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The present work describes the synthesis of iron oxide nanoparticles by thermal decomposition of Fe-precursors in argon and vacuum environments with control over particle size distribution, phase composition and the resulting magnetic properties. The Rietveld analysis of X-ray diffraction data revealed the crystallinity as well single-phase $\gamma$-$\text{Fe}_2\text{O}_3$ nanoparticles prepared under vacuum, whereas argon environment leads to the formation of multi-phase composition of $\gamma$-$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ (90%) and wustite (10%). Synchrotron x-ray absorption near edge structure (XANES) indicates that the predominant phase in both the samples is $\gamma$-$\text{Fe}_2\text{O}_3$, which is subsequently verified from the Mössbauer spectra. DC magnetic measurements indicate behavior typical of superparamagnetic system validated by Mössbauer analysis. However, further investigation of ac susceptibility by typical Néel-Arrhenius and Vogel Fulcher magnetic models suggest an influence from interparticle interactions on the overall magnetic behavior of the system.

**Synthesis, phase composition, Mössbauer and magnetic characterizations of iron oxide nanoparticles**

**Introduction**

Magnetic iron oxide based nanoparticles have become the center of huge attraction among the scientific community because of their increasing number of applications in various fields [1]. Recently, much attention has been paid towards the superparamagnetic $\text{Fe}_3\text{O}_4$ nanoparticles not because of their complex magnetic behavior, but also their suitability in various biological applications [2-3]. However, one of the most significant tasks in the synthesis of iron oxide nanoparticles is the control over the phase purity, which hinders to distinguish between pure magnetite and maghemite phase, as their crystal structures are very close. Furthermore, $\text{Fe}_2\text{O}_3$ has been predicted to be half metallic at 300 K and hence is expected to produce 100% spin polarization of an electric current passing through [4]. Thin films of $\text{Fe}_3\text{O}_4$ nanoparticles have been shown to display very interesting magneto-resistance values in comparison to thin films prepared by physical methods and are expected to lead to the development of magneto-electronic devices with enhanced magneto-transport properties [5]. Beside these, at nanoscale regime, Fe$^{3+}$, in $\text{Fe}_3\text{O}_4$ ([Fe$^{3+}$]$\alpha$[Fe$^{3+}$Fe$^{3+}$]$\beta$)$\delta$$_4$O with A- and B-sites is reported as the main cause of it, but at the same time the presence of large number of defects and/or of a spin canting in volume is also not ignored. Therefore, along with the compositional control there is current requirement for the fine to oxidation state hence may change the nanoparticle composition and properties, particularly at the surface. Therefore, the reproducibility of iron oxide nanoparticle (IONPs) with desired controlled phase compositions and magnetic properties is a challenging task, and equally important from applications point of view. In this regards, researchers are trying to optimize the synthesis conditions leading to reproducible sizes and compositions and hence the desired magnetic properties of nanoparticles. Moreover, a very important issue is to better understand the synthesis recipe in order to have a better control over the size/shape distribution and hence to establish a good relation with size and structure dependent magnetic properties.

Different synthesis strategies have been found in the literature for obtaining the iron oxide nanoparticles with well-defined size/shape and phase composition [6-8]. However, among these, the synthesis by thermal decomposition of metal precursor in a high boiling solvent appears to be the most interesting because it permits a good control over the size and morphology of the nanoparticles [9-10]. This is mainly due to the fact that the synthesis recipe is simple with one iron precursor, one type of organic ligand, and a high boiling point organic solvent. However at the same time, despite a lot of optimized synthesis reports, the influences of some synthesis parameters remain unclear such as the inert atmosphere in the three-neck flask during refluxing [11]. As observed with other synthesis routes, the magnetic moment of superparamagnetic iron oxide is much lower than that of bulk phase magnetite or its fully oxidized form: maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$). Spin canting layer at the nanoparticle surface is reported as the main cause of it, but at the same time the presence of large number of defects and/or of a spin canting in volume is also not ignored. Therefore, along with the compositional control there is current requirement for the fine...
structural and magnetic characterizations as a function of the
nanoparticle size to establish size-dependent magnetic properties.
In the present paper, we have performed synthesis either in an
inert atmosphere or in controlled vacuum in the three-necks round
bottom flask on the phase purity of iron oxide nanoparticles (IONPs)
and studied their magnetic properties. First synthesis has been
performed out in an argon atmosphere, whereas the second one
carried out in vacuum (10⁻³ mbar) through a simple rotary pump.
The rest of the synthesis conditions were exactly same in both the
cases. These nanoparticles have been investigated structurally and
magnetically, through x-ray diffraction (XRD), high resolution
transmission electron microscopy (HR-TEM), Soft X-ray absorption
Spectroscopy (SXAS), Mössbauer spectroscopy (MS) at 300 K, and
magnetic measurements in both ac and dc modes in order to
correlate the structural and hence magnetic properties.

