Thermal annealing induced enhancement of room temperature magnetic memory effect in Fe-doped NiO nanoparticles

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AFFILIATIONS
Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan

ABSTRACT
We report room temperature (RT) ferromagnetism and magnetic memory effect in Ni$_{0.95}$Fe$_{0.05}$O nanoparticles (NPs) synthesized by hydrothermal method followed by post-annealing in an ambient atmosphere. The temperature and time-dependent magnetization measurements show that the effect of post-annealing at higher temperatures leads to enhancement in the intraparticle interactions. The enhanced intraparticle interaction has provided additional magnetic anisotropy energy resulting in RT ferromagnetic (FM) properties and enhanced magnetic memory effect. The findings from this study will be useful for the development and understanding of RT FM materials to facilitate the integration of spintronic devices.

I. INTRODUCTION
NiO is an antiferromagnetic (AF) transition metal oxide (TMO) having the Neel transition temperature $T_N$-$523$ K. At the nanoscale, because of the size effect and point defects, NiO exhibit anomalous structural, magnetic, and optical properties which open up a way for a wide range of applications. The magnetic and optical properties of NiO nanoparticles (NPs) can be altered further through annealing or by doping foreign elements such as iron. Fe has ionic radius comparable to Ni ($r_{\text{Fe}^{3+}} = 0.063\text{nm}, r_{\text{Ni}^{2+}} = 0.069\text{nm}$), is recognized as one of the most convenient dopants, which provides an easy substitution of Ni by Fe ions. At high Fe content, 4:1 defect clusters (four octahedral Ni$^{2+}$ vacancies surrounding Fe$^{4+}$ tetrahedral interstitial) could be formed in the core of the NPs, resulting in the transition from spin-glass like NiO to the cluster-glass system. An enhanced low-temperature magnetic memory effect (MME) has been reported from cluster-glassy Ni$_{1-x}$Fe$_x$O NPs. Contrary to Fe-doped NiO, at high enough annealing temperature ($T_A$) pure NiO NPs exhibit bulk like AF properties. The thermal treatment affects the size, morphology, surface roughness, releases intrinsic stress, and consequently improves the structural and magnetic properties. Therefore, in this study, post-annealing of hydrothermally synthesized Ni$_{0.95}$Fe$_{0.05}$O NPs was carried at various $T_A$.

II. EXPERIMENTAL DETAILS
The details about the hydrothermal synthesis of Ni$_{1-x}$Fe$_x$O NPs have been reported in our previous work. In this work, post-annealing of Ni$_{0.95}$Fe$_{0.05}$O NPs was carried out using tube furnace with a heating rate of 5 °C/min from 400 to 700 °C at an interval of 100 °C for 2h in an ambient atmosphere. The sample was allowed to cool down naturally. The XRPD data were collected at the National synchrotron radiation research center, Hsinchu, Taiwan (TLS 01C2...
beamline, \( \lambda = 0.68889 \) Å). The magnetic measurements were carried out using a SQUID magnetometer (MPMS3, Quantum Design, USA).

III. RESULTS AND DISCUSSION

The most intense (111) and (200) diffraction peaks corresponding to space group \( Fm \bar{3} m \) of NiO is visible in the 2D plot of the XRPD patterns (Figure S1a). The line-width of the diffraction peaks narrow down with the increase of \( T_A \). Williamson-Hall (W. H.) plot:

\[
\beta = \beta_{\text{size}} + \beta_{\text{strain}} = \frac{1}{\cos \theta} \left( \frac{\lambda^2}{d_{\text{XRPD}}} + 4\sin \theta \right),
\]

where the intercept and slope of a linear fit in the W-H plot (Figure S1b) gives the inverse of grain size \( (d_{\text{XRPD}}) \) and the strain \( \eta \), respectively. The value of \( \eta \) drops exponentially from 0.32(14) to 0.050(7)% and the value of \( d_{\text{XRPD}} \) increases from 10(3) to 37(2) nm with the increase of \( T_A \) from 400 to 600°C.

The value of \( \eta \) and \( (d_{\text{XRPD}}) \) obtained from 700°C are very close to those obtained from 600°C samples (Figure S1c). The drop in \( \eta \) and the increase of \( (d_{\text{XRPD}}) \) suggest an improvement in the crystallinity of NPs with \( T_A \), possibly due to defect reduction. Figure S1d depicts the Rietveld refined \(^1\) (red line) XRPD spectra (open dots) of 400°C samples using GSAS-II software package \(^1\) confirming the existence of a single NiO phase in 400 to 700°C samples (refined spectra from 500 to 700°C samples are shown in Figure S2). Inset of Figure S1d shows the \( T_A \) dependency of lattice constant \( a \) which drops exponentially and at and above 600°C shows a constant value \( 4.1785 \) Å very close to bulk NiO standard (4.1777 Å).\(^1\) The lattice expansion in small-size NPs could be related to size effect, disordered surface and Fe-doping induced nickel vacancy defects.\(^3,5,9\)

