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Rheological investigations on mn-zn-dy ferrofluid

K. V. Zipare, S. S. Bandgar, and G. S. Shahane*
Department of Electronics, DBF Dayanand College of Arts and Science, Solapur, MS, India
*Email:shahanegs@yahoo.com

ABSTRACT

Oleic acid coated Mn-Zn-Dy ferrite nanoparticles with different Dy-content were used to prepare kerosene based ferrofluid and investigated for its rheological behavior. XRD confirms the synthesis of single crystalline phase of Mn-Zn-Dy ferrite nanoparticles. The introduction of the oleic acid does not affect the crystalline structure of the nanoparticles but enhanced uniform dispersion of the nanoparticles in the carrier liquid. The magnetic measurements show superparamagnetic nature of the samples. The synthesized ferrofluids behaved as Newtonian fluids in the absence of the magnetic field, which naturally reflected the lack of large aggregates. However, under the magnetic field, viscosity increased because of formation of string-like clusters of nanoparticles oriented in the field direction. The viscosity decreases with increase in Dy-content and can be correlated to the modifications in saturation magnetization as a result of replacement of Fe^{3+} ion by Dy^{3+} ion thereby modifying the superexchange interaction between the A and B sublattices.

KEYWORDS: Mn-Zn-Dy ferrofluid, magnetic properties, rheological behavior.

INTRODUCTION

A ferrofluid is an electrically nonconductive colloidal suspension consisting of carrier liquid and magnetic nanoparticles. The novelty of ferrofluids is that the fluid flow and properties may be controlled by an external magnetic field and thermal field. Since the discovery of the unique properties of ferrofluids, several applications for ferrofluids have been considered ranging from biomedical and technical to scientific applications (Caruntu *et al., 2007;* Drbohlavova *et al., 2009;*

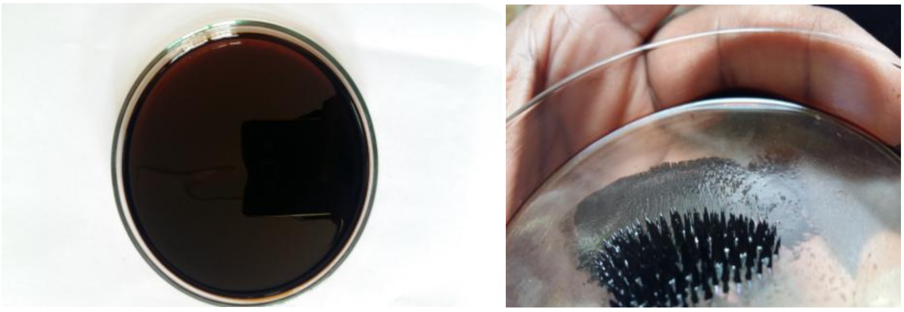
Scherer *et al., 2005; Zhuang et al., 2012*). Ferrofluid whose magnetic properties are strongly dependent on temperature is commonly referred as temperature sensitive ferrofluid (TSF). Recently, the temperature sensitive ferrofluids have been used in heat transfer enhancement and energy conversion devices (Nkurikiyimfura *et al., 2013;* Engler *et al., 2008;* Bozhko *et al., 2004*). One of the interesting and important features of ferrofluid is its ability to change rheological behavior under the action of external magnetic field.In different applications, the key parameters that dominate the process performance are viscosity and thermal conductivity of the ferrofluid. Quantitative understanding about the transport properties becomes important as the application of the magnetic nanofluid develops into thermal engineering. Its magnetically induced rheological effects are useful for designing magnetofluidic devices. This paper describes the synthesis, characterization and rheological behavior of ferrofluid formed with oleic acid coated Mn-Zn-Dy ferrite nanoparticles.

