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Ph.D. Programme: Inorganic Chemistry

Title of the Thesis: **Preparation and characterization of magnetoelectric core@shell nanoparticles**

Short Description

Brief summary of the thesis and its results: This thesis investigates the synthesis and characterization of magnetoelectric core@shell nanoparticles that exhibit unique properties at different temperatures.

After a well written and organized introduction that highlights the state of the art of magnetism at different length scales, the main characterizations and the multifunctional magnetic materials, followed by an experimental method chapter, the thesis is organized in 6 subchapters dealing with different results. The first subchapter of the thesis focuses on the size-dependent surface anisotropy constant and surface disorder of $CoFe_2O_4$ nanoparticles. Three different sizes of these nanoparticles, with identical shape, chemical composition, and surfactant percentage, were analyzed without interparticle interactions. This investigation revealed, for the first time, that particle size influences surface spin disorder. Additionally, it was experimentally confirmed that the surface anisotropy constant remains size-independent within the studied size range.

The second subchapter of the thesis examines the heat generation of cubic $CoFe_2O_4$ nanoparticles for magnetic fluid hyperthermia applications. The study focuses on the characterization of cubic cobalt ferrite nanoparticles with a narrowed dispersion size (15 nm), that were capable of reaching 42°C within three minutes. Cytotoxicity and biocompatibility tests indicated that the sample is both biocompatible and low in toxicity, making it a promising candidate for hyperthermia treatments.

The thesis then shifts focus to multiferroic materials, specifically the structural and magnetic properties of Re-substituted $BiFeO_3$. The importance of Re doping to stabilize weak ferromagnetic behavior is demonstrated. All the results reported in the first subchapters are of high relevance and have been published on highly recognized international journals.

Then, in a fourth subchapter, this thesis explores the disentanglement of anisotropy contributions in Mn-mixed ferrite nanoparticles. This part of the work shed light, thanks to combined refinement of the SAXS ana SANS scattering, on the magnetic properties observed from IRM-DCD protocols in a previous publication of the group. It is shown that the magnetocrystalline anisotropy increases with the Co/Mn ratio. Again, the SANSPOL technique is used with high competence to unequivocally study the physical properties of the magnetic core at the microscopic level.

Finally, the thesis presents still unpublished results on the synthesis and characterization of magnetoelectric $CoFe_2O_4$@$BaTiO_3$ and $CoFe_2O_4$@$NiFe_2O_4$ core@shell nanoparticle systems. If the attempts to synthesize $CoFe_2O_4$@$BaTiO_3$ with reproducible conditions met with failure in giving reproducible results, the selection of $NiFe_2O_4$ for the shell material provided uniform and homogeneous core@shell NPs. $NiFe_2O_4$ was chosen due to its ferroelectric transition below 98 K, minimal lattice mismatch with $CoFe_2O_4$, and well-established synthesis process. Three distinct core@shell systems with uniform morphology and size distribution (<20%) were successfully synthesized and fully characterized. Magnetoelectric (ME) coupling was detected in one of these samples, which exhibited a ferroelectric transition and coupling at 10 K. This report, in which for the first time the ME coupling is observed for such a core@shell magnetic nanoparticle is of high interest and most surely will be the object of further investigations.

Commentary on individual aspects of the thesis: The research fields identified to focus the aims of the thesis, through targeted experimental research, are original and the quality of the work confirmed by the strict actuality of the selected topics, organized in 6 sub-chapters dealing with the synthesis, characterization and magnetic properties of nanoparticles. The PhD candidate, Marianna, has used with high competence, a series of different characterization techniques, ranging from small-angle neutron scattering, small-angle X-ray scattering, powder X-ray diffraction, and macroscopic magnetization to transmission electron microscopy, EDS, TGA ICP and polarization measurements.

