Influence of grain size dispersion on the magnetic properties of nanogranular BaTiO$_3$-CoFe$_2$O$_4$ thin films

J. Barbosa[1], B.G. Almeida[1,*], J.A. Mendes[1], D. Leitão[2], J.P. Araújo[2]

[1]Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

[2]Dep. de Física and IFIMUP, Universidade do Porto, Rua Campo Alegre, 687, 4169-007 Porto, Portugal

*Tel. +321253604063, Fax. +351253678981, e-mail: bernardo@fisica.uminho.pt

Abstract

Thin film nanogranular composites of cobalt ferrite (CoFe$_2$O$_4$) dispersed in a barium titanate (BaTiO$_3$) matrix were deposited by laser ablation with different cobalt ferrite concentrations (*x*). Their structural and magnetic properties were characterized. The films were polycrystalline and composed by a mixture of tetragonal-BaTiO$_3$ and CoFe$_2$O$_4$ with the cubic spinel structure. A slight (111) barium titanate phase orientation and (311) CoFe$_2$O$_4$ phase orientation were observed. The lattice parameter of the CoFe$_2$O$_4$ was always smaller than the bulk value indicating that the cobalt ferrite was under compressive stress. From atomic force microscopy a broad distribution of grain sizes was observed in the nanocomposites, with a significant amount of smaller grains (<40nm) from the CoFe$_2$O$_4$ phase. The magnetic measurements show an increase of the magnetic moment from the low concentration region where the magnetic grains are more isolated and their magnetic interaction is small, towards the bulk value for higher CoFe$_2$O$_4$ content in the films. A corresponding decrease of coercive field with increasing cobalt ferrite concentration was also observed, due to the higher inter-particle magnetic interaction (and reduced stress) of the agglomerated grains.

Introduction

Recently, composite thin films formed by mixing a magnetostrictive material (such as $CoFe_2O_4$) in a piezoelectric matrix (such as $BaTiO_3$) have attracted much interest, both from the fundamental point of view as well as applications [1,2]. In addition to possessing ferroelectricity and magnetism in each individual phase, they are shown to exhibit a coupling between their magnetic and electric degrees of freedom, the so called magnetoelectric effect. In these composites it is the elastic interaction between the piezoelectric and magnetostrictive materials that is providing the coupling mechanism inducing the magnetoelectric response [1-3]. Thus, their electric and magnetic properties are strongly dependent on phase morphology and internal stress distribution.

Here, nanogranular thin films of cobalt ferrite ($CoFe_2O_4$) dispersed in a barium titanate ($BaTiO_3$) matrix were deposited by laser ablation with different cobalt ferrite concentrations, as well as pure barium titanate and cobalt ferrite films (end members). Their structural and magnetic properties were characterized.

Bulk $CoFe_2O_4$ has a cubic inverse spinel structure [4] and presents a high magnetocrystalline anisotropy and magnetostriction [5,6]. $BaTiO_3$ is a well studied piezoelectric perovskite [6,7]. At high temperatures it has a cubic structure, but below ~395 K $BaTiO_3$ transforms to a tetragonal structure, that remains at ambient temperature. The high temperature cubic phase is paraelectric and the ambient temperature tetragonal phase is ferroelectric.

Experimental

The nanogranular $BaTiO_3$ - $CoFe_2O_4$ thin films were prepared by pulsed laser ablation, on platinum covered Si(001) substrates. Details of their deposition conditions are in [8]. The ablation targets were prepared by mixing $CoFe_2O_4$ and $BaTiO_3$ powders with cobalt ferrite

weight concentrations x = 20%, 30%, 40%, 50%, 60% and 70%. They were then compressed and sintered at 1200ºC during 1 hour. The end members targets, barium titanate and cobalt ferrite, were also prepared in this way. The structural studies were performed by X-ray diffraction (XRD) and were carried out with a Philips PW-1710 diffractometer using Cu Kα radiation. Atomic Force Microscopy (AFM) using a Digital Instruments NanoScope in no contact mode was used in order to analyze the surface microtopography. The magnetic properties were measured with a Quantum Design MPMS SQUID magnetometer. The X-ray diffraction spectra measured on the laser ablation targets showed that they were polycrystalline and composed by mixtures of tetragonal-$BaTiO_3$ and $CoFe_2O_4$ with the cubic spinel structure.