EXPERIMENTAL DETAILS

Synthesis of ferrofluid is a two-step process; syntheses of magnetic nanoparticles with narrow size distribution and desired magnetic properties and then subsequent dispersion of these nanoparticles in suitable carrier liquid. Mn-Zn-Dy ferrite nanoparticles of the composition $Mn_{0.5}Zn_{0.5}Dy_xFe_{2-x}O_4$ (x= 0.05, 0.1, 0.15 and 0.2) were synthesized by a facile chemical co-precipitation method (Shahane*et. al.2010;*Zipare *et al. 2015*). AR grade $MnCl_2$, $ZnCl_2$, $FeCl_3$ and $DyCl_3$ were used as starting materials. For synthesis, $MnCl_2$ (1M), $ZnCl_2$ (1M), $FeCl_3$ (2M) and $DyCl_3$ (0.2M) were mixed in their stoichiometric ratio and homogenized at room temperature. Oleic acid was used as surfactant to prevent agglomeration of particles. The pH of the solution was adjusted by adding 1M NaOH solution. The mixture was then heated at 80^{o}C for about one hour. The particles were collected at this stage by magnetic decantation method and washed several times with de-ionized water to remove unwanted residual of salts. Oleic acid was then added and the mixture was heated at 70^{o}C for about 15 min. so as to coat the particles with oleic acid. For the synthesis of ferrofluid, a known quantity of wet slurry of oleic acid coated Mn-Zn-Dy ferrite nanoparticles was dispersed in kerosene using ultrasonic processor UP200S. The fluid was then centrifuged at 12,000 rpm for 15 min to separate out the larger size particles. The X-ray diffraction (XRD) patterns of the samples were recorded on Rigaku make powder X-ray diffractometer (Model- XRG 2KW) using CuKα radiation (λ=1.54059 Å). The magnetization measurements were carried out by vibrating sample magnetometer VSM Lake Shore Model 7307. The rheological behavior of the ferrofluid was investigated using MCR300 Rheometer, M/s Anton Paar GmbH. A special plate-plate spindle, TG16-MRD, was employed for all the measurements. A coaxial magnetic field in perpendicular direction to the sample was applied during the rheological measurement. The measurements were performed using a constant temperature thermostatic bath (± 0.1°C). The gap between measuring plate and the sample was precisely maintained i.e. 0.3 mm with 0.3 ml of magnetic fluid.

RESULTS AND DISCUSSION

The nature of synthesized ferrofluid can be observed under the influence applied magnetic field. Fig. 1 shows the synthesized ferrofluid in the absence and presence of magnetic field. The beautiful spikes are observed when ferrofluid is subjected to the external magnetic field.



(a) **(b)**

Fig 1: Synthesized ferrofluid (a) in the absence and (b) in presence of magnetic field.

Fig 2 shows the XRD patterns of the samples prepared with varying concentration of Dy in Mn-Zn ferrite. The 'd' values and intensities of observed diffraction peaks match with the single crystalline spinel form of the Mn-Zn ferrites (JCPDS Card No. 074-2401).

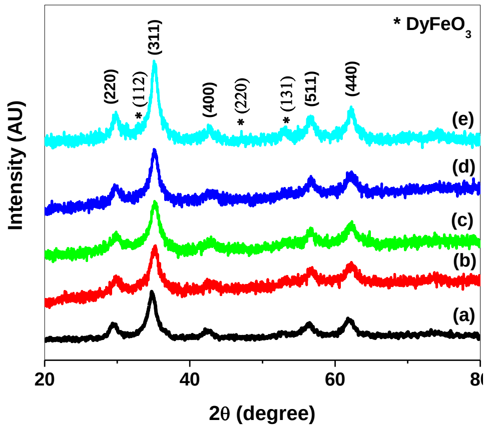


Fig 2: XRD patterns of $Mn_{0.5}Zn_{0.5}Dy_xFe_2O_4$nanoparticles: a) x=0, b) x=0.05, c) x=0.1, d) x=0.15 and e) x=0.2.

However, for x=0.2 very small peaks of $DyFeO_3$ are observed indicating separate phase formation of $DyFeO_3$ for higher doping concentration (PDF#47-0069). X-ray diffraction pattern shows broad peaks indicating ultrafine nature and small crystallite size of the samples.

The lattice parameters were calculated for all the compositions and the values are listed in Table 1. It is observed that lattice parameter increases from 8.4536Å to 8.4839Å with increase in Dy-concentration. The observed increase in the lattice parameter of Mn-Zn ferrite with Dy substitution may be attributed to the replacement of smaller Fe^{3+} ions (0.067nm) at the octahedral site by larger Dy^{3+} ions (0.104nm) (Song *et al., 2010;* Ji *et al., 2016;*). This causes an expansion of unit cell and hence distorts the crystal structure.The strain induced in the material and the crystallite sizes were determined by Williamson-Hall plots and the values are listed in Table 1. It is observed that crystallite size is of the order of 6-8 nm for all these samples.

To study the effect of Dy-substitution on magnetic properties the magnetic measurements were carried out on these samples at room temperature using vibrating sample magnetometer. Fig 3 displays the magnetization curves for $Mn_{0.5}Zn_{0.5}Dy_xFe_{2-x}O_4$ ferrite with different Dy-content.

