# Dilute magnetic semiconductors

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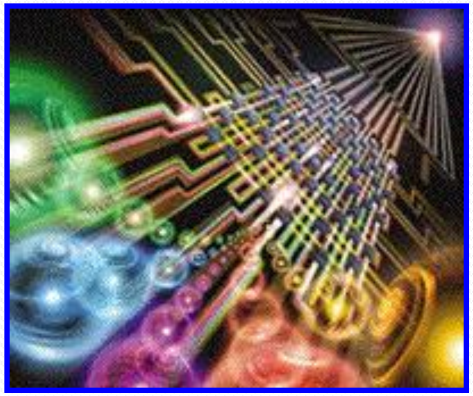
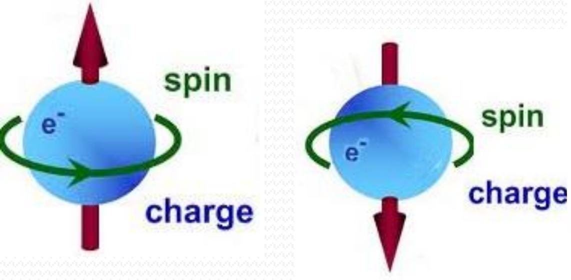
Doctoral study, programme physics

# Spintronics



- Spintronics (a neologism meaning "spin transport electronics"), also known as magnetoelectronics or spin electronics.




Terminal

Memory storage


Magnetic sensors

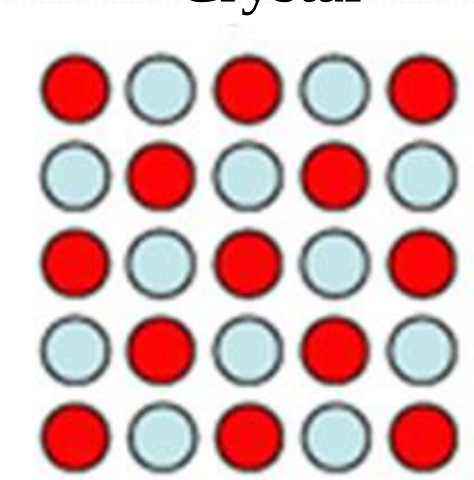
Quantum computing

# Primary requirements for spintronic materials:

- Room temperature ferromagnetism.
- Compatible with electronic devices.
- Semiconducting and ferromagnetic properties should coexist at room temperature.

# Dilute Magnetic Semiconductors (DMS)

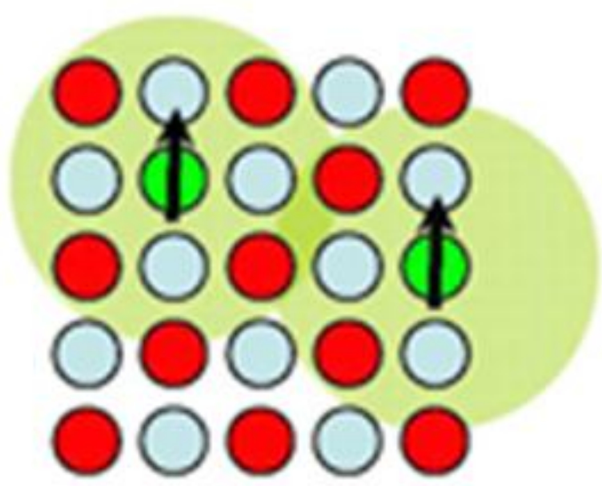
Nonmagnetic Semiconductor Crystal



Add TM Ions

**Mn, Fe, Co**

Ferromagnetic DMS



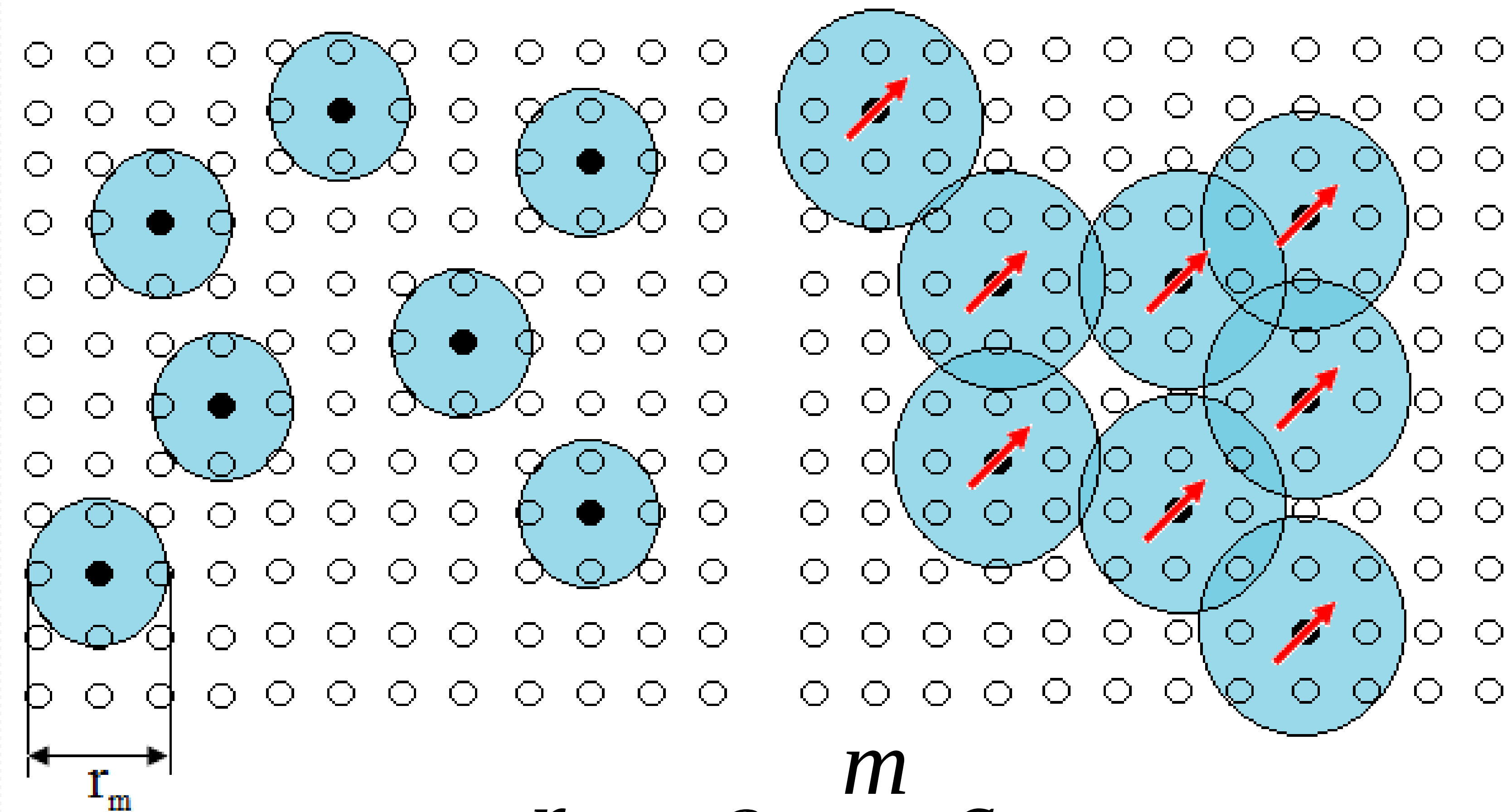
**GaAs, ZnO, AlN, $TiO_2$**

**Typical representatives.**

**- Mn-doped GaAs**

**- Mn-doped ZnO**

# When the magnetic coupling occur in the doped semiconductors?

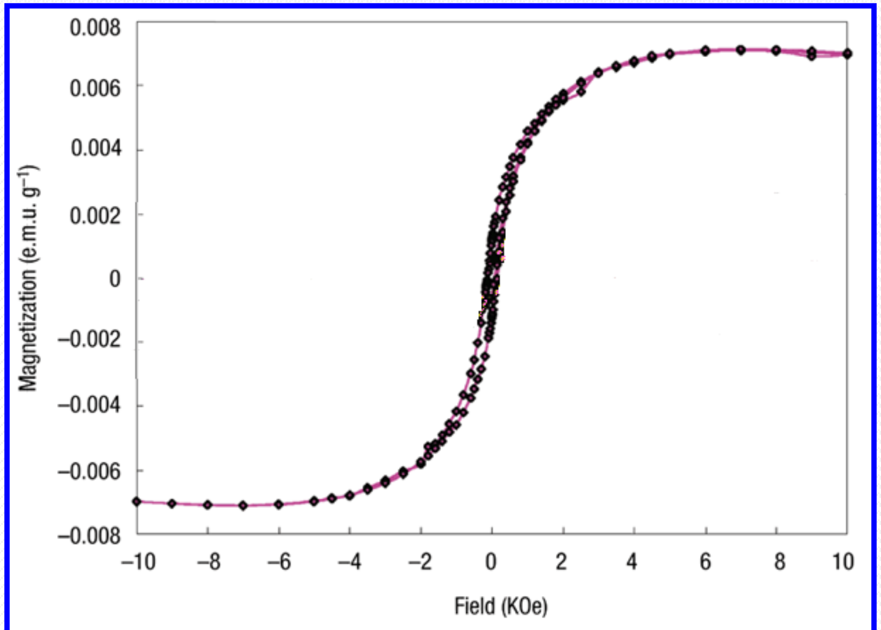



$$r_m = \varepsilon_r \frac{m}{m^*} a_0$$

# Ferromagnetism in bulk Mn-doped ZnO

- No trace of any secondary phase or other impurities was found.
- Room temperature ferromagnetism discovered in Mn doped ZnO [1].

