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Room Temperature Ferromagnetic-Dielectric Coupling of Iron Oxide Thin Films –Microwave based Sol-Gel Method

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ABSTRACT

Currently there is an active search of new materials that display coupling between electric and magnetic properties at room temperature. Room temperature coupling between ferromagnetic and dielectric orders will help in not only improving the current device efficiency but will also open new eras for applications in future spintronic and data storage devices. Among various materials of interest attention is devoted to iron oxide due to its stability and high Curie temperature. However, preparation of phase pure iron oxide is difficult due to strict oxidation kinetics. Alternate to conventional sol-gel synthesis is the use of electromagnetic radiations (microwaves) where formation of "hotspots" results in localized heating of the sol. This localized heating is strongly dependent on power of radiations used. We here report alternate to conventional sol-gel method using electromagnetic radiations with changes in percentage of power used as 25%, 50%, 75% and 100%. Films prepared using 25% and 75% of the total power exhibits amorphous nature. Transition from amorphous to crystalline α-Fe_2O_3 phase takes place at 50% power. γ-Fe_2O_3 phase is obtained 100%. Saturation magnetization and dielectric constant of 0.003emu and 33.96 (log f = 5.0) is obtained for α-Fe_2O_3 phase at 50%. Saturation magnetization and dielectric constant of 0.017emu and 84.199 (log f = 5.0) is obtained for γ-Fe_2O_3 phase at 100%. Enhanced coupling of magnetic and dielectric properties is obtained at room temperature for γ-Fe_2O_3 phase.

1. INTRODUCTION

For Industrial and technological applications, ferromagnetic and antiferromagnetic thin films have found deep interest due to their tunable magnetic properties. Use of magnetic thin films vary from dyes and pigments to latest century applications including data storage devices, advancement of spintronics devices like (GMR, TMR), electrochromism and energy storage contrast agent for the use of cancer treatment (Riaz et al. 2013; Riaz et al. 2014a-c; Monti et al. 2012; Cornell et al. 1996).

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Crystallographic states of iron oxide exists in maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), and hematite (α-Fe_2O_3). These phases exhibit tunable magnetic and structural properties depends on the oxidation state of iron and its interactions with oxygen atom. One of important iron oxide phase is Fe_3O_4 (magnetite) that shows variety of applications in gas sensors, catalyst and especially in spintronics. Both magnetite and maghemite have similar inverse spinel cubic structure but major difference in their structure is that in magnetite, one third octahedral sites occupy by Fe^{2+} cations while in maghemite, those sites are vacant. Different nature of hematite phase is obtained as compared to both magnetite and maghemite. It depicts hexagonal corundum structure with antiferromagnetic behavior (Takayama et al., 2013; Riaz et al., 2013; Yogi et al., 2012). Spin orbital coupling in the range of temperature 260 – 950 K, produces uncompensated canting in the crystal phase of hematite. Uncompensated magnetic moments of cations Fe^{3+} exhibits its weak ferromagnetic or canted ferromagnetic behave.

A very define route of formation of thin films of iron oxide has been adopted i.e. use of electromagnetic radiations with frequency of 2.45GHz. Use of electromagnetic radiations during sol synthesis provides localized heating effects as compared to conventional heating method. Rate of reaction becomes fast and duration of synthesis reduces from days to minutes. One of the major advantages of this type of synthesis is to obtain iron oxide pure phase without post heat treatment at room temperature (Acharya et al. 2011; Phani et al. 2006; Phani et al. 2007).

In the current study, the prime focus is to prepare pure phase of thin films of iron oxide with the change of power of electromagnetic radiations as 25%, 50%, 75% and 100% of total power in sol-gel route and correlate the magnetic and dielectric properties. Coupling of these two properties at room temperature is also investigated.

2. Experimental Details

A precursor of iron nitrate (Fe $(NO_3)_3.9H_2O$) was used and ethylene glycol and water was used as solvent. DI water was added in iron nitrate and ethylene glycol at room temperature and subjected to 25%, 50%, 75% 100% of total power for sol synthesis.

