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Dielectric and magnetic properties of ferrite/poly(vinylidene fluoride) nanocomposites

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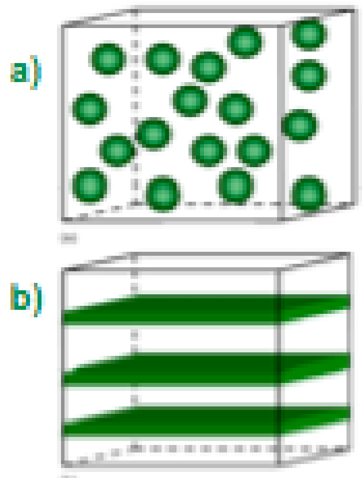
INTRODUCTION

- Hybrid Multiferroic Materials are excellent candidates as memory elements, smart sensors, etc.

- Magnetoelectric ones (ME) are composed of a magnetostrictive and a piezoelectric material

- Two main types:
  a) granular
  b) laminate



- Two-phase granular composites with ferrite grains and a ferroelectric matrix have good properties for the magnetoelectric effect.

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… INTRODUCTION

- Poly(vinylidene fluoride) (PVDF), is a semicrystalline polymer, and one of the largest pyro- and piezoelectric polymers.
- It presents four crystalline phases (α, β, γ, δ)
- The polar β-phase shows the largest piezoelectric,pyroelectric and ferroelectric coefficients, as well as a high dielectric constant
- Usually obtained by mechanical stretching of the non-polar α -phase

IN THIS PAPER

- PVDF-based nanocomposites with Co or Ni ferrites fillers are investigated
- The polar β- phase of the polymer is nucleated by the ferrites, giving a simplified processing method for the preparation of magnetoelectric composites

EXPERIMENTAL

- $CoFe_2O_4$ (35–55 nm) and $NiFe_2O_4$ (20–30 nm) nanoparticles (Nanoamor)
- PVDF (Solef 1010) density = 1.78 g cm^{-3} (Solvay)

- PVDF-Ferrite films (thickness ≈ 40–50 μm) prepared by spreading the solution on a clean glass substrate
- Weight 0.001% to 50% (Co-ferrite), 5% to 50% (Ni-ferrite)

- Scanning electron microscopy (SEM): Leica Cambridge S360
- X-ray diffraction (XRD): Philips PW1710

- Dielectric constant: automatic Quadtech 1929 Precision LCR meter + Linkam THMSE 600 oven (1 Hz to 1 MHz, 150 to 425 K)

- Zero-field-cooled (ZFC) field cooled (FC) curves: 75 Oe, 4 to 600 K VSM)
- Room temperature hysteresis loops: VSM (−10 to +10 T)

RESULTS

- Good dispersion of the ferrite nanoparticles within the polymer is achieved at all concentrations
- For low Co or Ni ferrite concentrations, the microstructure of PVDF is spherulitic (10-100 µm) α-phase (Fig 1a,b)
- For c = 0.08 or higher, the spherulitic structure is destroyed and the polymer agglomerates on the ferrite particles (Fig 1c,d)
- Ferrite nanoparticles result in the α to β phase transformation (Fig 2)
- Nucleation of the β-phase is stronger for the Co-ferrite nanoparticles (Fig 3)
- This variation is attributed to the different filler/polymer surface interactions

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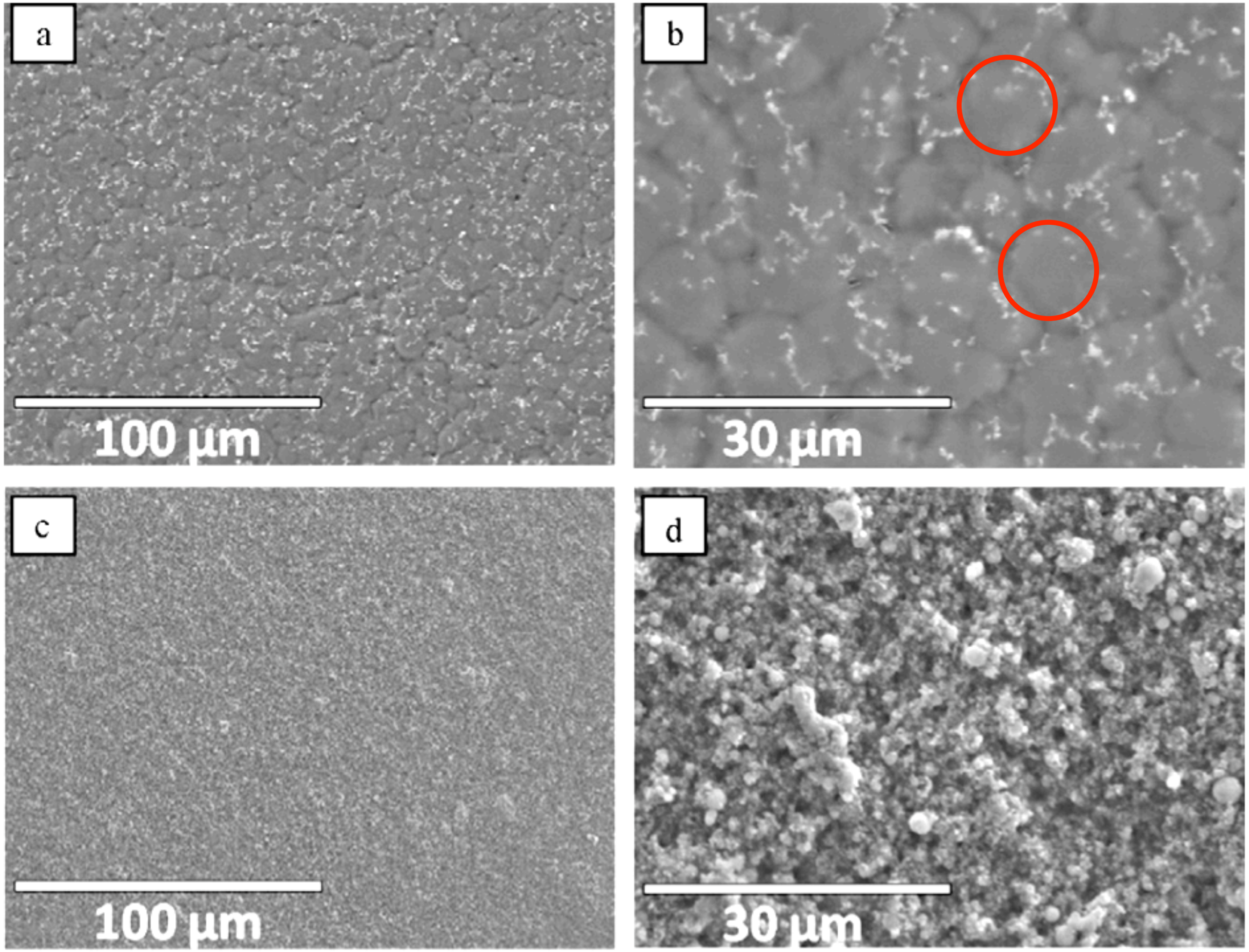