Discussion

Figure 1 shows the X-ray diffraction spectra measured on the nanocomposite thin films with cobalt ferrite concentrations in the range 20% - 100%. The peaks were fitted using pseudo-Voigt functions in order to determine their angular positions, intensities and integral widths. Figure 2a) shows the relative intensity between the (111) peak and the (110),(101) peaks of the $BaTiO_3$ phase and between the (222) and (311) peaks of the $CoFe_2O_4$ phase, in the films, for different cobalt ferrite concentrations. The (110),(101) peaks are the most intense ones in bulk tetragonal-$BaTiO_3$, while the corresponding one in the bulk cubic-spinel-$CoFe_2O_4$ is the (311) peak.

The films are polycrystalline and composed by a mixture of tetragonal-$BaTiO_3$ and $CoFe_2O_4$ with the cubic inverse spinel structure. However, as the concentration of the cobalt ferrite increases, the relative intensity of the (111) $BaTiO_3$ peak increases, indicating a progressively more oriented growth of this phase. The opposite occurs with the (311) peak from the $CoFe_2O_4$ phase. From figure 1 and figure 2a), as x increases the (222) peak starts to

appear, while the intensity of the (311) peak only slightly changes, indicating a progressive increase of the polycrystallinity of the $CoFe_2O_4$ phase with increasing cobalt ferrite concentration.

The grain sizes as measured from the X-ray diffraction peak widths for both phases ((112) for $BaTiO_3$ and (311) for $CoFe_2O_4$), were determined by using the Scherrer equation [9]. They are shown in figure 2b) for the different nanocomposite films and are in the range 20nm to 100nm. However, as the concentration of the cobalt ferrite increases, the grain size of the $BaTiO_3$ phase decreases, from 91.5 nm to 30nm, up to 50% $CoFe_2O_4$ content beyond which the $BaTiO_3$ grain size fluctuates in the interval 25-35nm. On the other hand the cobalt ferrite grain size does not show a clear trend with increasing cobalt ferrite concentration, fluctuating in the range 25nm to 30nm.

The lattice parameter of the cobalt ferrite phase was determined from the X-ray diffraction spectra measured on the nanocomposite films. For $CoFe_2O_4$ it was obtained from the (311) peak position and varied monotonically from 8.26Å in the sample deposited with cobalt ferrite concentration $x = 20\%$, to 8.35Å in the sample deposited with $x = 70\%$ and 8.38Å in the pure $CoFe_2O_4$ film. Comparing with the bulk $CoFe_2O_4$ lattice parameter ($a = 8.3919$Å), in the films the cobalt ferrite is under compressive stress that relaxes as its concentration progressively increases.

To further characterize the distribution of grain sizes in the films, AFM microtopography measurements were performed and they are shown in figures 3a) and 3b) for the particular cases with $x = 20\%$ and x = 60%, respectively. From the micrographs, the number of grains with a size falling on a particular range was determined and histograms were made in order to obtain their size distribution. Figures 3c) and 3d) show the histograms for the samples with the x = 20% and x = 60%, respectively. Since, from X-ray diffraction, the grain sizes of the phases composing the films are below 100nm and the AFM micrographs show the

existence of a significant number of grains up to ~220 nm, this indicates the presence of a broad distribution of grain sizes of the phases composing the films. Additionally, the calculated cobalt ferrite values obtained from the Scherrer equation are smaller than the ones for the $BaTiO_3$ phase, indicating that a significant amount of the smaller grains belong to the $CoFe_2O_4$ phase. Also, since from the X-rays diffraction results the grain size of the $CoFe_2O_4$ phase does not change much from sample to sample, thus its size distributions on the different films (in percentage) are similar, with similar average values.

Figures 4a) and 4b) show the magnetic moment hysteresis loops obtained on the nanocomposites at the temperatures T = 10 K and T = 300 K, respectively. The loops were measured on the films plane and corrected by subtracting the diamagnetic contribution from the substrate. Taking the value of the magnetic moment at the higher applied magnetic field (60kOe) and dividing by the volume of the magnetic phases in the films (according to the $CoFe_2O_4$ percentages), the saturation magnetization (Ms) was determined. Figure 5a) shows Ms for the nanocomposites, at the temperatures T = 10 K and T = 300 K (room temperature). Figure 5b) shows the coercive field (Hc) (at 10 K and 300 K) obtained from the same hysteresys loops. A progressive increase of the saturation magnetization and decrease of the coercive field of the thin films, with increasing $CoFe_2O_4$ concentration, is observed.

