Conferinta Diaspora in Cercetarea Stiintifica si Invatamantul Superior din Romania
21-23 septembrie 2010

FUNCTIONAL PROPERTIES OF MULTIFERROIC COMPOSITES WITH CORE-SHELL STRUCTURE

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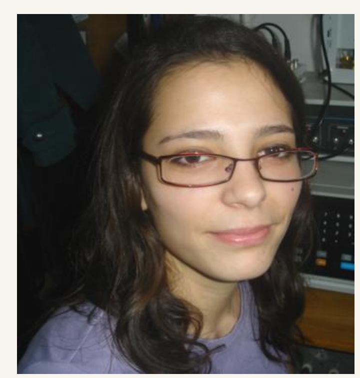

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RESEARCH TOPICS

Ferroelectrics

- Grain boundary and grain size effects in $BaTiO_3$- based ceramics

Multiferoics

- Single-phase: $BiFeO_3$- based ceramics (pure, doped and solid solutions)

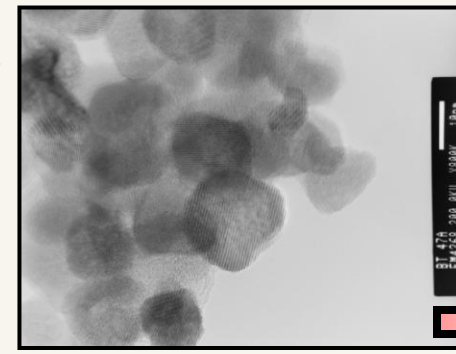
- Ferroelectric-magnetic composites

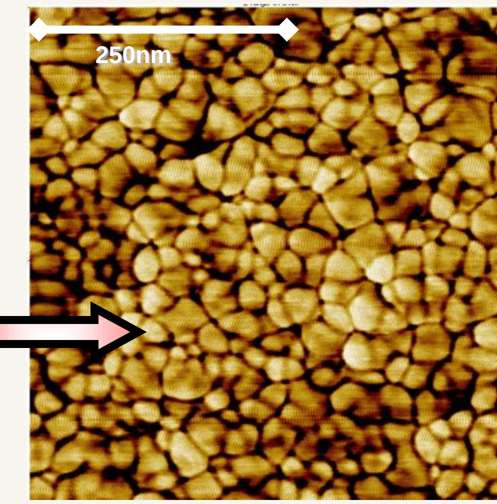
MAIN RESULTS

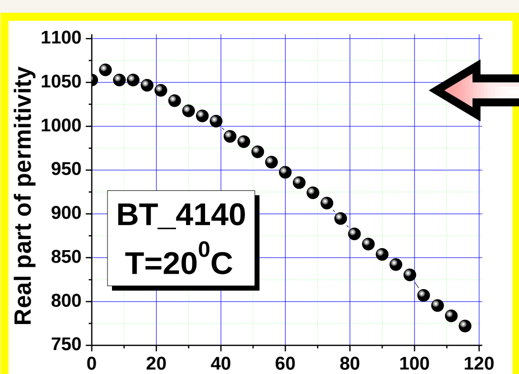
Ferroelectrics

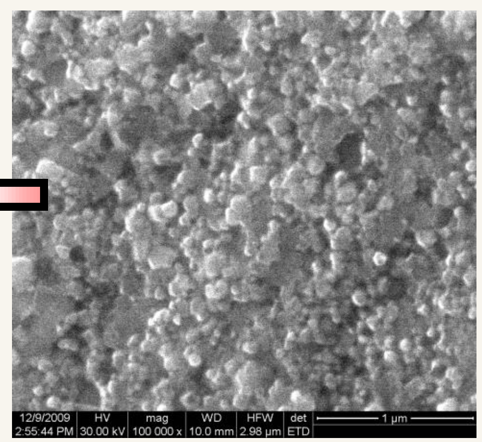
- **Grain boundary and grain size effects in $BaTiO_3$ – based ceramics**

- grain size & grain boundary phenomena in dense nanostructured ceramics (down to ~30nm)
- phase transitions; ferroelectric-relaxor crossover
- tunability $\varepsilon(E)$









- ***Collaboration with dr. Catalin Harnagea, INRS-EMT, Univ. Québec, Varennes, Canada (former group member)***

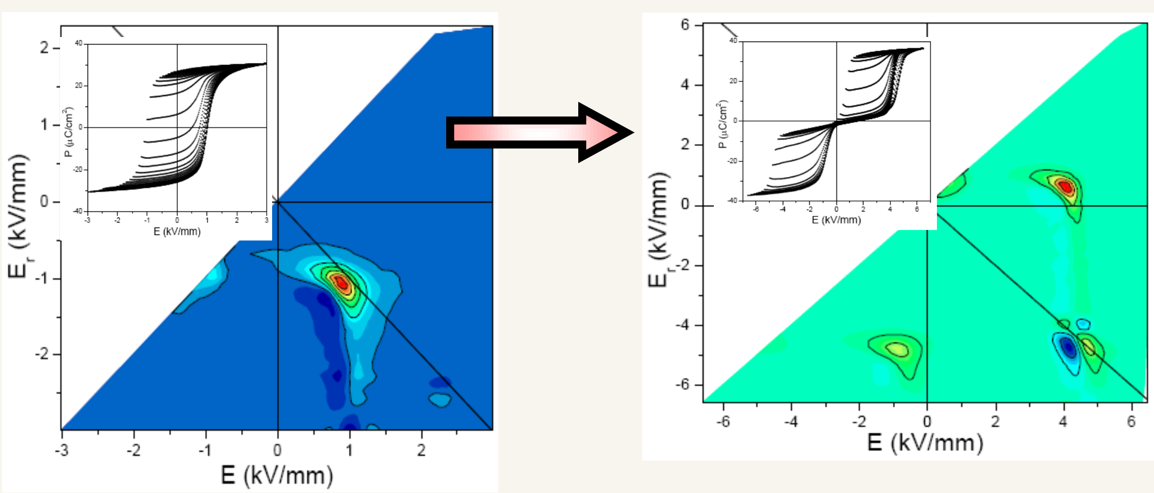
- ***NATO Grant; Romanian CEEX-FEROCER grant, Bi-lateral agreement Romania-Italy (Genova), European COST 525 and 539 Actions***

MAIN RESULTS

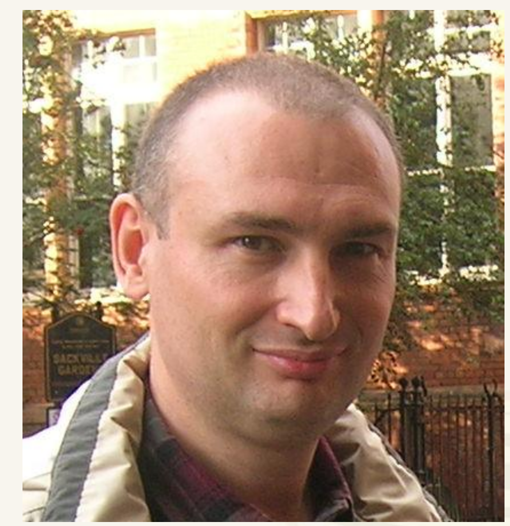
Ferroelectrics

- **Study of PZT (MPB) and PLZT (ferro-antiferro) by first order reversal curves (FORC) method and modeling**

-Study of the switching characteristics (based on the Preisach distribution over bias and coercivity)



FE-AFE crossover



- ***Collaboration with dr. Dan Ricinschi , Tokyo Inst. of Technol, Japan (former group member)***

- ***Bi-lateral agreement Romania-Italy (Faenza), Bi-lateral agreement Romania-Japan (Osaka)***

MAIN RESULTS

Multiferroics

- Single-phase: $BiFeO_3$- based ceramics (pure, doped and solid solutions)

ECAPD IX Roma

SAPIENZA Università di Roma

9th European Conference on Applications of Polar Dielectrics
Roma, August 25th-29th 2008

Award

The International Advisory Board of the 9th European Conference on Applications of Polar Dielectrics (ECAPD9) held in Roma (Italy) from August 25th to 29th 2008 selected the contribution titled

Functional properties of the
(1-x)$BiFeO_3$ – x$BaTiO_3$ solid solutions

presented by

Felicia Prihor

as one of the six best works of the conference.

Roma, August 29th 2008

On behalf of the International Advisory Board
Prof. Francesco Michelotti
Conference Chair

Sponsored by

LOT Oriel Group Europe

HAMAMATSU

- ❖ *(1-x)$BiFeO_3$ – x$BaTiO_3$ solid solutions*
- ❖ *$BiFeO_3$ – doped with: Mn, Cr, Sc, La, etc…*

- ***Romanian CNCSIS-AC CONSMEMF grant, European COST MP0904 Action***

MAIN RESULTS

Multiferroics

In-situ prepared ferroelectric-magnetic composites

(i) using templates: (Ni,Zn)Fe_2O_4, $CoFe_2O_4$ with $BaTiO_3$ and (Pb,Zr)TiO_3

(ii) core-shell approach: Fe_2O_3@$BaTiO_3$

Premiul I in competitia nationala a Societatii Romane de Ceramica, reprezentant al Romaniei la *Student contest of the European Ceramic Society, Cracovia, 2009*

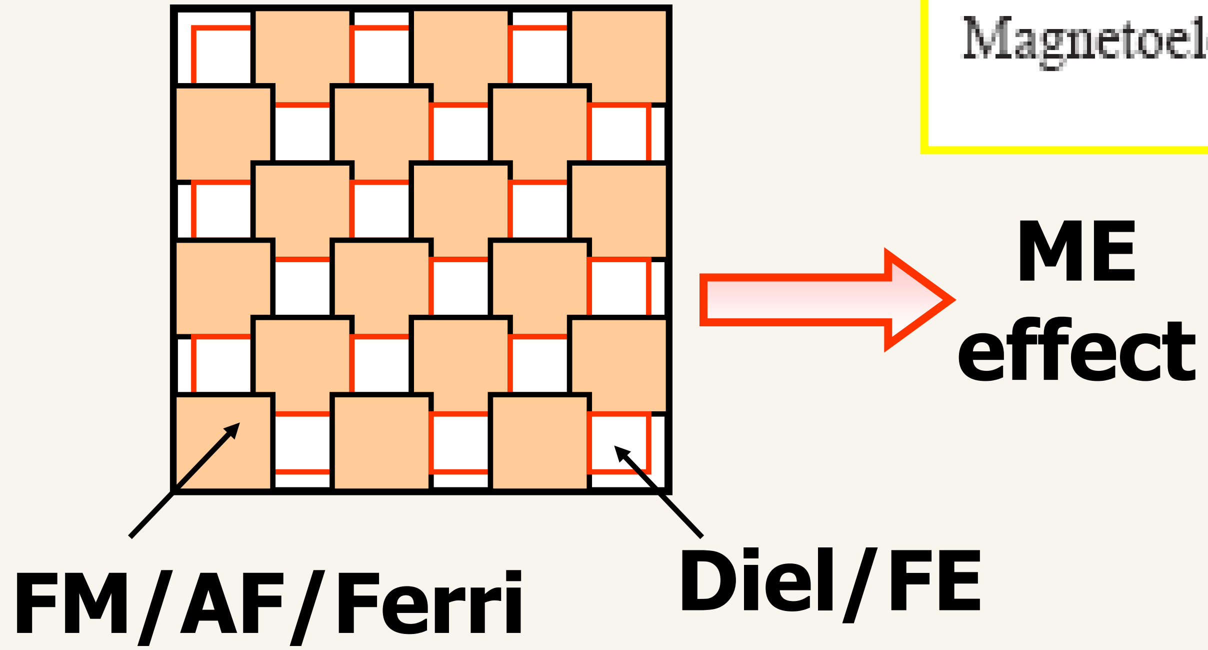
- ***Romanian grants PN II_RU_TE_187/2010, FSE-POSDRU* 89/1.5/S/49944, 89/1.5/S/63663**

I. Introduction

<u>Composite materials:</u> combining di-similar materials in compact structures in order to obtain new properties (***sum***, ***combinatory*** or ***product*** properties) and ***multifunctionality***.

Magnetoelectric (ME) composites coupling via magnetostrictive-piezoelectric effect:

$$\text{Magnetoelectric} = \frac{\text{electrical}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}}.$$



• *J. Van Suchetelene, Philips Res. Rep. 27, 28 (1972)*

Methods for producing ME composites

➢ **Mixing of the phases separately prepared**

The large majority of publications reported the use of this method to obtain ME composites.

