published by Kim *et al.* [114] for the $CoFe_2O_4$ powders and those by Wakabayashi *et al.* [111, 112] for $CoFe_2O_4$ - based thin films. The major feature of the L_3 - edge peak around 778.9 eV is linked to Co^{2+} ions in the A-site while at 779.6 eV to the B - site. The applied annealing revealed a slight enhancement of the second peak, which was more middle T_A , confirming the temperature-driven cation distribution modification well described by XRD and Raman methods.

As one may see, the heat treatment does not significantly change the absorption L-edge lines. The visible slight differences are associated with proven cations redistribution in A and B - sites. By analyzing the Fe L - edge lines, there is no expected trace of divalent iron. However, we cannot exclude a trace of such a species, which, as was shown theoretically by Chen *et al.* [115] and confirmed experimentally by Zhou *et al.* [109] and Crocombette *et al.* [116], could be expected in the spinel lattice as the additional configuration $Fe^{2+} \underline{2p}3d^7$ (B site) with the 1.5 eV hybridization energy between trivalent and divalent states in B-sites. Nonetheless, in the current research, if there exists a tiny contribution from divalent iron, it would be rather an effect of disordered dead magnetic layer shell also associated with the structural changes in the inverse-to-mixed spinel structure or/and the presence of Fe/Fe-Si states on the CFO core surface as proved by analysis of $Fe2p$ core level lines.

Fig.16a displays the comparison of O K - edge XAS spectra for all selected measured samples from the CFO@SiO₂ series acquired in TEY and PFY modes. As seen, both applied methods are reflected in spectra of similar shapes. However, in PFY modes, a structure between 529 – 534 eV is more pronounced. In many oxides, the O K-edge XAS line is the effect of the electron transition from O 1s core level to O 2p unoccupied states, which in oxide compounds are hybridized with the orbitals of neighbouring ions, here, namely Co, Fe and Si in the spinel crystal lattice. Thus, the first distinguished peaks in the photon energy range 529 – 534 eV are denoted in Fig.16a. as A may be an effect of (Co/Fe) 3d – Si 2p states hybridized with O 2p. By a closer glimpse at A region, one may observe a two-peak structure well seen in PFY spectra, which could be linked to two crystallographically placed Co²⁺/Fe³⁺ states in tetrahedral and octahedral sites corresponding to t_{2g} and e_g molecular orbitals as σ and π (Co/Fe) – O bonds, respectively [115-121]. Such states are modified slightly over annealing in the middle T_A due to various cation distribution and their interaction via oxygen anions. As shown by Tsai *et al.* [122], the surface effects, lattice defects, and modification within the core-shell structure may evidently influence the low-energy part of O K-edge XAS spectra.

The broad features dominated noticeably in the higher photon energy range between 535–550 eV representing (Co/Fe) 4sp – Si 3sp states hybridized with O 2p. In this case, a broad double peak marked as with two-maximum region C (peaked around 537.4 eV and 539.3 eV) and broad D (peaked around 541.1 eV) can be associated with a very slight core-shell structural modification over annealing. Indeed, SiO₂, contrary to NFO@SiO₂ [41], is stable, and no significant crystallization was observed. Thus, the stability of the CFO@SiO₂ core-shell structure is well justified by O K-edge XAS spectra.

The silicon XAS states were measured on two different absorption edges, namely by TEY on the Si L-edge (see Fig.16b) and by PFY on the Si K-edge (see Fig.16b). First, the TEY spectra are typical as for other Si-based compounds [122-128]. The double peak, denoted as A with two visible features, peaked around 105.8 eV and 106.5 eV and is associated with the Si2p_{3/2} and Si2p_{1/2} double-peak transitions to antibonding a_{1g} orbital (Si3s -like states). The splitting between both peaks ΔE = 0.6 is larger than Si2p spin-orbit splitting, but its origin is a spin-orbit interaction. The high-intensity peak labelled as B extended in the photon energy around range 107– 110 eV represents the dominated Si 2p-t_{2g} (3p-3s) transition. This kind of effect was already noted by Wu *et al.* [128]. Nonetheless, Mo *et al.* [127] explained the origin of such states, based on the dipole transition selection rule, as Si 3s or 3d states hybridized with O 2p. In contrast to previous XAS analysis for NFO@SiO₂, where a significant crystallization of amorphous silica was manifested, in the current studies, this peak is stable, proving once

again the stability of amorphous silica shell over the applied heat treatment processing even though various forms of silica exhibit similarities in the L-edge absorption spectra, as proved by *Li et al.* [125]. The broad low-intensity feature noted as region C in the photon energy range between 110 eV – 114 eV may be described as a probable multiple scattering process, as evidenced in many Si-based polymorphs [117, 121, 125]. The broad peak marked as D around 115 eV resembles the transition $\text{Si}2p - e (3d-3p)$ states. A partial shifting of such states is evidenced at specific annealing temperatures, and some features on L-edge XAS spectra could be a trace of very weak partial crystallization of the SiO_2 shell, more likely its surface exposed due to lower probing depth in TEY mode.

The Si K-edge spectra acquired in PFY mode revealed a significantly different shape than in amorphous silica (a-SiO_2) [125]. Thus, the central peak ascribed as A is noted at the photon energy range of 1846 – 1852 eV, and the second broad one denoted as C at the photon energy range of 1860 - 1875 eV. The A peak does not correspond to the peak marked in L - edge spectra by the exact letter cause in this case, the transition to $\text{Si}1s - \text{Si}3s$ is a dipole state forbidden. Thus, for K - edge spectra, the first narrow dominated A peak can be associated with a transition from $\text{Si}1s$ to antibonding t_{2g} with a majority $\text{Si}3p$ character. On the contrary, such a transition is not allowed for L - edge spectra. The following broad peak, denoted as C, represents the transition $\text{Si}1s - t_{2g}$ with main $\text{Si}3d$ -like states. The splitting between A and C peaks in K-edge spectra is stable over annealing and equals about 17 eV. It is worth underlining that between both peaks, there are somewhat visible weak states marked as B (around 1586 eV), especially for higher annealing temperatures, which could be assigned to $\text{Si}1s$ - e.g. transition with main $\text{Si}3d$ -like states. The splitting between B and C states of about 11 eV is in good agreement with previously reported by *Li et al.* [125]. As shown by the authors, some features in the L-edge and K-edge XAS spectra for Si-based compounds are modified over the sample form and coordination number of Si atoms. However, the comparison of Si K- edge and L-edge spectra in our case reveals the bond mixing of Si $3p$ and $3s$ orbitals and Si $3p$ and $3d$ orbitals. The shape of both types of spectra resembles mainly amorphous SiO_2 (a-SiO_2). Also, the local structure of a-SiO_2 has a tetrahedral 4:2-coordination symmetry, where the transition of Si $2p$ electrons to the t_2 state of high $\text{Si}3p$ -like character becomes dipole allowed. It is worth underlining that both L-edge and K-edge lines are almost unchanged upon annealing, proving the stability of the silica shell, which remains amorphous. Thus, based on XAS spectra analysis, there is unequivocal evidence that SiO_2 crystallizes over with T_A , which is in agreement with XRD data. This is contrary to previous studies of NFO@SiO_2 core-shell structures, where the crystallization of the silica shell was induced by annealing to $T_A = 900^\circ\text{C}$ [41].