The previous AFM and X-ray diffraction results indicate that, in the nanocomposite thin films, the cobalt ferrite phase nanograins present a broad range of sizes, with a significant amount of smaller grains, although their average grain size and size distribution do not change much with the $CoFe_2O_4$ concentration. Due to the magnetocrystalline anisotropy, the Co-ferrite particles are magnetically monodomain for sizes smaller than 40 nm [10,11], while the bigger $CoFe_2O_4$ particles (larger than 40 nm) divide into domains. Magnetization vector rotation is considered to be the mechanism responsible for the hysteresis of small particles and the corresponding coercive field is proportional to the magnetocrystalline anisotropy [4].

On the other hand, the bigger cobalt ferrite grains are polydomain and the corresponding coercivity is proportional to the stress in the films [4].

For low concentrations, the $CoFe_2O_4$ grains are more isolated and ferromagnetic interactions between them are weak. Thus, the magnetic moment of these isolated grains is more difficult to align along the applied magnetic field, particularly for the smaller grains (<40nm) which are monodomain. Additionally, both the increased coercivity of the smaller grains and the stress in these films, increasing the coercivity of larger grains, contribute to a higher coercive field of the nanocomposites. As the cobalt ferrite concentration increases, the nanograins start to form larger clusters composed by less isolated nanoparticles. Then, the magnetic interparticle interaction increases and the saturation magnetization progressively increases towards the bulk $CoFe_2O_4$ value, as observed in figure 5a). Since the number of magnetically isolated small particles (and their contribution to Hc) is decreasing with the growing cobalt ferrite content in the nanocomposites the overall coercive field of the films decreases with increasing $CoFe_2O_4$ concentration, as shown in figure 5b). The reduction of stress (and the corresponding Hc from bigger grains) contributes to the decreasing of Hc.

Also, from 10 K to 300 K the coercivity and magnetization of the nanocomposites are strongly reduced, (fig. 5). This is due to the corresponding decrease of the magnetocrystalline anisotropy of $CoFe_2O_4$ [4,10]. Consequently, the loops measured at 10 K are not fully saturated, whereas at 300 K they saturate for applied fields near or below 60 kOe, as shown in figure 4b) for the sample with x = 50 %.

Conclusions

Detailed structural and magnetic measurements were performed on nanogranular composites of cobalt ferrite dispersed in a barium titanate matrix. The $BaTiO_3$ phase presented a tetragonal structure, while the cobalt ferrite had the cubic spinel structure, and a

broad distribution of grain sizes was present in the films. Due to the smaller isolated particles the magnetic moment was difficult to align along the applied magnetic field, hindering saturation and broadening the hysteresys cycles. However, the increased (small and big) particle agglomeration in bigger polycrystalline clusters with increasing $CoFe_2O_4$ concentration, induced a higher magnetic inter-particle interaction, causing a bigger magnetization and a reduction of the coercive field with increasing cobalt ferrite content. The decrease of the magnetocrystalline anisotropy of the cobalt ferrite with increasing temperature induced a corresponding decrease of the coercivity and magnetization, and a less difficult saturation of the hysteresis loops of the films.

Acknowledgments

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Figure captions

Figure 1: X-ray diffraction spectra of the samples deposited with $CoFe_2O_4$ concentrations in the range 20%-100% (a), and SEM micrograph obtained on the film with $x = 40\%$ (b). The vertical lines mark the peak position of the bulk $CoFe_2O_4$ cubic spinel phase (**---**), and the tetragonal-$BaTiO_3$ phase (—). The peaks marked with an S are from the substrate.

Figure 2: In a) are the relative intensities and in b) the grain sizes of the $BaTiO_3$ and $CoFe_2O_4$ phases, for different $CoFe_2O_4$ concentrations. The values in a) were determined by dividing the intensities of the (111) and (110),(101) peaks for $BaTiO_3$ and the intensities of the (222) and (311) peaks for $CoFe_2O_4$.

Figure 3: AFM micrographs obtained on the films with cobalt ferrite concentrations of a) $x = 20\%$ and b) $x = 60\%$. Their corresponding grain size histograms are in c) and d), respectively.

Figure 4: Magnetic moment hysteresis cycles of the nanocomposite $(BaTiO_3)_{1-x}$-$(CoFe_2O_4)_x$ films, measured at a) T=10 K and b) T=300K.