**Experimental Section**

**Synthesis of iron oxide nanoparticles**

The size of iron oxide nanoparticles (IONPs) has been controlled
during synthesis by performing it in either inert atmosphere or
vacuum using a standard inert gas/vacuum manifold system
commonly known as Schlenk line. The synthesis were carried out in
a standard three neck round bottom flask using thermal
decomposition of Fe (acac)₃ (2.0 mmol) in the presence of 1-
octadecene (20 ml) and the surfactants oleic acid (8 ml) and
oleylamine (12 ml) either in pure Argon flux or vacuum. The above
mixture was gently heated at 120°C for 60 minutes under
continuous argon or vacuum with intermediate stirring. The above
mixture was slowly heated up to a final temperature of 315°C for 60
minutes with heating rate of ~ 6 °C/min. The solution was then
cooled down to room temperature under normal conditions and
the nanoparticles were washed adding excess of ethanol and
centrifugation at 4500 rpm for 20 minutes. This procedure was
repeated 3-4 times by dispersing the NPs in non-polar solvent,
adding excess of ethanol and centrifugation. Finally, the
nanoparticles were dispersed in toluene (concentration of 0.05
g/ml) for the long-term storage with 2-3 drops of oleylamine.

**Characterizations**

The particle diameter and its distribution were measured by means
of HRTEM (200 keV JEM 2010 microscope) by drying a toluene
dispersion of the nanoparticles on a carbon coated copper grid. The
structure was determined by X-ray diffraction (XRD) (XPERT
Powder PANalytical) with Cu Kα radiations. The Rietveld refinement
analysis of XRD patterns were performed using the DBWSTools2.3
refinement program [12, 13] A pseudo-Voigt function was selected
to fit the observed peak profiles of the identified crystalline phase.
The average crystallite size was calculated using all Bragg reflections
by the Scherrer equation. The full width at half maximum (FWHM)
of each peak was corrected with a standard sample of LaB₆. Further
details of crystallite size calculation and profile function can be
found in Ref. [14, 15]. Mössbauer spectrum was also measured
employing a homemade Mössbauer spectrometer working in a
constant acceleration mode and equipped with a ⁵⁷Co (Rh) source
with an activity of 50 mCi. The isomer shift values were referred to
α-Fe foil at room temperature. X-ray absorption spectroscopy (XAS)
measurements across Fe L₃ and O K-edge were performed at the
SXAS beamline (BL-01) of INDUS 2 synchrotron source at RRCAT,
Indore. XAS data were collected in total electron yield (TEY) mode
at RT under ultra-high vacuum conditions. Pre and post edge
correction of normalized XAS data were performed using Athena.
The magnetic properties were measured on dried powder sample
using SQUID (Quantum Design) magnetometer with fields up to 40
kOe and temperatures from 5-300 K. The ZFC and FC measurements
were carried out as follow: the sample was first cooled down from
300 K to 5 K in a zero magnetic field, then a static magnetic field (H
= 50 Oe) was applied and M(T) was measured during warming up
from 5 K to 300 K; finally the sample was cooled down to 5 K under
the same field and M(T) was measured during the cooling cycle.
The real and imaginary parts of the ac magnetic susceptibility were
measured at frequencies between 10 Hz < f < 10 kHz in external ac
field amplitude of 10 Oe on a commercial Physical Property
Measurement System (PPMS) in the temperature range 5-300 K.