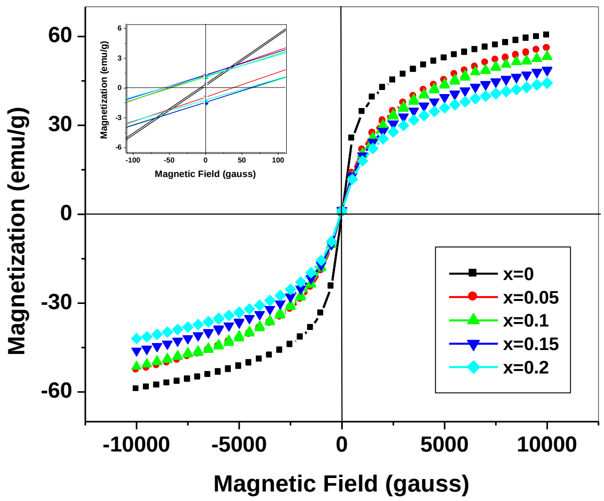


Fig 3: Magnetization curves of $Mn_{0.5}Zn_{0.5}Dy_xFe_2O_4$nanoparticles

As in normal behavior, the magnetization of all the samples increases with increasing applied magnetic field and tends towards saturation value for fields higher than 10,000 Gauss. The magnetization curves demonstrate superparamagnetic behavior of all these samples with negligible remanence and coercivity. The values of saturation magnetization (M_S), remanence (M_R) and coercivity (H_C) for all doping concentrations are listed in Table 1.

When referred to the effect of Dy-substitution for Fe^{3+} it is expected to enhance the magnetization. However in the present case it is observed that the saturation magnetization decreases with increase in Dy-substitution. The decrease in saturation magnetization can be correlated to modifications in the exchange interactions as a result of the structural modifications due to Dy-substitution. The 4f electrons of Dy^{3+} do not have strong exchange interaction with the 3d electrons of Fe^{3+}. Hence the magnetic moments of Dy^{3+} ions are randomly oriented at room temperature. They are not strongly interacting with each other and behave as paramagnetic-like-defect atoms occupying the B-site. This results in much weaker Fe-O-Dy interaction as compared to stronger Fe-O-Fe interaction. Hence magnetization decreases with increase in Dy-content. To understand the effect of Dy-substitution on viscosity, a magnetoviscous effect was carried out for all these samples. Fig 4 show plots of the steady state shear viscosity in the absence and presence of the magnetic field as a function of shear rate for various compositions. From the graphs it is seen that in the absence of the magnetic field, the ferrofluids behave essentially as a Newtonian fluid having a rate-insensitive viscosity because no large aggregates of the nanoparticles were formed therein. An increase in the magnetic field leads to strong changes in the viscosity.

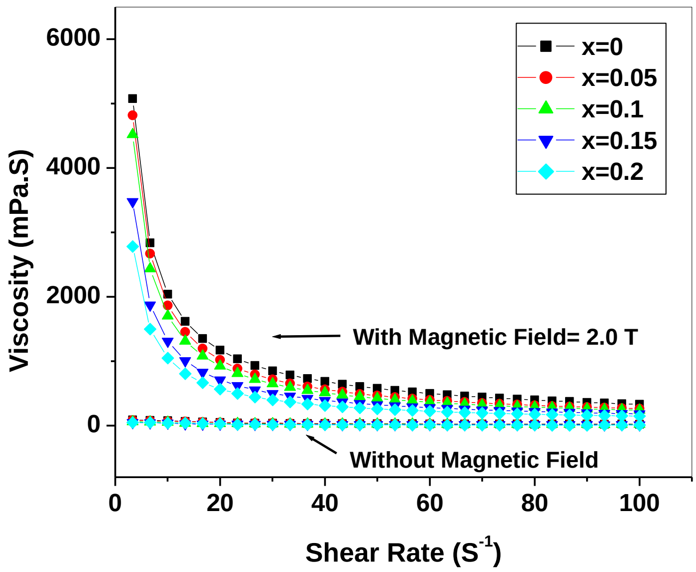


Fig 4: Study state shear viscosity vs shear rate

This phenomenon, the magnetoviscous effect, has been attributed to the formation of chain-like clusters due to strong inter-particle interaction in the presence of a magnetic field (Qiao *et al., 2010*). Superparamagnetic particles under the action of an external magnetic field, acquire induced magnetic dipoles and these dipoles interact to form long chains. As the field strength increases, the interaction between magnetic nanoparticles dominates the thermal motion of the individual nanoparticles and they start forming chains. The hindrance of rotation of these chains gives rise to an increase in viscosity under the influence of a magnetic field (Chand *et al.,.2013*). The viscosity of sample is higher at low shear rate and decreases with increasing shear rate. This shows a shear thinning behavior of the ferrofluids. Shear thinning of well-dispersed suspensions can be linked to the modifications in the structure and arrangement of interacting particles (Shankar *et al., 2012*). Shearing may cause the particles to orient in the direction of flow and its gradient. This can break agglomerates and hence reduce the amount of solvent immobilized by the particles. The interaction forces may then decrease and cause a lowering in the flow resistance and the apparent viscosity of the system. Thus, the viscosity of the fluid decreases rapidly with increasing shear rate (Shahnazian *et al., 2008*).