On copper substrate films were deposited. Etching of copper substrate was done by diluted HCl. DI water was used to rinse substrate separately. Acetone and isopropyl alcohol was used to agitate ultrasonically for (10 & 15) minutes respectively. On clean copper substrate, films were deposited at 3000rpms for 20sec. Post thermal treatment in vacuum was done on iron oxide thin films at 300˚C for 60 mins and at applied magnetic field 500Oe.

Structural and morphology of thin films of iron oxide were studied using Bruker D8 Advance X-Ray Diffractometer (XRD). Magnetic characterization was done with the use

of Lakeshore's 7407 Vibrating Sample Magnetometer (VSM). 6500B Precision Impedance Analyzer was selected to observe iron oxide thin films dielectric properties.

3. Results and Discussion

With the variation in power of radiations used as 25%, 50%, 75%, 100% XRD patterns are shown in Fig.1. With the change power used, phase transition occurs. At 25%, amorphous behavior is obtained as shown in Fig. 1(a). This includes heating mechanism as magnetic loss. Heating of material with use of electromagnetic radiations (frequency 2.45GHz) produces randomly oriented domains in magnetite thin films. Magnetic field variation in electromagnetic radiations is resonant with the spin motion thus, producing strong interaction between spin magnetic moment and magnetic field. At 50% and 75% (Fig. 1(b & c)) all peaks (104), (110), (202), (204), (217), matches to pure hematite phase .The most important key role factor that use of electromagnetic radiations gives the effect that arise from volumetric heating. Volumetric heating is the beneficial advantage of use of radiations. Moreover, at 100%, phase shifts from hematite to pure maghemite occurs. Peaks corresponding to (311), (320), (321), (400), (410), (530), (533), (622) confirms the pure phase of maghemite formation in Fig.1 (d).

Major difference in hematite and maghemite phase is the occurrence of space on cationic sub lattices of maghemite. Use of high power electromagnetic radiations produces vacancies thus converting hematite to maghemite at 100% power.