Fig. 1. SEM images of $CoFe_2O_4$/PVDF nanocomposites with ferrite volume fractions of 0.02 (a and b) and 0.25 (c and d).

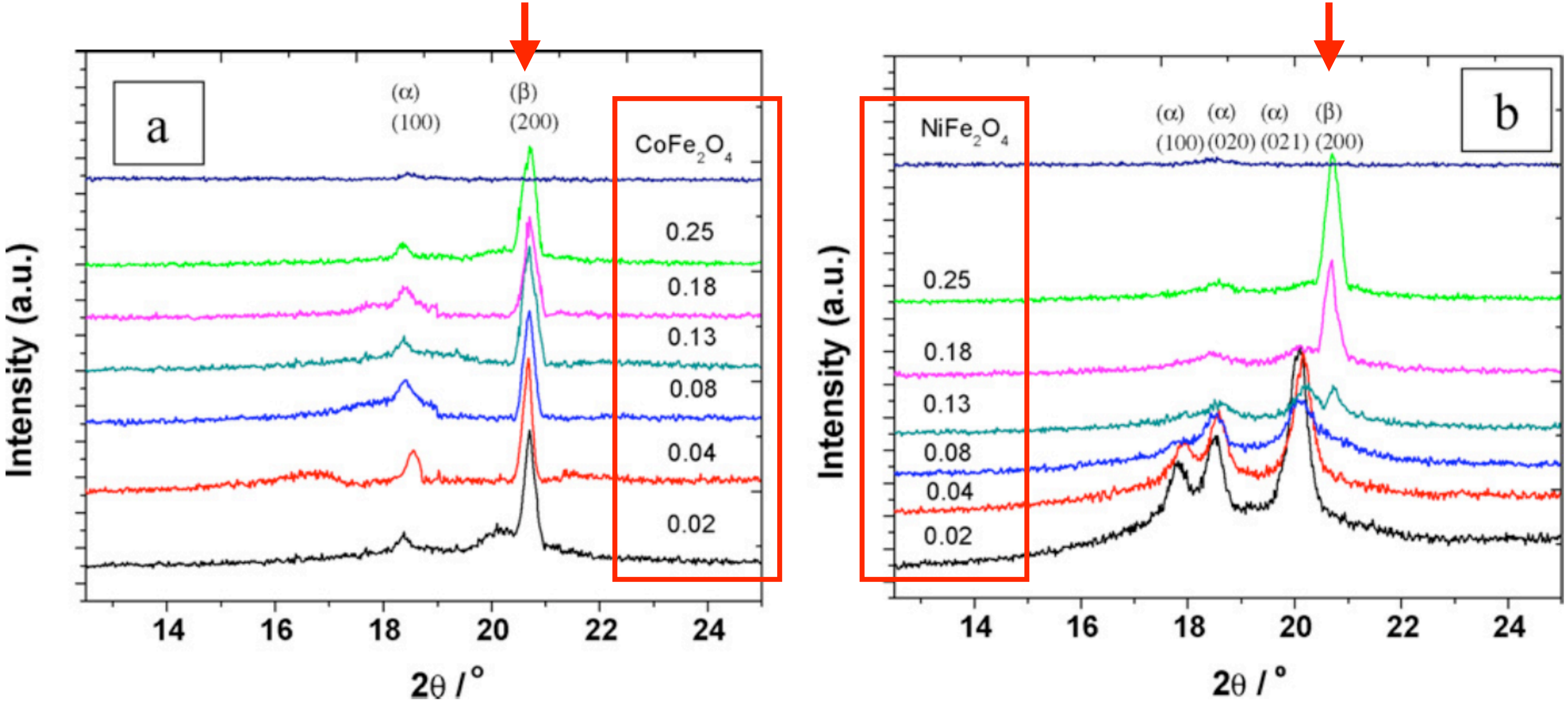

Fig. 2.- XRD patterns for (a) $CoFe_2O_4$/PVDF (b) $NiFe_2O_4$/PVDF nanocomposites with different volume fractions of ferrite.