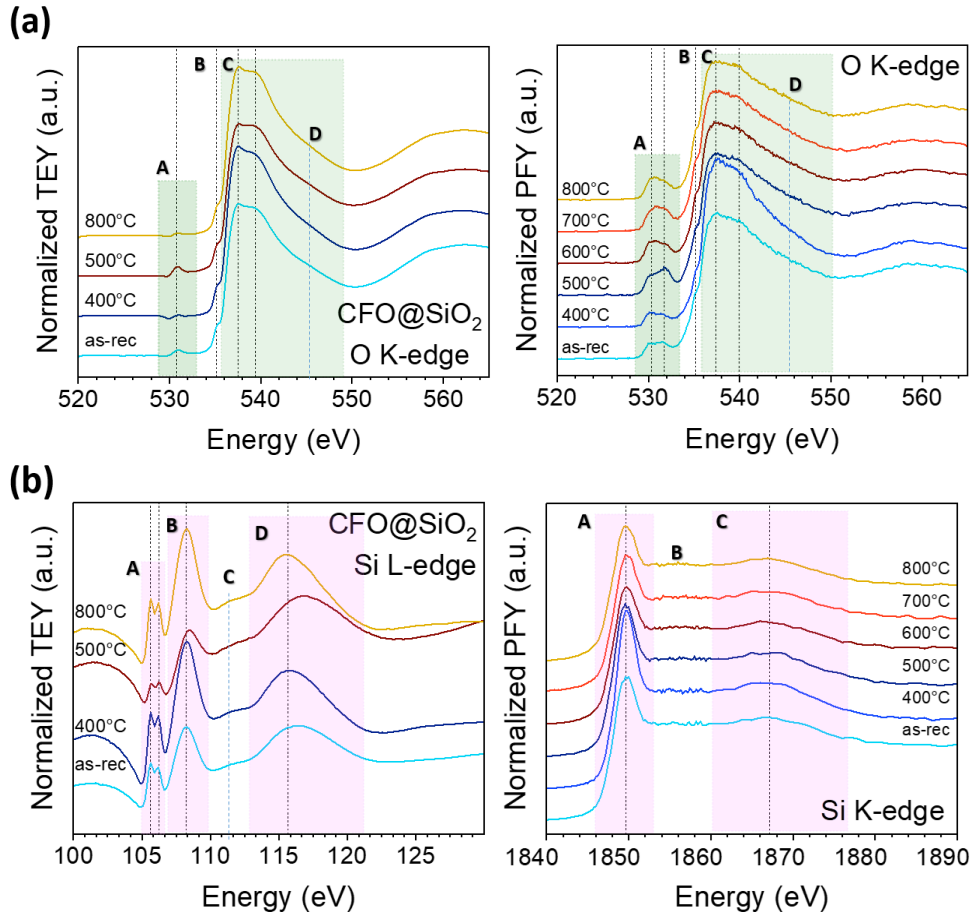


Fig.16. The comparison of XAS spectra in CFO@SiO₂ composites (a) O -K-edge and (b) Si L-edge and K-edge measured in TEY and PFY modes, respectively.

3.7. Magnetic properties

Fig.17a shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves measured at an external field of $H_{DC} = 100$ Oe and in the temperature range of 5-350K for exemplary samples as-received and annealed at $T_A = 400, 600$ and 800°C . All measured $M(T)$ curves display a noticeable $M_{FC}-M_{ZFC}$ difference at a low-temperature regime, which value is reduced with the sample processing from 1.48 emu/g (as-received) to 12.7 emu/g ($T_A = 800^\circ\text{C}$). The shape of the FC curve, which becomes flat as the temperature decreases, indicates strong interparticle correlations in all measured samples. The M_{ZFC} curves in all cases are raised with the temperature, but the maximum is barely detectable in the available T range. Obviously, for superparamagnetic nanoparticles, the FC and ZFC curves should overlap above the blocking temperature (T_B), which is the maximum temperature (T_{max}) in ZFC curves. In our case, such overlapping occurs above 350 K, meaning that in such a range, all measured composites exhibit rather ferrimagnetic arrangements of magnetic moments and most of the CFO nanoparticles are blocked. The source of such magnetic behaviour is the indirect interaction between two magnetic sublattices, A – tetrahedral and B-octahedral, which is

realized via oxygen anions. It is well established that T_{max} is proportional to the particle size, and usually, when particle size is larger, such a value is shifted to higher temperatures. It is worth underlining that the point where FC and ZFC bifurcate is called the irreversibility temperature T_{irr} , corresponding to the blocking process of larger particles. In our case, the distribution of particle size is significant, as manifested by TEM analysis, and therefore, the T_{irr} is larger than the available measurement temperature range. However, as can be noted from Fig.17a, there are some peculiarities below T_{max} at the temperatures denoted as T_I . For the as-received sample, such a hump is around $T_I \approx 285$ K, and for annealed samples around $T_I \approx 319$ K ($T_A = 400^\circ\text{C}$), $T_I \approx 297$ K ($T_A = 600^\circ\text{C}$), but for the sample annealed at the last stage ($T_A = 800^\circ\text{C}$), such additional hump is not visible. The origin of $M(T)$ peculiarities is probably attributed to the freezing effect of smaller particles leading to the spin-glass states. Such behaviour was already observed, e.g. by *Demirci et al.* [10], where for pure CoFe_2O_4 , the additional hump was found at 320 K. On the contrary, *Li et al.* [14] explained such an effect as a possible presence of the Verwey transition between 100 – 150 K, which is not a realized scenario in our case.

It is worth noting that in the case of magnetic nanoparticles, there are two essential critical sizes, namely (i) the superparamagnetic blocking radius (D_B) and (ii) the critical domain size (D_{crit}). The first one determines the classification of nanoparticles as SPM, where thermal fluctuations overcome the magnetocrystalline anisotropy energy for NPs smaller than D_B . The second one defines the critical size of single-domain nanoparticles and NPs below the D_{crit} transform from a multidomain state to a single domain. Both sizes can be expressed as:

$$D_B = \left(\frac{6k_B T_B}{K} \right)^{\frac{1}{3}} \quad D_{crit} = \left(\frac{36\sqrt{AK}}{\mu_0 M_S^2} \right) \quad (17)$$

where T_B is a blocking temperature, K is a magnetocrystalline anisotropy constant, A is an exchange constant, M_S denotes a saturation magnetization for a bulk compound, k_B is a Boltzmann constant and μ_0 is vacuum permeability. Considering that of the bulk CoFe_2O_4 , the K was found as 290 kJ/m^3 , the blocking radius for $T_B = 300$ K was found as $D_B \approx 4.4 \text{ nm}$ [14] while the critical domain size was estimated as ten times higher $D_{crit} \approx 40 \text{ nm}$ [8, 129].

By analyzing the average size of studied CFO cores in CFO@SiO_2 composites, we can claim that in all cases, CFO is above the published value of D_B and below the D_{crit} and hence, we could expect single domain particles with an average size higher than D_B . Nonetheless, some CFOs are smaller than D_B due to a significant size distribution. Thus, some peculiarities in magnetic properties could be expected in such a scenario.

Due to the available $M(T)$ measurement apparatus being only 350 K to estimate the T_{max} values, a Gauss function approximation of ZFC curves was made. The obtained T_{max} values are changed from $T_{max} \approx 360 \pm 7$ K (as-received) to $T_{max} \approx 376 \pm 4$ K ($T_A = 800^\circ\text{C}$). Interestingly, for the sample annealed at $T_A = 400^\circ\text{C}$, such a value is the lowest $T_{max} \approx 333 \pm 1$ K. Ayyappan *et al.* [130] summarized the T_B dependence versus particle size. As shown, for 2-3 nm, the blocking temperature was found to be 100 - 160K, but for 12 nm, it was drastically raised to about 390 K. The values above 300 K were also found by Demirci *et al.* [10] for particles of about 20 nm. In addition, Grigorova *et al.* [12] proved a significant increase in T_B from 1250 K to 623 K versus annealing temperatures from 325 °C to 700 °C, respectively. This effect is due to the temperature-driven CFO crystallization process, also confirmed by Omelyanchik *et al.* [28]. Parma *et al.* [25] estimated $T_B \approx 177$ K for 3 nm-sized CFO in the SiO₂ matrix. Thus, the CFO blocking temperature is independent of the particle size and can be tuned by heat treatment.