Hysteresis curve at Room temperature for 2 at. % Mn-doped ZnO




In general, the solid solubility of transition metals in semiconductors is low.


1. P. Sharma, A. Gupta, K. V. Rao et. al. Nature Materials 2, p. 673 - 677 (2003)

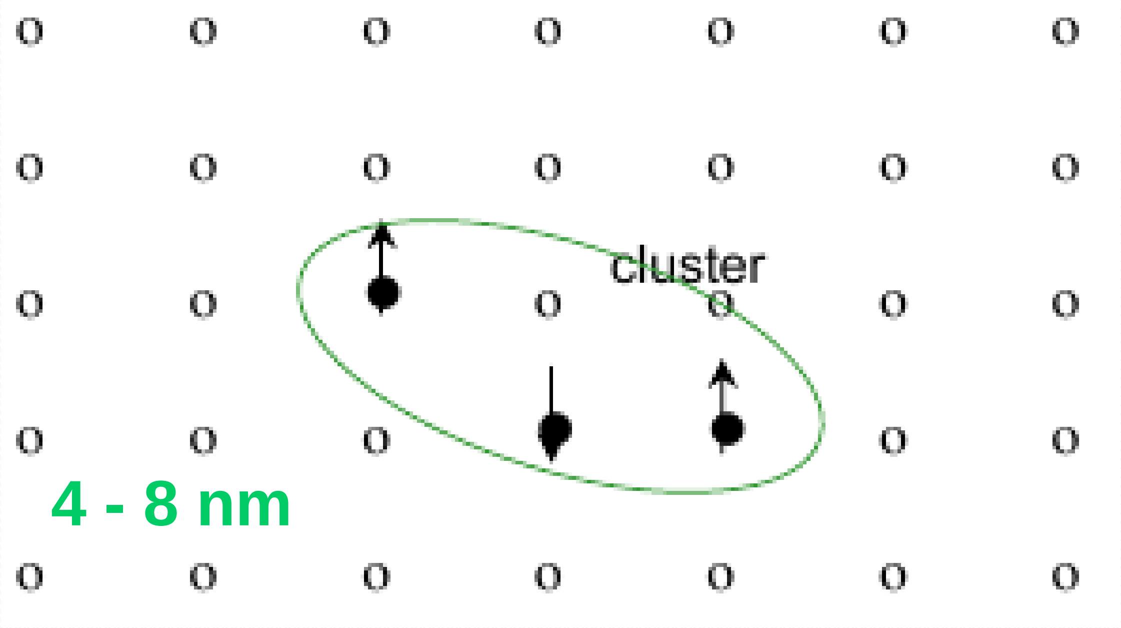
# Type of impurity source of magnetism in DMS systems

- Clusters \ Segregations
- Secondary Phases (Spinels)
- Extrinsic impurity

- SQUID magnetometer

(superconducting quantum interference devices)

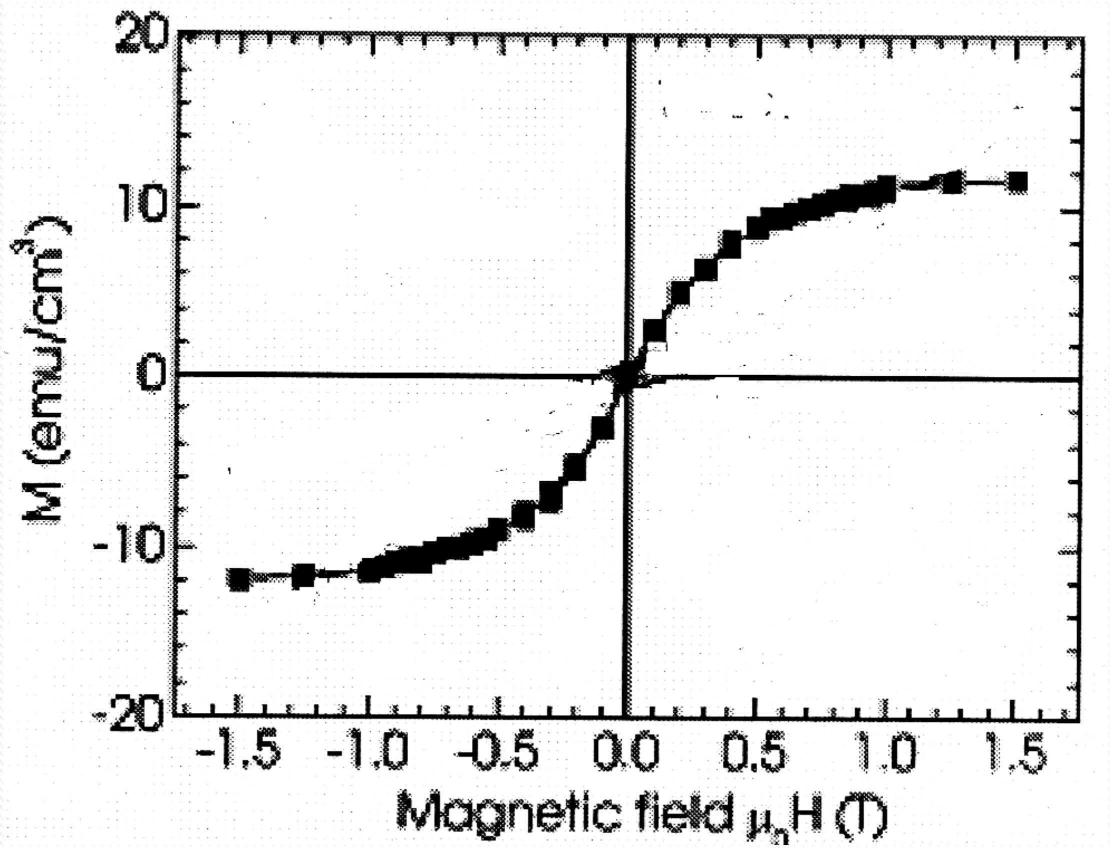
# Clusters




- Nanoclusters of the TM ion form the most obvious candidates for impurity sources of magnetism.

# Secondary Phases (Spinels)

Hysteresis curve for $ZnCo_2O_4$ phase in the Co-doped ZnO




general formula

$A^{2+}B_2^{3+}O_4^{2-}$

3. X. Wang, J. Xu, X. Yu, et. al., Applied Physics Letters 91, p. 031908, 2007

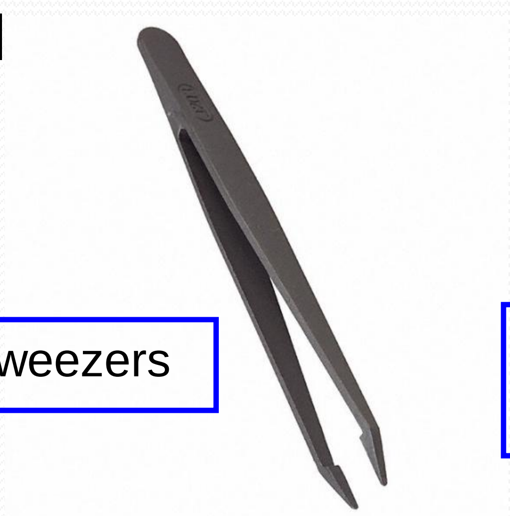
# Extrinsic impurities

- Magnetic moment of small amount extrinsic impurity is

$$\mu = 5*10^{-6}\ emu$$

- Abraham undertook a systematic study of the growth of $HfO_2$ thin films [2].

- No ferromagnetic signal



- Teflon tweezers

- Observation of a magnetic signal

- Stainless steel tweezers

2. D.W. Abraham, Frank, MM, Guha, S, Appl. Phys. Lett. 87, p. 252502, 2005

# Metal doped $In_2O_3$

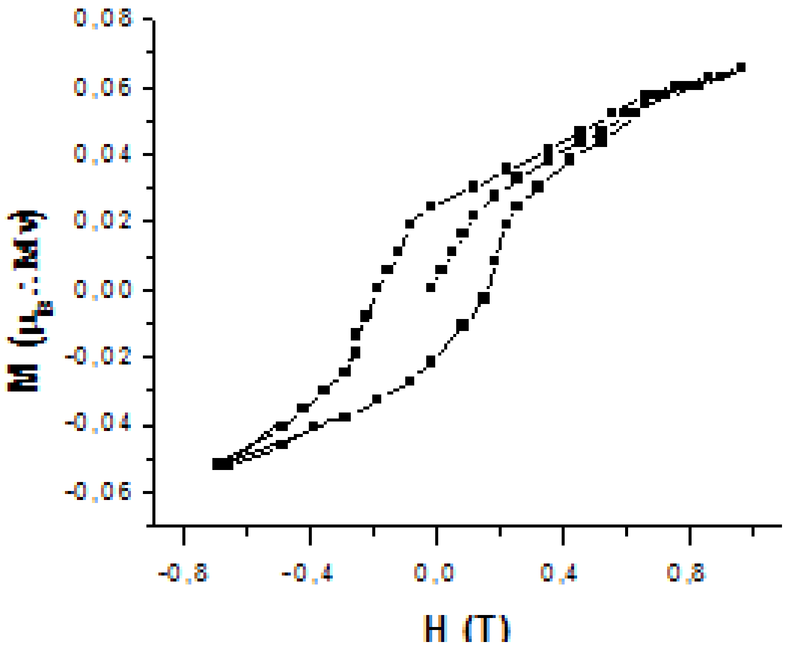
- 1. Nanocrystalline $In_2O_3$ is diamagnetic.
- 2. Bulk TM-doped (M = Cr, Mn, Fe, Ni, Cu) $In_2O_3$ is intrinsically paramagnetic, with a paramagnetic effective moment originating from the dopant.
- 3. Magnetic behaviour in bulk material are linked to the presence of small amounts of magnetic secondary phases in the samples.