Peaks identify the respective α, β phases

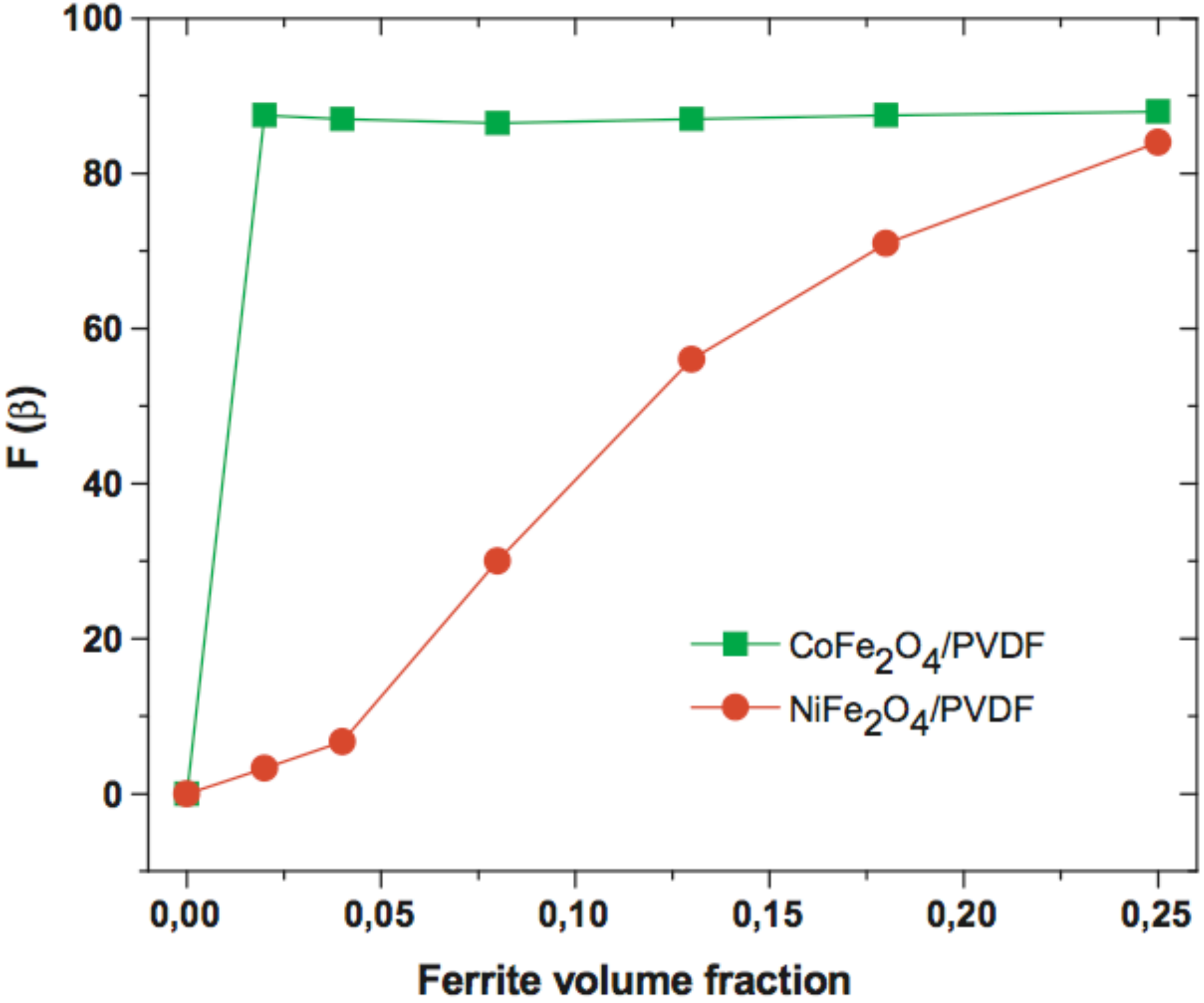

Fig. 3. β-Phase of the PVDF as a function of ferrite content

… RESULTS

- Increase of ε for the composites with respect to the pure polymer (Figs 4,5)
- The higher values are obtained for the $CoFe_2O_4$ nanocomposites (Figs 4,5)
- Dielectric losses also increase, but stay lower that 0.3 (Fig 5)
- Explained by the early nucleation of the β-phase of the polymer (polar nature and larger dielectric constant than the α-phase)
- Dielectric losses also reflects the differences between the α and β-phases of PVDF (larger for the Co-ferrites that nucleate the polar β-phase)

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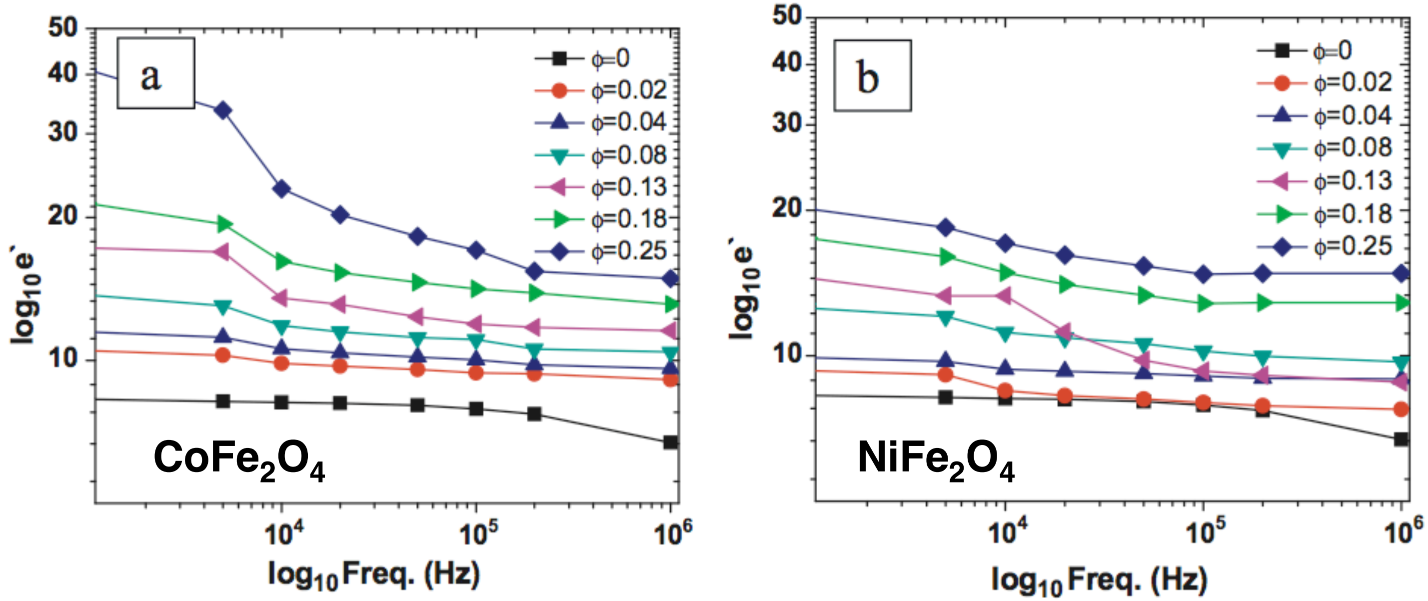