➢ **In situ preparation of the composites:**

- coprecipitation, gel-combustion

- *P. Padmini et al., J. Mater. Chem. 4, 1875 - 1881 (1994)*
- *L. Mitoseriu et al., J. Eur. Ceram. Soc. 27, 4379–4382 (2007)*
- *A. Iordan et al., J. Eur. Ceram. Soc. doi:10.1016/j.jeurceramsoc.2009.03.031*

- core-shell powder composites

- *F. Caruso, Adv. Mater. 13, 11 (2001)*
- *C. Huber et al., Ceram. Inter. 30, 1241-1245 (2004)*
- *Y.S. Koo et al., Appl. Phys.Lett. 94, 032903 (2009)*
- *Y. Deng et al., Adv. Mater. 21, 1-6 (2009)*
- *M.S. Park et al., Phys. Rev.B 79, 024420 (2009)*

→ **followed by appropriate sintering to obtain dense ceramics.**

II. Our approach

❖ to produce ME powder composites with core-shell structure using **innovative combined wet chemistry** and **solid-state methods**;

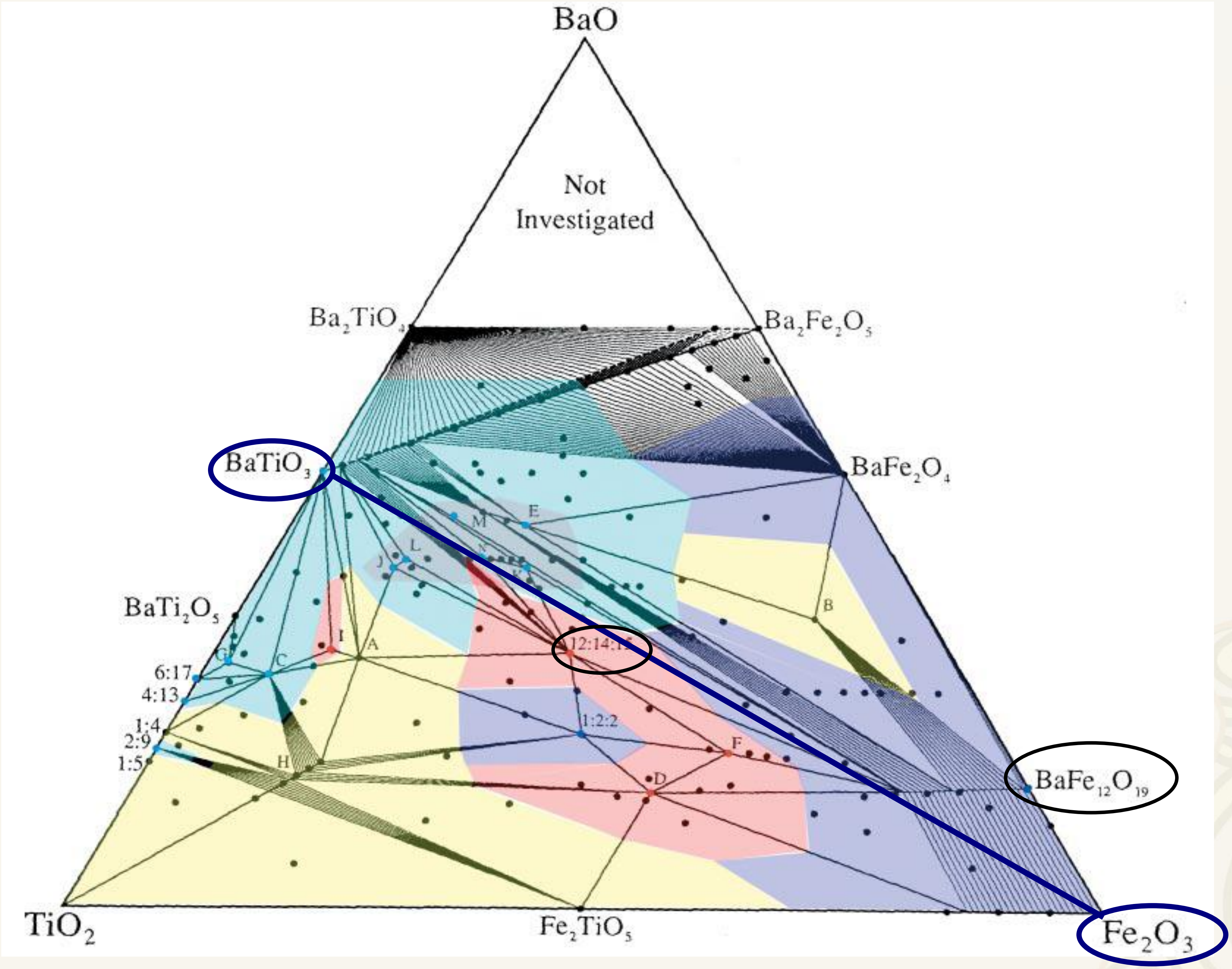
❖ appropriate **sintering strategy** to control

(i) phase assemblage (isolation of the magnetic phase: 0-3 connectivity)

(ii) controlling the chemical reactions at interfaces (nanoscale composition and coupling);

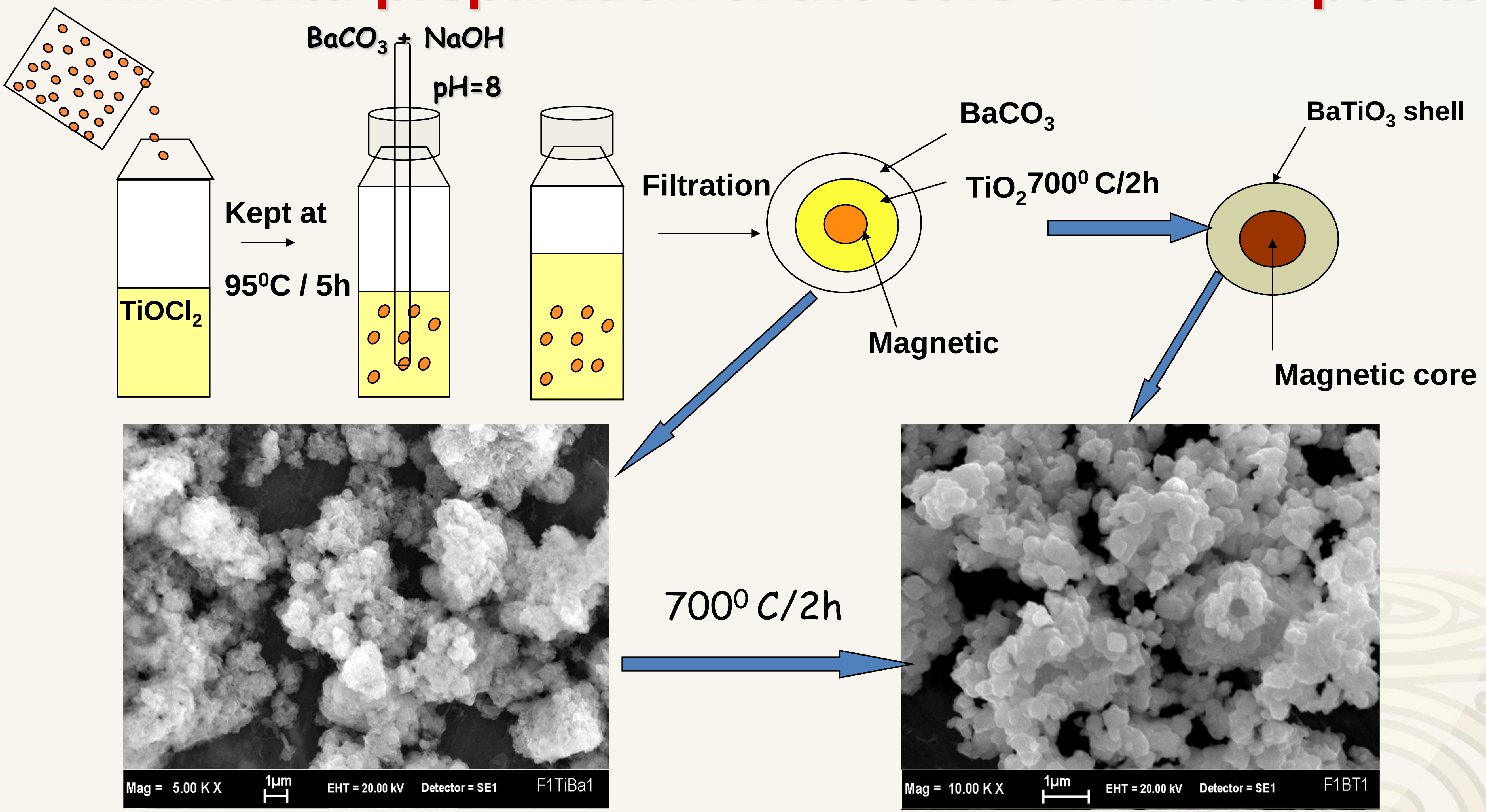
❖ expected to drive towards **new functional properties**.

Choosing the appropriate system



•*T. Siegrist, et al., Eur. J. Inorg. Chem. 14831501 (2003)*

III. In situ-preparation of the core-shell composite



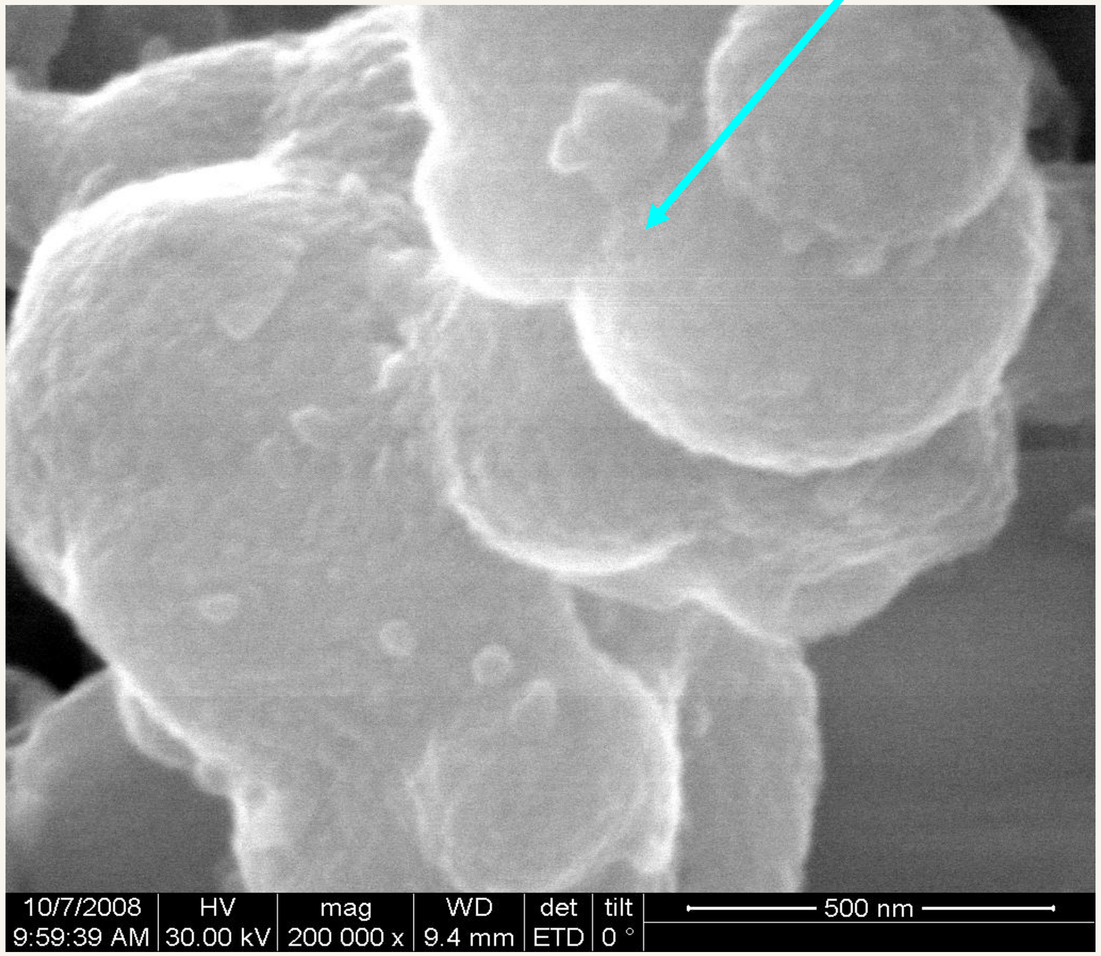
$\alpha Fe_2O_3@TiO_2@BaCO_3$ before calcination

