



# The effect of Er doping on local structure of magnetite nanoparticles

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## Abstract

In this work  $\text{Fe}_3\text{O}_4\text{:Er}$  nanoparticles (NPs) with the characteristic size of  $\sim 11$  nm were synthesized via classic co-precipitation method. Electron microscopy and X-ray diffraction were employed to probe the morphology and structure of the samples. Results revealed that samples synthesized in the  $Fd\text{-}3mZ$  structure with lattice constant close to that of pure magnetite.  $^{111}\text{In}$  probe generator was incorporated at synthesis in order to map the evolution of hyperfine magnetic field with temperature using time differential perturbed angular correlation (TDPAC) spectroscopy. The TDPAC results are discussed in terms of the effect of Er dopant on the magnetic properties and local structure of the NPs.

**Keywords** Magnetic nanoparticles · Coprecipitation · TDPAC

## 1 Introduction

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is a ferrimagnetic compound formed by Fe(II) and Fe(III) cations, it has an inverse spinel crystal structure. Bivalent ions occupy octahedral sites, whereas the trivalent Fe is equally distributed between tetrahedral and octahedral sites [1].

Magnetite can be doped by rare earth (RE) elements that have large magnetic moments in order to increase the saturation magnetization and thus allow an enhanced potential for applications in certain areas of biomedicine [2].

The use of RE dopants in nanoparticulated ferrites can also influence the optical properties of these compounds, since in the field of optical nanothermometry the luminescence of lanthanide ions is used to approach thermal sensing at the nanoscale [3, 4].

Time-differential perturbed angular correlation (TDPAC) spectroscopy allows insights to the local magnetic field at the atomic sites occupied by the probe isotopes that act as

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impurities in the magnetic compounds making it possible to distinguish between different regions within the particles (such as core and surface), in addition to providing information about the quality of the crystallites and phase transitions. Thus, the TDPAC in cubic metal monoxides may be employed for understanding the chemistry of defects in the compounds [5, 6].

In this work we report the production of 10 at.% erbium doped magnetite ( $\text{Fe}_3\text{O}_4\text{:Er}$ ) through the classic co-precipitation method. We investigate the effect of the dopant on the local magnetic structure of the nanoparticles (NPs) with the TDPAC technique.

## 2 Experimental

$\text{Fe}_3\text{O}_4\text{:Er}$  was produced according to the classic method of Massart (1981) [7] with adaptations in the stoichiometric calculations for dopant introduction. Iron (II) chloride (Alfa Aesar 99%), iron (III) chloride (Alfa Aesar 99%), erbium (III) acetate (Sigma-Aldrich 99.9%), and ammonia solution (Casa Americana) were used as reagents for the synthesis. 200 mL of deaerated purified water were transferred to a three-neck flask. Then iron chlorides and erbium acetate were added and remained under mechanical stirring in an inert atmosphere. After 10 min, the ammonia solution was added to reach pH 10. This solution remained under mechanical stirring for 40 min. After that the specks were allowed to precipitate to the bottom of the three-neck flask. The solvent was then removed, and the residue was washed with deionized water and acetone. NPs were vacuum dried for 6 h resulting in a black, loose, and highly responsive to external magnetic fields powder.

Subsequently, the sample was divided into two parts, one part remained intact, and the other part was subjected to the heat treatment process at 500 °C for 4 h.

When unexposed to measurements the samples were stored under vacuum to prevent oxidation.

For TDPAC spectroscopy it was necessary to incorporate the radioactive probes into the samples. In the case of  $^{111}\text{In}$  generator,  $^{111}\text{InCl}_3$  solution was added at synthesis together with iron chlorides before the addition of ammonia water.