Magnetic phenomena in DMS have been attributed to experimental artefact, such as influence of synthesis conditions or measurements errors.

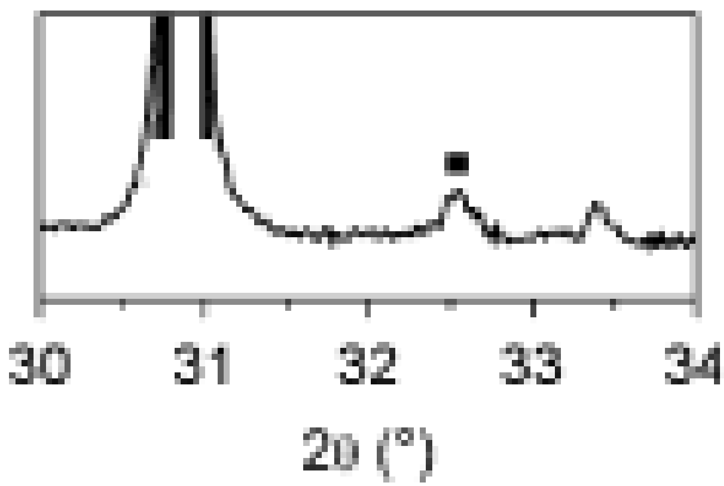
7. D. Berardan, E. Guilmeau, D. Pelloqun et. al. Journal of Magnetism and Magnetic Materials 320, p. 983-989, 2008.

# Mn – doped $In_2O_3$

Hysteresis loop in Mn-doped $In_2O_3$

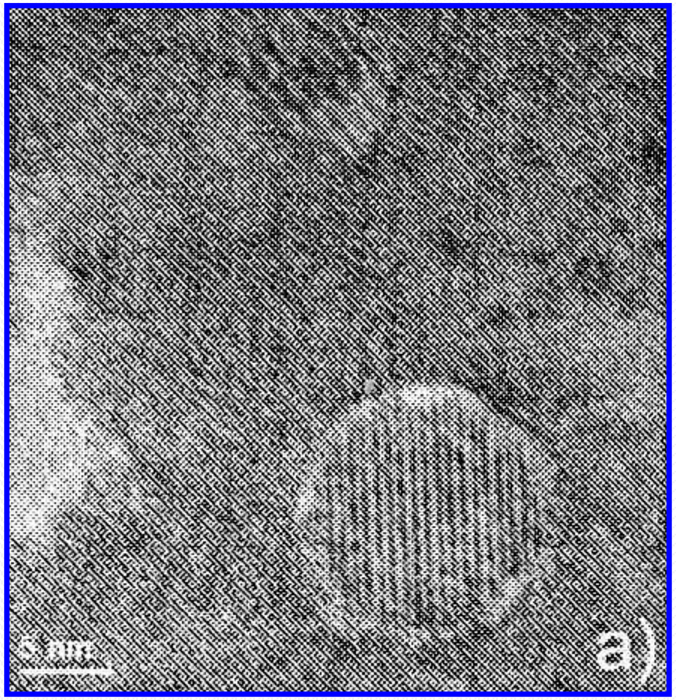



XRD spectrum from the sample showing the presence of oriented $Mn_2O_3$ fractions.




4. Wakano T., Fujimura N., Morinaga Y., Abe N., Ashida A. Physics E 10, 260, 2001

# Transmission electron microscope (TEM)

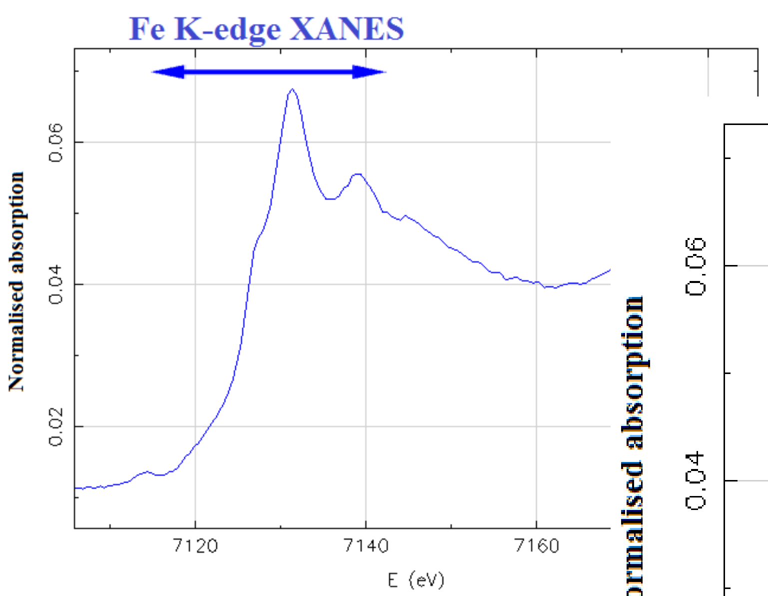



High resolution TEM of Ge:Mn film showing $Mn_5Ge_3$ clusters

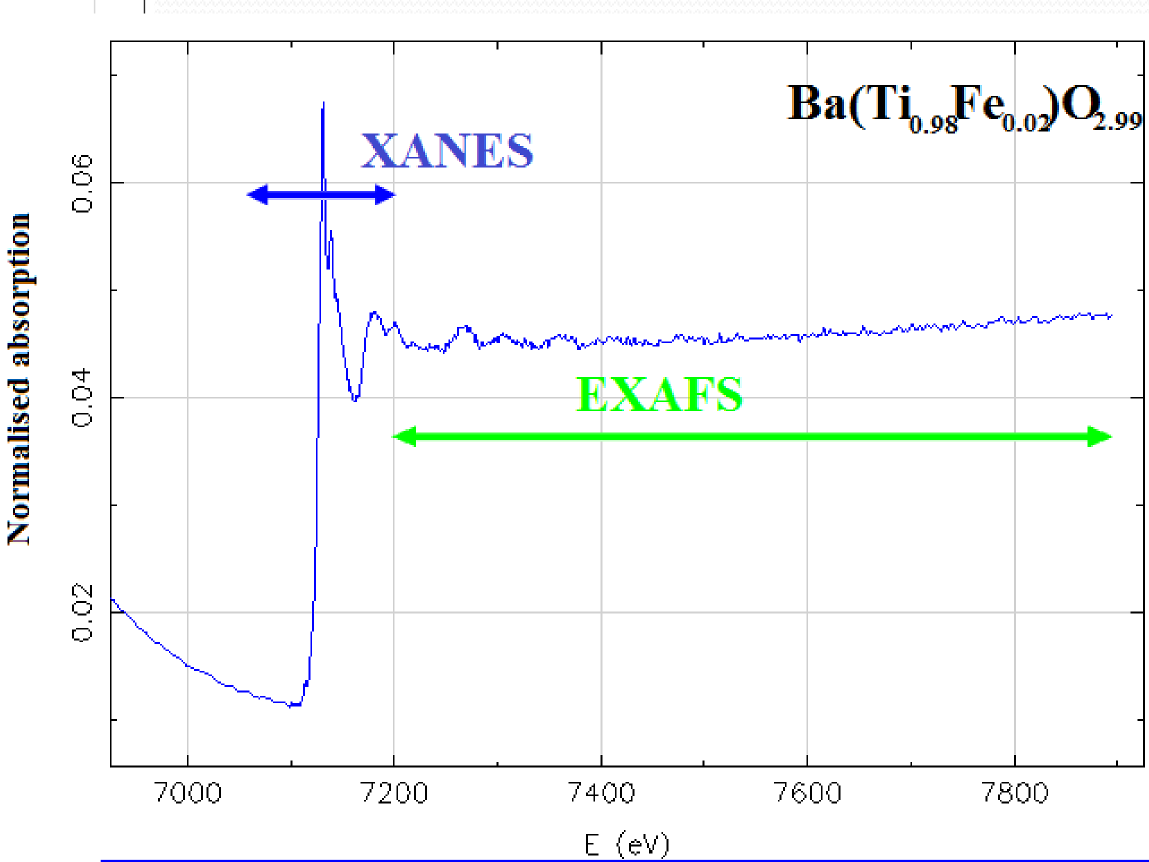
- The dilution of TM ions used to dope these DMS materials means that it is quite conceivable that the cross section does not contain any such impurities.[6]

6. O. Kazakova, R. Morgunov, J. Kulkarni, et. Al. Physical Review B (Condensed Matter and Materials Physics) 77, p. 235317, 2008.