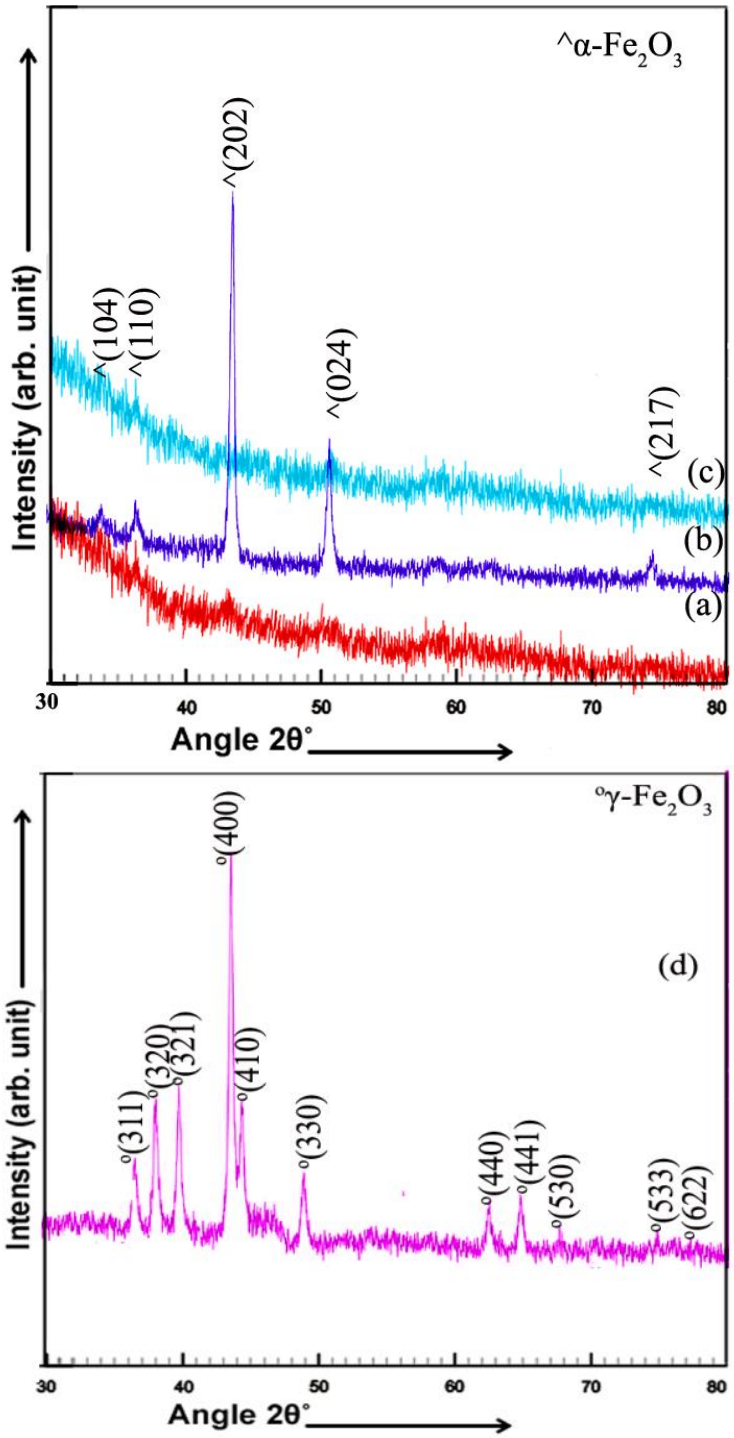


Fig. 1 XRD patterns for thin films of iron oxide prepared with power of (a) 25%; (b) 50%; (c) 75%; (d) 100%

Increase in crystallite size by varying power can be seen in Fig. 2(a). Growth rate and nucleation plays an important role in wet chemical routes as sol-gel (Acharya et. al 2011). Fast nucleation leads to less number of monomers that are responsible for formation of particle with decrease in size of crystallite. As power is enhanced to 75%, this phenomenon can be explained. In contrast, large crystallite size occurs due to slow nucleation and large number of monomers. Electromagnetic radiations also increase the temperature of sol/ solvent during reaction. Energy transferred selectively happens in the material as compared to conventional heating in which high intrinsic temperature around the ions is present and such localized heating control the nucleation rate. High crystallite size, low dislocation density and strain at 50% and 100% is due to phase pure α-Fe_2O_3 and γ-Fe_2O_3 as was observed in Fig. 1.