Figure 5: Saturation magnetization (a) and coercive fields (b) obtained from the hysteresis cycles, at T=10K and T=300K. The horizontal lines mark the bulk values reported at 5K and 300K [12].
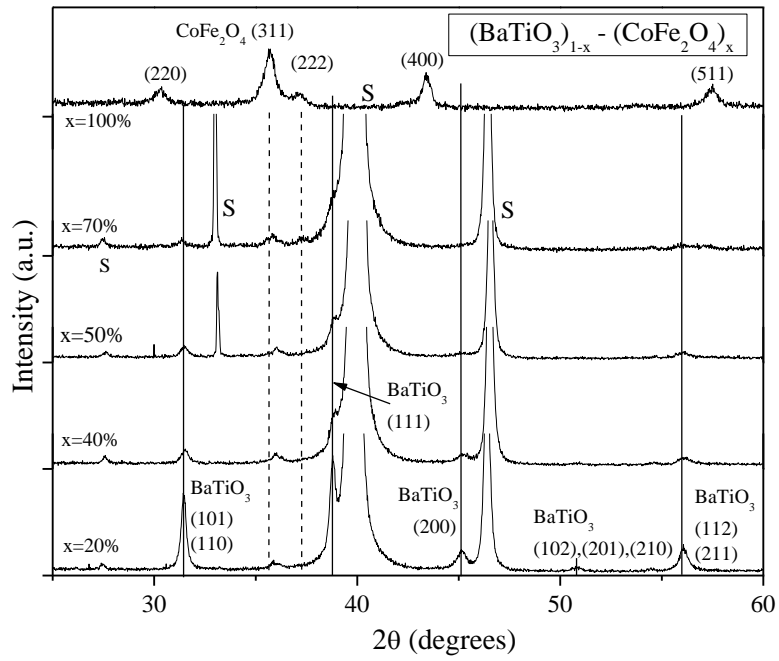
Figure 1