Fig. 4. Frequency-dependent dielectric constant at RT

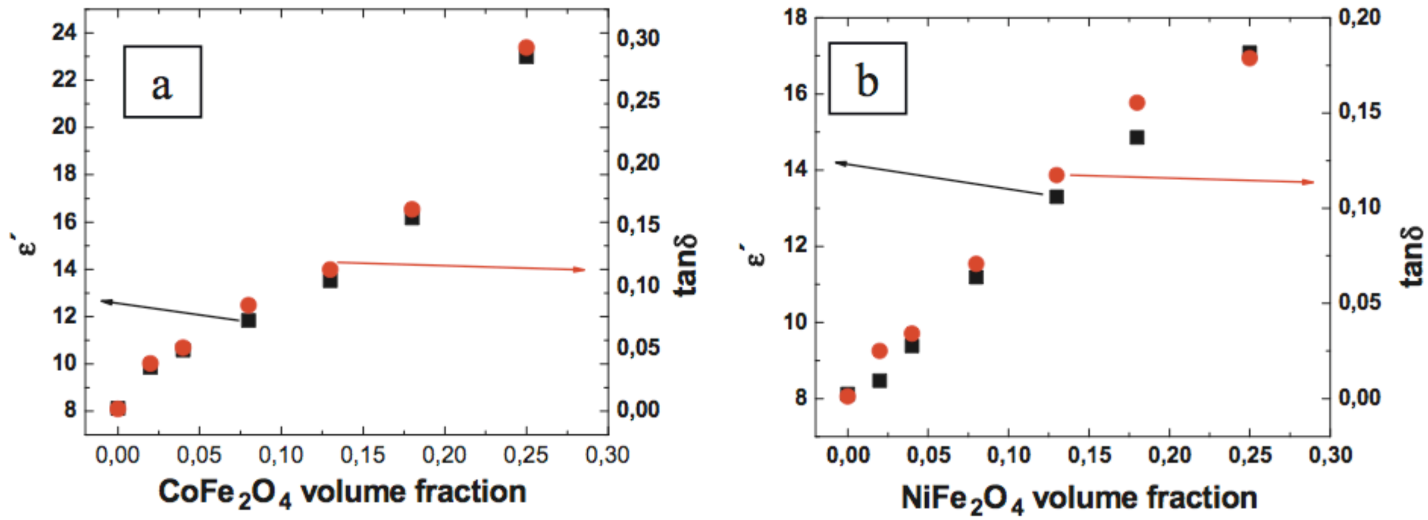

Fig. 5. Dielectric constant and losses at 10 kHz (RT)

… RESULTS

- Dielectric relaxation assigned to cooperative segmental motions within the amorphous phase (β-relaxation) has been studied (Fig 6)
- Shows a similar behavior as in the pure polymer
- Dynamics analyzed by the Vogel–Fulcher–Tammann (VFT) formalism (Fig 7)
- Parameters of the β-relaxation are the same as in the β -phase obtained by stretching from the α-phase (Table 1)
- Ferrite particles make the composites more fragile (m factor) than the pure α -phase. Values are similar to the β-PVDF

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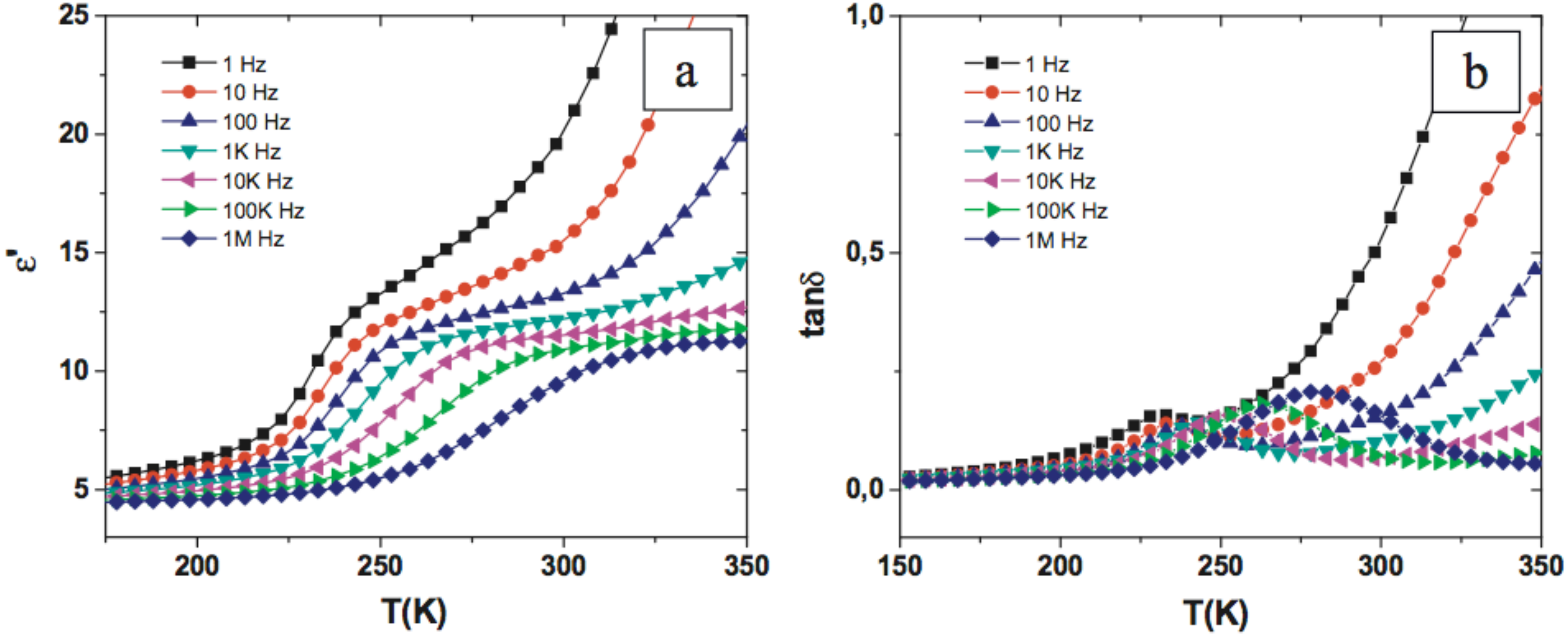