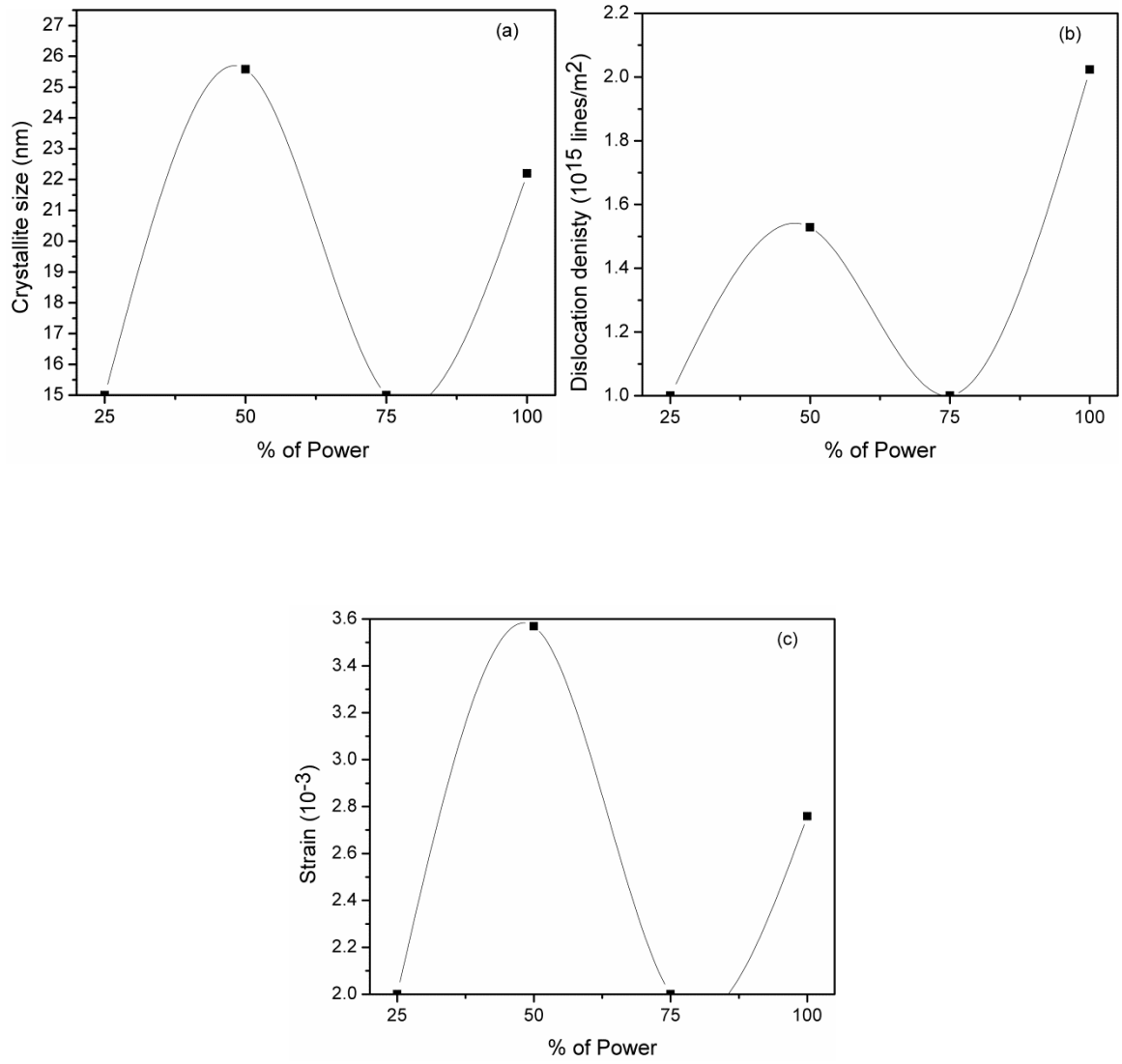


Fig. 2 a) Crystallite size, b) Dislocation density and c) Strain for thin films of iron oxide with the change in % of power used

Fig. 3(a) exhibits temperature M-H curves of iron oxide thin films. 25% power, paramagnetic nature of curve is obtained. This confirms the not appropriate formation /no formation of iron oxide phase. At 50%, formation of hematite phase is obtained but with the low saturation magnetization values. Ferromagnetic nature is obtained at power of 100% with high saturation values. This behavior confirms the transition from hematite to maghemite phase which confirms results explained in Fig.1. Ferromagnetic behavior of maghemite phase is observed at100%. Electric and magnetic fields heating align all the domains in maghemite and net magnetic moment becomes strong shows ferromagnetic behavior.

Fig.3 (b) exhibits saturation magnetization plotted for changes % of total power used. High saturation magnetization is obtained at 100% and this is purely confirmation of transition to maghemite phase formation. Decrease value of saturation magnetization at 25% exhibits the hematite phase.

Fig.3 (c) explains coercivity plots. At 100%, ferromagnetic results are obtained with low coercively. Low coercively exhibits the transition of phase from hematite to maghemite.