# X-Ray Absorption Spectroscopy (XAS)

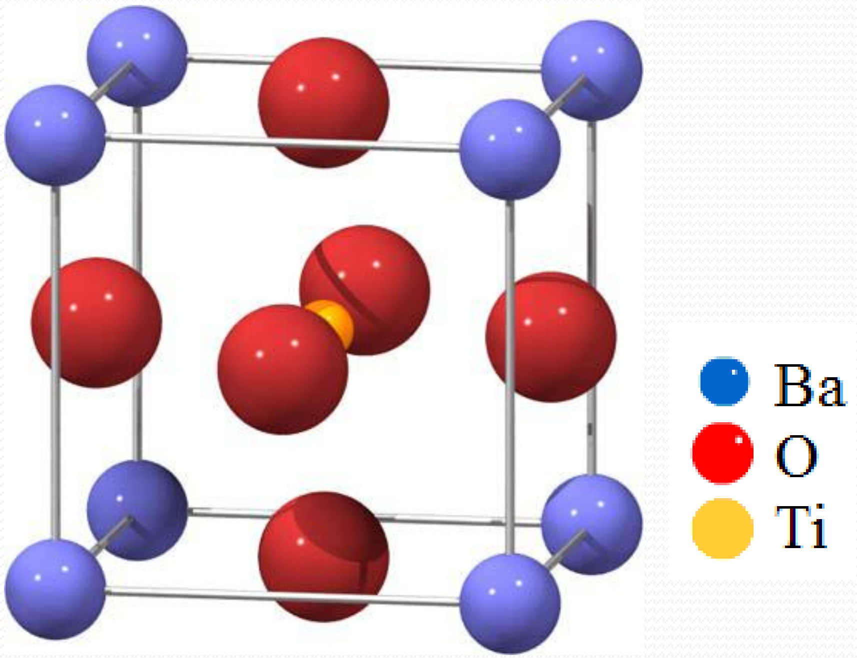



Fe K- edge XANES spectra of $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$




Normalised Fe K-shell absorption spectra of $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$

# Fe doped $BaTiO_3$




- $BaTiO_3$ – ferroelectric material with perovskite structure

Doping with iron:

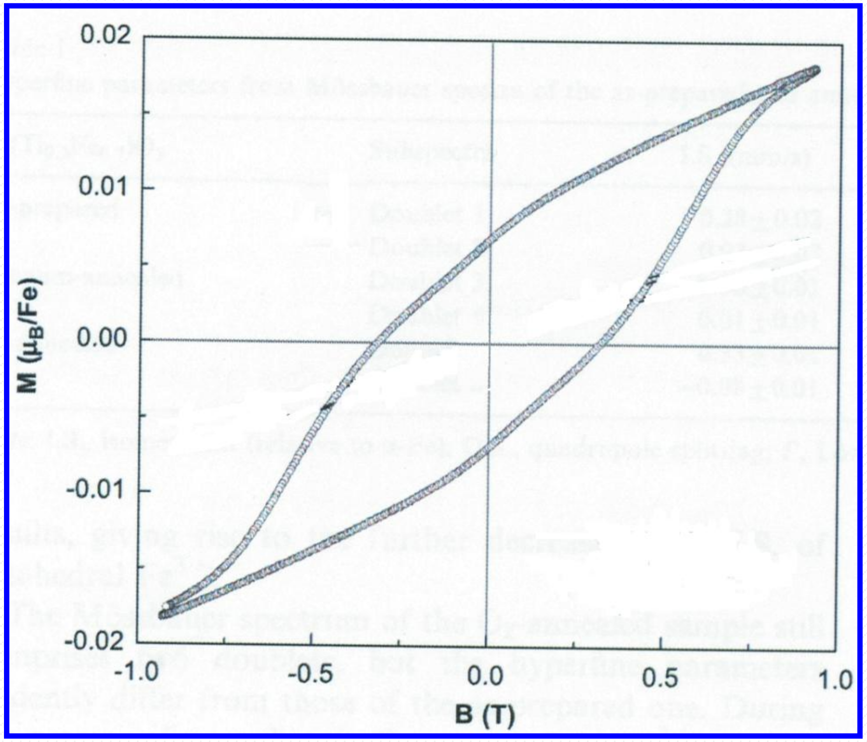
$$Ba^{2+}(Ti_{1-x}^{4+}\ Fe_{x}^{3+})O_{3-x/2}^{-2}$$

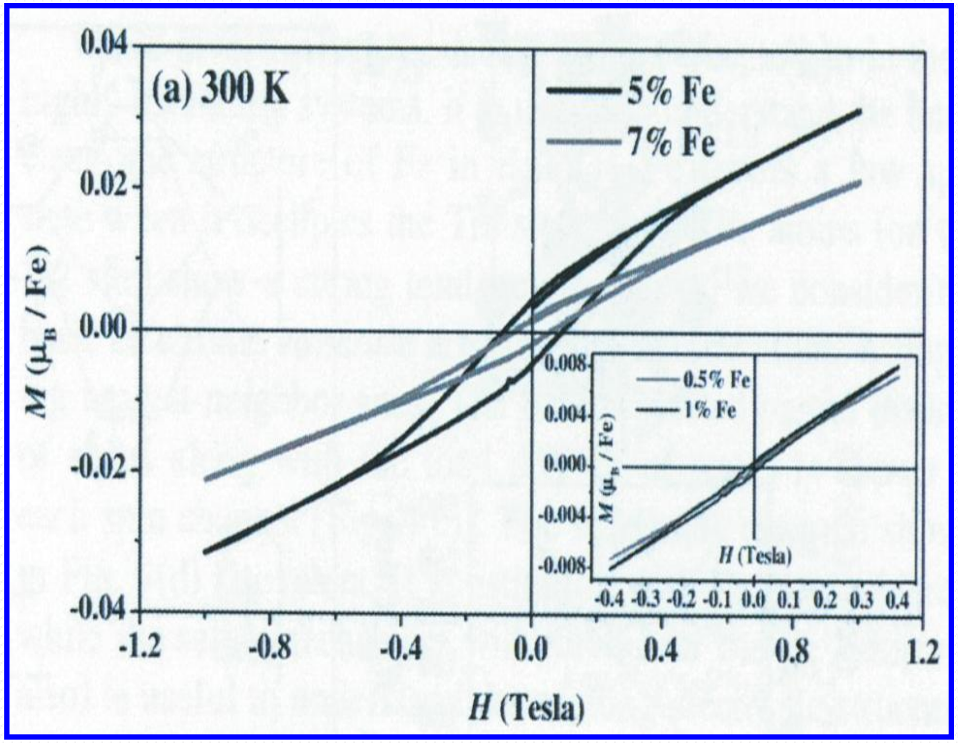
aliovalent substition

# Room temperature ferromagnetism in Fe doped $BaTiO_3$

Room-temperature M–H curves of the O2-annealed $Ba(Ti_{0.3}Fe_{0.7})O_3$ ceramic [8]

Room temperature M(H) loops from samples $Ba(Ti_{0.95}Fe_{0.05})O_3$ and $Ba(Ti_{0.93}Fe_{0.07})O_3$ [9]