Fig. 6. ε' and $\tan\delta$ vs. temperature for the sample with 0.08 volume fraction of $CoFe_2O_4$ at several frequencies between 1 Hz and 1 MHz.

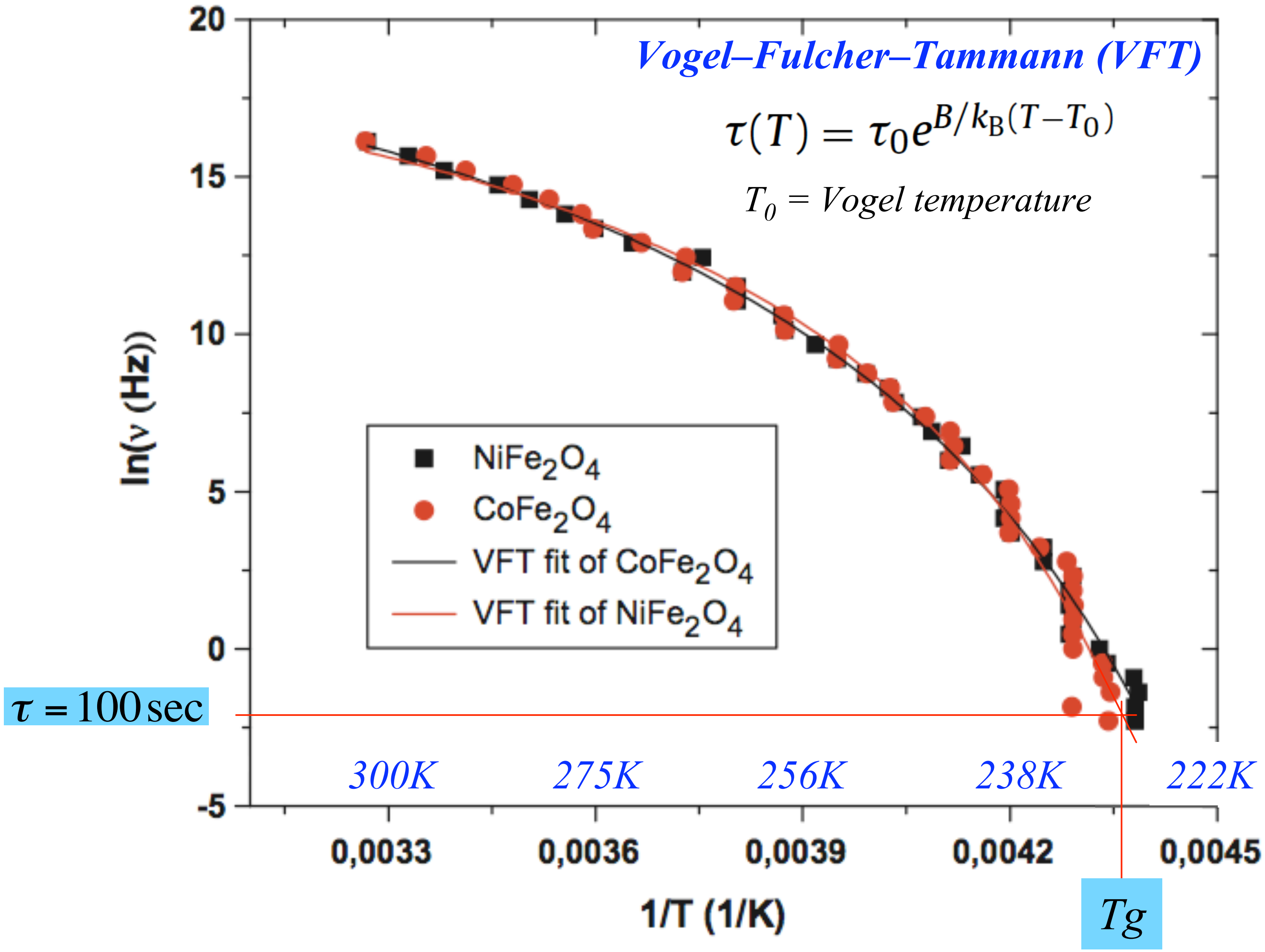

Fig. 7. VTF fittings of the β-relaxation of $CoFe_2O_4$/PVDF and $NiFe_2O_4$/PVDF with 0.08 of ferrite volume fraction.

