Superparamagnetic behaviour of nano-particles of Ni-Cu ferrite

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The nano-particles of Ni₀.₈Cu₀.₂Fe₂O₄ with a log-normal size distribution of the median diameter of 9 nm and standard deviation of 0.60 have been synthesized by the chemical co-precipitation method followed by annealing at 500°C. The cubic spinel structure in single phase has been confirmed by X-ray diffraction. Reduction in saturation magnetization has been explained on the basis that the magnetic moments in the surface layers, outside the core are in a state of frozen disorder. The dc magnetization is measured which show that the nano-particle sample is super-paramagnetic above the blocking temperature of 250 K. Secondly, the departure of fc curve from the zfc curve is suggestive of temporal relaxation.

Keywords: Nano-particles, Spinel ferrite, Magnetism, Super-paramagnetic behaviour

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1 Introduction

Magnetic nano-particles of spinel ferrites are of great interest both in fundamental science and in technical applications, e.g., ferrofluid technology, magnetocaloric refrigeration, magnetic resonance imaging enhancement and high-density data storage. Nanocrystalline ferrites have attracted considerable attention, as their physical properties are significantly different from those of bulk due to fundamental changes in co-ordination, symmetry and confinement. Super-paramagnetism, collective magnetic excitation, low saturation magnetization, enhanced coercivity, metastable cation distribution, etc., are some of the phenomena, which have been observed in nanocrystalline of various ferrites. Below a critical size, magnetic particles become single domain in contrast to the usual multi-domain structure of the bulk magnetic materials and exhibit interesting magnetic properties such as super-paramagnetism, quantum tunneling, etc. The super-paramagnetic properties, such as the blocking temperature and coercivity, can be controlled by varying the size of the nano-particles. The nanocrystalline ferrite is being synthesized by various techniques such as sol-gel, hydrothermal, reverse micelle synthesis and combustion. The present work has been taken up to study the magnetic behaviour of nano-particles of Ni₀.₈Cu₀.₂Fe₂O₄ prepared by chemical co-precipitation method followed by annealing.

2 Experimental Details

A ferrofluid comprised of Ni₀.₈Cu₀.₂Fe₂O₄ in the nano-size range has been prepared using wet chemical process. Ni(NO₃)₂.6H₂O, Cu(NO₃)₂.3H₂O, FeCl₃.6H₂O and NaOH of 99.5% purity have been taken as the starting materials. The oleic acid has been used as surfactant and kerosene has been used as the dispersing medium. In order to obtain narrow distribution of particle sizes, the fluid was centrifuged at 12,000 rpm. For obtaining dried particles of this ferrite, carrier liquid from the ferrofluid has been removed by repetitive washing with acetone. The powder was then annealed at 500°C in air.

X-ray diffraction (XRD) patterns have been recorded at 300 K, using Fe Kα(1.9373 Å) radiation with Mn filter, on a Philips make powder diffractometer model PW 1840. A silicon disc (cubic a = 5.431 Å) has been used as standard sample for calibration. The dc magnetization measurements have been made on the PARC make vibrating sample magnetometer (VSM) model 155. For temperatures down to 20 K, a closed cycle refrigerator cryostat has been used.

3 Results and Discussion

Fig. 1 shows the XRD pattern of nanoparticle sample. All the Bragg reflections have been indexed, which confirm the formation of cubic spinel structure in single phase. The value of lattice parameter is
8.308 Å as, which is close to 8.345 Å, the reported value for bulk sample of Ni$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$. Considerably broadened lines in the XRD pattern are indicative of the presence of nano-sized particles. Average crystallite size estimated with the help of Scherrer equation using the width of 311 line is 9 nm.

Fig. 2 shows magnetization versus magnetic field ($M$-$H$) curves recorded at 300 and 20 K. In Fig. 2, $M$-$H$ curve recorded at 300 K clearly indicates zero retentivity and coercivity, which suggest a super-paramagnetic behaviour at 300 K and blocking temperature, is below 300 K. The hysteresis curve recorded at 20 K provides non-zero values of retentivity of 17 emu/g and coercivity of 512 Oe and shows that even at a magnetic field of 8 kOe, the samples do not indicate sign of magnetic saturation. The saturation magnetization ($M_s$) has been obtained by extrapolation of $M$ versus $1/H$ curve to $1/H \to 0$, and it gives a value of 45 emu/g, which is much less than 60 emu/g, the value for bulk sample of Ni$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$. Taking the analogy observed in nano-particles of Fe$_{2.9}$Zn$_{0.1}$O$_4$ (Ref. 17) and NiFe$_2$O$_4$ (Ref.18) by the magnetization measurements, we may attribute to the much reduced $M_s$ in the nano-particle sample to the outside core of ordered moments, those in the surface layer are in a state of frozen disorder.

In Fig. 3, we show Langevin function fitting on the $M$-$H$ curve at 300 K along with Langevin function fitting (open circles).
distribution for the particle sizes and taking the reported value of $M_s = 60 \text{ emu/g}$ for bulk particles of $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$, the Langevin function fitting is obtained for size distribution with median diameter $D_m = 8.9 \text{ nm}$ and standard deviation $\sigma = 0.60$. The median diameter $D_m$ is in good agreement with that obtained by XRD measurements.

Fig. 4 shows variation of magnetization $M$ as a function of temperature in the range 20-300 K in an external field of 100 Oe recorded in zero field cooling (zfc) and field cooling (fc) modes. In the zfc magnetization measurements the sample was cooled in the zero field from 300 to 20 K and after stabilization of the temperature, a measuring field of 100 Oe was applied. The data were then recorded while heating the sample. In the fc magnetization measurements, the sample was cooled from 300 to 20 K in the presence of the magnetic field of 100 Oe and then measurements were carried out while heating in the same field.

In Fig. 4, the zfc curve exhibits a broad peak around 250 K, which is suggestive of blocking at around 250 K. Above 250 K, the nanoparticle sample would be in a super-paramagnetic state, which is also suggested by Fig. 2. The small kinks in zfc and fc curves at ~ 250 K occurred due to instrumental error only. The blocking temperature ($T_B$) is the threshold point of thermal activation for the whole nano-particle sample. When the nano-particles are cooled in zero magnetic field, the magnetization direction of each nano-particle align with its easy axis as temperature decrease below $T_B$. Due to the random orientation of the easy axes among the nano-particles, overall susceptibility is almost zero since the applied field is too small to overcome the anisotropy alone. Above $T_B$, magnetic anisotropy is overcome by thermal activation and the magnetization direction of each nano-particle simply follows the applied field direction. Consequently the nano-particles become super-paramagnetic and show paramagnetic properties. Fig. 4 shows a divergence between zfc and fc curve, which is a characteristic feature of super-paramagnetic behaviour, which is attributed to the temporal relaxation. Such a divergence originates from the anisotropy barrier blocking of the magnetization orientation in the nano-particles cooled with a zfc process. Although the deviation of fc and zfc curves starts at 300 K which suggests that some particles are having blocking temperatures higher than 250 K.

4 Conclusions

Nano-particles of $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ have been synthesized by chemical co-precipitation method followed by annealing. Langevin function fitting of the super-paramagnetic $M$-$H$ curve at 300 K yields a log-normal particle size distribution with median diameter $D_m = 8.9 \text{ nm}$ and standard deviation $\sigma = 0.60$. The sample shows typical super-paramagnetic behaviour with a blocking temperature of 250 K, which arises from competition between thermal energy and magnetic anisotropy energy. The dc magnetization measurements suggest that outside a core of ordered moments, those in the surface layer are disordered.

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References