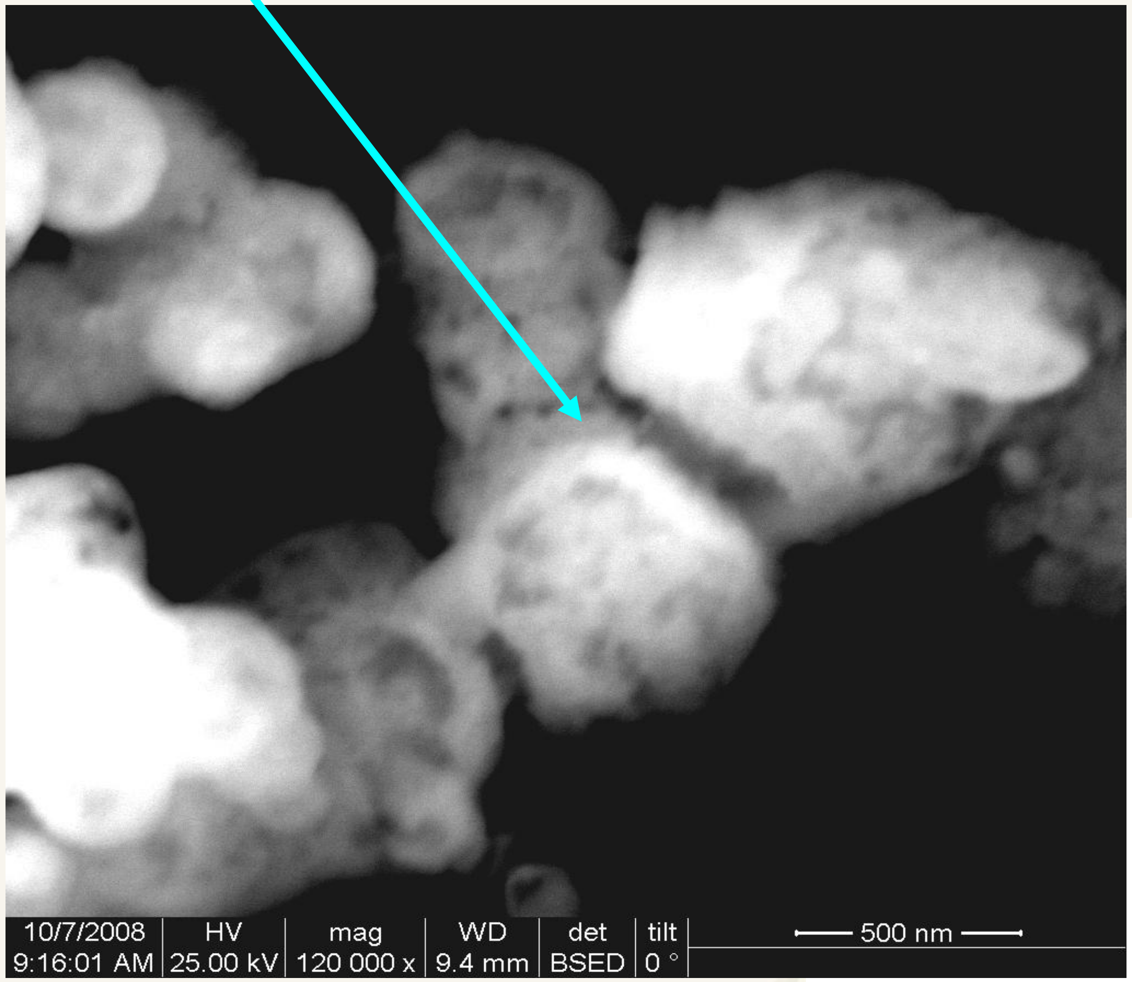
$30\%\alpha Fe_2O_3@70\%BaTiO_3$ (after calcination)

- *M.T. Buscaglia et al. Chem. Mater. 22, 4740-4748 (2010)*

IV. Microstructural characterization

Powders - The magnetic phase perfectly covered by $BaTiO_3$ shell
⇒ spherical nanocomposites with **0-3 connectivity.**

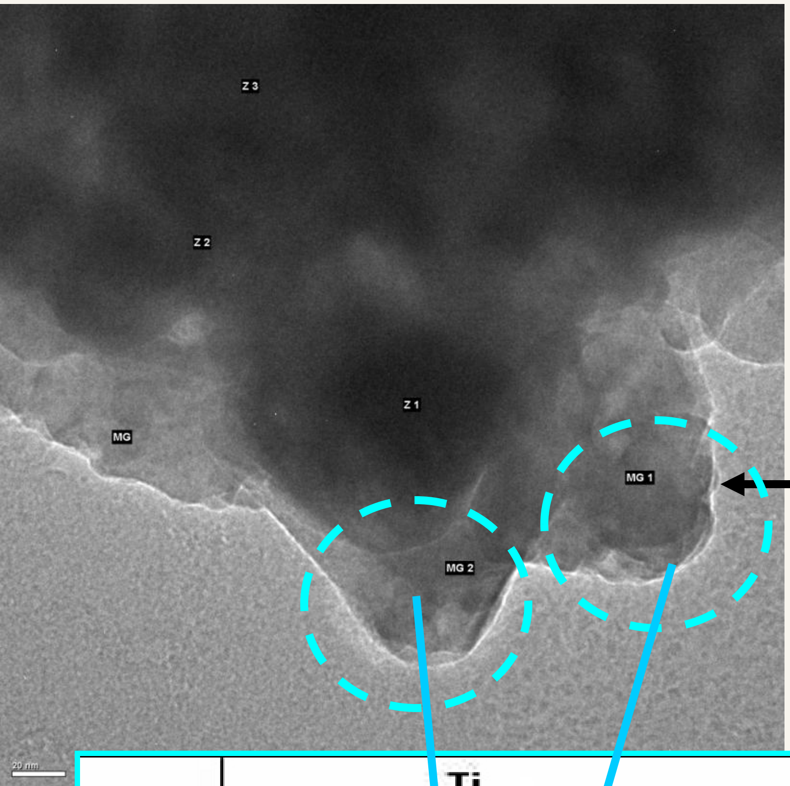


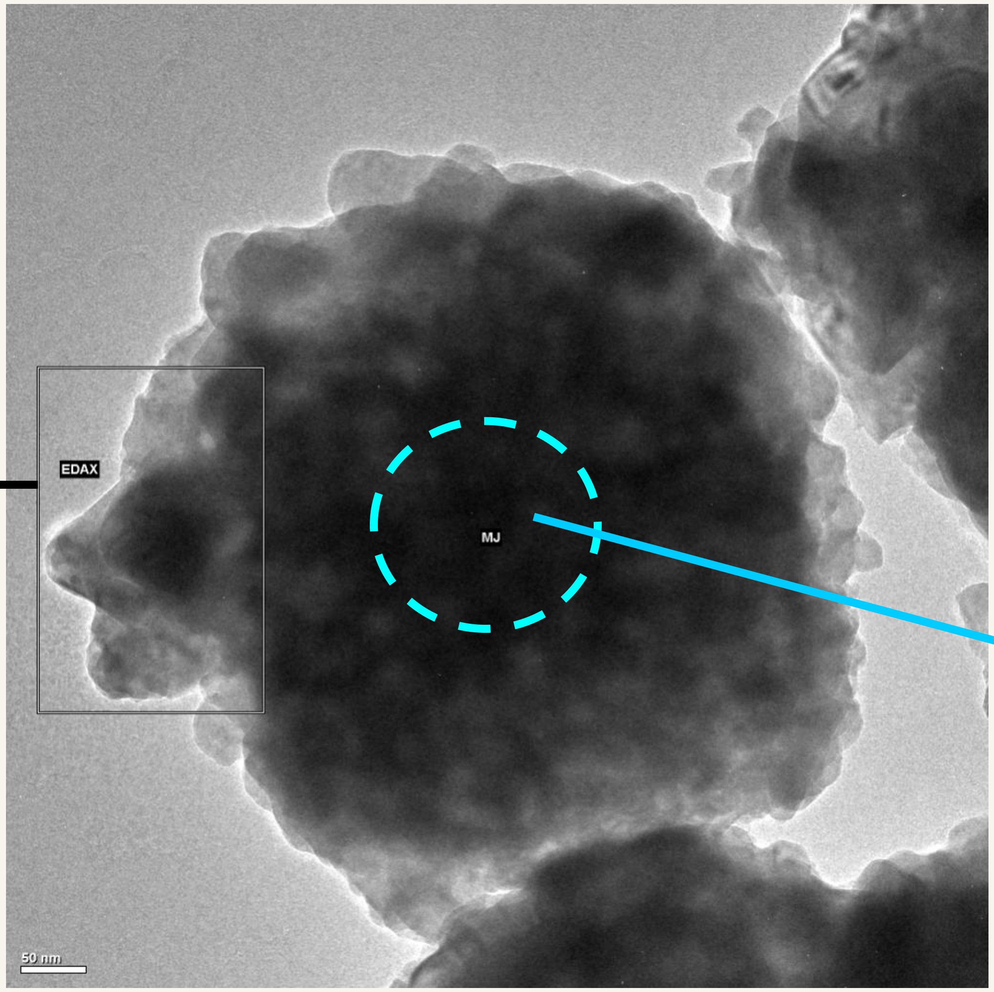


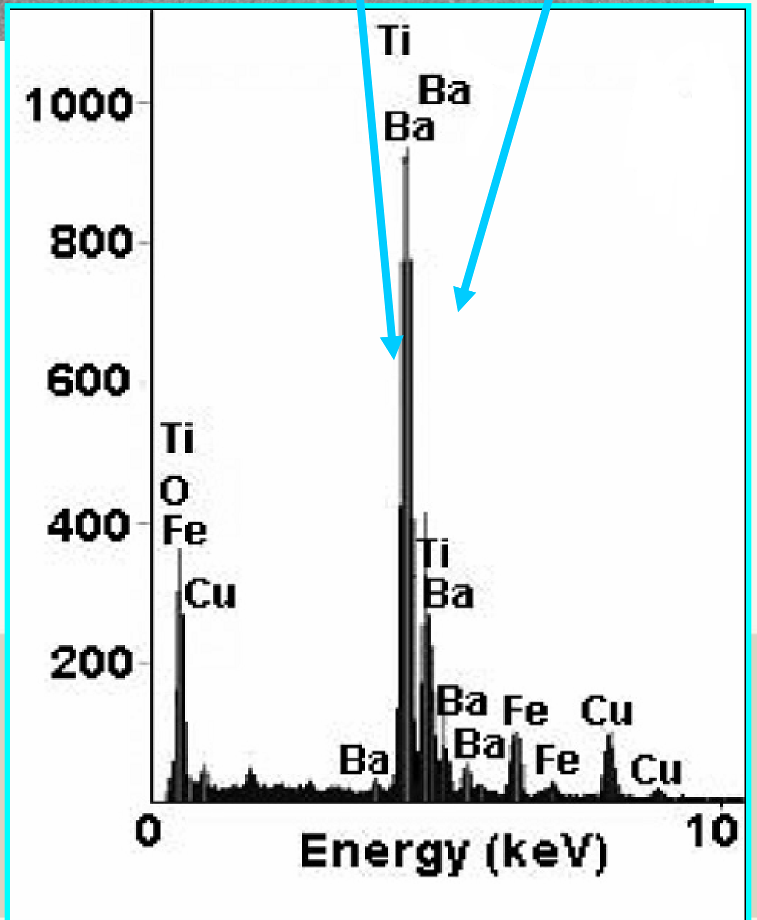
→ Nanoscale phase intermixing and core-shell structures