**Results and discussion**

The phase purity and composition has been checked using powder
XRD method and their Rietveld analysis. Figure 1 shows the powder
XRD patterns for the two sample of iron oxide prepared under
argon flux and vacuum. By analyzing the XRD patterns, it is
confirmed that the brownish black powder obtained in case of
sample prepared under argon consisted mainly of maghemite/magnetite (γ-Fe₂O₃/Fe₃O₄) (90(2) %) as well as wustite
FeO phase (10(4) %), whereas the sample prepared under vacuum
confirmed the formation of maghemite (γ-Fe₂O₃) as the major
phase. Here we would like to mention that the most intense peaks
of the FeO phase ((111), 20 ≈ 36.5°; (200), 20 ≈ 42.8°; (220), 20 ≈
62.1°) are overlapped with the Bragg peaks (222), (004) and (044)
of the γ-Fe₂O₃/Fe₃O₄ phase. Thus, theses peaks cannot be pulled
apart among the others. However, the two major oxides of Fe
namely maghemite (γ-Fe₂O₃) and magnetite (Fe₃O₄), are both cubic
inverse spinels and structurally very similar to each other.
Figure 1 (left panel) X-ray diffraction patterns for iron oxide nanoparticles (IONPs) samples prepared under argon or vacuum conditions, (right panel) showing the colloidal dispersion in toluene (a) argon, (b) vacuum condition. The labels indexed identify the miller indices (peaks most intense) of the phases $\gamma$-Fe$_2$O$_3$/Fe$_3$O$_4$ (in black) and FeO (in blue). The inset show the planes (200) and (004) of FeO and $\gamma$-Fe$_2$O$_3$/Fe$_3$O$_4$ phases, respectively.

Further from the XRD patterns, it is evident that the reflection lines are quite broad, suggesting the miniaturization of the powder crystallites into nanosized particles. Using the full width half the maximum (FWHM) and positions of the most intense peaks extracted from Rietveld refinement we have estimated the particle sizes. The average particle sizes were calculated without considering the possible contributions of crystal strain to the observed broadening by using Scherrer’s equation;

$$D = \frac{k\lambda}{B\cos\theta}$$

where $D$ is the average particle size, $k$ is a shape factor for which a value of 0.9 is used and $\lambda$ is the wavelength of the incident X-ray. Here $B = (B_M^2 + B_S^2)^{1/2}$, where $B_M$ is the FWHM of the XRD peak and $B_S$ is the standard instrumental broadening. The average particle size calculated using eq. (1) are 7.4 nm and 5.1 nm for argon and vacuum condition, respectively and consists of nanosized particles for which superparamagnetic effects should be expected.

Figure 2 highlights the micro-structural features of both iron oxide nanoparticles. Here Figs. 2a, e display the representative low resolution TEM image for the IONPs synthesized in Argon atmosphere as well as in vacuum along with their high resolution images, respectively.

Figure 2 TEM images for iron oxide samples prepared in Argon atmosphere (a-c) and vacuum (d-f) along with their particle size distribution histograms.

In Fig 2(b, e) the faceted-spherical shape can be clearly observed and we observed that there is no agglomeration among the particles owing to the organic capping on their surfaces. Evidently the nanoparticles obtained under argon atmosphere are more polydisperse as compared to the ones obtained under vacuum condition (Figure 2). The reason of this remarkable difference aforementioned synthesis paths are not clearly understood yet. The detailed explanation of this issue is beyond the scope of this paper, where more systematic experiments at different vacuum levels are required as the boiling point of 1-octadecene changes as a function of atmospheric pressure. However, the vacuum path is promoting a narrower single-step process of nucleation and growth of nanoparticles, which means narrow particle size distribution. It is observed in the images (see Fig. 2a, b) that most of the particles show an inner contrast variation suggesting probably the existence of two phase structure consisting of $\gamma$-Fe$_2$O$_3$/Fe$_3$O$_4$ and FeO. Moreover, we have also seen the absence of such a contrast variation in most of the particles which could be explained by complete oxidation of those particles during the washing process or thereafter. Selected area electron diffraction (SAED) was also performed in order to see the crystallinity of the samples and the corresponding patterns are shown in ESI Figure S1. However, it was not possible to quantify the interplanar distance of each electron diffraction ring, but the observed results hints towards a better crystallinity of both the samples.