It is worth emphasizing that in the case of DC measurements, the relaxation time (τ_m) equals $\tau_m = 10^2$ s and, therefore, the blocking temperature T_B identical to maximum temperature T_{max} for uniaxial particles is expressed as:

$$T_B = \frac{\Delta E_a}{25k_B} = \frac{K_{eff}V}{25k_B} \quad (18)$$

where ΔE_a denotes the effective activation anisotropy energy barrier with the effective anisotropy constant K_{eff} , the particle volume V and k_B is the Boltzmann constant. Considering the T_{max} estimated from ZFC curves and the average particle size from TEM approximating the particle shape as spherical, the value of the K_{eff} constant could be determined, and the product of both parameters gives the value of the effective activation anisotropy energy barrier. As known, there are several features contributing to the ΔE_a values as intrinsic NPs anisotropy, such as (i) magnetocrystalline or stress anisotropy, (ii) shape anisotropy, (iii) surface spin disorder in the so-called magnetic “dead layer” with a specific thickness D_L and (iv) the inter-particle dipolar or exchange interactions. The effective anisotropy constant estimated for CFO encapsulated in SiO₂ shells based on ZFC dependence measured at 100 Oe and approximated to obtained T_{max} can be estimated by taking into account the average d_{TEM} values. Thus, the effective anisotropy constant is modified from about $(7.86 \pm 0.65) \times 10^5$ erg/cm³ (as-received) to $(8.16 \pm 0.45) \times 10^5$ erg/cm³ (annealed at $T_A = 800^\circ\text{C}$) (see Table III). Interestingly, K_{eff} is the highest for moderate annealing temperatures, which might be an effect of shape anisotropy, considering the significant particle size distribution for such annealing conditions. The assessed values are in reasonable agreement with those previously reported. The blocking process of

smaller and larger particles and various T_B related to the type of the used synthesis is reflected in noted differences in K_{eff} . As found, e.g. by *Omelyanchuk et al.* [28], the effective anisotropy constant for CFO annealed at 800°C equals $2.3 \times 10^5 \text{ J/m}^3$ and is reduced from $7.9 \times 10^5 \text{ J/m}^3$ for the sample annealed at 700°C. The increase in the heat treatment up to 900°C will lead to further reduction even up to $1.9 \times 10^5 \text{ erg/cm}^3$. *Jummaa et al.* [38] manifested the dependence of anisotropy constant with particle size. As seen, such a parameter was reduced with the increased particle size and a simultaneous decrease in saturation magnetization. The noted correlation directly affected cations distribution and the CFO – SiO₂ mixing ratio. As it is well known, effective anisotropy is considered as an interplay between core size and surface effects, including the cation distribution in the spinel lattice. Thus, the change in the core structure, cation distribution, degree of spin canting and larger magnetocrystalline anisotropy might be induced by higher T_A .

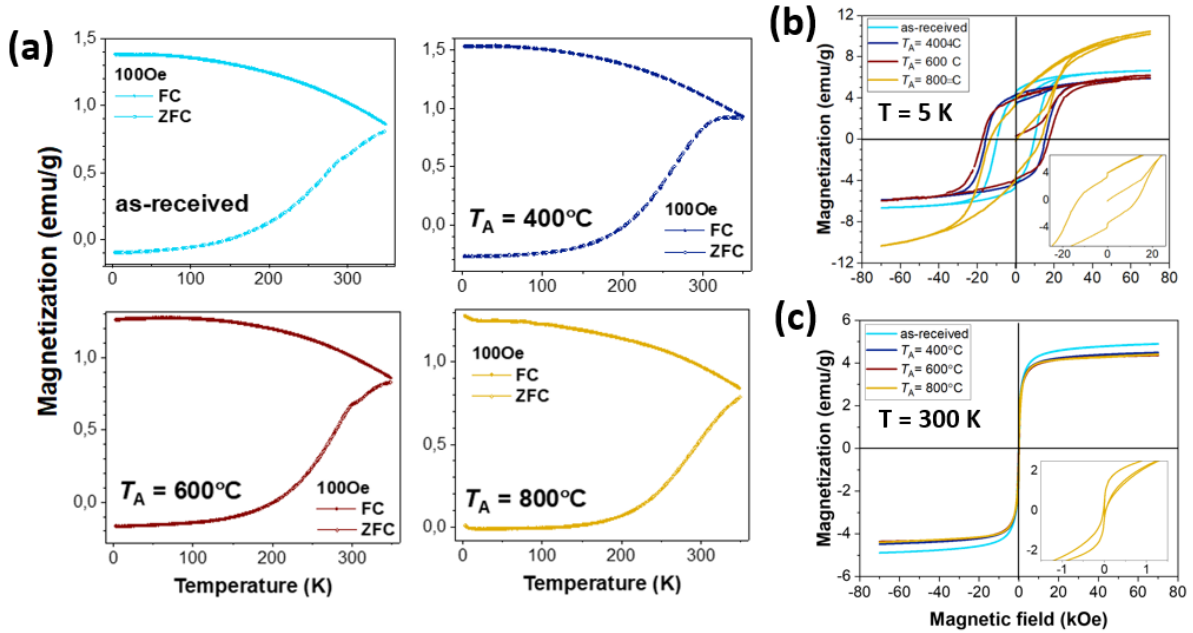


Fig.17. (a) Temperature dependence of DC magnetization as FC- ZFC curves measured at $H_{DC} = 100 \text{ Oe}$ and **(b)** hysteresis loops measured at 5 K and 300 K (RT) for as-received and selected annealed CFO@SiO₂ composites.

The evolution of magnetic hysteresis loops $M(H)$ acquired at 5 K and 300 K versus annealing temperature is shown in Fig.17b. The shape of measured loops at low temperatures resembles the ferromagnetic behaviour of all analyzed samples due to the ferrimagnetic alignment between the two magnetic A and B sublattices. The non-saturated behaviour observed at the highest applied external field may originate from the magnetic core-shell-like morphology of CFO with magnetically ordered cores and disordered shells [131, 132]. Comparing the measured hysteresis loops, we may infer that the heat treatment process modifies the magnetic properties noticeably. As observed, for the samples annealed at $T_A = 800^\circ\text{C}$, the