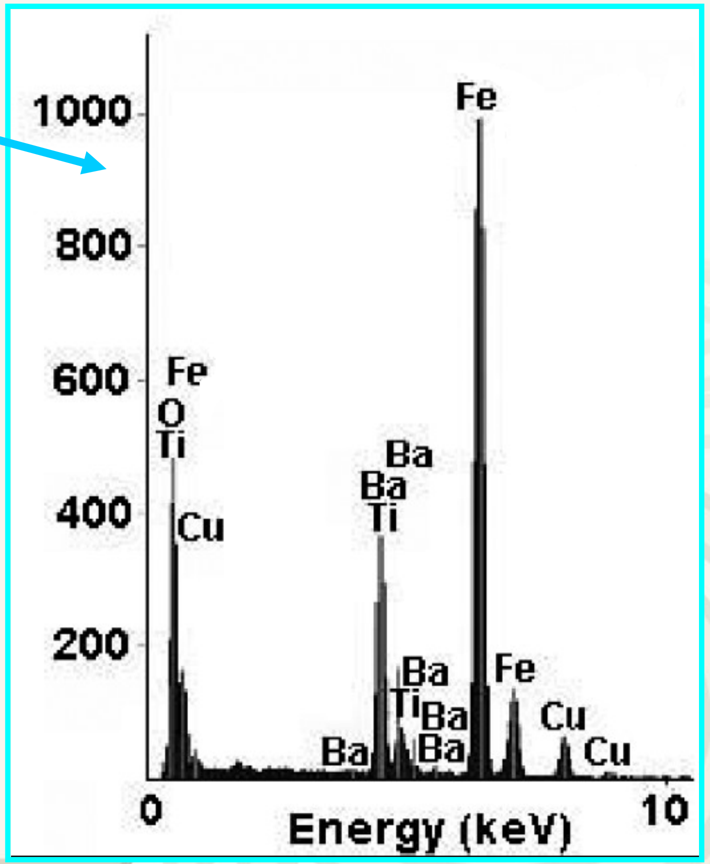
TEM-EDS analysis

- To estimate the local chemical composition and confirm the formation of the **core-shell structure**