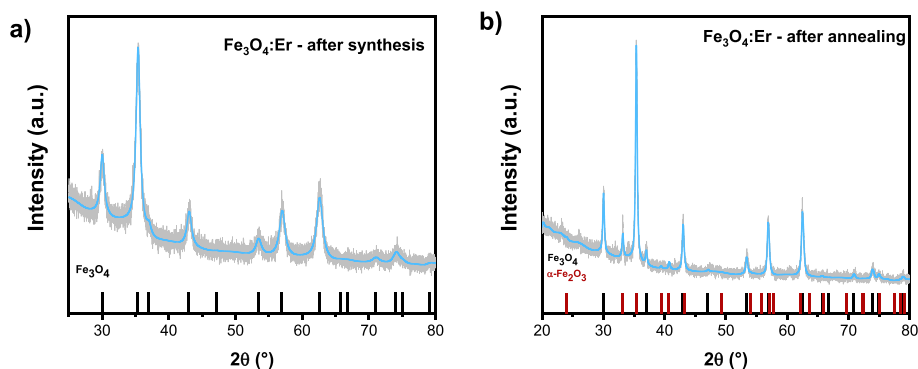
XRD analysis of the samples was carried out at Rigaku SmartLab of 3 kW ( $\text{Cu } K_\alpha$ ) diffractometer using a step scanning technique in the  $2\theta$  range 20–80 at 1°/min rate. GSAS II was employed for Rietveld refinement of the data.

Transmission electron microscopy (TEM) images were taken at JEM-2100 by Jeol and processed with ImageJ complemented by MATLAB scripts.

TDPAC experiments were performed at an analogue 4  $\text{BaF}_2$  detector spectrometer. PACfit was employed for data analysis and  $R(t)$  refinement.

## 3 Results and discussion

The  $\text{Fe}_3\text{O}_4\text{:Er}$  crystalline structure was probed with XRD as shown in Fig. 1. The reflections revealed a cubic structure with space group  $Fd\bar{3}mZ$  [8], a single magnetite phase is distinguishable at the diffraction pattern in Fig. 1a with estimated lattice parameter of 8.373 Å. This could be an indication of the incorporation of the dopant into the matrix, however, the value is close to that of conventional magnetite (8.394 Å). Crystallite size estimated with the Scherrer equation is ~ 11 nm.



**Fig. 1** XRD patterns of the Fe<sub>3</sub>O<sub>4</sub>:Er nanoparticles **a** after synthesis and **b** after 4 h annealing at 500 °C

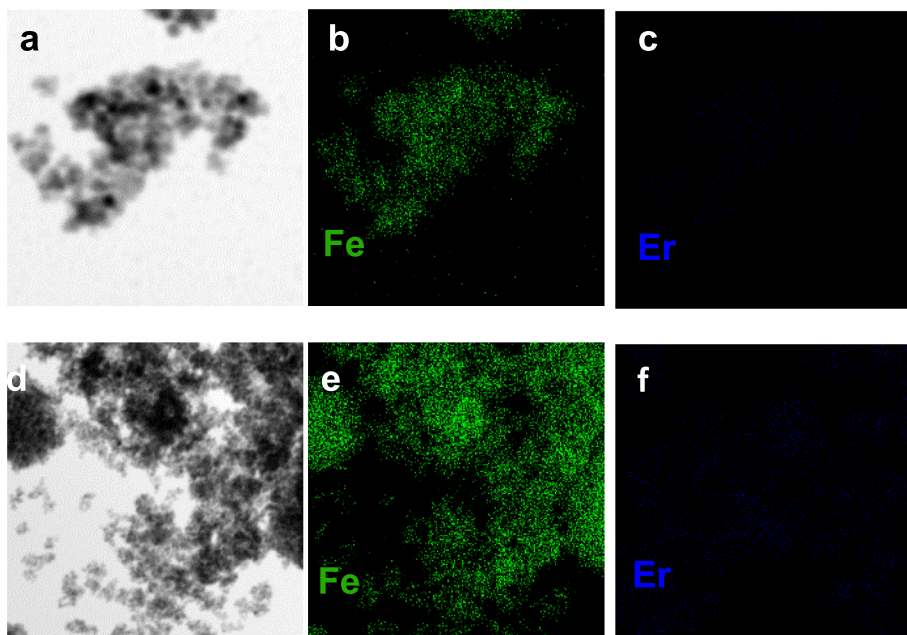
Magnetite may be easily oxidized, and the characteristic reflections of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) can be observed in post-annealing samples as shown in Fig. 1b. No reflections that could be attributed to Er oxides were detected which could support the hypothesis on substitutional doping. However, the difference in the atomic radii of Er and Fe is 25%, which violates Hume-Rothery rules for substitutional solid solutions. Together with the absence of the trace of Er oxide reflections in the patterns, this may be interpreted as the relaxation of dopant ions in the irregular environment.