saturation magnetization value is the largest, which underlines the effect of the temperature-driven crystallization process. As manifested, the CFO core size is considerably larger at $T_A = 800^\circ\text{C}$. Compared to lower T_A and as-received samples, the raised M_S can be explained by the domination of the CFO cores ordered magnetic moments. The observed low-temperature non-saturated $M(H)$ behaviour, as in many other known ferrites, can be associated with the interplay between the possible existence of strong inter-particle interactions and the core-shell-like morphology of magnetic NPs having a ferrimagnetic core and spin-glass-like surface layer. However, the CFO@SiO₂ samples measured at 300K are typical S-shaped hysteresis with significantly lower remanence, and negligible coercivity might suggest the superparamagnetic behaviour. Here, the hysteresis exhibits more saturated behaviour, which is consistent with FC-ZFC curves. Comparing the M_S values for all measured samples, we may infer that the lowest value was found in the range $T_A = 400 - 600^\circ\text{C}$, which is in fair agreement with all other parameters. Thus, for such a temperature range, the inversion factor of Co²⁺ at the A site is the lowest, leading to different magnetic arrangements between the A and B sites. The exact M_S values might be estimated by many different approaches. The most common one is simply the extrapolation of high-field curves to zero. Thus, the M_S values for CFO nanoparticles encapsulated in the SiO₂ shells are modified versus annealing temperature from 5.85 emu/g (as-received) to 6.73 emu/g ($T_A = 800^\circ\text{C}$) and 4.61 emu/g (as-received) to 4.08 emu/g ($T_A = 800^\circ\text{C}$) estimated at 5K and 300 K respectively (see Table III). Notwithstanding, it is worth underlining that M_S is significantly lower than for pure CFO nanoparticles [1-17] due to the size effects tuned by synthesis type, annealing process and, as a consequence, various cations distribution. As demonstrated, the slight increase of M_S for higher T_A can be linked to the domination of the ordered magnetic moments in the magnetic core of particles, which undergo the crystallization process. As shown, at 5K, the $M(H)$ hysteresis loops reveal quite significant coercivity (H_C) changes from 9.3 kOe (as-received) to 13.1 kOe ($T_A = 800^\circ\text{C}$) with a noticeable maximum value for samples annealed at $T_A = 400 - 600^\circ\text{C}$ (see Table III). At room temperature, coercivity has almost vanished, indicating the possible SPM behaviour. The enhancement of magnetic parameters after the annealing process is consistent with the effects noticed by e.g. Chaudhuri *et al.* [18], Wang *et al.* [20], Mitra *et al.* [21] and Dippong *et al.* [31-33].

Table III. Magnetic parameters estimated as-received and selected annealed CFO@SiO₂ composites.

Magnetic parameters			Annealing temperature T_A (°C)			
			as-received	400	600	800
determined at $H_{DC} = 100$ Oe	$M_{FC} - M_{ZFC}$ (emu/g) at 5K		1.48 ± 0.01	1.81 ± 0.01	1.43 ± 0.01	1.27 ± 0.01
	T_{max} (K)		360 ± 7	333 ± 1	351 ± 1	376 ± 4
	$K_{eff} \times 10^5$ erg/cm ³		7.86 ± 0.65	24.96 ± 2.69	12.75 ± 0.85	8.16 ± 0.45
determined from the hysteresis loops	M_{9T} (emu/g) ± 0.01	5K	7.38	7.01	6.20	8.44
		300K	5.22	4.53	4.61	4.56
	M_S (emu/g)	5K	5.85	5.03	4.67	6.73
		300K	4.61	4.19	4.16	4.08
	M_R (emu/g) ± 0.05	5K	4.46	4.33	3.92	3.69
		300K	0.67	0.32	0.61	0.42
	M_R / M_S	5K	0.76	0.86	0.83	0.55
		300K	0.15	0.08	0.15	0.10
	H_C (kOe) ± 0.05	5K	9.72	15.44	17.45	13.06
		300K	0.10	0.04	0.08	0.03

The hysteresis loop squareness expressed by the M_R/M_S ratio at 5 K is significantly larger than the theoretically predicted by the Stoner–Wohlfarth (S-W) model [131, 132]. Thus, the magnetic interaction between CFO core nanoparticles is considerably effective. Such a large ratio may indicate the mixed multi-domains and single-domain particles emphasizing the dominant participation of larger multi-domains, similarly as shown by *de Lima Alves et al.* [9] and *Demirci et al.* [10]. What is more, such an enhanced ratio might be an effect of the interplay of anisotropy and various magnetization processes in the core and on the surface of particles due to possible surface spin disorder, which can also explain the hysteresis loop shape at lower temperature regimes, especially seen for as-received composites. However, at RT, the S-W criterium $M_R/M_S < 0.5$ is fulfilled, and the ratio is lower than 0.2 for all measured samples, proving the domination of non-interacting uniaxial CFO single-domain particles with the randomly oriented easy axis at this temperature range. Thus, obviously, by extrapolation to zero, lower M_S values than M_{9T} are obtained (see Table III). Afterwards, by employing the calculated from XRD cations distribution an estimation of the magnetic moments in A-tetrahedral and B-octahedral sublattices can be carried out. As manifested, the selection of the synthesis method affects the distribution of magnetic cations in A and B sites, leading to ferrimagnetically coupled A and B magnetic moments by super-exchange interactions via oxygen anions [131]. However, in the case of inverse or mixed spinel ferrites the adopted two A-B sublattice Néel model describing such a magnetic arrangement is often insufficient. Accordingly, the alternative *Yafet–Kittel* (Y-K) approach [133-136] based on the three sublattice model is adopted. According to the Y-K model, the B – B-magnetic sublattice is, in

fact, composed of two B1 and B2 sublattices forming the triangular lattice. Each of them has equal in magnitude but oppositely canted magnetic moments with the *Yafet-Kittel* canting angle denoted as α_{YK} , which can be determined by the following formula:

$$m_{exp}(\mu_B/f.u) = M_B \cos \alpha_{YK} - M_A \quad (19)$$

where the (m_{exp}) value is estimated from $M(H)$ by the extrapolation to zero, the theoretical M_B and M_A magnetic moments are simply calculated considering cation distribution in the crystal lattice from XRD diffraction and theoretical values of cationic moments as $\text{Co}^{2+} - 3\mu_B$ and $\text{Fe}^{3+} - 5\mu_B$. The discrepancies between the theoretical and experimental magnetic moments are explained in the Y-K model by the surface spin canting effect. Considering the aforementioned approach, the estimated canting angle slightly depends on the T_A . Thus, the values estimated at low temperatures 5 K for as-received sample equal: $\alpha_{YK} \approx 58.5 \pm 1$ (as-received), $\alpha_{YK} \approx 56.8 \pm 1^\circ$ (annealed $T_A = 400^\circ\text{C}$) and $\alpha_{YK} \approx 58.1 \pm 1^\circ$ (annealed $T_A = 800^\circ\text{C}$). Similarly, at room temperature, such values are just slightly modified as follows: $\alpha_{YK} \approx 58.9 \pm 1^\circ$ (as-received), $\alpha_{YK} \approx 57.4 \pm 1^\circ$ (annealed $T_A = 400^\circ\text{C}$) and $\alpha_{YK} \approx 59.2 \pm 1$ (annealed $T_A = 800^\circ\text{C}$). It is worth underlining that the obtained YK parameters are noticeably higher than previously calculated for NFO@SiO₂ composites annealed at the same temperatures [41], which confirms the larger surface disorder for CFO-based core-shell nanocomposite, including the significant particle size distribution.

The thickness of the magnetically disordered layer (D_L) [136, 137] as the MDL can be estimated according to the model proposed by *Pereira et al.* [135], employing the expression below at a given temperature:

$$M_{S(CFO)} = M_{S(CFO)}^{bulk} \left(\frac{d_{TEM} - 2D_L}{d_{TEM}} \right)^3 \quad (20)$$

where $M_{S(CFO)}$ represents the experimental value of the saturation magnetization for CFO cores with the corresponding values of average d_{TEM} particle size from TEM analysis; $M_{S(CFO)}^{bulk}$ is the saturation magnetization value for the bulk CFO adopted from the *Grigorova et al.* [12] paper as 80 emu/g. It is worth emphasizing that the MDL thickness considerably affects the surface anisotropy compared to volume one [131]. Thus, the estimated MDL thickness based on the above equation is almost sustained regardless of the samples heat treatment and equals about $D_L \approx 3.5 \pm 0.2$ nm (as-received), $D_L \approx 2.2 \pm 0.1$ nm ($T_A = 400^\circ\text{C}$), $D_L \approx 3.2 \pm 0.1$ nm ($T_A = 600^\circ\text{C}$) and $D_L \approx 3.7 \pm 0.4$ nm ($T_A = 800^\circ\text{C}$). As seen, the lowest value was noted for the sample annealed at $T_A = 400^\circ\text{C}$, for which the largest size distribution was demonstrated with the lowest value of the average particle size. The comparable MDL thickness regardless of samples

processing confirm considerable samples stability as manifested by other complementary methods. It is well known that D_L coincides with the interactions of surface core atoms with atoms of functionalized surface [137]. Thus, if the shell exhibit well - defined stability over annealing the thickness of MDL should also be only slightly modified, which was herein confirmed for CFO@SiO₂. Ayyappan *et al.* [130] evidenced the MDL thickness as 1.3 nm of 11 nm sized CFO and reported value is in the known range between 0.5 – 1.5 nm for the cobalt ferrite nanoparticles. Such a disorder layer thickness is also in a good agreement with values demonstrated for other ferrites [41, 137-139] and its exact value is not only dependent on the NPs size but also on the employed synthesis method.