It is not very straightforward to distinguish between two forms iron oxide namely maghemite ($\gamma$-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) from the XRD patterns, therefore x-ray absorption spectroscopy has been used to understand the oxidation states of Fe for these two samples. Figure 3 shows X-ray absorption near edge spectra (XANES) across Fe $L_3,2$ edges (fig 3(a)) and O K edges (fig 3(a)) for iron oxide nanoparticles along with reference compound $\gamma$-Fe$_2$O$_3$.
Fe L$_{2,3}$ edge XANES probes the unoccupied 3d states of Fe via electron transitions from spin orbit split levels 2p$_{3/2}$ to 3d (L$_2$ edge) and 2p$_{1/2}$ to 3d (L$_3$ edge). Due to crystal field splitting L$_2$ and L$_3$ edges are further split into t$_{2g}$ and e$_g$ levels (marked for L$_3$ edge). A careful observation of L$_3$ edge shows that t$_{2g}$ feature is suppressed in nanoparticles; suppressed relatively more in the nanoparticles prepared in vacuum. Weaker (stronger) t$_{2g}$ feature in L$_3$ edge of Fe is indicative of less (more) un-occupancy in t$_{2g}$ state, which is the case for Fe$^{2+}$ (Fe$^{3+}$), so supporting the situations for Fe$_2$O$_3$: Fe$^{2+}$ & Fe$^{3+}$ (γ-Fe$_2$O$_3$; only Fe$^{3+}$). Slightly increased t$_{2g}$ feature for nanoparticles prepared in argon is indicative of increased Fe$^{3+}$ content (indicative of presence of γ-Fe$_2$O$_3$). Oxygen K edge features here are clearer for disentangling the γ-Fe$_2$O$_3$ and Fe$_2$O$_3$ phases. Features at around 530 eV in XANES at O K edge probes the unoccupied 3d states, split into Fe t$_{2g}$ transition of O 1S electrons into O 2p states (hybridized with Fe 3d electron transitions from spin orbit split levels 2p$^{4}$). Intensity ratios of t$_{2g}$ and e$_g$ features (~ 530 eV) for vacuum nanoparticles mimics the O K edge feature of Fe$_2$O$_4$ reported in literature [17]. Features t$_{2g}$ and e$_g$ in argon nanoparticles show deviation from Fe$_2$O$_3$ feature and tendency of γ-Fe$_2$O$_3$ features, due to presence of slight admixture of γ-Fe$_2$O$_3$.

$^{57}$Fe Mössbauer spectroscopy is a powerful tool to characterize IONPs undergoing superparamagnetic (SPM) relaxation. Figure 4 shows the Mössbauer spectra recorded for the two samples at 300 K, while the values of the Mössbauer hyperfine parameters, derived from the fitting of the recorded Mössbauer spectra, are listed in Table 1. Here, the dots in Fig. 4 represent the experimental data and solid lines through data points are least squares fittings. The 300 K Mössbauer spectrum of the both samples shows relaxation effects owing the nanometric particle size. In both samples a doublet contribution corresponding to superparamagnetic is recognized. The sample prepared in argon atmosphere, according with its bigger size, also presents a distributed sextet component characteristic of collective magnetic excitation (CME) phenomena. In this case, the fitting was made using one distribution of hyperfine fields and one doublet. The corresponding values of the Mössbauer hyperfine parameters (see Table 1), in particular the isomer shift values, are typical of high-spin Fe (III) atom in iron (III) oxides [18]. There is no indication of presence of the Fe$^{2+}$ valence state, which confirms that both samples are solely of Fe$_2$O$_3$ origin.

**Table 1** Values of the Mössbauer hyperfine parameters, derived from the Mössbauer spectrum recorded 300 K, where isomer shift (IS), quadrupole splitting (QS), mean magnetic hyperfine field ($B_{hf}$), relative area % and assignments of individual spectral components are shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component (Area)</th>
<th>IS (±0.01 mm/s)</th>
<th>QS (±0.01 mm/s)</th>
<th>$B_{hf}$ (±0.1T)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>Doublet (14%)</td>
<td>0.34</td>
<td>0.84</td>
<td>-</td>
<td>Fe$^{3+}$ SPM component</td>
</tr>
<tr>
<td></td>
<td>Sextet (86%)</td>
<td>0.34</td>
<td>-</td>
<td>15.8</td>
<td>Fe$^{3+}$ CME component</td>
</tr>
<tr>
<td>Vacuum</td>
<td>Doublet (100%)</td>
<td>0.33</td>
<td>0.85</td>
<td>-</td>
<td>Fe$^{3+}$ SPM component</td>
</tr>
</tbody>
</table>

Figure 4 Mössbauer spectra for the iron oxide nanoparticles at 300 K prepared in (a) argon atmosphere, and (b) Vacuum conditions.