Vogel–Fulcher–Tammann (VFT)

$$\tau(T) = \tau_0 e^{B/k_B(T-T_0)}$$

Fragility parameter

$$m = \frac{B/kT_g}{(\ln 10)(1 - T_c/T_g)^2}$$

High m = fragile, small m = strong

Table 1
Vogel–Tammann–Fulcher and fragility parameters for the β-relaxation for α and β-PVDF and for the $CoFe_2O_4$/PVDF and $NiFe_2O_4$/PVDF nanocomposites with 0.08 of ferrite volume fraction.

Sample	τ_0 (s^{-1})	B (eV)	T_0 (K)	T_g (K)	m
α-PVDF	5.96E−13	0.13	168.00	213.00	67.00
β-PVDF	3.00E−12	0.06	201.50	228.67	99.00
$CoFe_2O_4$/PVDF	4.93E−10	0.05	205.28	227.10	117.68
$NiFe_2O_4$/PVDF	9.29E−11	0.07	197.18	225.08	97.08

… RESULTS

- RT hysteresis loops of $CoFe_2O_4$ and $NiFe_2O_4$ composites (Fig 8) similar to pure ferrites (no interaction with the polymer)
- $CoFe_2O_4$-ferrite hysteresis loop with Hc= 2,7 kOe and reaches saturation
- $NiFe_2O_4$ - ferrite almost absence of hysteresis, remanence and coercivity (superparamagnetic?)
- Saturation magnetic moment Ms determined by Arrott plots increases linearly with ferrite content (Fig. 9) Well dispersed non interacting particles
- In-plane and out of plane M(H) loops similar → random orientation (Fig 10)

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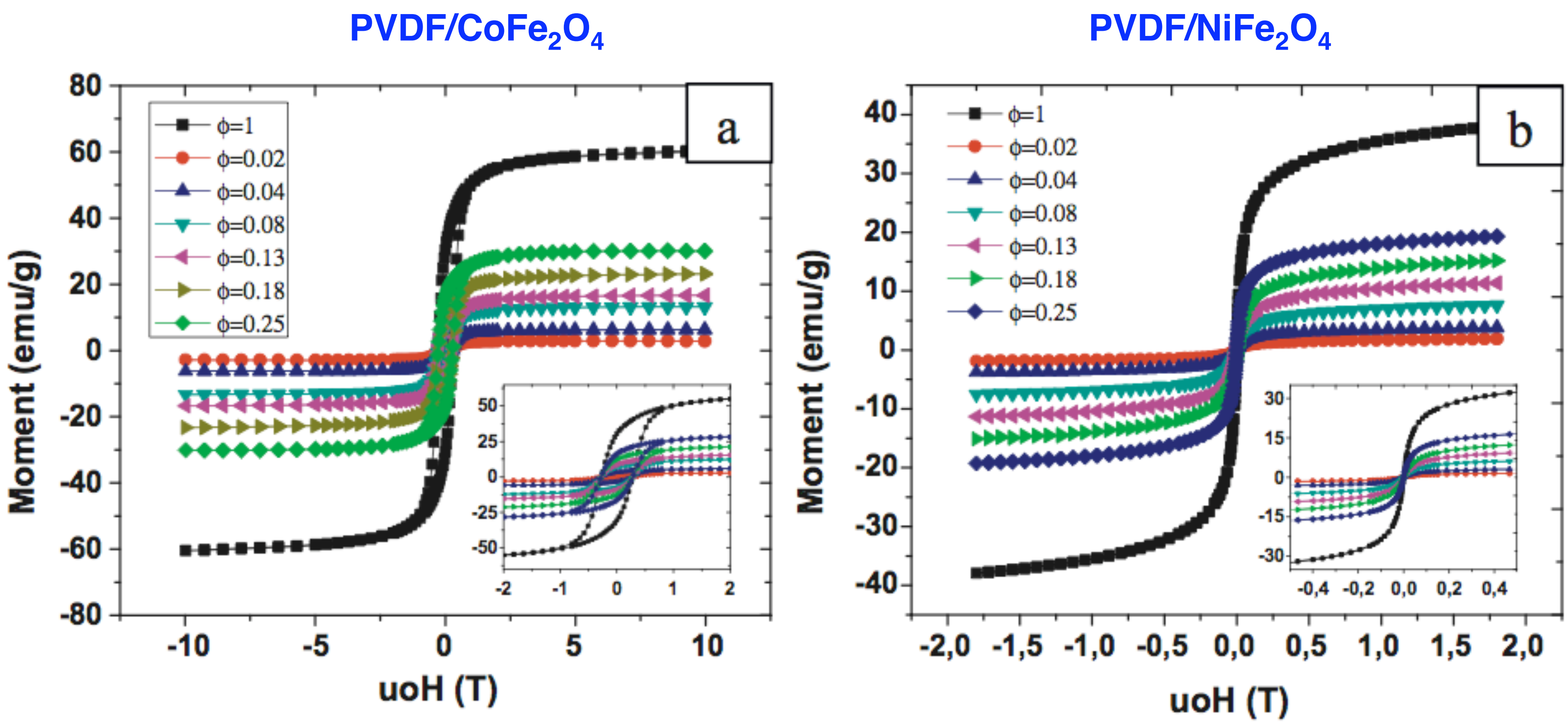