3.8. Mossbauer spectrometry

The Mössbauer spectrometry (MS) acquired at room temperature (RT) revealed the existence of both magnetic (MP) and non-magnetic (NMP) phases for all studied CFO@SiO₂ nanocomposites (see Fig.18). The fitting model considered the discrete hyperfine magnetic field (H_{hf}) distribution for the magnetic component and quadrupole doublet for the non-magnetic component. The model, which has been developed on the basis of a thorough analysis of the available data, reflects the dynamics of the magnetization of CFO nanoparticles as a function of their size distribution and temperature, as well as the topological disorder of the iron atoms in the CFO spinel structure. Fig. 18b illustrates the evolution of the hyperfine field distribution shape as a function of annealing temperature obtained through spectral fitting. As the annealing temperature increases, the distribution narrows, and its maximum shifts toward higher field values. This behaviour indicates that higher temperatures facilitate the diffusion of Fe³⁺ ions from a disordered state (nanoparticles) into a more ordered arrangement, forming progressively larger polycrystals. This interpretation is consistent with XRD, TEM microscopy, and magnetometry results. For the first two samples in the CFO@SiO₂ series, namely as-received and annealed at 200°C, the distribution is broad. For higher applied annealing temperatures, the distribution width is reduced and the mean and the most probable field value (but called H_{max}) of H_{hf} increase (see Fig.18c right bottom panel). Such an effect corresponds to the crystallization process driven by annealing and is consistent with XRD and TEM data.

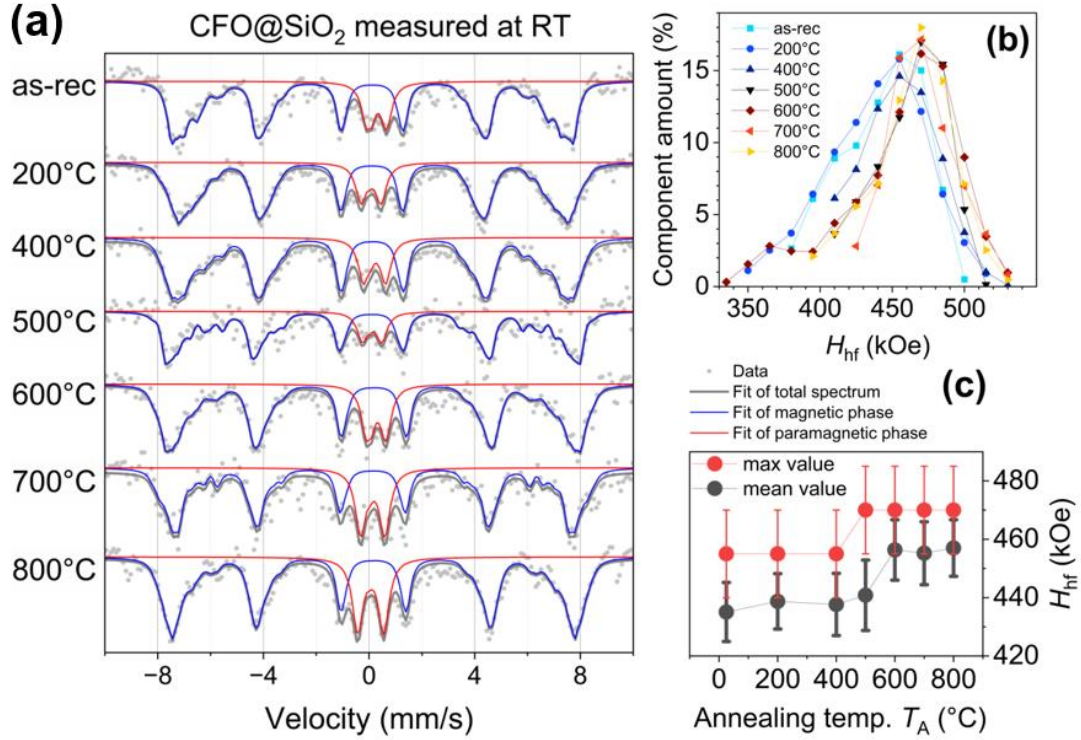


Fig.18. (a) Mössbauer spectra for CFO@SiO₂ composites measured at 300K (denoted as RT) annealed at different T_A ; **(b)** the hyperfine field distribution; **(c)** the mean and the most probable field values based on the hyperfine field distribution.

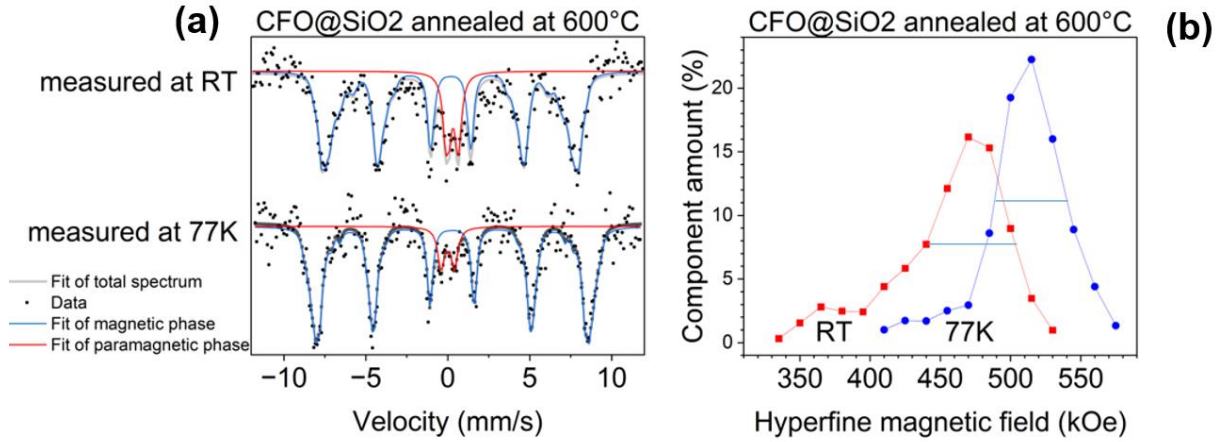


Fig.19. (a) Mössbauer spectra measured at 77K and 300K for CFO@SiO₂ annealed at $T_A = 600^\circ\text{C}$. The fit of the non-magnetic phase is denoted in red, and the magnetic phase is marked in blue. **(b)** The comparison of the distribution of hyperfine magnetic induction estimated at 77 K and 300 K.