This is quite expected in connection with their nano size with a large surface-to-volume ratio securing their complete oxidation during the synthesis. On the timescale of the Mössbauer spectroscopy, the nanoparticles of both samples presents thermally induced reversal of its magnetization direction at 300 K. Here, the doublet component belongs to the nanoparticles with thermally fluctuating super spins having relaxation times much smaller than the characteristic measurement time ($\tau_m$) of the Mössbauer spectroscopy, i.e. superparamagnetic relaxation; while the presence of a distributed sextet component corresponds to nanoparticles whose super spin thermally fluctuates between the energetically favored orientations with a relaxation time close to $\tau_m$, i.e. collective magnetic excitations. These two samples would show superparamagnetic features in their dc magnetization measurements at 300 K, however, this will be largely driven by finite-size and surface effects which can be depicted by a smaller saturation moment or lack of full saturation etc.

Further, we have performed magnetization (M) measurements as function of both temperature (T) and as well as applied magnetic field (H). Figure 5 shows the variation of M as a function of T in the range 5 - 300 K in an external magnetic field of 50 Oe recorded in zero-field-cooled (ZFC) and field-cooled (FC) modes for both the samples.
2 D is the size of iron oxide nanoparticles. Considering the value blocking temperature $T_{B}$ indicates a particle size distribution, whereas a fraction of the separation of ZFC and FC curves at a certain irreversibility $T_{IRR}$ confirms the nanoscale nature of iron oxide particles. In addition, in the ZFC curves, a characteristic superparamagnetic (SPM) peak calculated from the distribution of blocking temperatures for the iron oxide sample, (b) the mean blocking temperature $<T_{B}>$ of the nanoparticles is being blocked at around $T_{IRR}$. It is evident from Fig.5(a) that there is a sharp maximum in $M_{ZFC}$ curve ($\sim 53$ K for the sample prepared under vacuum as compared to other prepared in Argon atmosphere which is $\sim 195$ K), which indicates their mean blocking temperatures. Furthermore, the relatively sharpness of the ZFC curve peak for the sample prepared under vacuum and the fact that $T_{IRR}$ and $T_{MEAN}$ are quite close to each other ($T_{IRR} \sim 60$ K) can be taken as an indication of a narrow size distribution for this sample. It is worth mentioning that the generally distribution of blocking temperatures$(f(T_{B}))$ can be calculated as the temperature derivative of the difference between the $M_{ZFC}$ and $M_{FC}$ magnetizations $(d(M_{ZFC}-M_{FC})/dT$, allowing one to estimate correctly the mean blocking temperature $<T_{B}>$ [19-20]. The $<T_{B}>$ calculated from the distribution of blocking temperatures was found to be $\sim 56$ K and $\sim 235$ K (see Fig. 5b) for the sample prepared in vacuum and argon atmosphere, respectively. From the $<T_{B}>$, we have calculated the mean size using the Néel relaxation model for isolated particles, i.e.,

$$D=\frac{6K_{b}T_{B}}{ln(t_{f}/t_{0})/\pi K_{surf}}^{1/3}$$

where $K_{surf}$ is the anisotropic energy of iron oxide, $t_{f}$ the measurement time, $t_{0}$ is the frequency factor and D is the size of iron oxide nanoparticles. Considering the value $2 \times 10^{6}$ erg/cm$^{3}$, 100 s, and $10^{3}$ s$^{-1}$ for $K_{surf}$ for cubic iron oxide ($\gamma$-Fe$_{2}$O$_{3}$), $t_{f}$, and $t_{0}$, respectively, a value of 9.2 nm (argon) and 5.6 nm (vacuum) are obtained for the iron oxide nanoparticles, which are in a good agreement with XRD and TEM findings.

![Figure 5](image1.png)

Figure 5 (a) Zero-field-cooled (ZFC) and Field-cooled (FC) curves for the iron oxide sample, (b) the mean blocking temperature calculated from the distribution of blocking temperatures.

![Figure 6](image2.png)

Figure 6 MH curves for the iron oxide samples at (a) 300 K, (b) 5 K.