J. Barbosa, B.G. Almeida, J.A. Mendes, D. Leitão, J.P. Araújo, "Influence of grain size dispersion on the magnetic properties of nanogranular BaTiO$_3$-CoFe$_2$O$_4$ thin films"
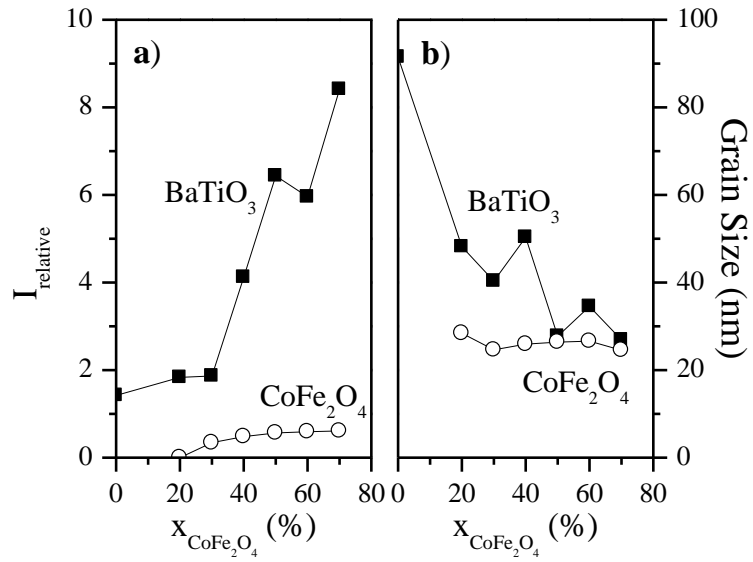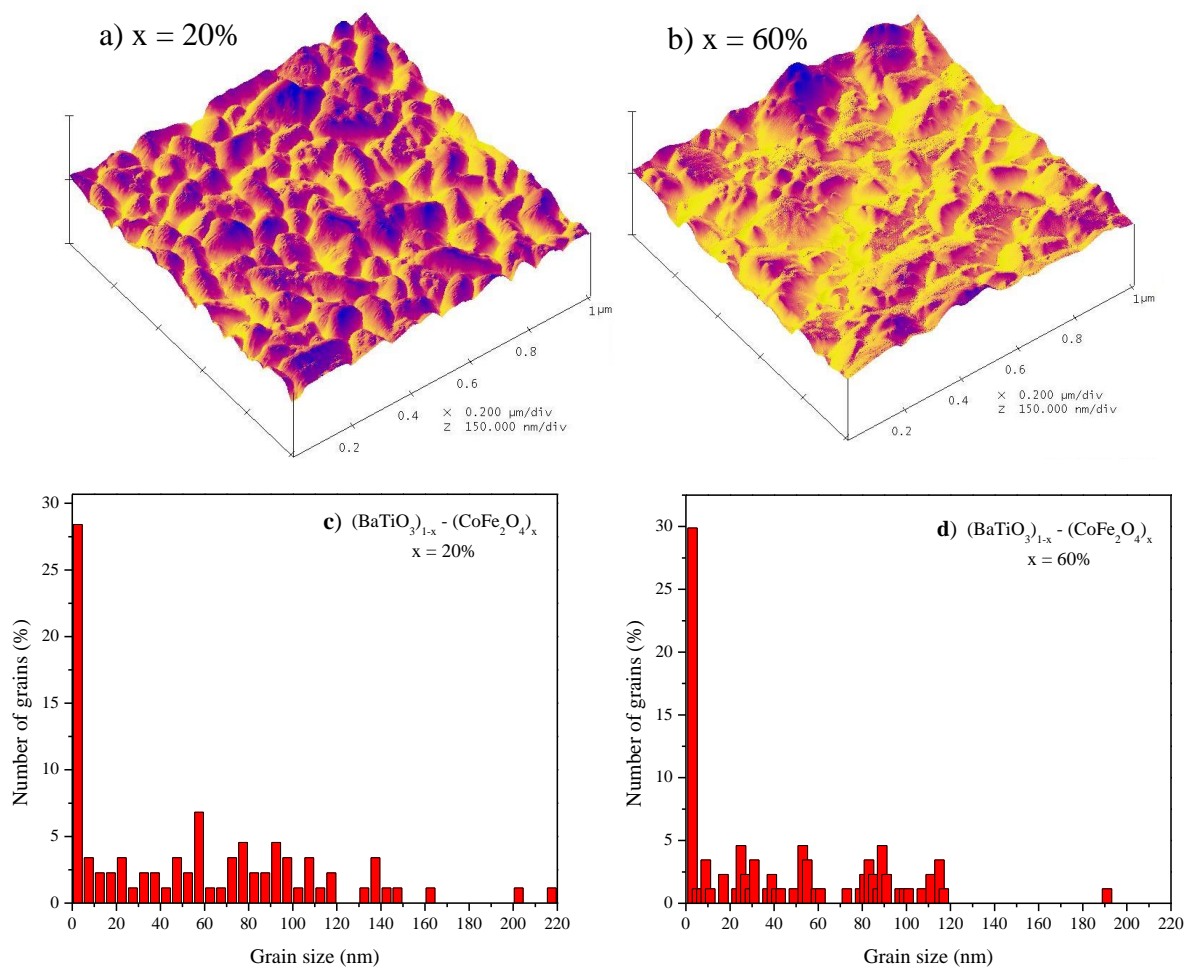
Figure 2