Fig. 8. RT hysteresis loops vs concentration

PVDF/$CoFe_2O_4$ **PVDF/$NiFe_2O_4$**

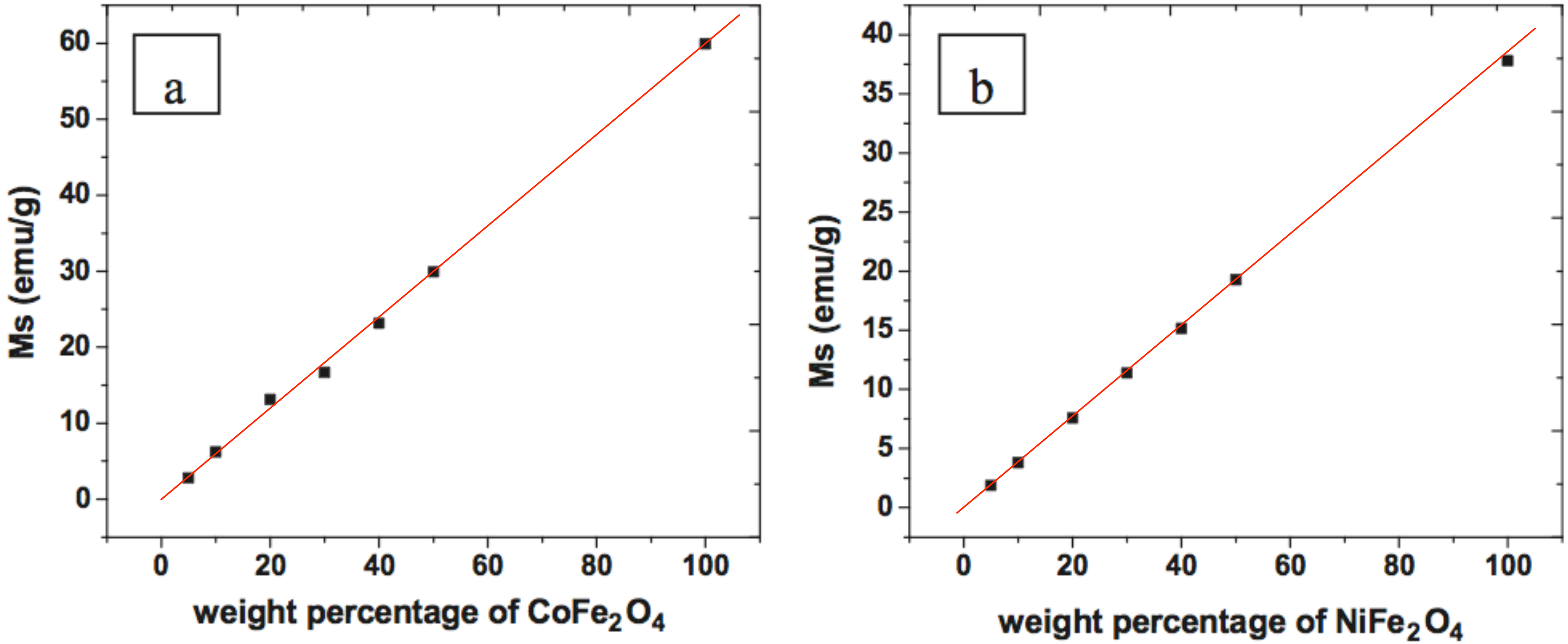

Fig. 9. RT Saturation magnetization vs concentration (Arrot plots)