XRD data also reveals an increase in the crystallite size of Fe<sub>3</sub>O<sub>4</sub>:Er from 11 to 29 nm upon annealing.

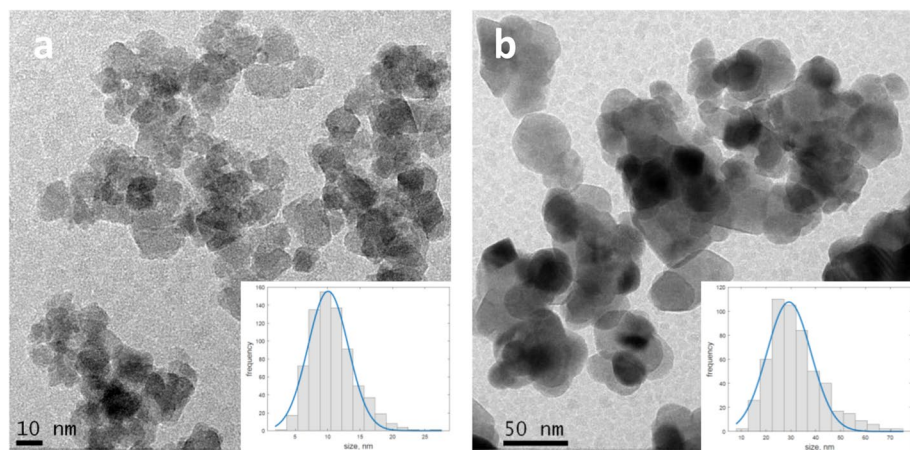
The distribution of the dopant in the samples before and after annealing was also mapped with Energy-dispersive X-ray spectroscopy (EDS), as shown in Fig. 2. Dopant distribution appears as homogeneous at EDS images. Comparing Fig. 2d, e and f, apart from the uniformity of Er distribution in the samples, one may speculate on its attachment to the formed structures.

TEM image of as synthesized NPs is shown in Fig. 3a. Their characteristic size is ~10 nm; the size distribution is relatively broad ( $\sigma \sim 3.1$  nm). After annealing the average size increased as expected, although a short annealing doesn't take the sample off the nanoscale. The mean size of the particles after annealing reaches  $30 \pm 8.9$  nm as shown in Fig. 3b. The particles demonstrate irregular shape before and after the treatment.

Figure 4 shows the spin rotation spectra measured with <sup>111</sup>Cd probe upon heating and cooling in the pre-annealed sample. One observes an easily distinguishable magnetic interaction. The evolution of the hyperfine magnetic field with temperature is shown in Fig. 4c and follows a Brillouin-like function, similarly to that of the pure Fe<sub>3</sub>O<sub>4</sub> sample. The values of the hyperfine field do not differ significantly between Er-doped and pure samples. Although the total angular momentum of Er<sup>3+</sup> ion is 3 times that of Fe<sup>3+</sup>, an approximate 6.6% increase in B<sub>hf</sub> near 0 K is prognosed in Fe<sub>3</sub>O<sub>4</sub>:Er with the help of our TDPAC data. The lack of significant effect of the presence of Er<sup>3+</sup> indicates that the dopant ions were pushed to the outer layers of the particles at synthesis. This correlates with the observed dominance of the distorted sites with broadly distributed V<sub>zz</sub> in our R(t) patterns. The latter remains in conformity with TEM results: the irregularity