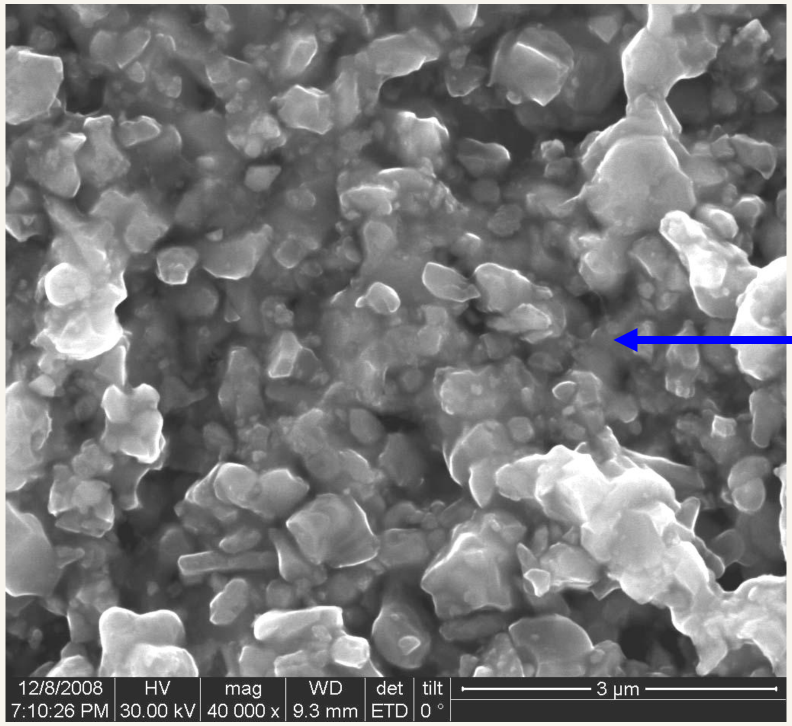


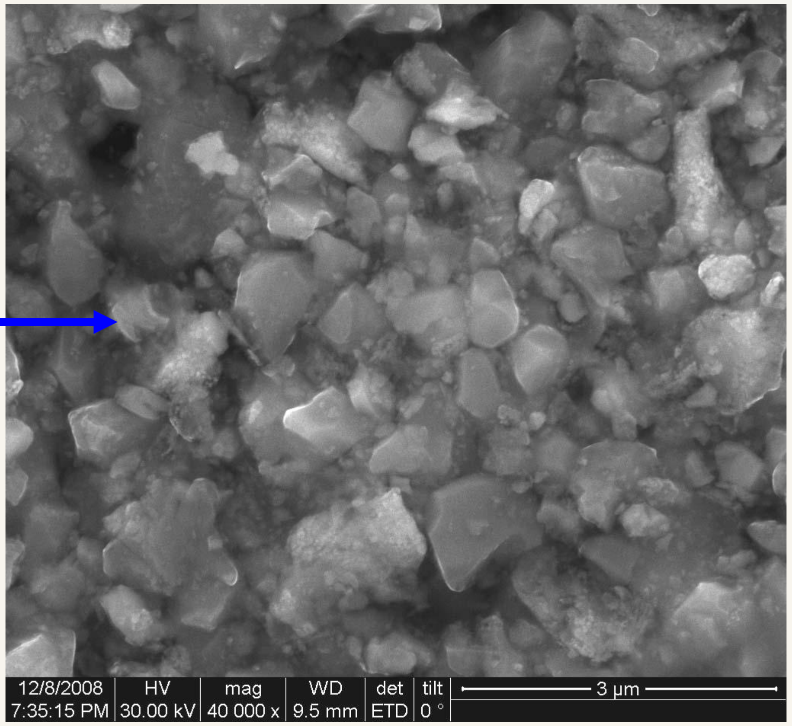






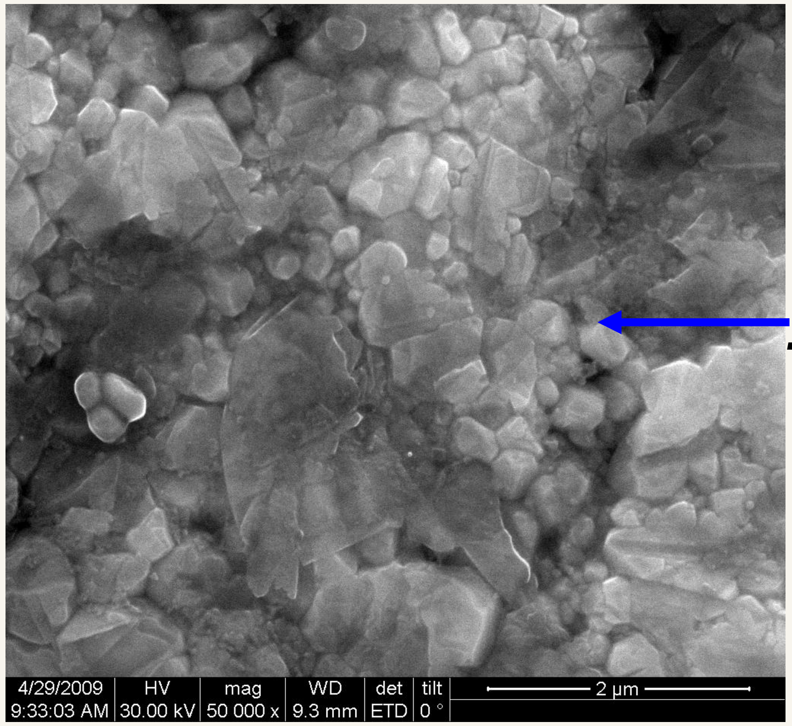
Ceramics

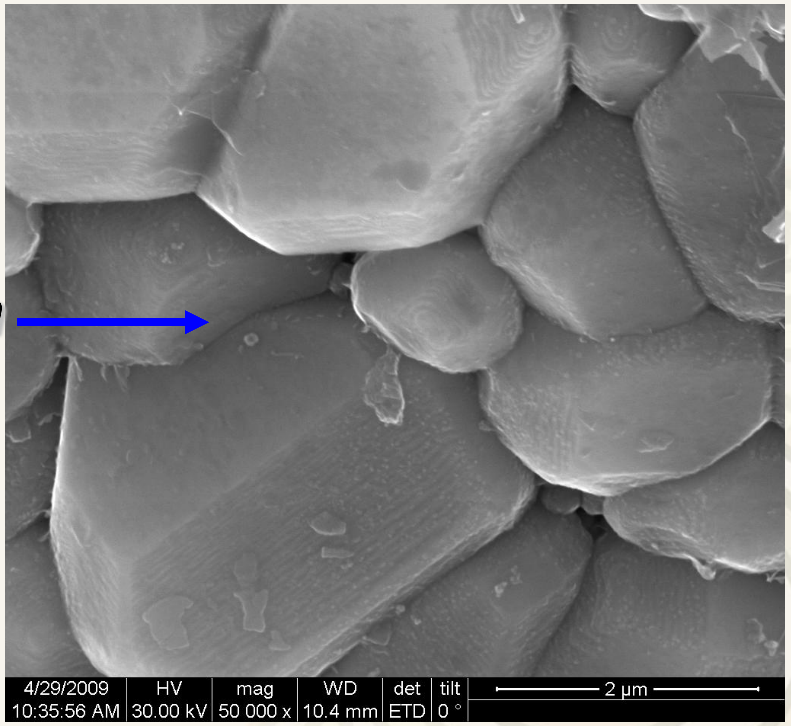




Traditional sintering at

1050^0C/1h and 1150^0C/1h





Spark Plasma Sintering at

1050^0C/4min and 1100^0C/3min

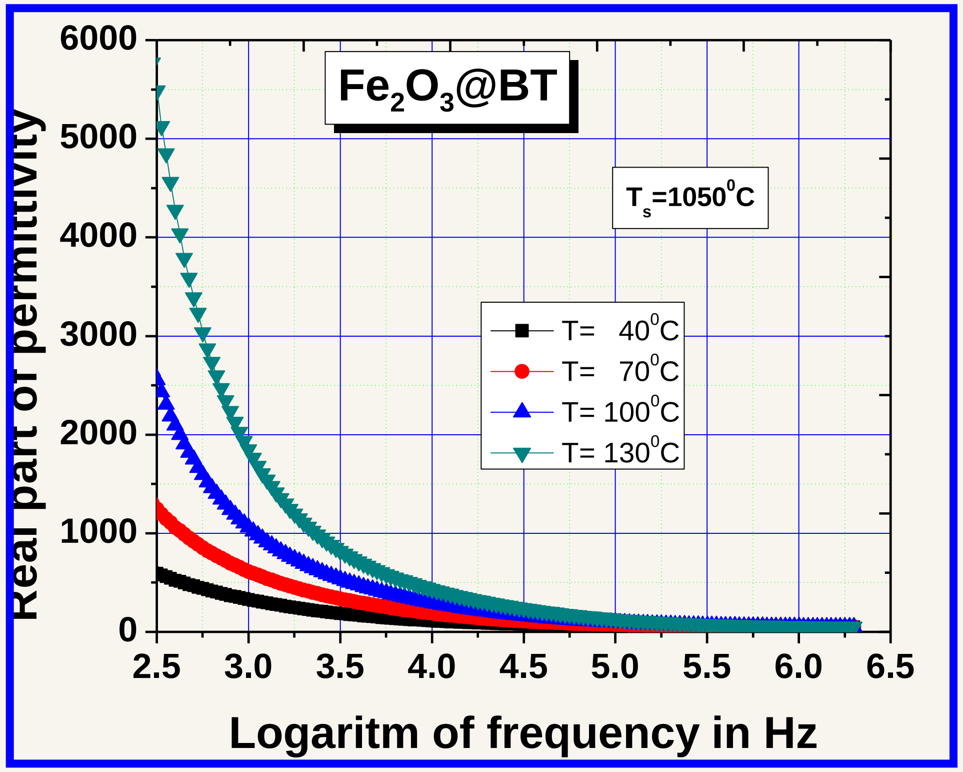
V. Functional properties

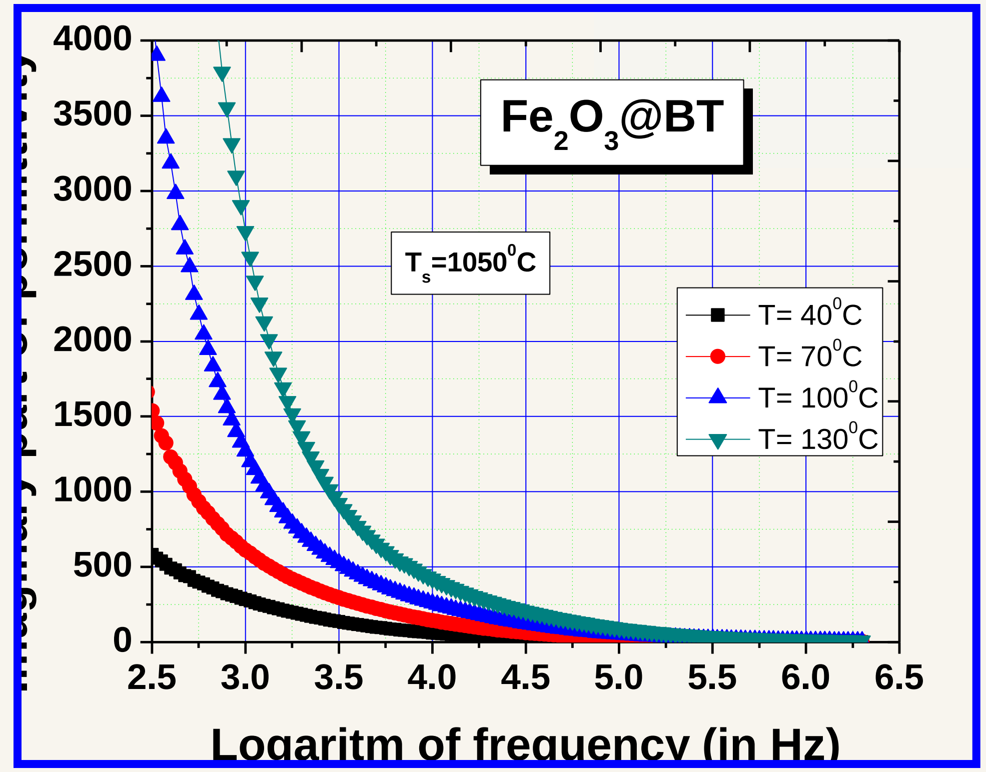
V.1 Impedance spectroscopy data

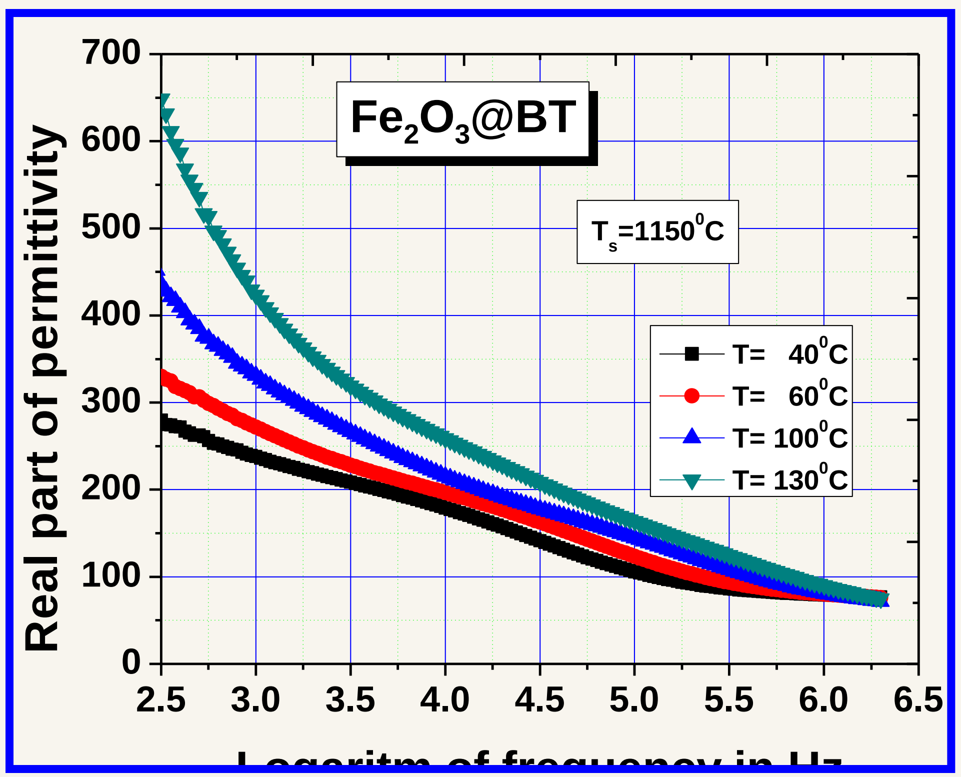
V.2 Dc-tunability

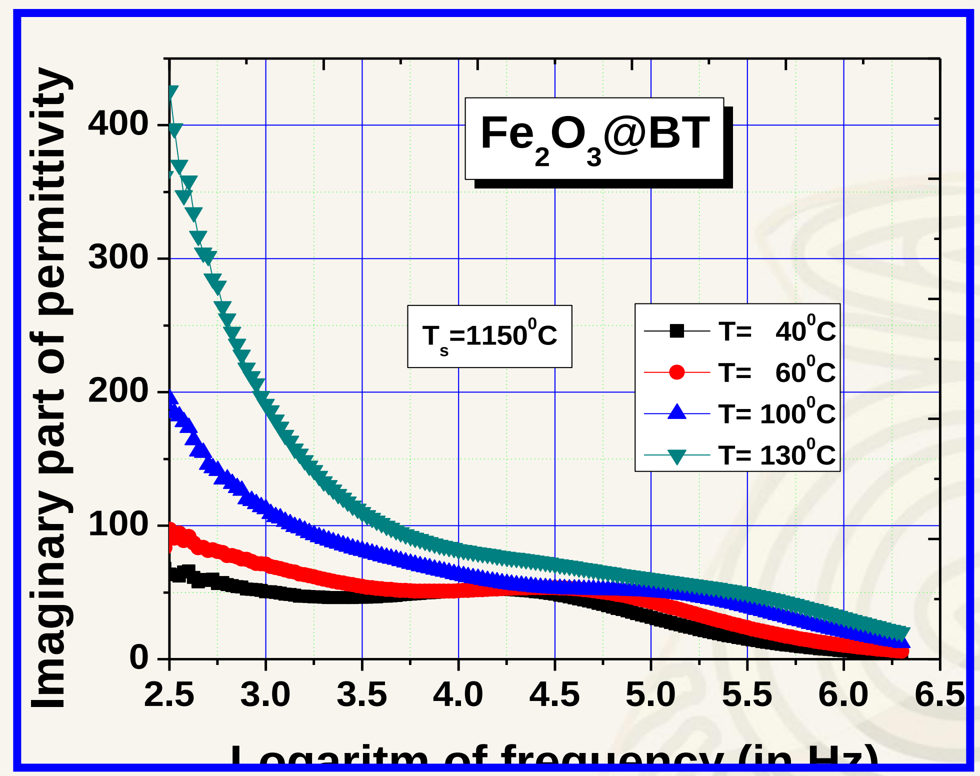
V.3 Magnetic properties

V.1 Impedance spectroscopy data