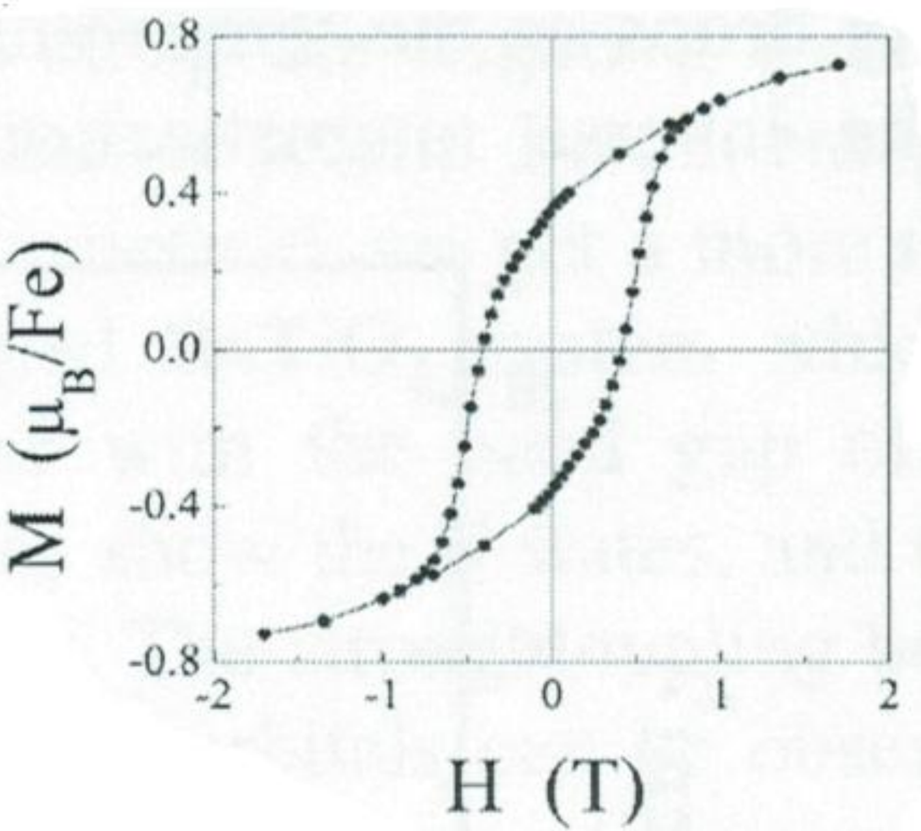


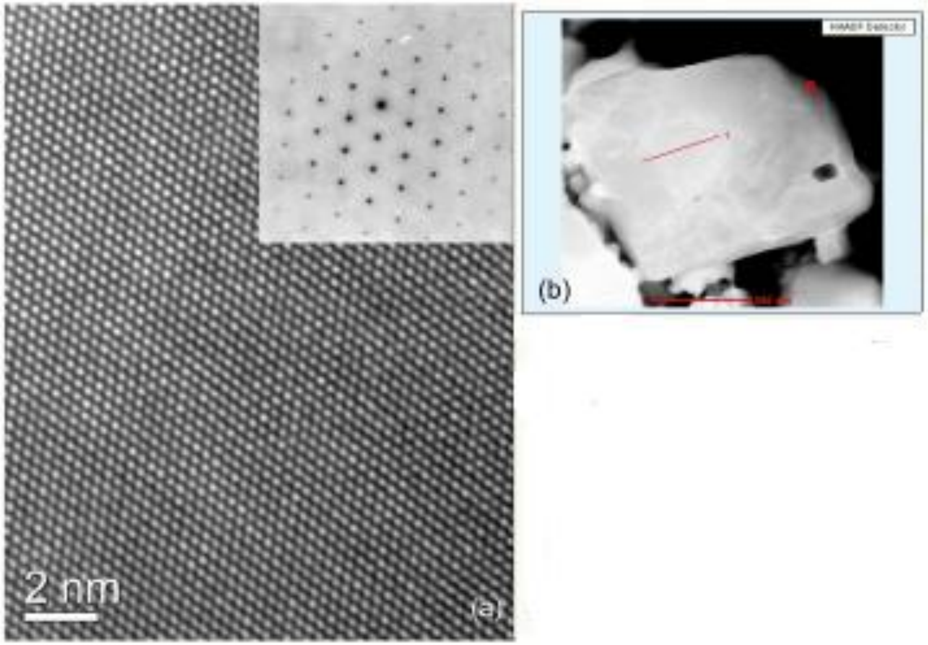

8. Fangting Lin, Dongmei Jiang, et al., Phisica B 403, p. 2525-2529, 2008.
9. Sugata Ray, Priya Mahadevan, et al. Physical Review B 77, p. 104416 (2008)

# Room temperature ferromagnetism in Fe doped $BaTiO_3$

Magnetic hysteresis loop of the $BaTi_{0.95}Fe_{0.05}O_3$ ceramics at room temperature




(a) High-resolution transmission electron microscopy of the $BaTi_{0.95}Fe_{0.05}O_3$ ceramics, and selected area electron diffraction in the inset; (b) transmission electron microscopy the $BaTi_{0.95}Fe_{0.05}O_3$ ceramics;




10. B. Xu, K. B. Yin, J. Lin, Y. D. Xia, et al., Physical Review B 79, p. 134109, 2009.

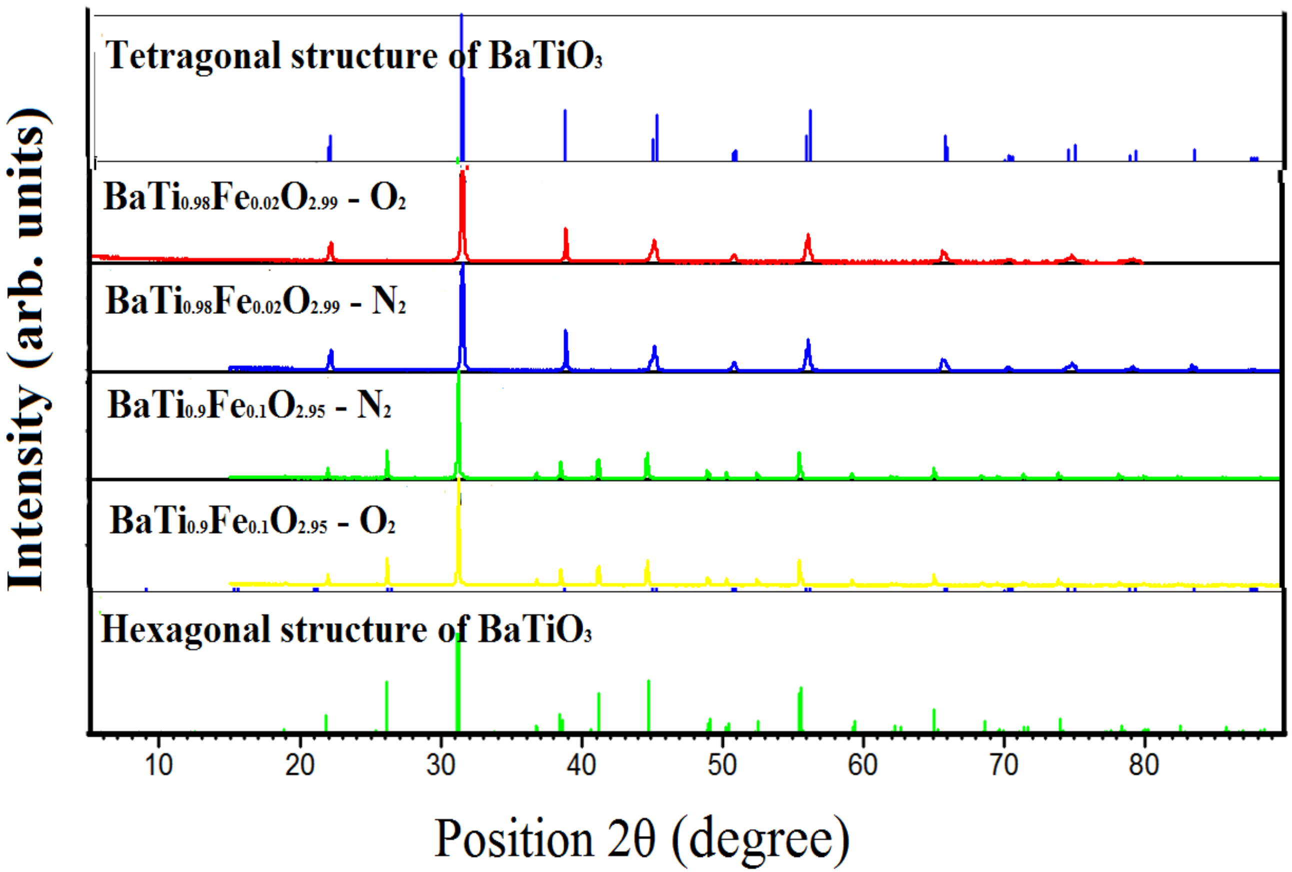
# Our study: Fe-doped BaTiO3

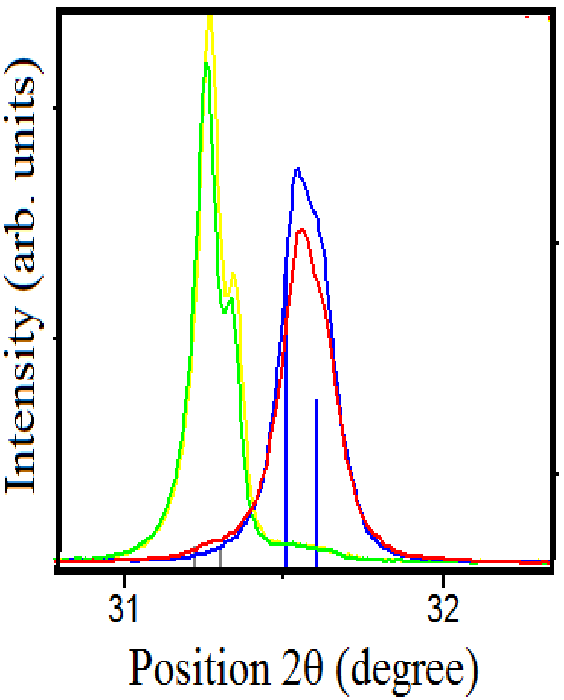
- The purpose of this research is detailed studies on the existence of the intrinsic magnetic ordering in Fe doped $BaTiO_3$.