Fig.19 compares the exemplary spectra for the CFO@SiO₂ sample annealed at $T_A = 600^\circ\text{C}$, measured at room temperature and 77 K, with a hyperfine magnetic field distribution. It can be observed that as the temperature decreased, the H_{hf} field distribution became increasingly refined for low H_{hf} values (see Fig.19b), and that the proportion of the non-magnetic component decreased in favour of the magnetic component (see Table IV). This trend may be interpreted as a variation in the magnetisation dynamics of CFO nanoparticles as a

function of temperature. The observed behaviour is similar to that of NFO@SiO₂ annealed at $T_A = 800^\circ\text{C}$ [41]: the most probable H_{hf} values occur when MS is measured at a lower temperature (77K). The results point to the fact that at 77 K, the magnetisation of CFO intermediate-sized particles, with a blocking temperature distribution between 77 K and 300 K, is blocked due to the dominance of anisotropy energies over thermal agitation, resulting in an increase in the magnetic component. At elevated temperatures (300 K), the smaller particles are in the superparamagnetic state and constitute the non-magnetic component. The H_{hf} values for samples measured at room temperature are lower than for bulk CFO [140], which may be the same reason as for the previously mentioned NFO@SiO₂ [41]. The hyperfine parameters obtained from the resolved MS spectra are presented in Table IV. The mean value of δ obtained for the magnetic component is 0.30 ± 0.03 mm/s for measurement at room temperature and 0.43 ± 0.02 mm/s for measurement done at 77K. As in the case of NFO@SiO₂ [40], the value measured at a lower temperature is more likely to correspond to the Fe^{3+} state of iron with a total spin of 5/2. The average value of the quadrupole shift (2ε) approaches zero, further confirming the cubic symmetry of the magnetic phase. The hyperfine parameter values of the non-magnetic component are consistent with those of superparamagnetic ferrite spinel nanoparticles, as previously reported in our paper on NFO@SiO₂.

Considering a broad particle size distribution, as manifested by TEM analysis, we may also estimate the distribution of blocking temperatures (T_B) based on the particle size distribution and using the superparamagnetic *Néel-Brown* model [141]. Employing such an approach to the Arrhenius law describing fluctuating magnetic moment between two stable equilibrium states with relaxation time $\tau_0 \approx 10^{-12}\text{s}$ as for assembly of spinel ferrites [142] and the value of instrumental relaxation $\tau_m \approx 10^{-8}\text{s}$ typical for Mössbauer measurement we can estimate the distribution of T_B based on the equation:

$$k_B T_B = \frac{K_{\text{eff}} V}{\ln\left(\frac{\tau_m}{\tau_0}\right)} \quad (21)$$

utilizing the particle size values from TEM data and K_{eff} determined from magnetic measurements. Thus, for the as-received sample, the blocking temperature changes from $T_{B(\text{min})} \approx 76$ K to $T_{B(\text{max})} \approx 73\,402$ K with an average of $T_{B(\text{avg})} \approx 7080$ K, for particle size distribution d_{min} , d_{max} and d_{TEM} , respectively. The applied annealing at $T_A = 400^\circ\text{C}$ reduces the estimated values to $T_{B(\text{min})} \approx 13$ K, $T_{B(\text{max})} \approx 65\,470$ K and $T_{B(\text{avg})} \approx 1792$ K, while further heat treatment to the final stage at $T_A = 800^\circ\text{C}$ modifies it to $T_{B(\text{min})} \approx 251$ K, $T_{B(\text{max})} \approx 48\,756$ K and $T_{B(\text{avg})} \approx 7125$ K. The apparent difference between herein calculated T_B values and those determined

from ZFC is caused by different characteristic measurement times τ_m . Thus, the two revealed MP and NMP contributions in Mössbauer spectra are well justified. For a given temperature, the MP sextet represents the ferrimagnetic blocked state for larger CFO particles, whereas the NMP doublet defines the superparamagnetic state for smaller CFOs. The MP dominates the whole spectra, which is in agreement with magnetic data. Mössbauer spectrometry is one of the valuable methods to determine cations distribution in the spinel ferrite lattice [9-11, 14, 27, 37], which corroborates with sample magnetic performance. However, to precisely determine the iron distribution in A-tetrahedral and B-octahedral sites, more accurate measurements in-field MS measurements would be more suitable in the future. To summarize, the observed changes in MS spectra are the effects of particle size distribution, cation distribution and the spin-canting effect of the CFO surface with the MDL, which was proved by magnetic analysis.

Table IV Mössbauer spectra parameters for CFO@SiO₂ spinel nanoferrites as-received and annealed up to $T_A = 800^\circ\text{C}$.

Annealing temperature T_A (°C)	Phase	Contents	Isomer shift	HWFM	Quadrupole shift/splitting	Hyperfine magnetic field (mean)	Hyperfine magnetic field (max)
			δ (mm/s)	Γ (mm/s)	$2\varepsilon/QS$ (mm/s)	$H_{hf(mean)}$ (kOe)	$H_{hf(max)}$ (kOe)
Spectra measured at RT:							
as-received	MP	86%	0.28 ± 0.02	0.18	0.02 ± 0.03	435 ± 11	455 ± 15
	NMP	14%	0.45 ± 0.03	0.24	0.63 ± 0.05	-	-
200	MP	87%	0.29 ± 0.02	0.18	0.06 ± 0.03	439 ± 10	455 ± 15
	NMP	13%	0.23 ± 0.03	0.24	0.66 ± 0.04	-	-
400	MP	87%	0.29 ± 0.02	0.18	0.02 ± 0.03	438 ± 11	455 ± 15
	NMP	13%	0.37 ± 0.03	0.24	0.74 ± 0.04	-	-
500	MP	89%	0.27 ± 0.02	0.18	0.05 ± 0.03	441 ± 13	470 ± 15
	NMP	11%	0.27 ± 0.05	0.24	0.64 ± 0.08	-	-
600	MP	85%	0.32 ± 0.02	0.18	-0.02 ± 0.03	456 ± 11	470 ± 15
	NMP	15%	0.43 ± 0.03	0.24	0.62 ± 0.04	-	-
700	MP	79%	0.31 ± 0.02	0.18	0.03 ± 0.03	455 ± 11	470 ± 15
	NMP	21%	0.30 ± 0.03	0.24	0.82 ± 0.04	-	-
800	MP	79%	0.33 ± 0.02	0.18	0.00 ± 0.03	457 ± 10	470 ± 15
	NMP	21%	0.22 ± 0.02	0.24	0.90 ± 0.03	-	-

4. Conclusions

In the current research, we are focused on the influence of the heat treatment-driven modification of the CFO@SiO₂ core-shell nanocomposites. As shown, the physical properties

can be tuned by slightly applying the multistage annealing procedure at the temperature regime $T_A = 400\text{-}800^\circ\text{C}$.

As we have found in all studied nanocomposites, the CFO cores crystallize in the cubic inverse spinel structure with Fe^{3+} and Co^{2+} cation distribution in A-tetrahedral and B-octahedral sites in the cubic unit cell. The slight dependence of the inversion degree of magnetic ions was demonstrated versus T_A by PXRD and Raman spectroscopy with emphasis on the minimum degree of inverted structure for $T_A = 400^\circ\text{C}$. This feature is associated with significant microstructural non-uniformity, linked to the various than for other samples particle size distribution. It is worth underlining that SiO_2 is almost stable regardless of the annealing without its evident crystallization, which positively infers potential bioapplications. Noticeable but subtle growth of CFO cores from about $d_{\text{TEM}} \approx 11.9$ nm to about $d_{\text{TEM}} \approx 13.2$ nm was evidenced by TEM analysis proving the stability of nanoparticles in the overall annealing process. However, a drop to $d_{\text{TEM}} \approx 6.9$ nm was found in the middle T_A regime, accompanied by a significant particle distribution. In addition, the amorphous SiO_2 shell size of about 40 nm is almost unchanged, and no trace of core-shell degradation is detected. The nanocomposite chemical composition was also unveiled by EDS, which confirmed the formation of CFO@ SiO_2 composites.