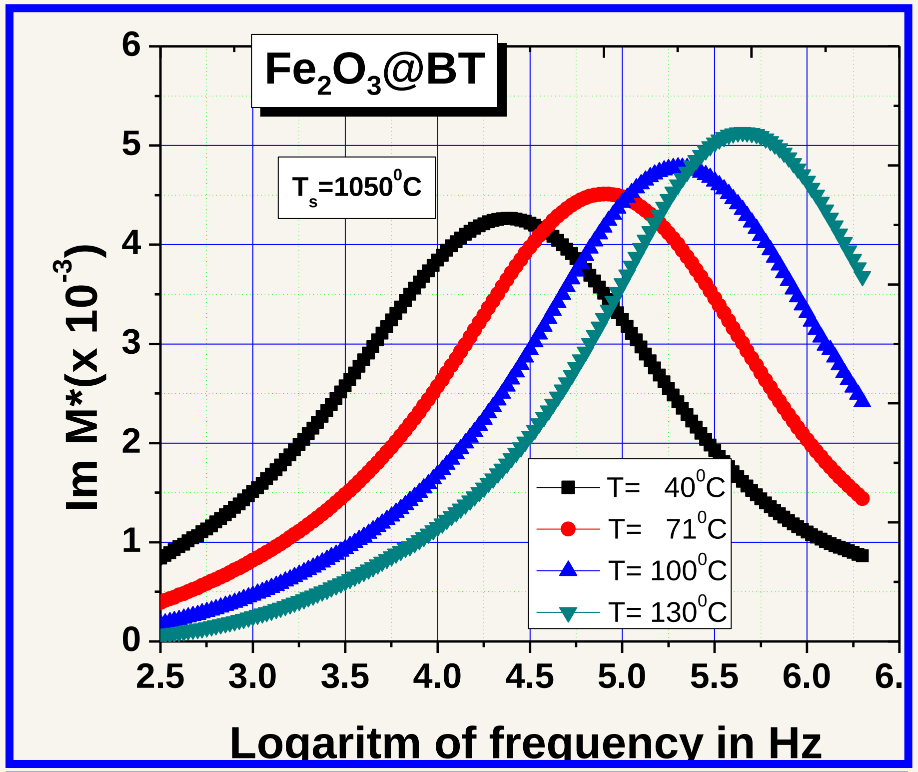


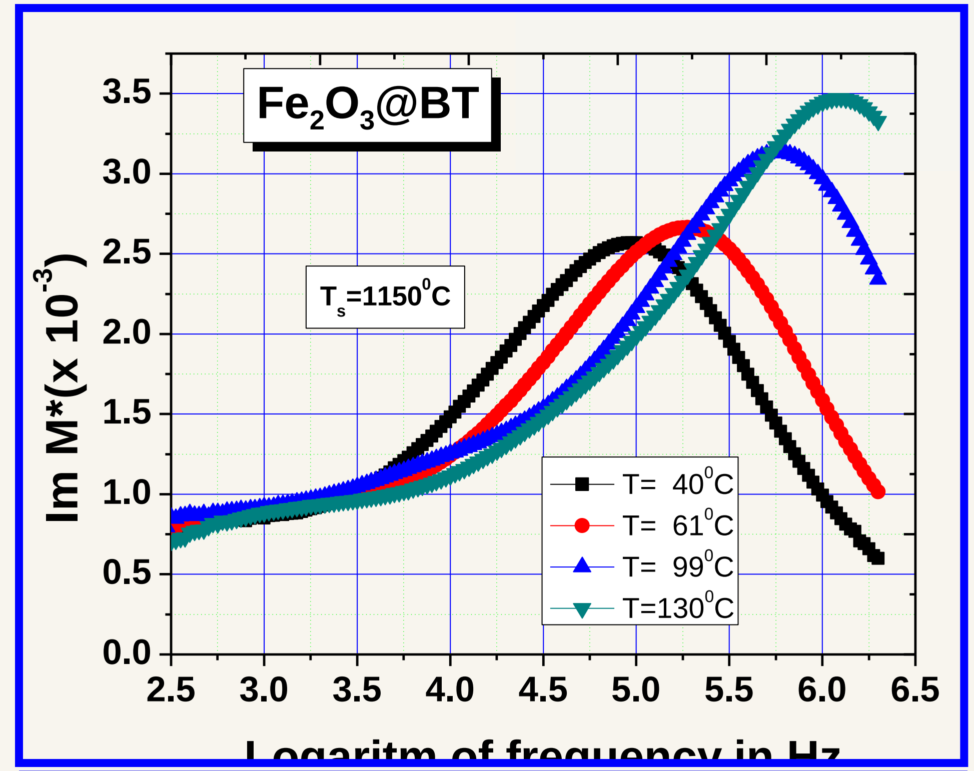


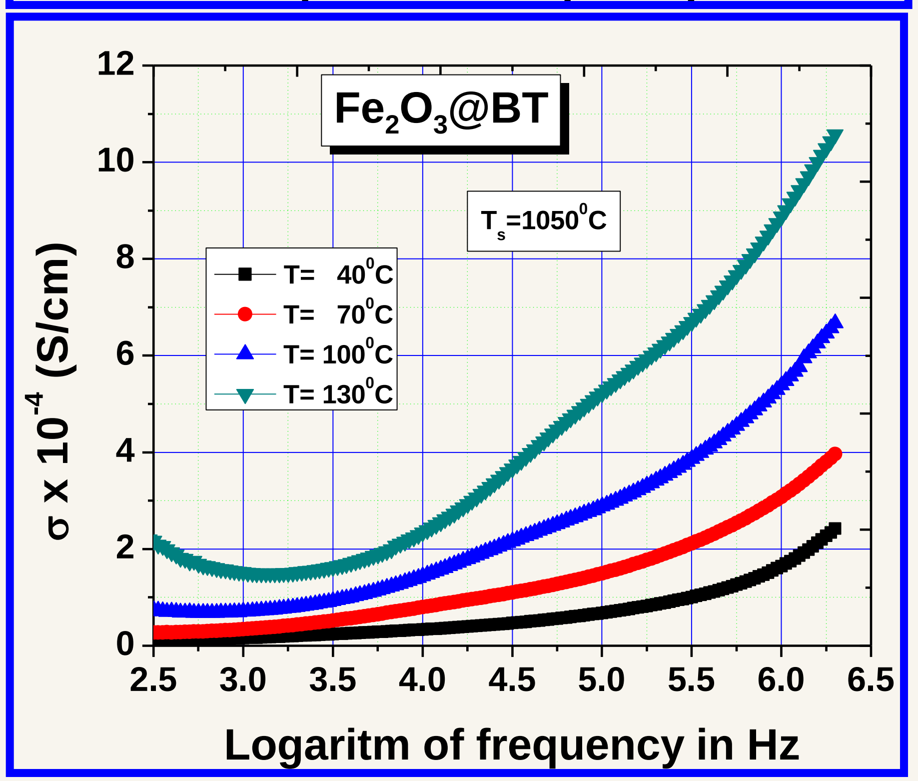


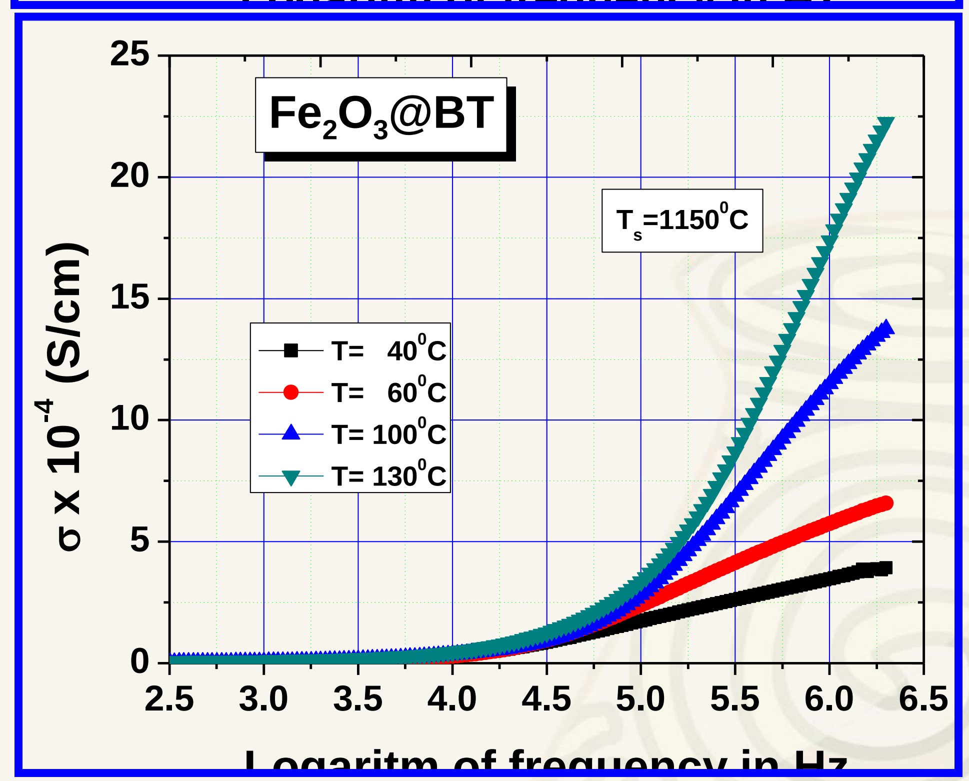


Dielectric modulus and conductivity



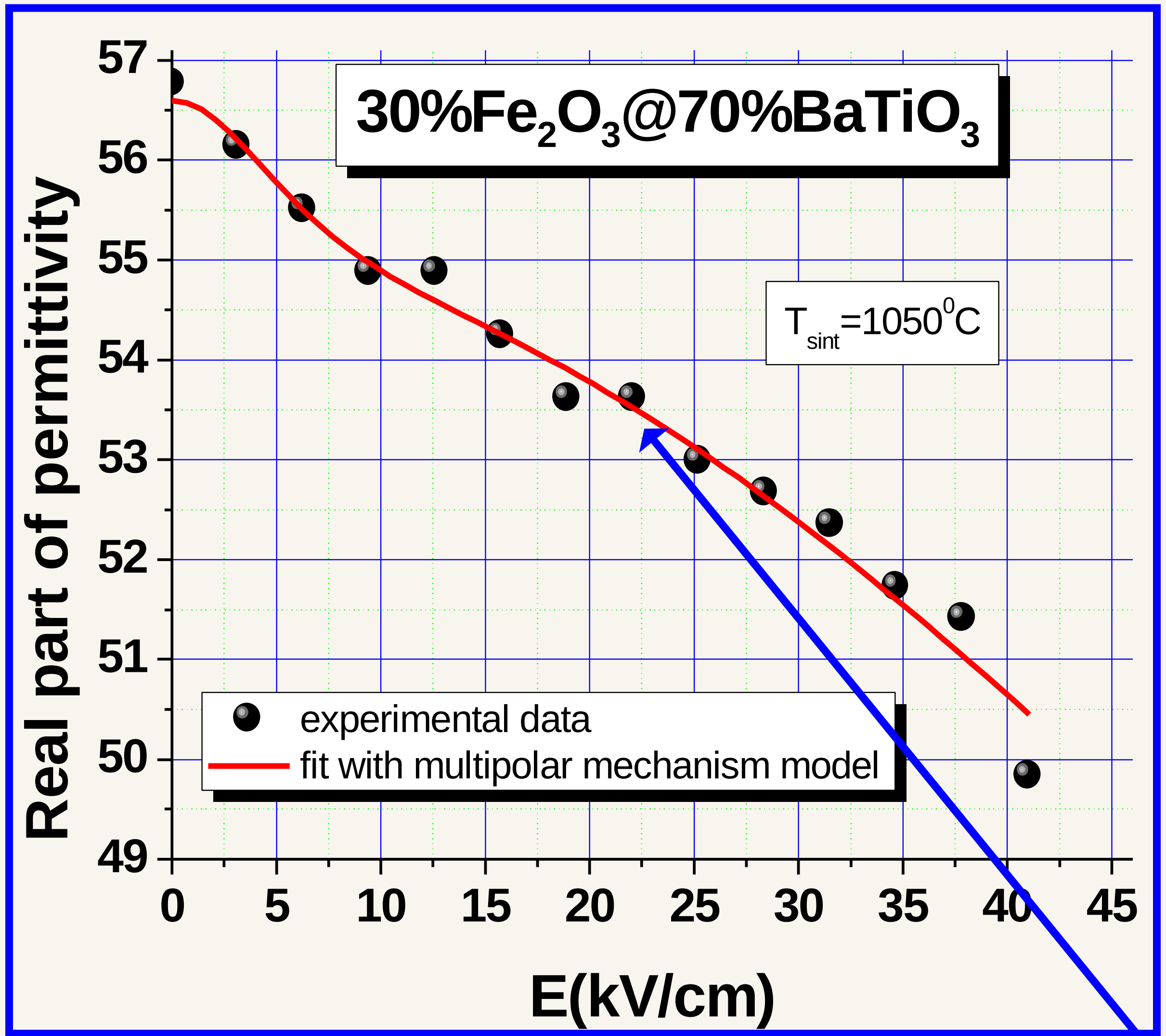






• *L.P. Curecheriu et. al , J. Appl. Phys. 107, 104106, 2010*

V.2 Dc-tunability data



- A high tunability (n=20%), without tendency to saturation.

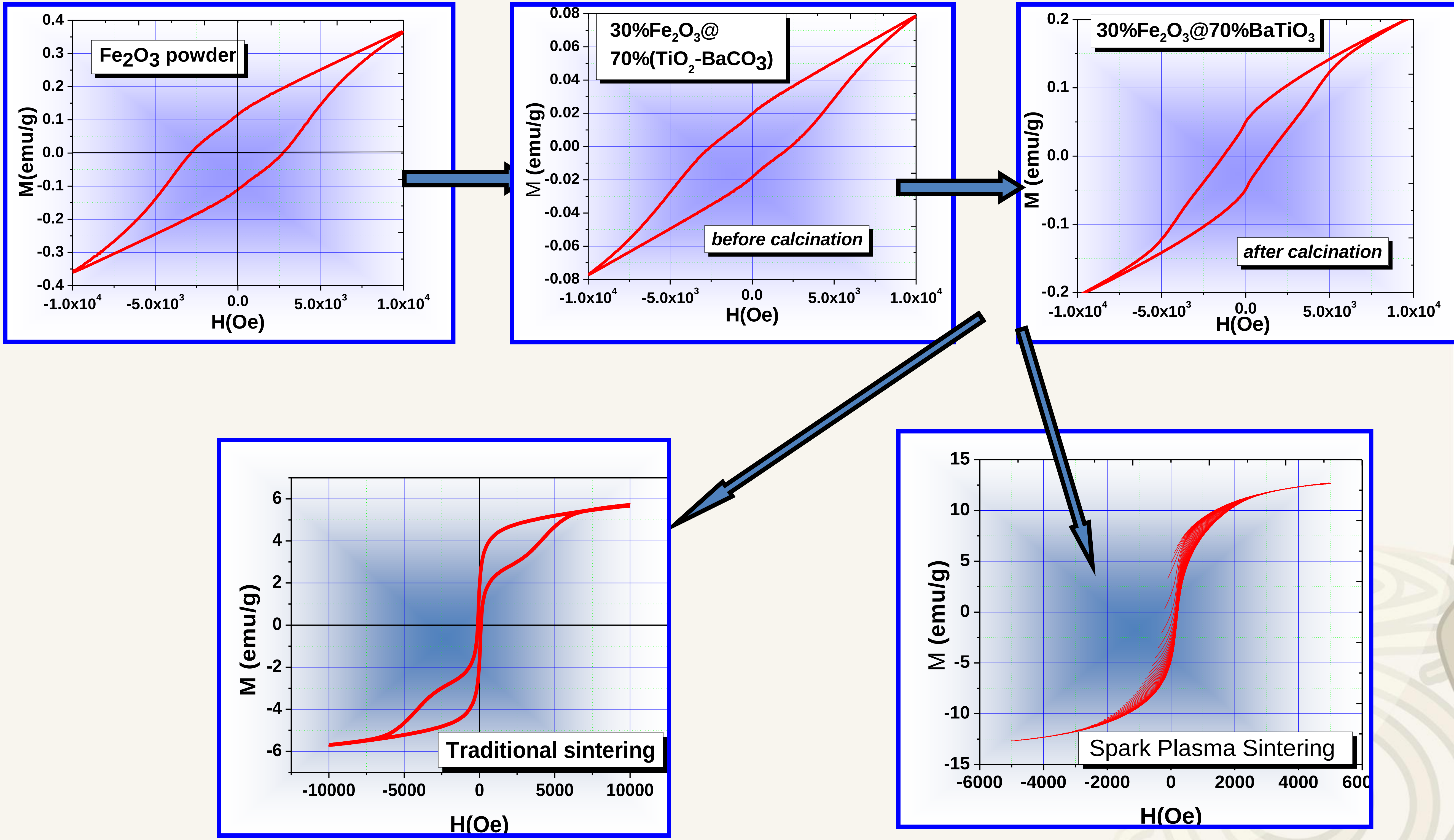
- A combination of more polarization mechanisms describes the exp. tunability data – to be investigated further in detail.