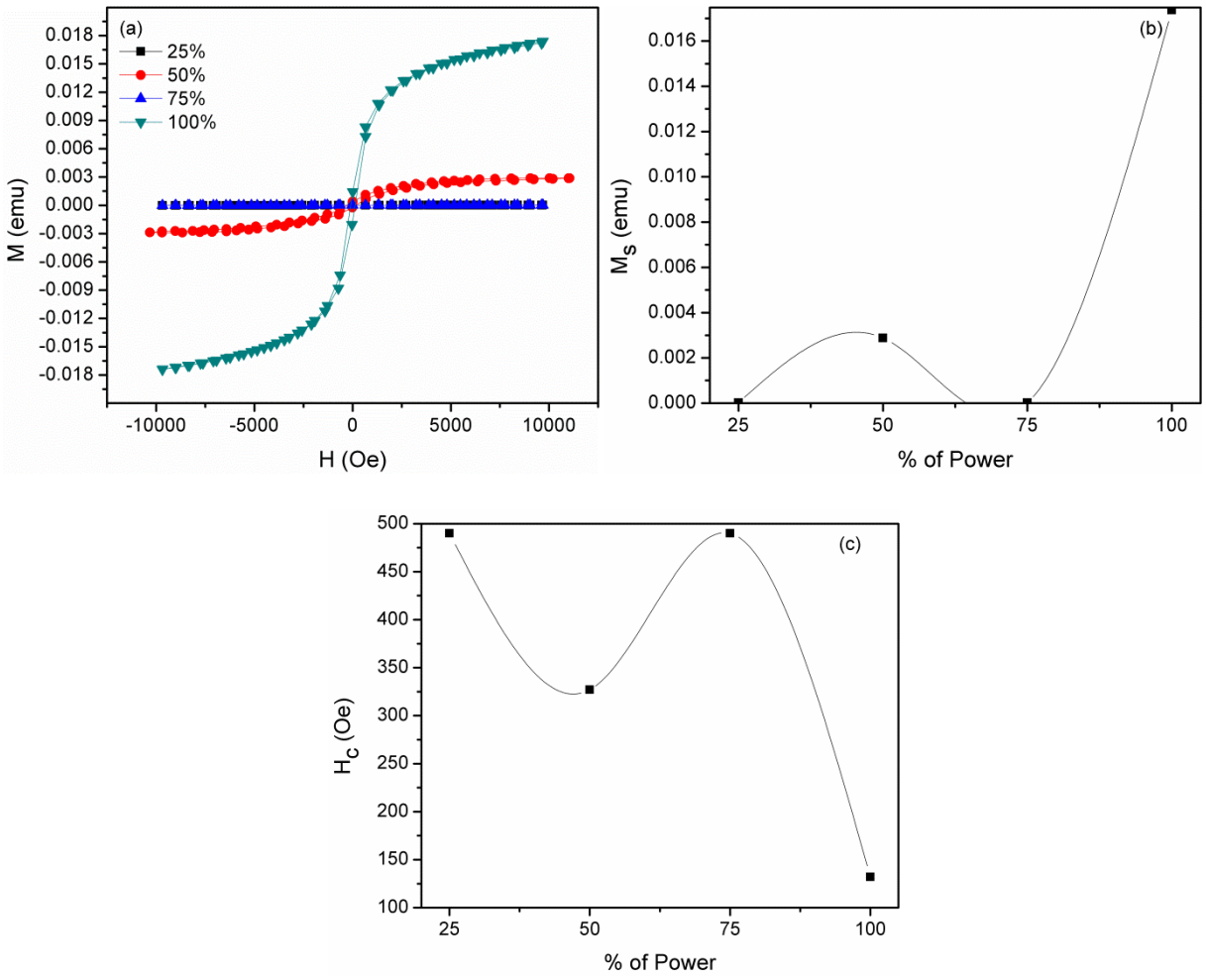
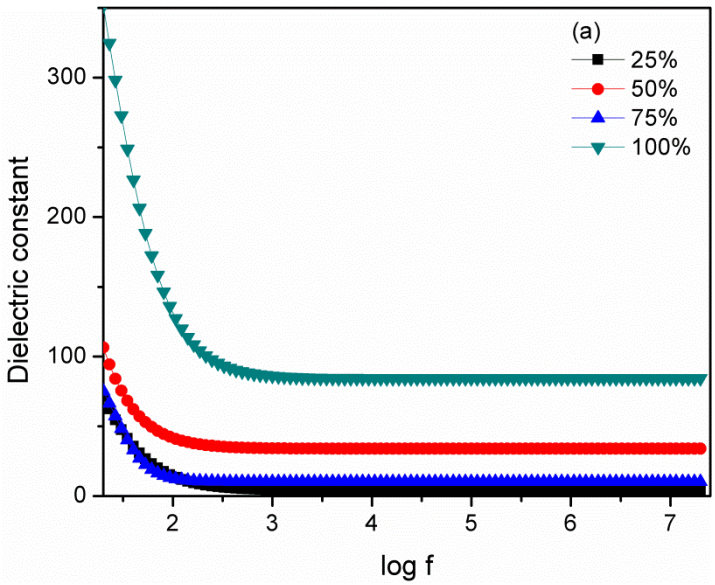