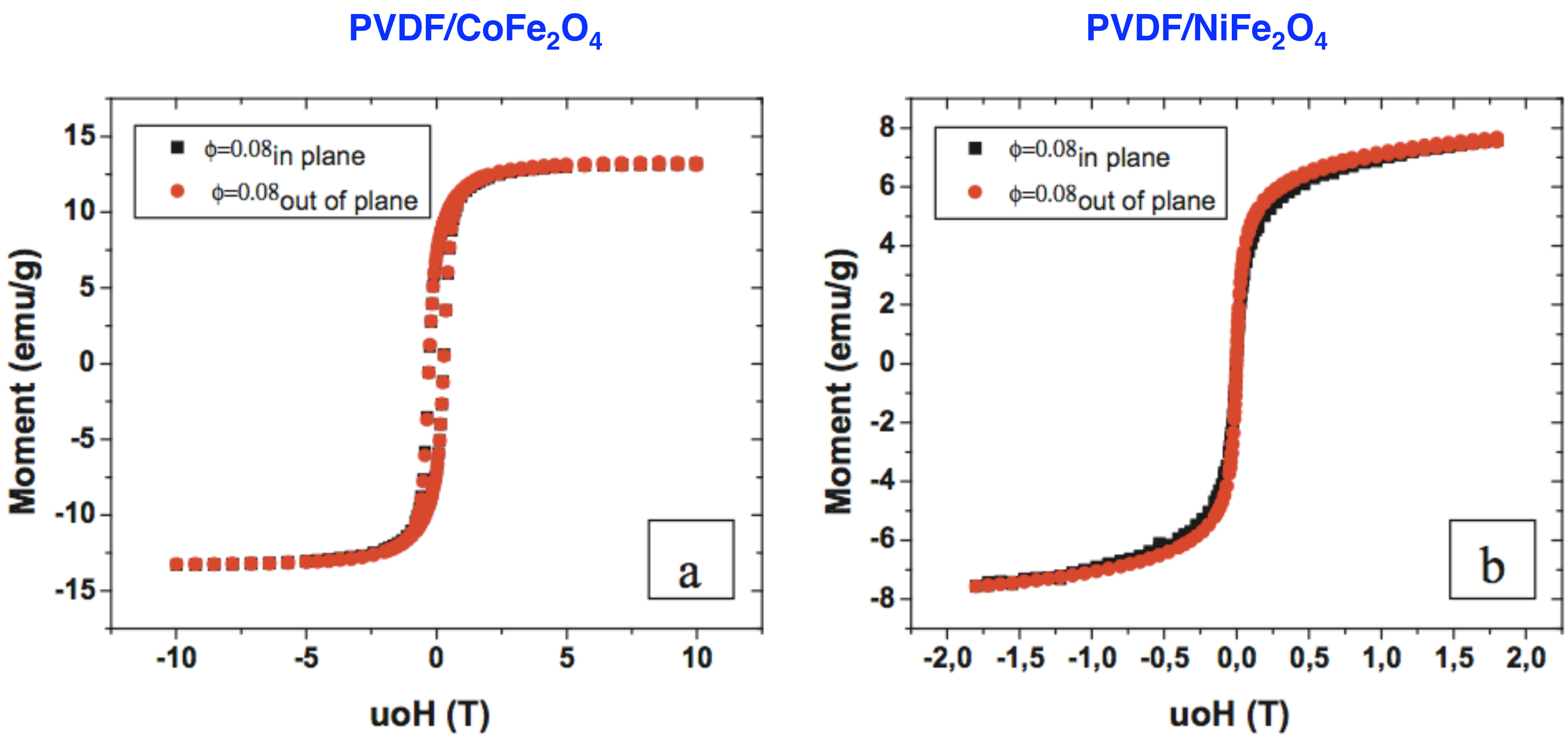

Fig. 10. RT in plane - out of plane hysteresis loops

… RESULTS

- ZFC–FC curves for $CoFe_2O_4$ and $NiFe_2O_4$ are similar in shape (Fig 11)
- Blocking temperatures T_b (525 K - $CoFe_2O_4$ and 275 K - $NiFe_2O_4$)
  Maxima (450 K - $CoFe_2O_4$, 225 K - $NiFe_2O_4$)
  Broad distribution of sizes
- At RT $CoFe_2O_4$ is ferromagnetic, $NiFe_2O_4$ almost superparamagnetic
- From approach to saturation:
  $CoFe_2O_4$, $K_{eff} = 1.58 \times 10^5$ ergs cm^{-3}, d≈30nm
  $NiFe_2O_4$, $K_{eff} = 0.14 \times 10^5$ ergs cm^{-3}, d≈50nm
  agree with the sizes given by supplier

$$T_b = \frac{K_{eff} V}{25 k_B}$$

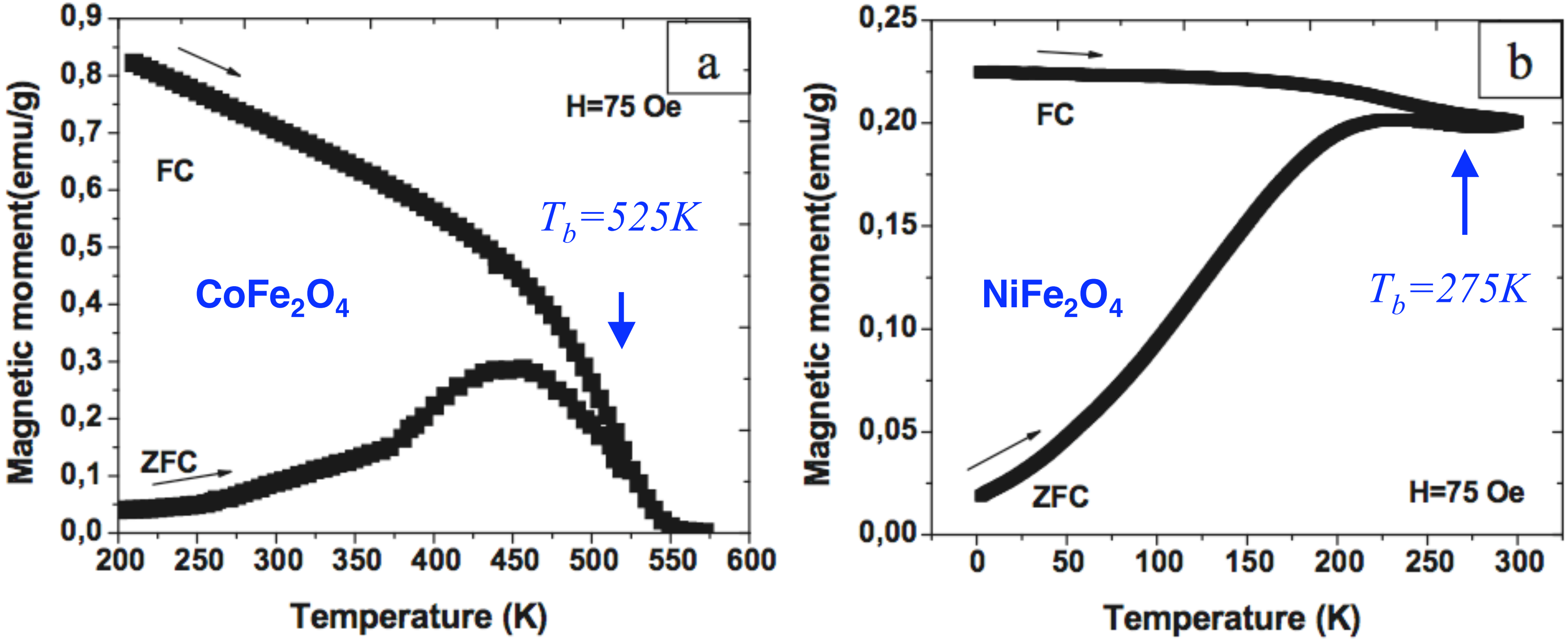

Fig. 11. ZFC-FC magnetization at 75 Oe

CONCLUSIONS

- $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles / PVDF composites were prepared.

- Nucleation of the β-phase of PVDF is more effective for the Co-ferrite nanoparticles
- The whole polymer is in ferroelectric phase for c= 0.02
- Larger Ni-ferrite content (c= 0.25) is needed for full ferroelectric phase

- The dielectric constant increases with increasing ferrite content
- The dielectric constant is larger for the Co-ferrite composites

- The β-relaxation of the amorphous part of the polymer is the same as the β - PVDF obtained by stretching

- Ferrite nanoparticles are homogeneously distributed within the composite
- $CoFe_2O_4$ /PVDF composites exhibit hysteresis loop (coercivity = 2.7 kOe)
- $NiFe_2O_4$ /PVDF composites are quasi-superparamagnetic (FC and ZFC)

Thank you

for your attention!