"Multipolar mechanism" model:

$$\varepsilon_r = \frac{\varepsilon_r(0)}{\{1+\lambda[\varepsilon_0\varepsilon_r(0)]^3 E^2\}^{1/3}} + \sum \frac{P_0 x}{\varepsilon_0}[\cosh(Ex)]^{-2}$$

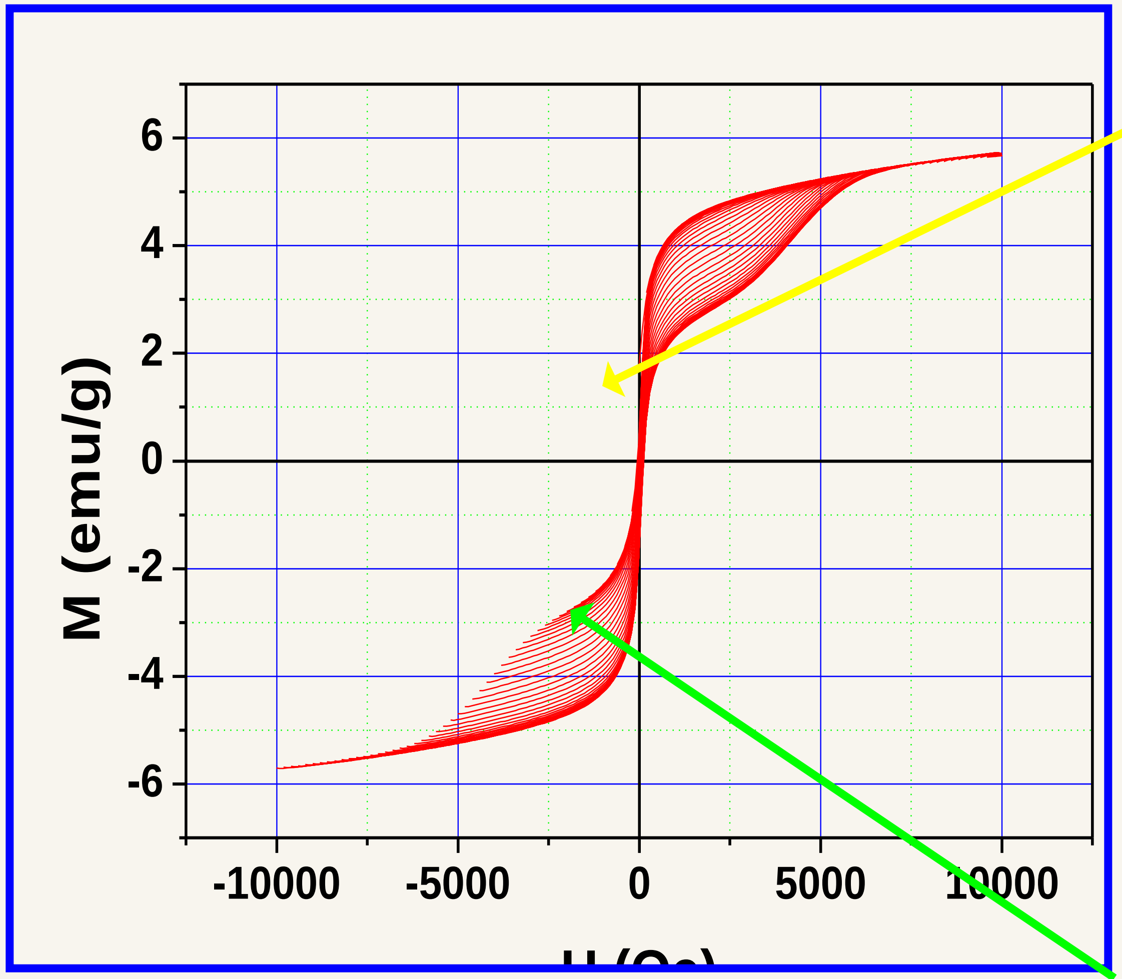
- *C. Ang , Z. Yiu, Phys. Rev. B 69, 174109 (2004)*

V.3 Magnetic properties

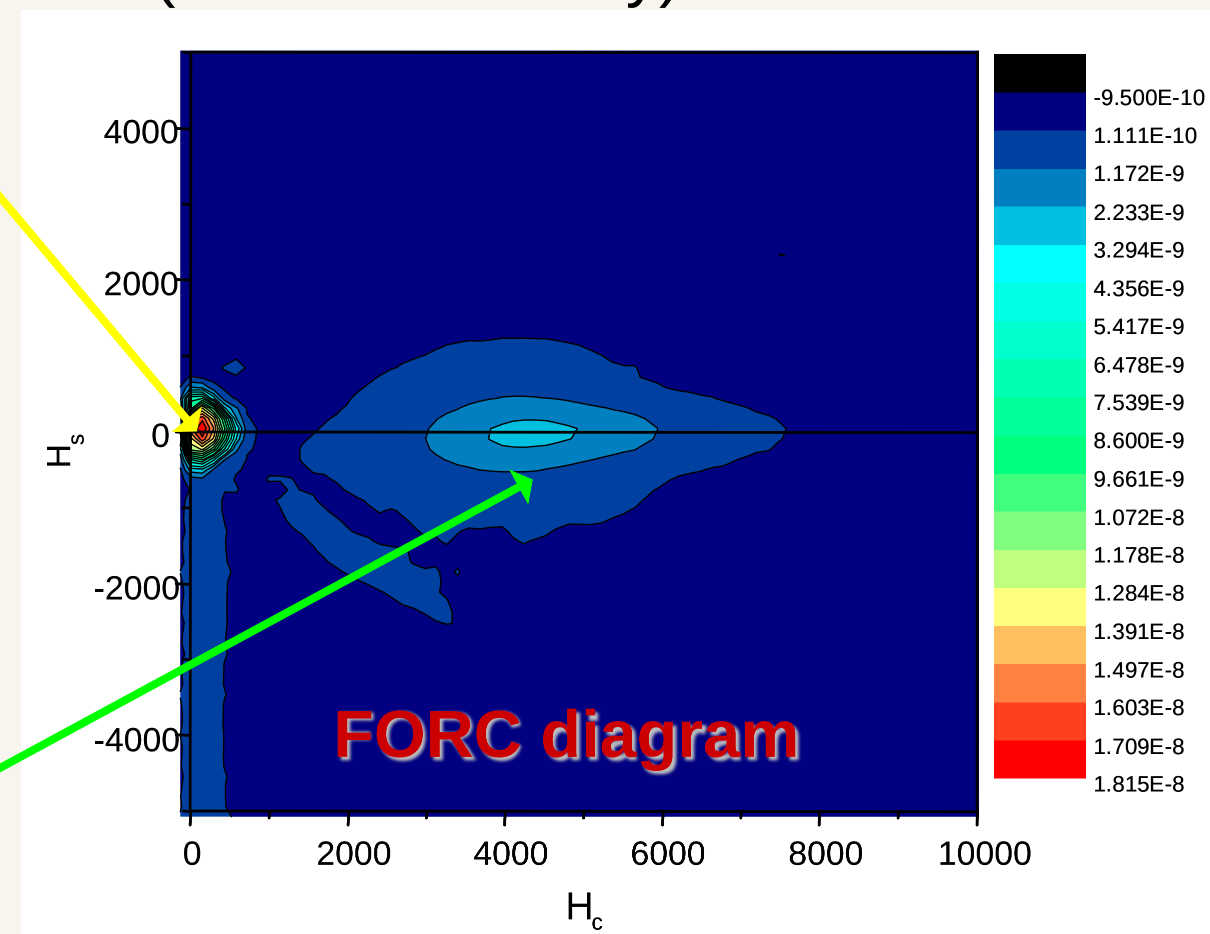


"PRODUCT PROPERTY"

Radically new magnetic properties in the nanocomposite – not present in the parent phases.



Soft phase (~ zero coercivity)

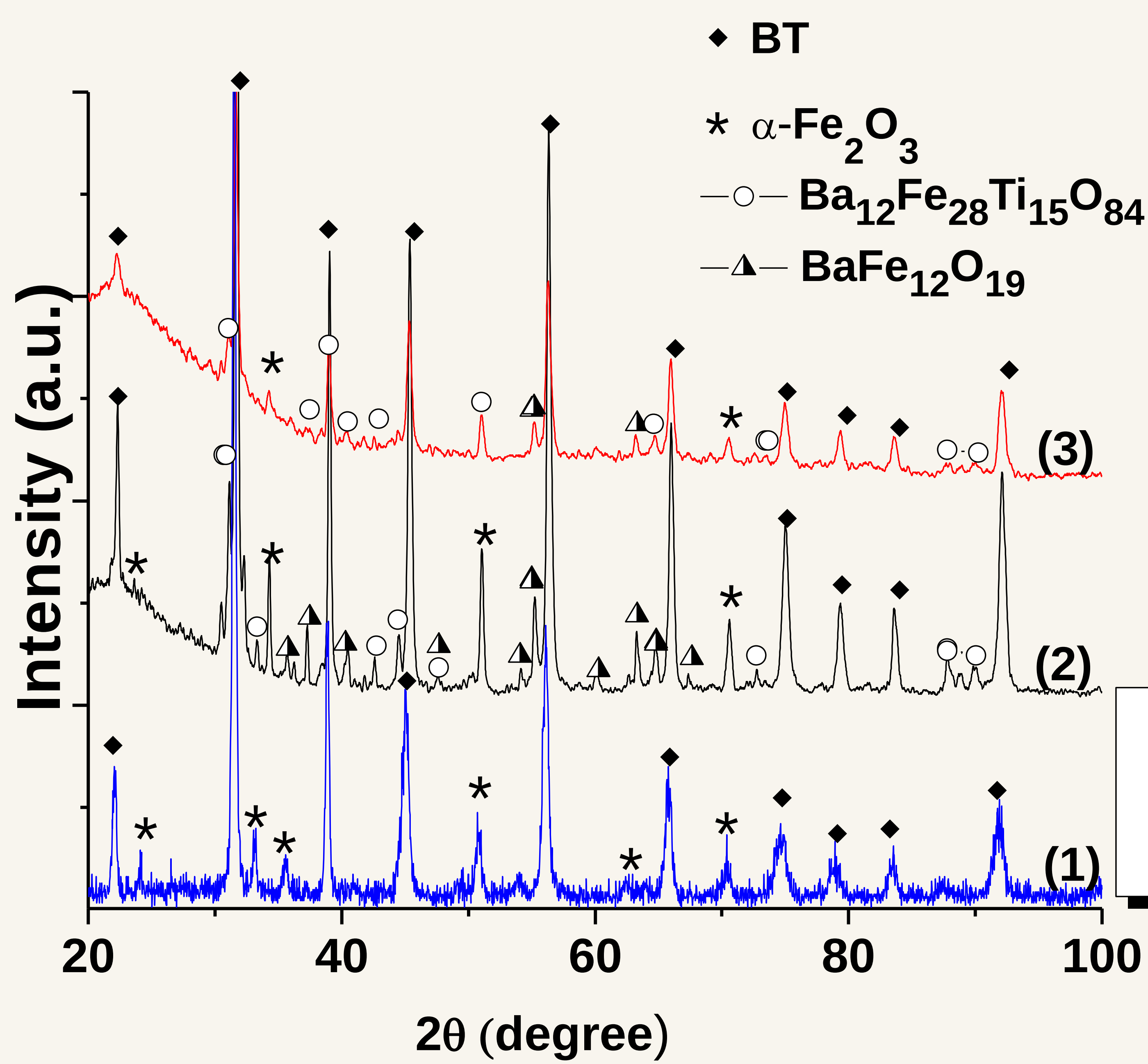


Hard magnetic phase

Very interesting: Two or more magnetic components due to the formation of secondary phases at interfaces.

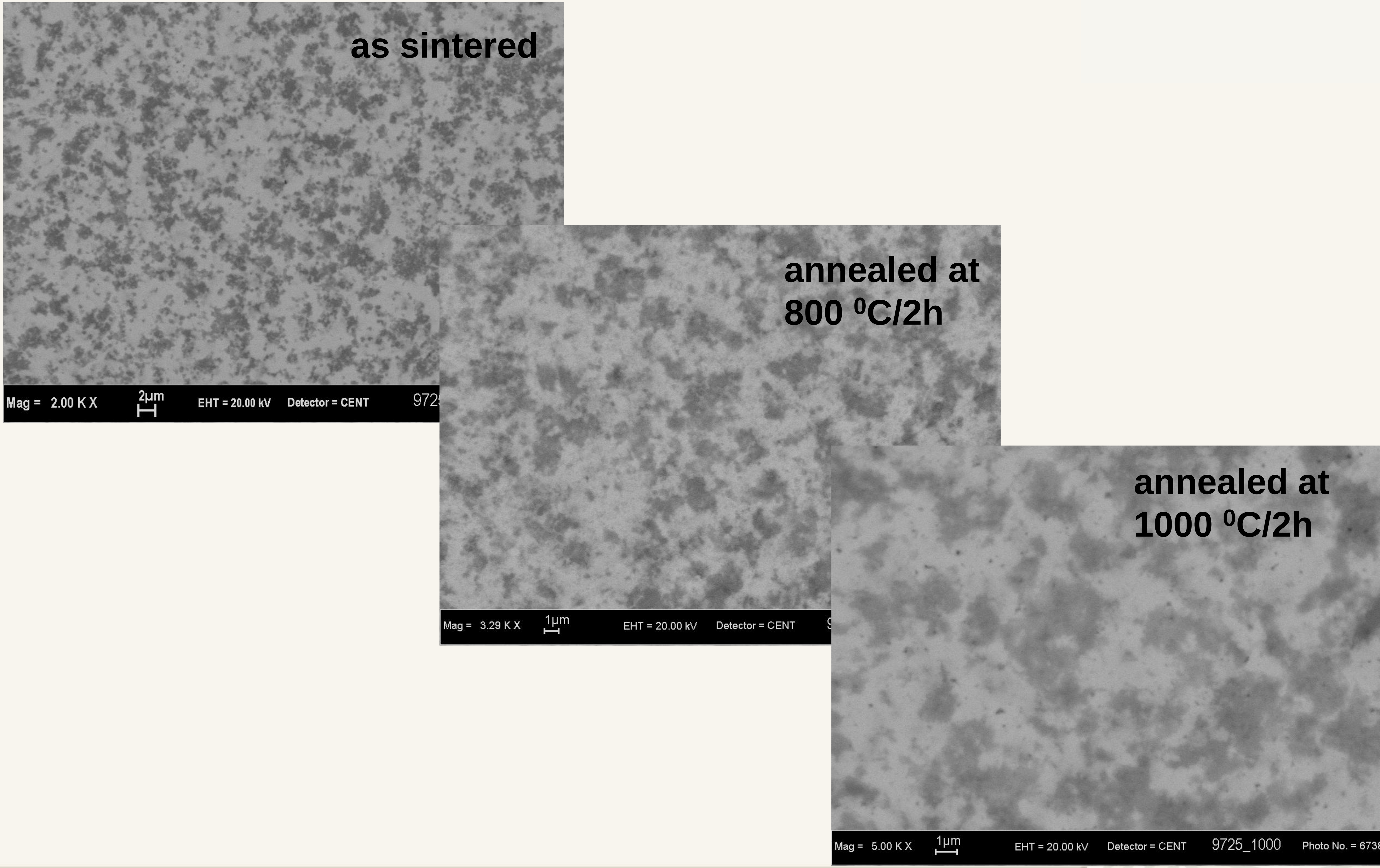
- *A. Stancu, et al. J. Appl. Phys. 93, 6620 (2003)*