Fig. 3. Thin films of iron oxide prepared with powers of (a) 25%, 50%, 75% and 100% of radiation power b) M_s as a function of % of power used. (c) H_c as a function of % of power used

A plot of dielectric constant and tangent loss with frequency is shown in Fig. 3. There is a sharp decrease in dielectric constant and tangent loss observation at increased frequency and at high frequency, it becomes constant. Space charge carriers require some time to make alignment in the field direction. At low frequency , charge carriers get enough time to arrange in the oscillating field direction while higher frequencies gives no chance to align charges in the field direction and constant behavior of dielectric constant and tangent loss is observed. Polarization occurs in the material due to structure inhomogeneity according to Maxwell- Wagner two layer model. Grain boundaries of high resistivity are separated by grains of low resistivity. Few electrons are able to reach grain boundary at high frequency thus exhibit decrease in dielectric constant.



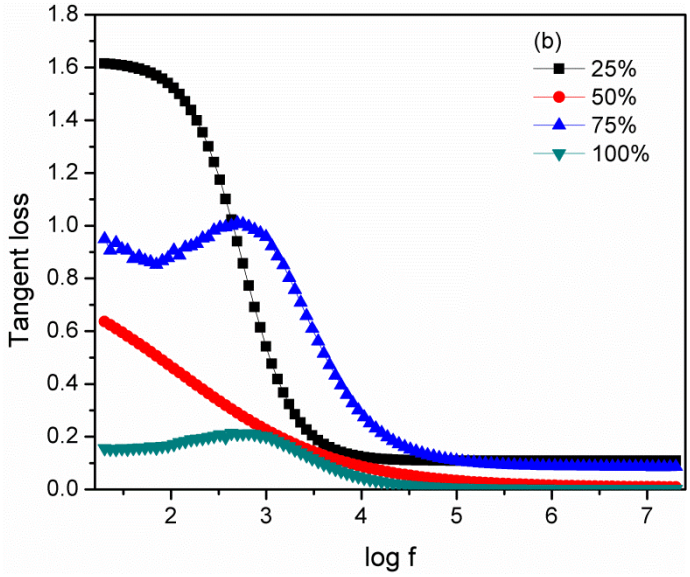


Fig. 4. (a) Dielectric constant as a function of log f (b) Tangent loss as a function of log f

Coupling between magnetic and dielectric properties strongly depends on the dielectric and magnetic field strength. Dielectric and magnetic coupling increases to maximum with the magnetic field. The coupling behavior is attributed to carrier transport across ant phase boundary. Presence of Fe^{2+} and Fe^{3+} produces dipoles locally that results in coupling effect.

4. Conclusions

Thin films of iron oxide was prepared using sol - gel technique. XRD results confirms the hematite pure phase at 25% power while at 100% power transition from hematite to maghemite takes place. Maghemite thin films showed high saturation magnetization and high dielectric constant. High dielectric constant arises due to high grain boundary resistance. All the results confirmed that at 100% highest saturation magnetization and dielectric constant was observed. Presence of Fe3+ and Fe2+ cations in iron oxide resulted in coupling between magnetic and dielectric properties at room temperature.

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