The magnetic performance is linked to the particle size and cations distribution in the ferrite lattice. The noted significant modification in the blocking temperature (T_B) from 360 K (as-received) to 376 K ($T_A = 800^\circ\text{C}$) with a 333 K minimum ($T_A = 400^\circ\text{C}$) is an effect of annealing-driven microstructural alteration. The estimated effective magnetic anisotropy constant, which in turn is the largest for $T_A = 400^\circ\text{C}$ refers to the considerable influence of the CFO surface and shape anisotropy. The spin-canting effect in the dead magnetic layer (MDL) was also identified by the *Yafet-Kittel* model. The determined change in the MDL thickness over annealing based on magnetic analysis is rather minor. The analyzed M_R/M_S ratio at low temperatures confirms the magnetic properties of studied nanocomposites with emphasis on the interplay between larger multi-domain and low-sized single-domain nanoparticles. Such an effect was also justified by the *Mössbauer* spectrometry, which confirms the mixture of the ferrimagnetic and SPM nanoparticles in the whole T_A temperature regime as two-fold *Mössbauer* spectra.

The XPS and XAS analysis confirmed the Fe^{3+} and Co^{2+} cation distribution over the tetrahedral A – and octahedral B – sites. The existence of possible Si-O-Co/Fe intermixing on the CFO surface was revealed by the complex electronic structure analysis. The stability of the

silica shell during heat treatment was assessed by XPS and XAS spectra. Thus, indubitably, the biocompatible silica shell as a CFO core coating acts as a protection against excessive grain growth during annealing, reinforcing the CoFe₂O₄@SiO₂ nanocomposites application possibility. The auxiliary low-cost and eco-friendly synthesis technology conditions and corroborated temperature-driven nanocomposite stability make the studied core-shell samples favourable and captivating materials as e.g. effective novel drug delivery systems or magnetic hyperthermia.

CRediT authorship contribution statement

A. Bajorek: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Funding acquisition, Project administration, Resources, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **A. Czempik:** Investigation, Data curation, Formal analysis, Visualization, Writing - review & editing. **F. Grasset:** Investigation, Formal analysis, Methodology, Resources, Writing - review & editing. **S. Auguste:** Investigation, Data curation. **M. Dulski:** Data curation, Investigation, Formal analysis, Writing - original draft. **M. Fijalkowski:** Data curation, Investigation. **E. Beyer:** Data curation, Investigation. **T. Sobol:** Data curation, Investigation. **B. Wolanin:** Data curation, Investigation. **E. Jankowska-Partyka:** Data curation, Investigation. **M. Zając:** Data curation, Investigation. **N. Randrianantoandro:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Project administration, Resources, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The data supporting the findings of this study are available within the article and its Supplementary Materials. Raw data will be available on request.

Acknowledgements

The research activities were co-financed by the funds granted under the Research Excellence Initiative of the University of Silesia in Katowice under the project Freedom of Research in the City of Science. This publication was partly developed under the provision of the Polish Ministry and Higher Education project Support for research and development with the use of research infrastructure of the “National Synchrotron Radiation Centre SOLARIS” under contract nr 1/SOL/2021/2. A. Bajorek and A. Czempik also acknowledge SOLARIS Centre for access to the PHELIX and PIRX beamlines, where measurements were performed under the granted SOLARIS/PHELIX/232103 and SOLARIS/PIRX/249037 proposals. The authors are grateful to Ludivine Rault for her assistance in TEM experiments performed on the Themis platform (ScanMAT, UAR 2025 University of Rennes-CNRS). This platform received financial support from the European Union through the European Regional Development Fund (ERDF) (CPER-FEDER 2007–2014). The authors are also grateful to Krystian Prusik for the TEM (Jeol JEM 3010) measurements included in the Supplementary Materials.

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The Editor of Journal of Magnetism and Magnetic Materials

Dear Editor,

Please find enclosed the manuscript entitled:

**Unlocking the hidden potential: exploring the fascinating properties of
CoFe₂O₄@SiO₂ nanocomposites driven by annealing**

Authors: A. Bajorek, A. Czempik, F. Grasset, S. Auguste, M. Dulski, M. Fijałkowski, E. Beyer, T. Sobol, B. Wolanin, E. Jankowska-Partyka, M. Zając, N. Randrianantoandro

to be considered for publication in ***Journal of Magnetism and Magnetic Materials***.

Herein, the effect of annealing on the structural and microstructural evolution of CoFe₂O₄@SiO₂ core-shell type nanocomposites is reported. The studied nanocomposites are part of a wide range of spinel ferrites-based nanomaterials studied towards various versatile possible applications, among which biomedical, e.g. targeted drug delivery systems, hyperthermia or cancer treatment, are among the most desirable. So far, CoFe₂O₄ nanoparticles have been synthesized by diverse and relatively low-cost methods such as e.g. sol-gel, co-precipitation, microemulsion, combustion, hydrothermal, citrate, and ball-milling, allowing tuning their physico-chemical properties. However, CoFe₂O₄ nanoparticles exhibit quite significant magnetic properties; their application in the field of biotechnology and nanomedicine, as in the case of many other spinel ferrite nanoparticles (SF-NPs), requires an encapsulation or coating by non-magnetic and biologically compatible shells to ensure well dispersed and homogeneous ultrafine NPs with the narrow particle size distribution. Thus, as a final product, the core-shell structure is obtained, where SiO₂ shell, e.g. (i) prevents SF-NPs aggregation, (ii) as a porous coating allows transport of gases from and to the ferrite core, (iii) can be used in active catalytic applications, (iv) provides a chemically inert surface allowing for its further functionalization and (v) stabilizes the metallic core from excessive modification over annealing, which is usually a key factor to enhance the core properties.

Considering the outstanding properties of such composites, which would indicate a huge application potential in many areas, they have to be accurately characterized by multi-technique approaches. However, despite many studies done so far, the properties of selected CoFe₂O₄@SiO₂ core-shell type nanocomposites have not been fully discovered and understood.

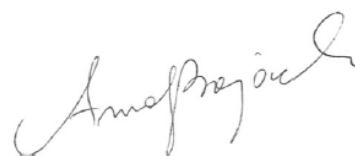
Thus, the submitted paper aims to annealing-driven the structural, microstructural and magnetic evolution of the CoFe₂O₄@SiO₂ core-shell composite. To achieve this goal, we have utilized a complementary multi-technique analysis. The deepened studies of the electronic structure by photoemission spectroscopy and using the synchrotron radiation for absorption spectroscopy correlated with structural, microstructural, and magnetic properties are one of the key novelty parts of the presented data compared to other research for CoFe₂O₄@SiO₂ nanomaterials.

The clear evidence of the Si-O-Ni/Fe intermixing on the interface between CFO and SiO₂ nanoparticles was confirmed by electronic structure analysis employing X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) by synchrotron radiation.