Inducing new magnetic phases by annealing



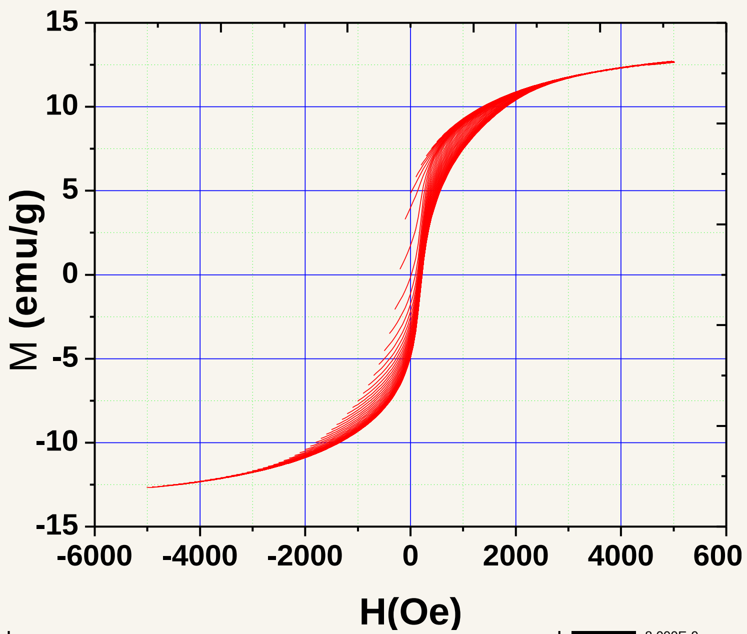
(1) SPS ceramic
(2) SPS anneling at $800^0C/2h$
(3) SPS anneling at $1000^0C/2h$

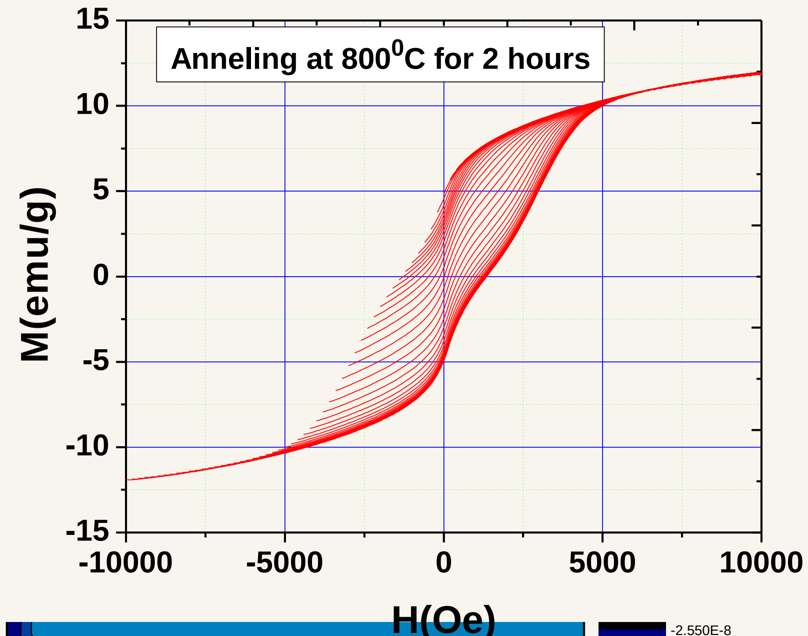
Confirmation of new magnetic phase from SEM

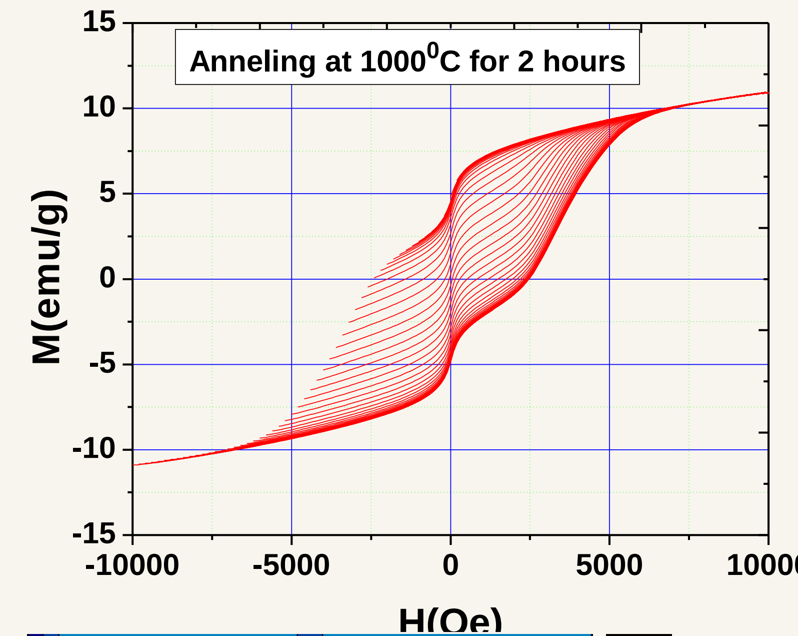


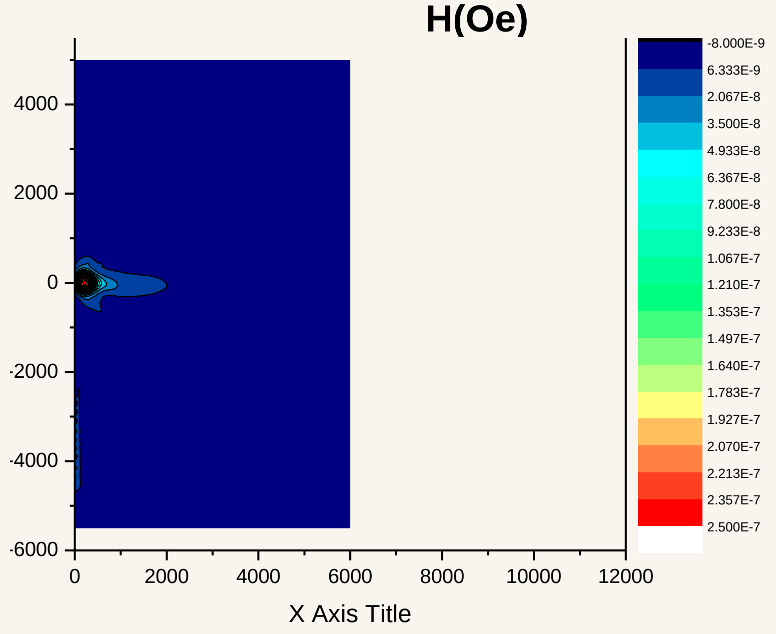
Confirmation of the presence of new phases by the magnetic measurements

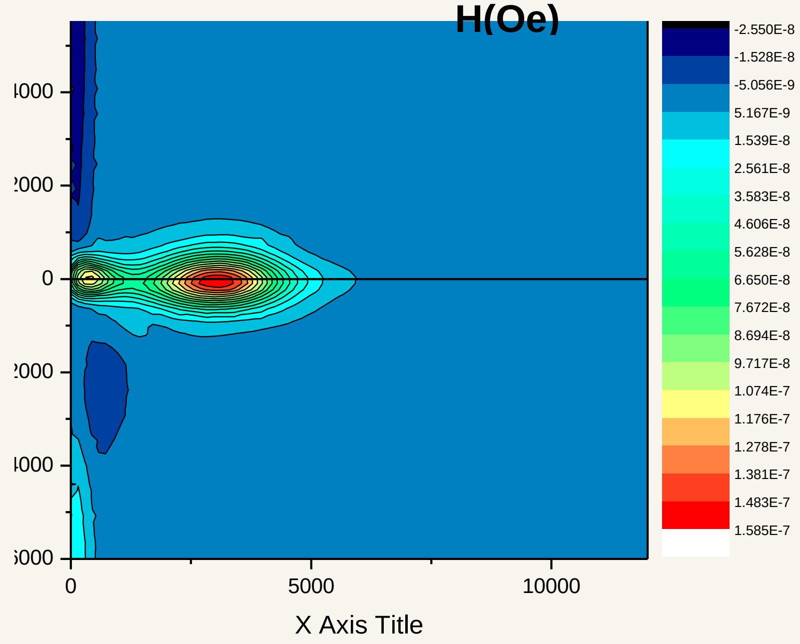
SPS – as sintered	SPS- annealing 800⁰C/2h	SPS- annealing 1000⁰C/2h

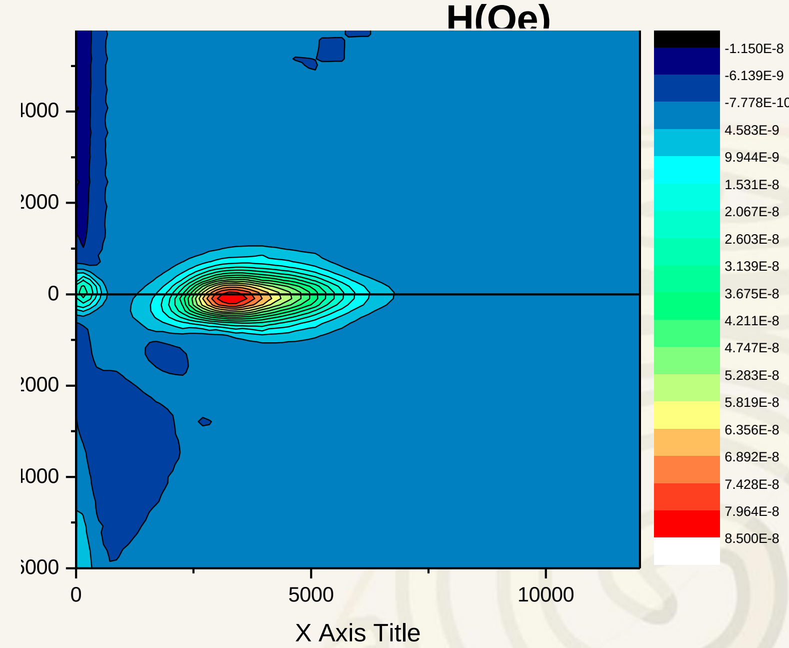












VI. Conclusions

☺ A ceramic material with **completely new magnetic** characteristics was designed and produced by the appropriate choice of the components, synthesis and sintering method:

☺ **Core-shell composite powders** with hematite core and barium titanate shell were prepared *in situ* by combined wet chemistry and solid state method;

☺ The sintered ceramics show multifunctional characteristics: **good dielectric properties and complex magnetic order;**

☺ Magnetic investigations demonstrated **coupled soft/hard magnetic components** at room temperature, as result of the nanoscale coupling and of interface secondary phases;

☺ The amount and coupling of the magnetic components are promoted by **controlling the chemical reactions at interfaces.**

Acknowledgements

- ROMANIAN GOVERNMENT FELLOWSHIP
- CNCSIS PN II-RU TE code 187/2010
- POSDRU FSE-POSDRU 89/1.5/S/49944

Thank you for attention!