The magnetization hysteresis loops recorded at 300 K and 5 K in ZFC mode. At 300 K, the sample shows zero coercivity and retentivity, indicating that the particles are in SPM state without saturation up to a field of 30 kOe, whereas at 5 K, the coercivity is $\sim 345$ Oe and $\sim 165$ Oe for the sample prepared in argon and vacuum condition, respectively. This can also be explained due to the fact that $\gamma$-Fe$_{2}$O$_{3}$ is magnetically softer than Fe$_{2}$O$_{4}$. Additionally, coexisting phases could induce more magnetic frustration than single magnetic phase, thereby inducing an increment of the coercivity for the sample prepared in argon atmosphere against the vacuum one. The saturation magnetization ($M_{S}$) of the sample prepared under vacuum is smaller than the one prepared under argon and bulk $\gamma$-Fe$_{2}$O$_{3}$. Roughly, this can be explained due to the fact the $M_{S}$ value of bulk $\gamma$-Fe$_{2}$O$_{3}$ (76 emu/g@293 K) is smaller than the value of Fe$_{2}$O$_{4}$ (93 emu/g@290 K) [21]. Here we note that nanoparticles prepared under vacuum are majority composed of $\gamma$-Fe$_{2}$O$_{3}$, whereas nanoparticles prepared under argon are of multi-phase composition with majority of $\gamma$-Fe$_{2}$O$_{3}$/Fe$_{2}$O$_{4}$. Reduced $M_{S}$ compared to bulk values are commonly ascribed to spin canting or defects at the particle’s outer surface [21]. Indeed, previous work has identified iron oxide nanoparticles that can be composed of Fe$_{2}$O$_{4}$, for example, which is a solid solution of the end members Fe$_{2}$O$_{4}$ and $\gamma$-Fe$_{2}$O$_{3}$ (both ferrimagnets, FM): Fe$_{1-x}$O (wüstite) an antiferromagnet, AFM; or Fe, a ferromagnet, FM. Further, we have measured the hysteresis curves for both the samples at 5 K in a field cooled ($H_{FC} = 70$ kOe) mode for both the samples (figures not shown here) and observed that the sample prepared in argon atmosphere displayed a measurable exchange bias of $\sim 40$ Oe at 5 K, whereas the hysteresis curve for the sample prepared under...
vacuum is symmetric about the origin. This further confirms the presence of exchange coupling between maghemite (ferromagnetic) and wustite (antiferromagnetic) phase for the sample prepared in argon atmosphere.

To have a deeper insight about these two samples, we have further performed temperature dependence of dc magnetization after ZFC and FC at different magnetic fields. It is observed that the magnetization increases with increasing magnetic field, while the \( T_B \) shifts to lower temperatures with increasing magnetic field, indicating the frozen spin glass state is gradually destroyed under large magnetic fields for both samples (see Figure 7 and 8). This coincides well with the other SG systems [22-25].

Figure 7 (a) \( T \)-dependent magnetization \( M(T) \) curves under FC and ZFC modes with different magnetic fields. Magnetization curves measured under different magnetic fields up to 1 kOe, and (b) its enlarged view for the sample prepared under argon flux.

Figure 8 (a) \( T \)-dependent magnetization \( M(T) \) curves under FC and ZFC modes with different magnetic fields. Magnetization curves measured under different magnetic fields up to 1 kOe, and (b) its enlarged view for the sample prepared under vacuum condition.

We have further investigated the temperature dependence of the ac susceptibility measurements at different driving frequencies in the range from 10 Hz-10 kHz (see Fig. 9(a-b)) for both samples prepared under argon flux or vacuum conditions. It is observed that \( \chi' (T) \) exhibits a strongly frequency dependent peak. As the frequency increases, the sharp peak shifts to higher temperatures, while the height decreases, suggesting a characteristics feature of typical SG behavior. The expected behavior of blocking processes is evident in the plots, i.e. the occurrence of a maximum at \( T_B \) which shifted towards higher temperatures and decreased in height with increasing frequency [26]. The effect that becomes visible upon sample cooling is directly related to the frequency dependence of \( T_B \) of the single-domain particles. Two key empirical relations are often used as tools to compare the frequency dependence of \( T_B \) namely, \( C_1 = \Delta T_B/T_B \log (f) \), independent of any model and \( C_2 = (T_B-T_0)/T_B \) where \( \Delta T_B \) is the difference between the \( T_B \) measured in the \( \Delta \log (f) \) frequency interval and \( f \) represents the ac magnetic field frequency [26]. The parameters \( C_1 \) and \( T_0 \) deliver a model-independent classification of the blocking/freezing process [26-28].