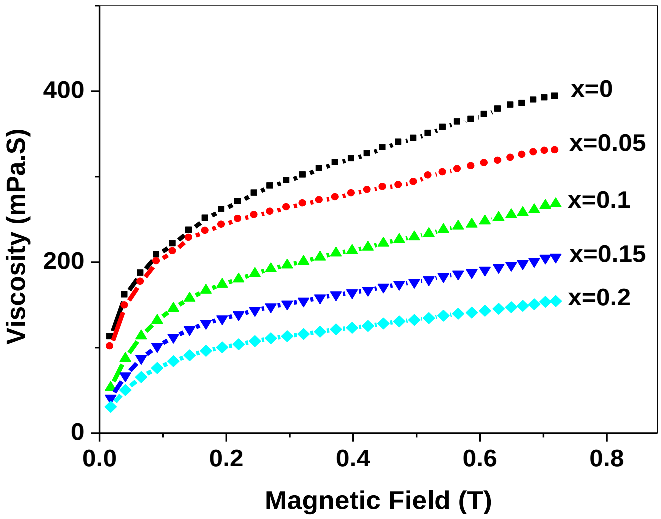


Fig 5: Variation of viscosity with applied magnetic field

The variation of viscosity with applied magnetic field (0-0.8 T) is shown in Fig. 5. It is observed that viscosity increases and tends towards saturation as magnetic field increases. This effect reveals that the formation of chain like structures is occurring as a function of magnetic field. In the system, due to the dipole-dipole interactions, the individual dipoles are arranged in a head to toe manner and tend to form a chain like structure in the direction of the force field. With the increase of magnetic field intensity, the interaction among magnetic particles increases and hence flow resistance increases (Shahnazian *et al., 2008*). Thus viscosity of FFs increases with applied magnetic field. For higher fields the viscosity tends to saturate and can be attributed to the fact that as field increases almost all particles gets aligned to form chains. Hence subsequent increase in the field has less effect on the viscosity. Fig. 6 shows the variation of steady state viscosity with Dy-concentration. The viscosity decreases with increase in Dy-concentration. The variation in viscosity can be correlated to the modifications in saturation magnetization as a result of replacement of Fe^{3+} ion by Dy^{3+} ion thereby modifying the superexchange interaction between the A and B sublattices.

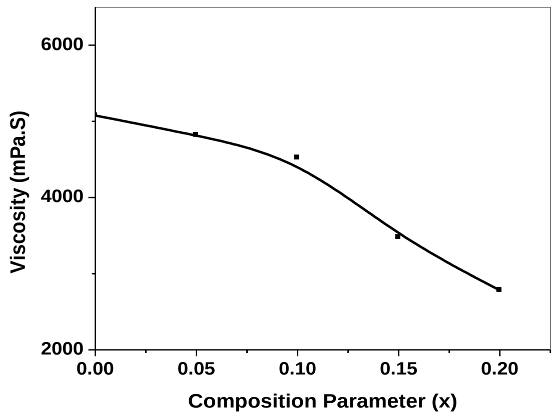


Fig 6: Variation of steady state viscosity with Dy-concentration

Table 1: Structural and magnetic analysis of Mn-Zn-Dy ferrite nanoparticles

Comp. (x)	Lattice Parameter (Å)	Crystallite Size (nm)	Strain	Ms (emu/g)	Mr (emu/g)	Hc (gauss)
0	8.4536	6.6	0.000969	60	0.4	8
0.05	8.4588	6.6	0.001005	56	1.1	49
0.10	8.4605	7.2	0.001909	53	1.26	51
0.15	8.4629	7.4	0.001899	48	1.4	57
0.20	8.4839	8.1	0.002323	44	1.23	58

CONCLUSION

Oleic acid coated Mn-Zn-Dy ferrite nanoparticles with different Dy-content were used to prepare kerosene based ferrofluid and investigated for its rheological behavior. The synthesized ferrofluids behaved as Newtonian fluids in the absence of the magnetic field, which naturally reflected the lack of large aggregates. However, under the magnetic field, viscosity increased because of formation of string-like clusters of nanoparticles oriented in the field direction. The viscosity decreases with increase in Dy-content and can be correlated to the modifications in saturation magnetization as a result of replacement of Fe^{3+} ion by Dy^{3+} ion thereby modifying the superexchange interaction between the A and B sublattices.

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