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a) x = 20%

b) x = 60%

c) $(BaTiO_3)_{1-x} - (CoFe_2O_4)_x$
x = 20%
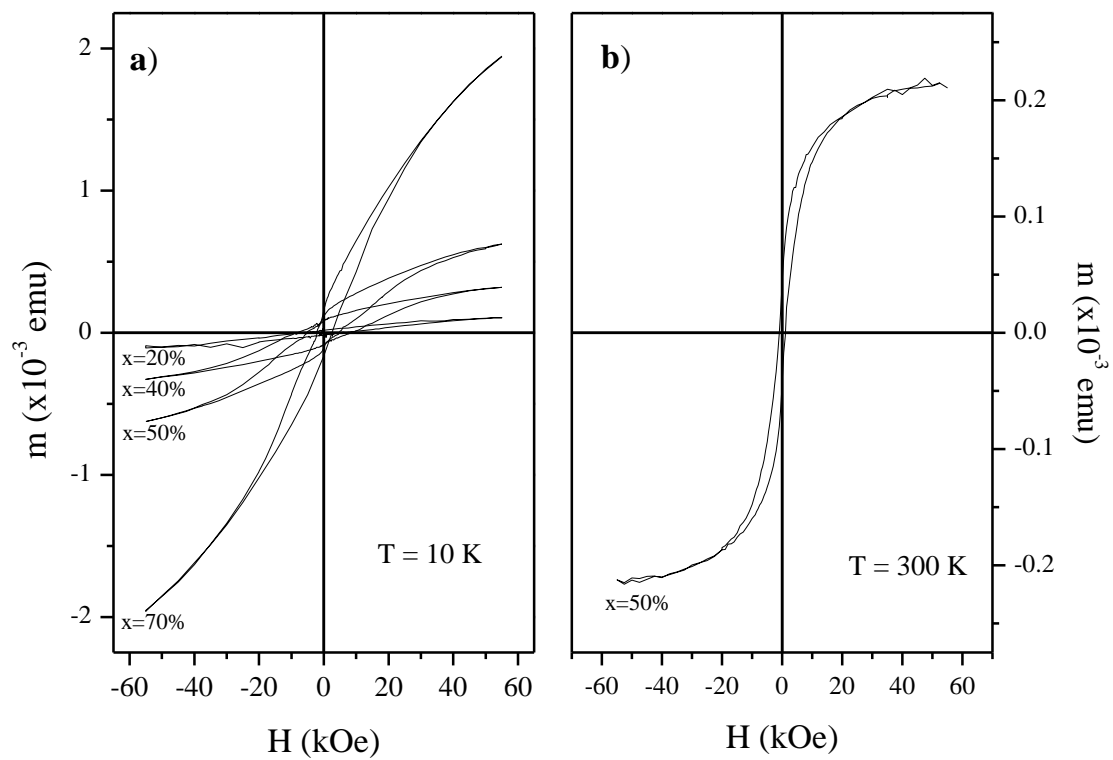
d) $(BaTiO_3)_{1-x} - (CoFe_2O_4)_x$
x = 60%

Figure 3

J. Barbosa, B.G. Almeida, J.A. Mendes, D. Leitão, J.P. Araújo, "Influence of grain size dispersion on the magnetic properties of nanogranular $BaTiO_3$-$CoFe_2O_4$ thin films"

Figure 4

J. Barbosa, B.G. Almeida, J.A. Mendes, D. Leitão, J.P. Araújo, "Influence of grain size dispersion on the magnetic properties of nanogranular BaTiO$_3$-CoFe$_2$O$_4$ thin films"
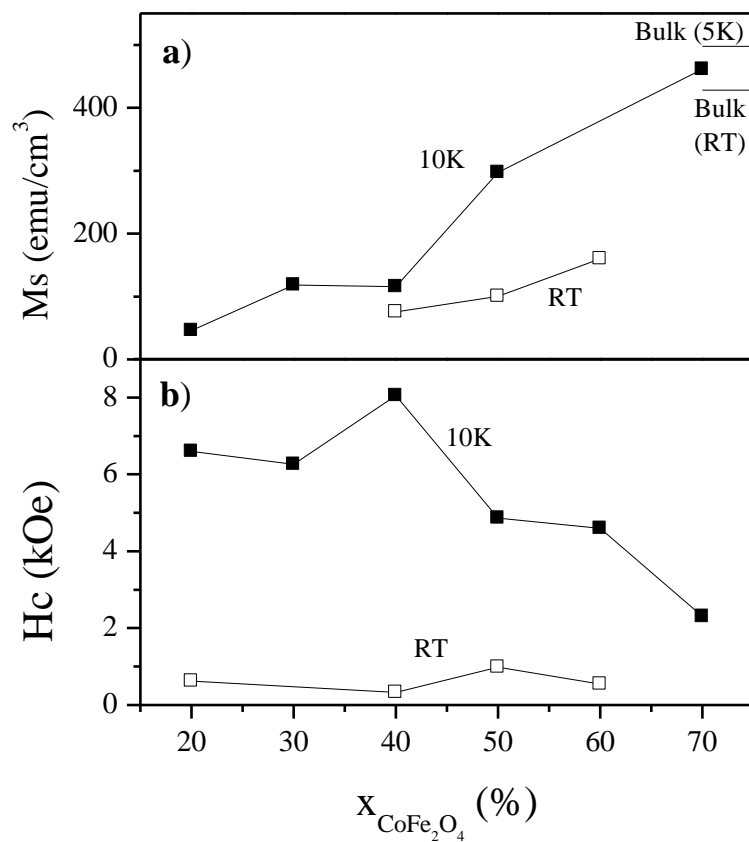
Figure 5

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