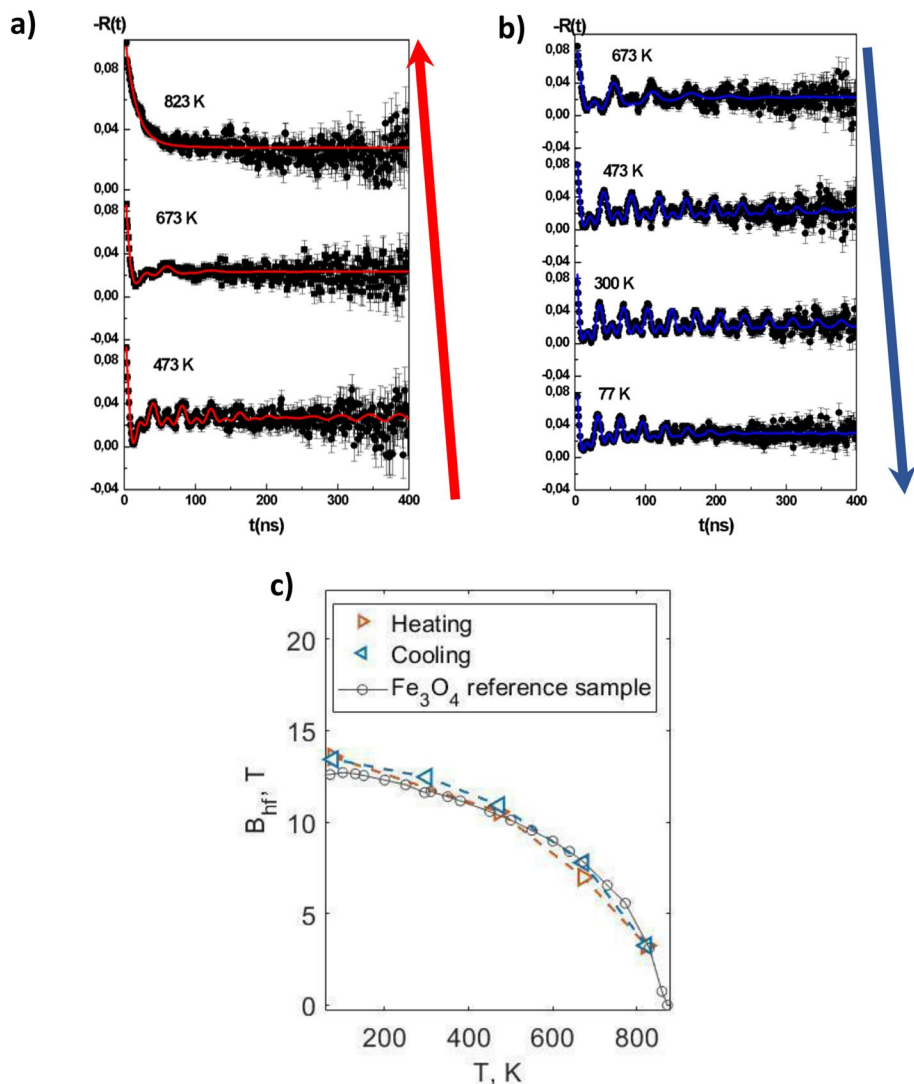


**Fig. 2** EDS scans of  $\text{Fe}_3\text{O}_4\text{:Er}$  before annealing at grayscale (**a**) and showing Fe (**b**) and Er (**c**) concentrations, as well as those after annealing (**d**, **e**, **f** respectively)



**Fig. 3** TEM images showing the morphology and size distribution of  $\text{Fe}_3\text{O}_4\text{:Er}$  NPs before (**a**) and after (**b**) annealing

of particle shapes emphasizes the large portion of the distorted sites associated with the outer layers.



**Fig. 4**  $-R(t)$  function of the  $\text{Fe}_3\text{O}_4:\text{Er}$  sample upon heating (a) and upon cooling (b). The evolution of the hyperfine magnetic field with temperature (c)

In contrast to XRD data, TDPAC did not allow to observe any contribution that might be associated with highly crystalline and defect-free hematite. We note, however, that structural irregularities that are minor for XRD may be drastic for TDPAC spectroscopy.

## 4 Conclusion

Magnetite NPs with nominal 10 at.% Er concentration were synthesized using a simple coprecipitation route. The average characteristic size of the particles was near 10 nm and increased to 30 nm upon annealing. A combined XRD, TEM/EDS and TDPAC study lead to the hypothesis on the Er concentration at irregular sites in the outer layers of the particles, but didn't exclude the possibility of the formation of amorphous agglomerates of RE oxide.

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