Specific comments on the professional, linguistic and formal aspects of the thesis: The results described in this thesis, can have a very good impact in basic research and possible future technological development. Magnetic materials find applications in a range of potential areas such as catalysis, data storage, gas sensors, battery technology, optoelectronics, biomedical, electromagnetic interference (EMI) shielding, etc. All these aspects, if further implemented, can be favourable toward a potential application.

Questions and suggestions for the thesis, final evaluation: The structure of the thesis is clear, the writing is quite fluent. The quality of the written English is good, and the aims well outlined at the end of the Introduction.
There are some minor inconsistencies and typos:

- Page 1, paragraph 1.1.2, line 11: "non-magnetic ion" instead of "non-atomic ion"
- Page 10, line 25, "single multiferroics" instead of "single of multiferroics"
- Page 12: "$CoFe_2O_4$@$BaTiO_3$" instead of "$BaTiO_3$@$CaFe_2O_4$"
- Page 31, line 8: "atom" instead of "atomic"
- Page 48, first paragraph: it seems to me that on the contrary to what it is stated negative values of ΔM are observed for the samples having Co/Mn molar ratios 6.1, 2.8 and 0.6.

As a general suggestion, in sub-chapter 3.4 the experimental procedure to obtain the target modified nanoparticles in the case of Mn ferrite NPs should have been reported in the appendix D. The work, after the well detailed and correctly referenced introduction, is well organized in five different subchapters, all functional to the target aim.

Questions:

- In sub-chapter 3.2, "Cobalt ferrite nano-cubes for magnetic hyperthermia applications" the sample's magnetic properties are studied both in the solid state and as dispersion in water and toluene: this last solvent is surely not applicable for *in vivo* applications. Why it is important to evaluate the magnetic properties of the samples in an aromatic organic solvent? Is this study relevant for *in vivo* hypothermia applications?
- Sub-chapter 3.3, "Rhenium substitutions effects on the structural, morphological and magnetic properties of bismuth ferrite: There are several examples of Ba and Ca substitution effects on bismuth ferrite to obtain remnant magnetization of the material. Why the choice of rhenium, a metal for which oxo compounds are of key importance in high oxidation state, especially V and VI?
- Sub-chapter 3.4, "Disentangling anisotropy contributions in Mn-mixed ferrite nanoparticles". The effect of Zn doping at different amounts for chemically enabling cobalt

ferrite nanoparticles in magnetostrictive strain sensing applications at low magnetic fields has been studied in the literature, as reported by Anantharamaiah and co-workers in Materials Science and Engineering B 266 (2021) 115080. In this study, irrespective of whether the zinc ion is substituted for Co or for Fe in the cobalt ferrite, better magnetic and magnetorestriction parameters of the doped samples have been observed due to the tetrahedral site preference of Zn (and also is non-magnetic nature). Do you think that it would be of interest also to study the substitution of Mn for Fe for the fine tuning of the magnetic behaviour of cobalt ferrite?

- Sub-chapter 3.5 and 3.6, $CoFe_2O_4$ core@shell nanoparticles. The choice of the experimental conditions employed to synthesize the $CoFe_2O_4$ cores for the preparation of $CoFe_2O_4$@$BaTiO_3$ and $CoFe_2O_4$@$NiFe_2O_4$ nanoparticles are different. In the first case, a procedure already adopted for the synthesis of cobalt ferrite nano-cubes (sub-chapter 3.2), involving a thermal decomposition method starting from $Co(acac)_2$ and $Fe(acac)_3$ in the presence of sodium oleate and oleic acid was followed. In the second case the $CoFe_2O_4$ core was synthesized by the decomposition of Co and Fe oleates in a bomb reactor. If in the first case cubic shaped nanoparticles are obtained, in the second, spherical morphology is observed. Is there a rationale for the different strategy used in the two cases? Would it be possible to grow a shell of $NiFe_2O_4$ on the cubic cobalt ferrite nanoparticles?

Final Evaluation:

The thesis is worthy of defence. No re-assessment is necessary.

Signature **Date,** 06/04/2024

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