# Our study: Fe-doped BaTiO3

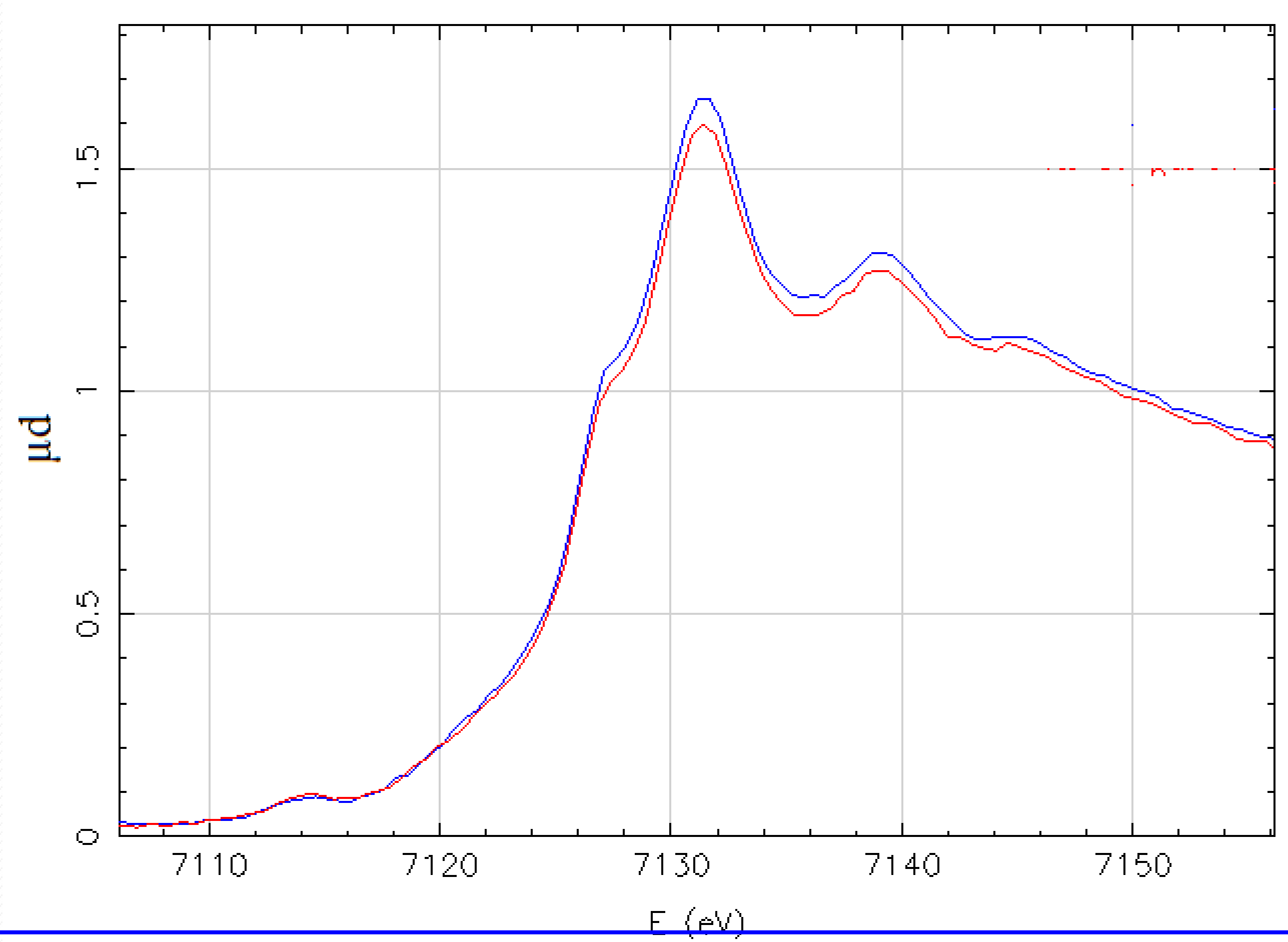
- Sample preparation:
  - Solid state reaction method.
  - $Ba(Ti_{1-x}Fe_x)O_{3-x/2}$, where x=2, 10 % of Fe –synthesis in nitrogen 1250°C/5h.
  - $Ba(Ti_{1-x}Fe_x)O_{3-x/2}$, where x=2, 10 % of Fe –synthesis in oxygen 1250°C/5h.
- X-Ray Diffraction (XRD).
- X-Ray Absorption Spectroscopy (XAS).
- Magnetic measurements.

# XRD patterns



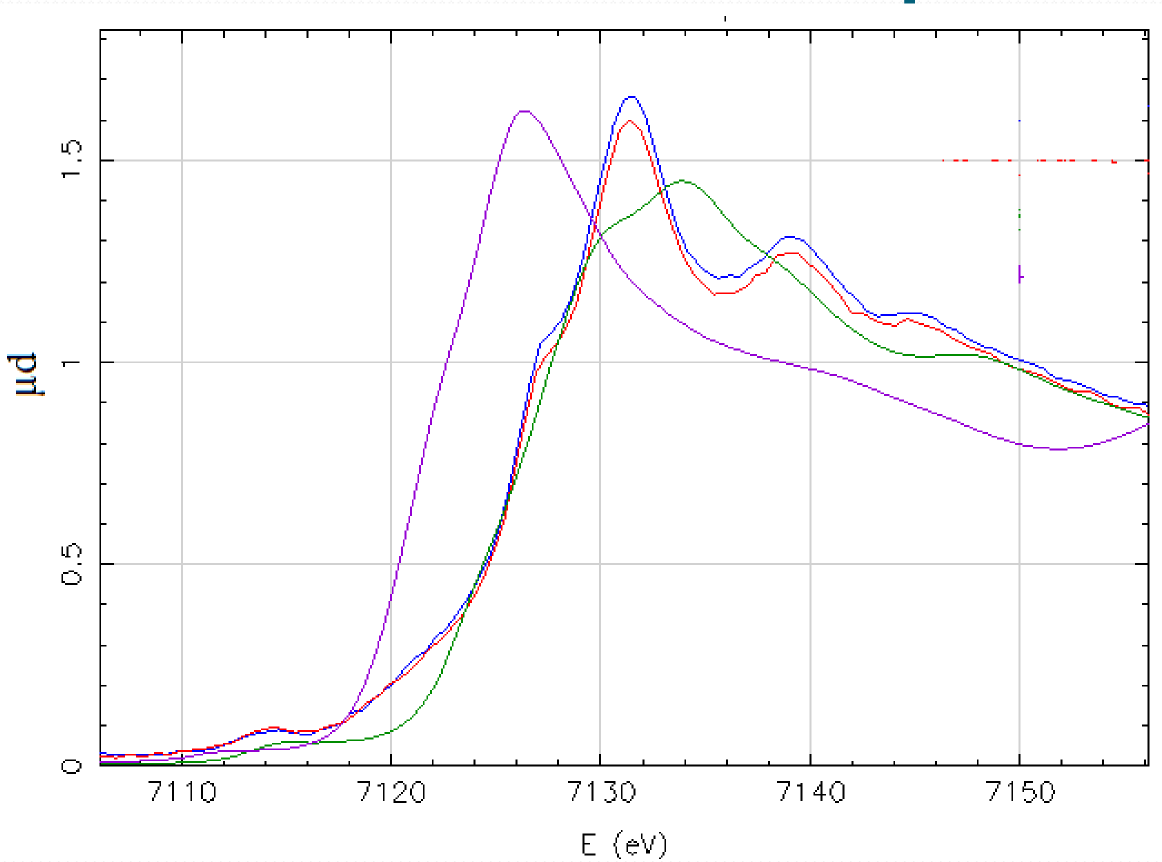



# Fe K-edge XANES spectra in $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$



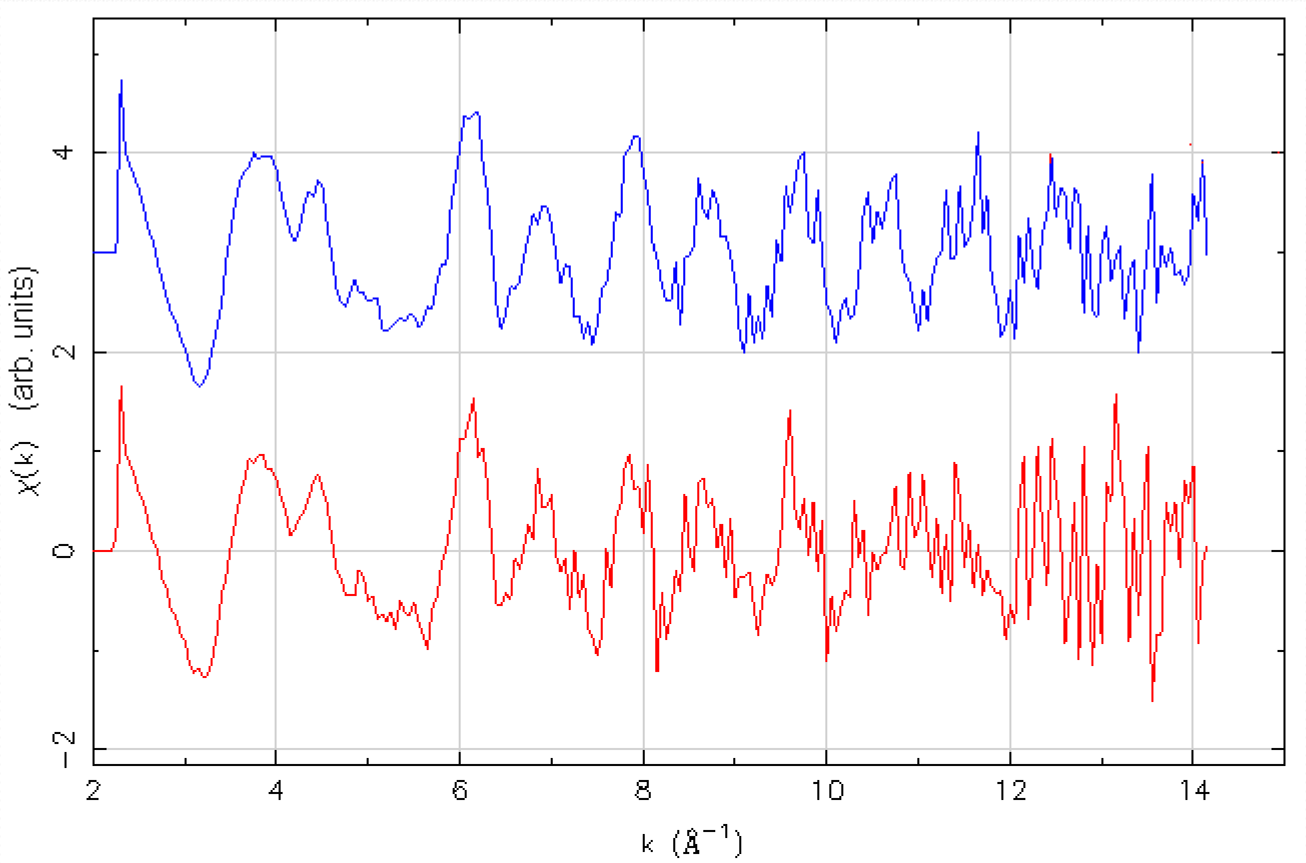

Fe K- edge XANES spectra of $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$
(blue line – annealed in nitrogen, red line – in oxygen)