This law is phenomenological and without physical significance near \( T_B \) and yet \( C_1 \) can be taken as indicator to screen different \( T_B \) in closely related materials. Figure 9(c) shows the variation of \( T_B \) in the classical Arrhenius and Vogel-Fulcher plot of \( \log (\tau) \) vs. \( 1/T \).

\[
\log (\tau) = \log (\tau_0) - \frac{E_B}{kT},
\]

where \( \tau = 1/f \) is the characteristic relaxation time constant (10\(^{-5}\) s < \( t_c < 10\(^{-12}\) s), \( E_B \) is the energy barrier of the NPs for the moment reversal [27]. Thus, \( E_B = K \), and \( K \) represents the effective anisotropy constant and \( V \) the volume of the particle. The terms \( E_B \) and \( K \) can be estimated from analyses of the experimental data. Even though the fitted straight-lines in Fig. 9(c) seem to well support the experimental findings; the fitted parameters obtained had no physical meaning for both the samples. Particularly, the \( \tau_0 \) values in both samples were found much smaller than those physically accepted, and \( E_B \) values were found too high as compared to the reference values of \( E_B = 8440 \) K
for iron oxide (calculated using $K = 5.5 \times 10^6$ erg/cm$^3$). Thus, the experimentally observed variations in $\chi'(T)$ for these samples were not consistent with the simple superparamagnetic blocking behaviour of independent particles. The data were then analysed by using the Vogel-Fulcher relation [26] and can be written as $\tau = \tau_0 \exp \left( E_a/k_B(T - T_0) \right)$. Here $T_0$ is an effective temperature with similar origin to that used to reproduce the dc susceptibility in the superparamagnetic regime and $T_0$ is the characteristic temperature signifying the onset of the blocking process.

Taking into account Vogel-Fulcher relation, the calculated fitted parameters are given in Fig. 9d, and can be compared with the values extracted by using the Néel-Arrhenius relation. The Vogel-Fulcher law provides more reasonable values of $\tau_0$ and $E_a$ for both samples, comparable to those observed for spin-glass (SG) systems [26]. For sample prepared under Argon flux, the energy barrier $(E_a/k_B)$ and effective temperature is enhanced by more than two times in comparison to vacuum one $(T_0 = 76$ K for vacuum, $T_0 = 172$ K for Argon). In this case, the VG fitting is giving the following values of the parameters: $\tau_0 = 1.0 \times 10^{12}$ s, $T_0 = 76$ K and $\tau_0 = 5.0 \times 10^{12}$ s, and $T_0 = 172$ K, respectively for the sample prepared in vacuum and argon atmosphere, respectively. A good agreement of the experimental data and Vogel-Fulcher (VG) law evidences that the phenomenon taking place at maximum of susceptibility is related to blocking of an assembly of interacting particles rather that a collective freezing that is occuring in a spin-glass system.

Conclusions

Synthesis method clearly shows the effect of argon and vacuum environments on the structure-property relationship of iron oxide nanoparticles. Detailed XRD, XANES and Mössbauer experiments suggest that the dominating chemical phase is $\gamma$-Fe$_2$O$_3$ for both the samples. Vacuum conditions result in narrow particle size distribution as compared to argon atmosphere. DC magnetization measurements revealed that nanoparticles are superparamagnetic above the blocking temperature. However, the analysis of ac susceptibility data shows that magnetic dynamics of these nanoparticles is strongly influenced by spin-glass features and is well described by the Vogel-Fulcher (VG) law for interacting superparamagnetic particles. On the other hand, endeavor to fit the data with Neel-Brown (NA) model for thermally non-interacting superparamagnetic (SPM) particles is unsuccessful and yields an unphysical small value of relaxation time constant $\tau_0$.

Acknowledgements

SKS is grateful to FAPEMA for providing financial support. Sarveena would like to thank UGC-DAE CSR, Indore Centre for financial support under CRS Scheme. JM would like to acknowledge the full support by Conicet. DKS is thankful to DST-India, New Delhi for the support through DST-Inspire faculty scheme. Mr. Rakesh Sah is thankfully acknowledged for help during XAS measurements.

References