Figure 1a–d shows the zero-filled-cooled (ZFC), field-cooled (FC), and temperature dependent magnetization \( M(T) \) curves at 200 Oe from 400 to 700°C samples. The value of magnetization initially drops and then shows an increasing behavior with \( T_A \) from 500°C. The ZFC curve of 400°C sample is characterized with a sharp upturn in the magnetization around freezing temperature \( T_f \) \( \sim \) 11 K (assigned to collective freezing of disordered surface spins),\(^20\) a broad maximum defined as blocking temperature \( T_B \) \( \sim \) 181 K (possibly originated from the uncompensated core) and an irreversible temperature \( T_{irr} \) above 350 K. At and above 600°C, \( T_f \) disappears, and \( T_B \) shifts to the maximum 378 K (700°C), which is far above the RT. An additional anomaly is also visible around \( \sim 278 \) K in ZFC of 700°C of which is not clear yet. Most importantly, a plateau-like region can be seen below \( \sim 200 \) K from 600°C related to collective spin behavior, and its strength enhances further on annealing at 700°C.\(^21\) The strength of collective spin behavior can be enhanced with the increase of interaction in an interacting atomic level magnetic clusters (super-spin-glass).\(^22\) In the present system, such a super-spin-glass system could be correlated with the presence of interacting 4:1 defect clusters (intraparticle interaction) in the core of NiO$_{0.95}$Fe$_{0.05}$O NPs, which enhance further with \( T_A \). Therefore, observed enhancement in \( T_B \) with \( T_A \) could be correlated with an enhanced intrinsic intraparticle interactions.

The effect of thermal annealing on an anisotropy energy barriers can be investigated by analyzing time-dependent magnetic moment relaxation \( M(t) \) curve using a stretched exponential function:\(^23\)

\[ M(t) = m_i - m_s \exp \left( -\frac{(t/t)^\beta}{} \right), \]

where the value of \( \beta \) lies between 0.35 to 0.44 far below < 1, suggesting an activation against multiple magnetic anisotropy energy barriers (Figure 2b). The cause for anisotropy energy barriers possibly bears a correlation to the signature of interparticle interactions which can be investigated by simulating the M(t) curve using a theoretical model: \(^24\)

\[ W(t) = -\langle d/dt \rangle \Delta M(t) = \tau^{-n}, \]

where the value of \( n \) is a function of particle density, temperature, and magnetic field.\(^23,24\) A plot of \( \ln W(t) \) versus \( \ln t \) is shown in Figure 2c, where the solid line represents a satisfactory linear fit. The fitted value of \( \beta \) lies between 0.35 and 0.44 far below < 1, suggesting an activation against multiple magnetic anisotropy energy barriers (Figure 2b).

Moreover, we have achieved RT FM properties and to utilize it for possible future applications, we have carried out FC MME measurements on post-annealed NiO$_{0.95}$Fe$_{0.05}$O NPs using a protocol suggested by Sun et al.\(^25\) Initially, FC-cooling curve was recorded at 200 Oe with a sporadic stops for \( t_{\text{tot}} = 2 \) h in zero field at various stopping temperatures \( T_{S} \) (designated as FC-cool). The relaxation of magnetic moment at various \( T_S \) in zero field resulted in the appearance of the step-like \( M(T) \) curve. During warming, the step-like magnetization curve was reproduced around \( T_S \) such that \( M(T) \) curve regains its FC cooling value above it (designated as FC-warm). The observed FC-memory response from 400 to 700°C samples is shown in Figure 3a–d, respectively. Low-temperature MME is obtained from 400 and 500°C; RT MME from 600°C and it enhances further on annealing at 700°C. The nature of the \( M(T) \) curve evolves with \( T_A \).
such that from 400 and 500 °C samples, a saturation like behavior is noticed in the low-temperature region. On the other hand, from 600 and 700°C samples, the value of magnetization increases and then shows decreasing behavior with the decrease of measuring temperature. The decreasing behavior of magnetization is generally assigned to an interacting spin-glass like system, whereas a non-interacting super-paramagnetic system shows an increasing magnetization with a decrease of measuring temperature. The observed glassy behavior from 600 and 700 °C treated sample mirrors the collective behavior originating from strong inter-cluster interactions.

IV. CONCLUSION

We report RT FM properties with an enhanced $T_B$ ∼ 378 K in Ni$_{0.95}$Fe$_{0.05}$O NPs achieved simply by performing post-annealing in an ambient atmosphere having the same crystal structure as that of parent NiO. An enhancement in both inter- and intra-particle interactions with post-annealing temperature is evident. The RT magnetic memory effect is accomplished in Ni$_{0.95}$Fe$_{0.05}$O NPs mediated through strong intrinsic intraparticle interactions, which can be tailored simply by varying the post-annealing temperature.

SUPPLEMENTARY MATERIAL

Supplementary material includes Rietveld refined XRPD spectra obtained from 500 to 700 °C annealed Ni$_{0.95}$Fe$_{0.05}$O NPs.

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