# Valence state of Fe in Fe doped $BaTiO_3$




Fe K- edge XANES spectra of $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$ (blue line – annealed in nitrogen, red line – in oxygen) and reference samples (light violet line– $FeSO_4$, green line – $Fe_2O_3$) with well known Fe valence state.

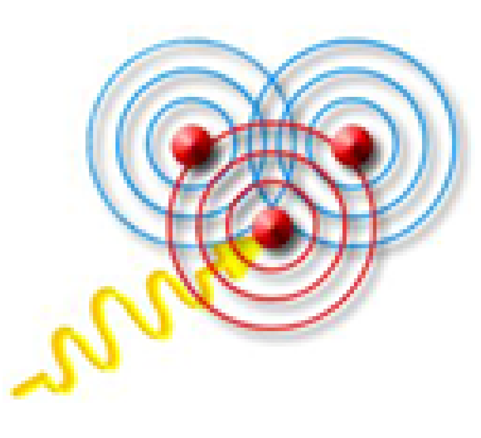
# EXAFS analysis




The EXAFS spectra χ(k) of Fe in $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$
(blue line – annealed in nitrogen, red line – in oxygen)

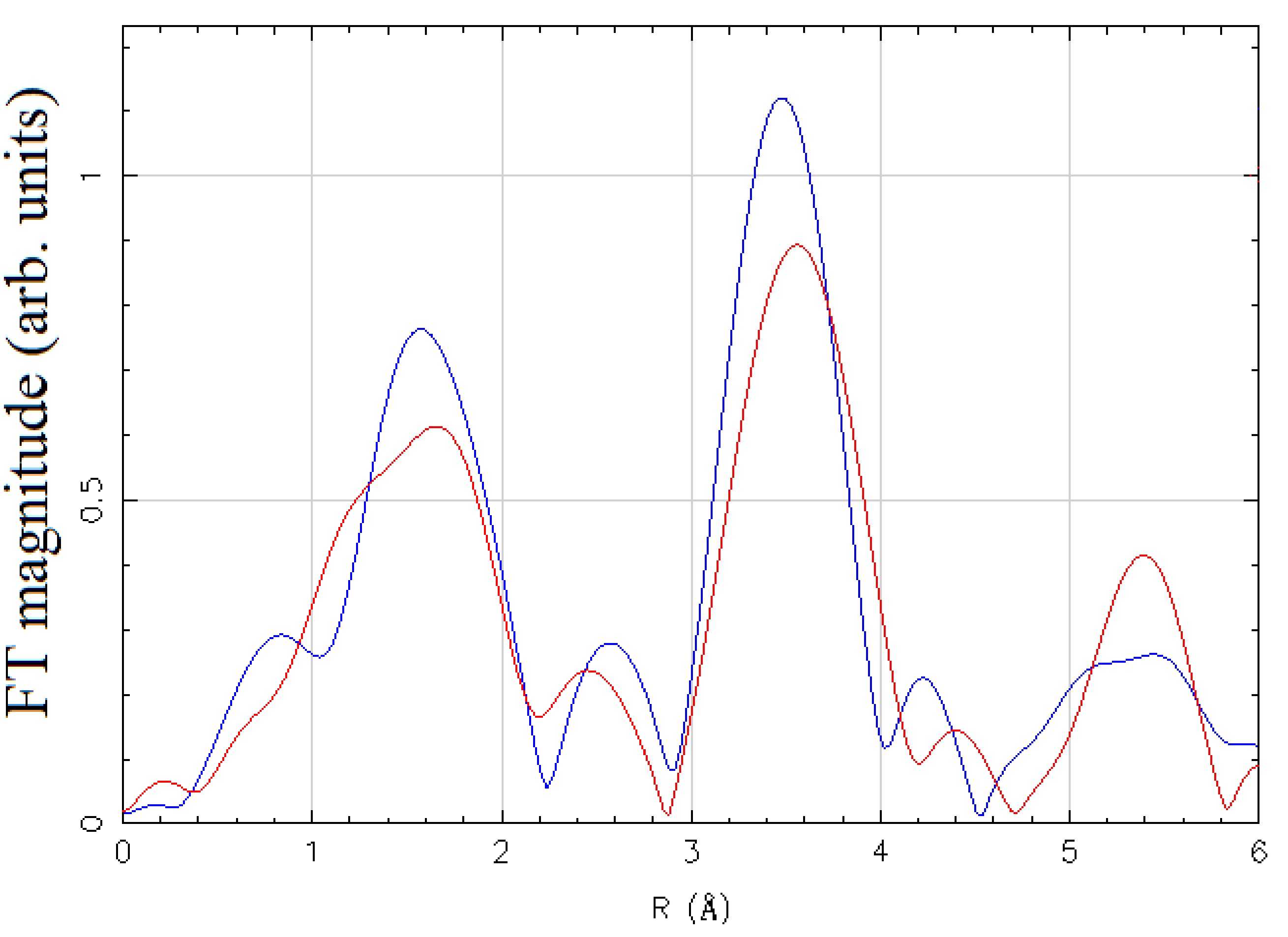
# EXAFS analysis

$$\chi(k) = \sum_i A_i(k)\sin(2kR_i + \delta_i),$$



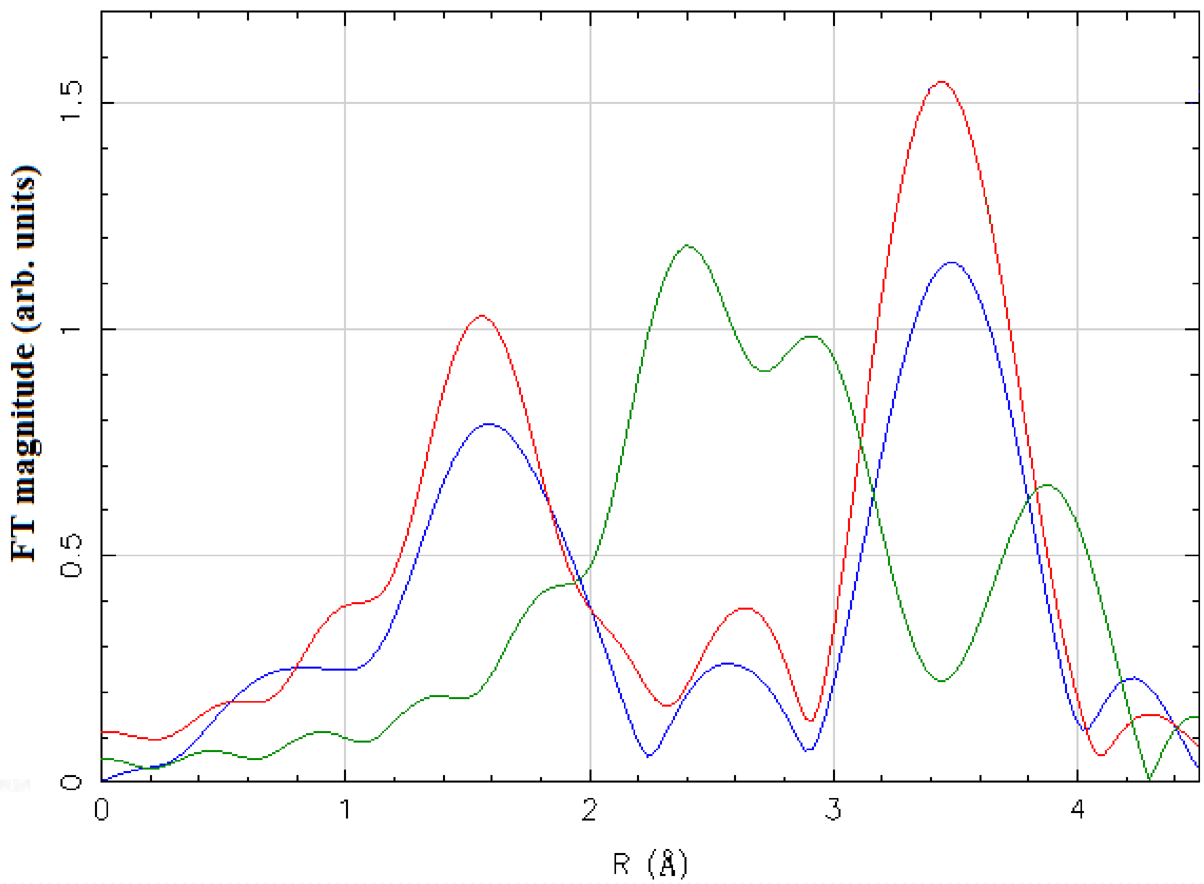
- with the atom-specific phase shift $\delta_i$ and the amplitude factor