The structural characterization revealed the stability of CFO cores with a noticeable, but subtle growth from about $d_{\text{TEM}} \approx 11.9$ nm to about $d_{\text{TEM}} \approx 13.2$ nm was evidenced over the annealing process. The presence of cubic inverse spinel ferrite structure with tetrahedral and octahedral trivalent iron occupancy is confirmed in all analyzed samples. The slight dependence of the inversion degree of magnetic ions was demonstrated versus T_A by PXRD and Raman spectroscopy with emphasis on the minimum degree of inverted structure for $T_A = 400^\circ\text{C}$. This feature is associated with significant microstructural non-uniformity, linked to the various than for other samples particle size distribution. It is worth underlining that SiO₂ is almost stable regardless of the annealing without its evident crystallization, which positively infers potential bioapplications. Additionally, the amorphous SiO₂ shell size of about 40 nm is almost unchanged, and no trace of core-shell degradation is detected. The nanocomposite chemical composition was also unveiled by EDS confirming the formation of CFO@SiO₂ composites. The magnetic performance is linked to the particle size and cations distribution in the ferrite lattice. The noted significant modification in the blocking temperature (T_B) from 360 K (as-received) to 376 K ($T_A = 800^\circ\text{C}$) with a 333 K minimum ($T_A = 400^\circ\text{C}$) is an effect of annealing-driven microstructural alteration. The estimated effective magnetic anisotropy constant, which in turn is the largest for $T_A = 400^\circ\text{C}$ refers to the considerable influence of the CFO surface and shape anisotropy. The spin-canting effect in the dead magnetic layer (MDL) was also identified by the *Yafet-Kittel* model. The determined change in the MDL thickness over annealing based on magnetic analysis is rather minor. The analyzed M_R/M_S ratio at low temperatures confirms the magnetic properties of studied nanocomposites with emphasis on the interplay between larger multi-domain and low-sized single-domain nanoparticles. Such an effect was also justified by the *Mössbauer* spectrometry, which confirms the mixture of the ferrimagnetic and SPM nanoparticles in the whole T_A temperature regime as two-fold *Mössbauer* spectra. The XPS and XAS analysis confirmed the Fe³⁺ and Co²⁺ cation distribution over the tetrahedral A – and octahedral B – sites. The existence of possible Si-O-Co/Fe intermixing on the CFO surface was revealed by the complex electronic structure analysis. The stability of the silica shell during heat treatment was assessed by XPS and XAS spectra. Thus, indubitably, the biocompatible silica shell as a CFO core coating acts as a protection against excessive grain growth during annealing, reinforcing the CoFe₂O₄@SiO₂ nanocomposites application possibility.

We hope that our detailed approach will expand and the existing state-of-the-art and the auxiliary low-cost and eco-friendly synthesis technology conditions and corroborated temperature-driven nanocomposite stability make the studied CFO@SiO₂ core-shell samples favourable and captivating materials suitable for potential application in many areas, including magnetic hyperthermia. For the above-exposed reasons and those explained in the manuscript, we believe that our results directly lie within the scope of this journal and have relevant implications for the scientific community with interests at the borderline between physics, chemistry and materials science. We are convinced of the current interest and timeliness of the subject and the importance of the conclusions drawn in the present manuscript. Thus, we would be grateful for considering the submitted paper for publication in the ***Journal of Magnetism and Magnetic Materials***.

On behalf of all authors
Dr hab. Anna Bajorek, prof. UŚ
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A. Bajorek: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Funding acquisition, Project administration, Resources, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **A. Czempik:** Investigation, Data curation, Formal analysis, Visualization, Writing - review & editing. **F. Grasset:** Investigation, Formal analysis, Methodology, Resources, Writing - review & editing. **S. Auguste:** Investigation, Data curation. **M. Dulski:** Data curation, Investigation, Formal analysis, Writing - original draft. **M. Fijałkowski:** Data curation, Investigation. **E. Beyer:** Data curation, Investigation. **T. Sobol:** Data curation, Investigation. **B. Wolanin:** Data curation, Investigation. **E. Jankowska-Partyka:** Data curation, Investigation. **M. Zając:** Data curation, Investigation. **N. Randrianantoandro:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Project administration, Resources, Supervision, Writing - review & editing.

Declaration of competing interest

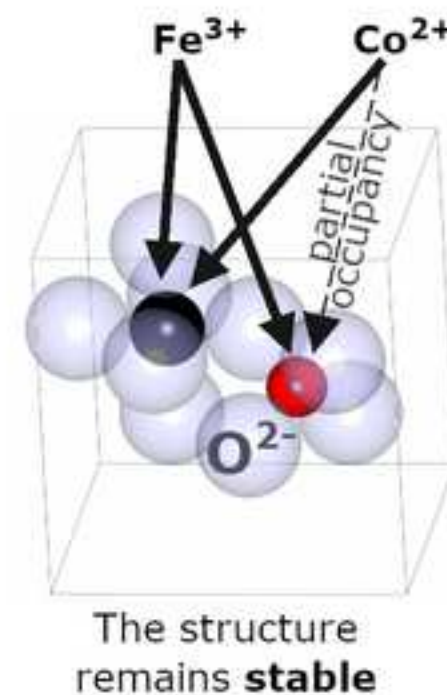
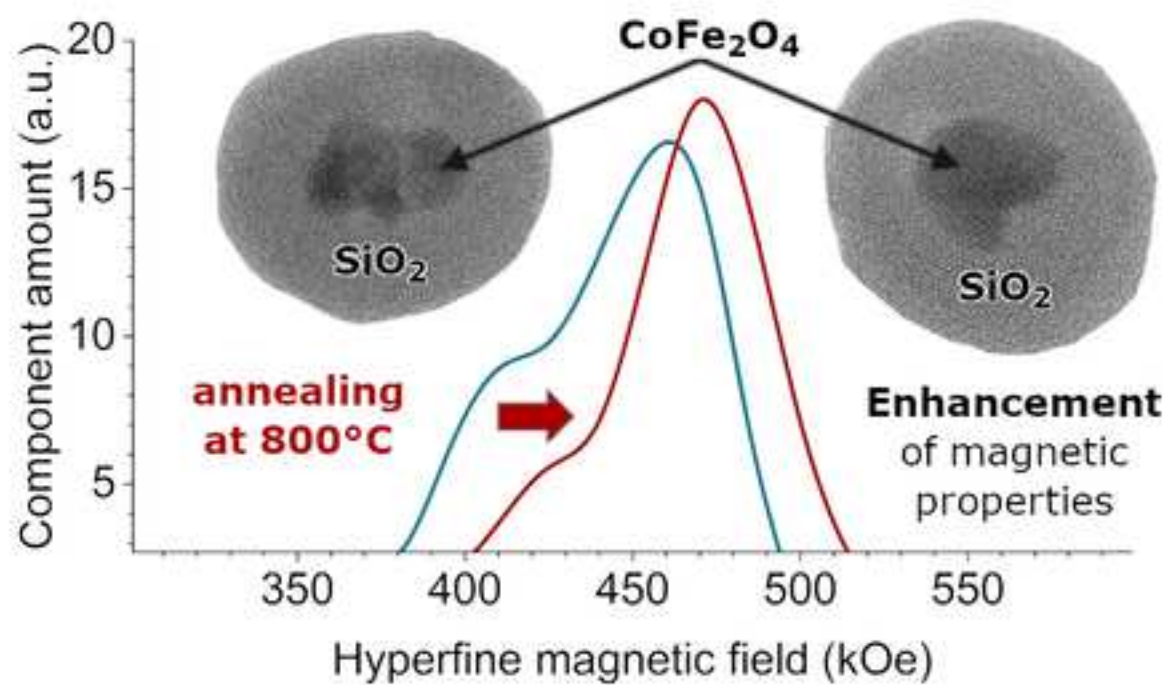
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

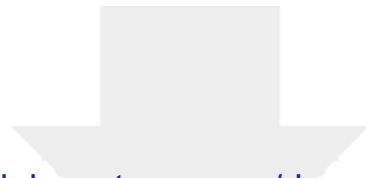
Data Availability

The data supporting the findings of this study are available within the article and its Supplementary Materials. Raw data will be available on request.

Highlights

- Physical properties of core-shell CFO@SiO₂ are tuned by annealing at $T_A=400-800^\circ\text{C}$
- A subtle growth of CFO cores crystallized in the cubic crystal structure with T_A
- The CFO is stabilized with a slight change in the inversion degree of magnetic ions with T_A
- Spin-canting effect in CFO dead magnetic layer (MDL) was identified by the *Yafet-Kittel* model
- XPS and XAS confirmed the Fe³⁺ and Co²⁺ cations distribution among A and B sites





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