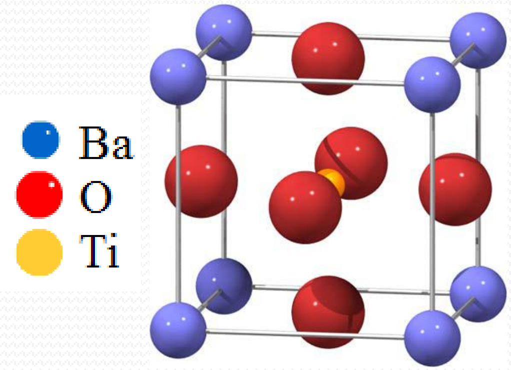
$$A_i(k) = \frac{N_i}{kR_i^2} S_0^2 F_i(k) e^{(-2k^2\sigma_i^2)} e^{-R_i\lambda_i}$$




- Red line - Fe K-edge Fourier transforms of Ba(Ti0.98Fe0.02)O2.99 annealed in oxygen.
- Blue line - Fe K-edge Fourier transforms of Ba(Ti0.98Fe0.02)O2.99 annealed in nitrogen.

# EXAFS analysis of Fe doped $BaTiO_3$



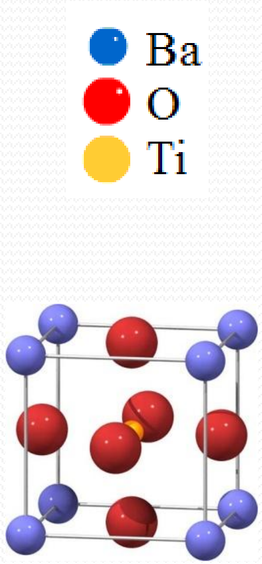



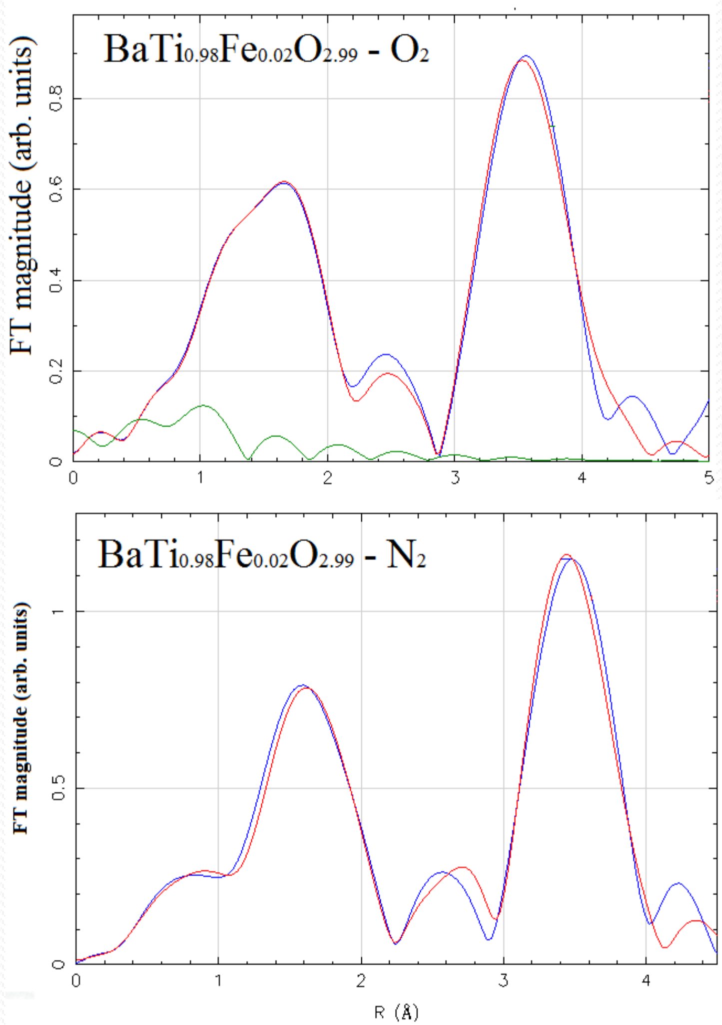

Blue line - Fe K-edge Fourier transforms of $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$ (experiment).

Red line - model of the undistorted $BaTiO_3$ structure around Ti site.

Green line - model of the undistorted $BaTiO_3$ structure around Ba site.

# EXAFS analysis of Fe doped $BaTiO_3$



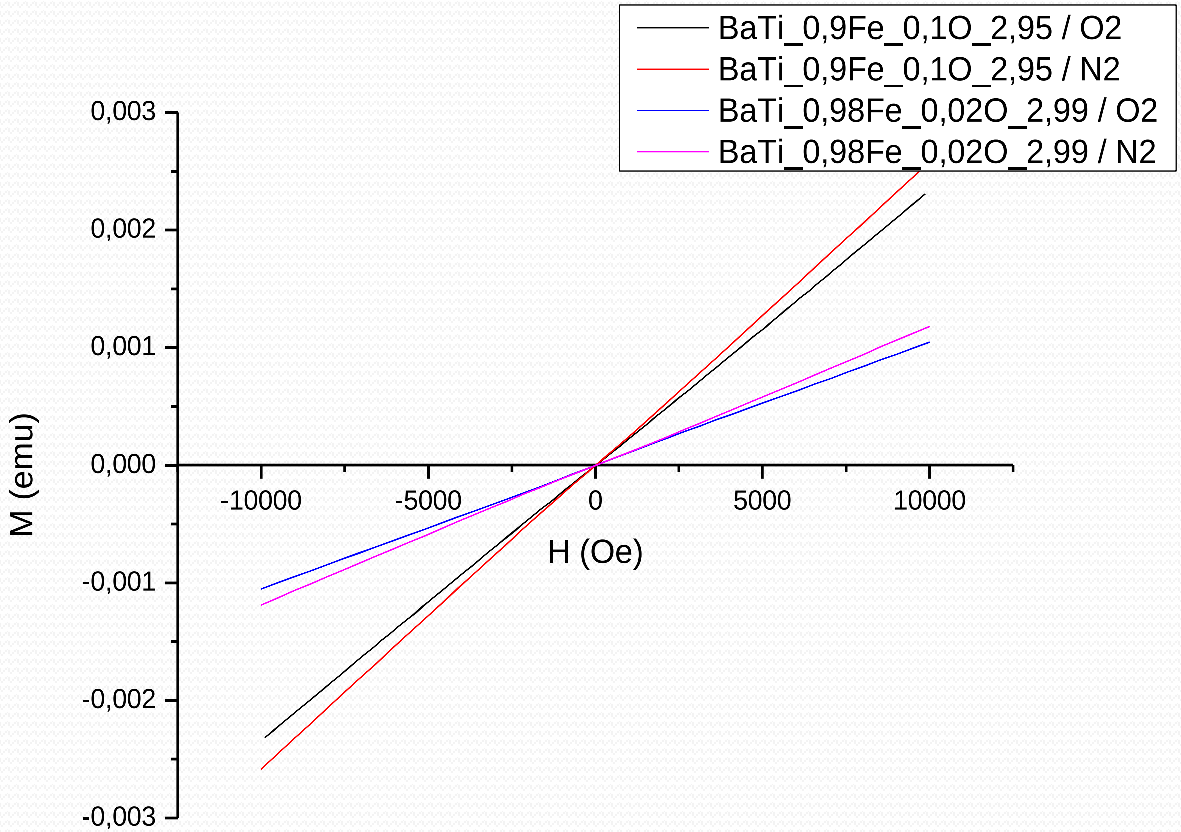




| Type | Number | Distance, A | Debye-Waller factor |
|---|---|---|---|
| O | 4 | 2.05(1) | 0.006(4) |
| O | 2 | **1.90(3)** | 0.006 (4) |
| Ba | 8 | 3.44(1) | 0.011(1) |
| Ti | 4 | 4.00(2) | 0.012(2) |

| Type | Number | Distance, A | Debye-Waller factor |
|---|---|---|---|
| O | 4 | 2.05(1) | 0.004(2) |
| O | 2 | **2.011(8)** | 0.0014 |
| Ba | 8 | 3.46(1) | 0.006 |
| Ti | 4 | 3.98(2) | 0.009 |

$$R_i, \sigma_i^2, N_i$$

# Magnetic measurements



# Conclusion

- We synthesized 4 samples of Fe-doped $BaTiO_3$ by solid state reaction method.
- No magnetic ordering exists in bulk Fe-doped $BaTiO_3$.
- All iron in $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$ samples is in trivalent form and $Fe^{3+}$ atoms substituted $Ti^{4+}$ on B sites of the perovskite $BaTiO_3$ host matrix.
- No impurities or secondary phases were observed in well-processed $Ba(Ti_{0.98}Fe_{0.02})O_{2.99}$.

***Thank you for your attention!!!***