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A study of effect of size of divalent metal on structural and magnetic properties of synthesized MFe_2O_4 (M=Mg, Ni, Cu and Ca) ferrite nanomaterials using citrate approach and annealed at 450°C.

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Abstract : *Ferrite nanoparticles, MFe_2O_4 (M=Mg, Ni, Cu and Ca) were synthesized using chemical based citrate precursor method. The citrate precursor was annealed at a single temperature 450°C only. The annealed powder was characterized using X-ray diffraction (XRD), Vibrating sample magnetometer(VSM) and Scanning Electron Microscopy (SEM). The average particle size was determined using Scherrer equation. They were found to be 13 nm, 23 nm, 11 nm and 43 nm for $MgFe_2O_4$, $NiFe_2O_4$, $CaFe_2O_4$, $CuFe_2O_4$ respectively and the prominent peak position for each ferrite was found at 35.355° 35.645°, 35.697° and 35.975° respectively. The height of the intensity peak position was largest (2700 cps) for Nickel ferrite and lowest for Cu-ferrite (880 cps). Magnetization, retentivity, coercivity and particle size have different values for each ferrite while annealing temperature 450°C was kept constant for all ferrite samples. Range of magnetization, retentivity and coercivity was observed from 10.486 emu/g to 32.727 emu/g, 0.108 emu/g to 6.283 emu/g and 13.382 G to 481.56 G respectively.*

Keywords : Ferrite, Nanoparticles, Divalent cations, Structural and Magnetic properties.

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Introduction:

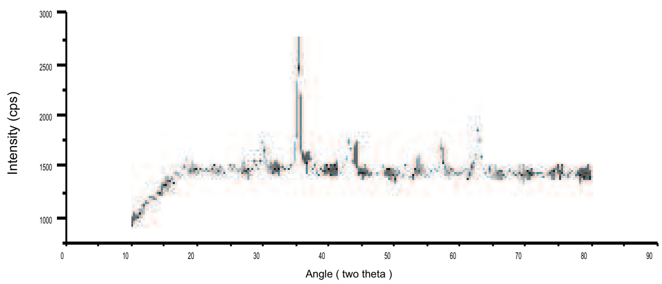
Nanoscience is the study of materials on the nanometric scale between approximately 1nm and 100 nm (Rotello 2003). Nanotechnology includes the integration of these nanoscale structures into larger material components and systems, keeping control over preparation of new and improved materials at the nanoscale. The unusual properties of nanoparticles (NPs) have accelerated growth in the production of nanoscale materials and the rapid increase of their applications in many areas has captured the attention of researchers, government, corporate sector and industry worldwide. Nanomaterial is currently used in water management, electronics, biomedicine, pharmaceuticals, cosmetics, environmental analysis and catalysis. Iron based oxide nanomaterials exist in many forms in nature, with magnetite (Fe_3O_4), maghemite (g-Fe_2O_3), and hematite (development and potential applications of nanomaterials for arsenic removal from contaminated groundwater containing Fe_2O_3) being probably the most common (Cornell and Schwertmann 2003). Nanoscience and nanoengineering can provide cost-effective options to restore contaminated groundwater (Biswas and Wu 2005). Many researchers have found application of Magnetic Nanomaterials in water purification to reduce concentrations of toxic components (e.g. metal ions, radionuclides, organic and inorganic compounds, as well as bacteria and viruses) . On the basis of magnetic response, the magnetic materials can be classified as paramagnets, ferro-magnets, ferrimagnets or antiferromagnets. Ferrites are iron based magnetic nanomaterials having ferrimagnetic behaviour. The spinel structure of ferrite is MFe_2O_4(where M= Cu,Ni, Ca, Mg and other divalent metals (Smit and Wijn1959; Ishino and Narumiya 1987). In this work we have prepared spinel ferrite based magnetic nanomaterials and studied their structural and magnetic properties.

Materials and Methods

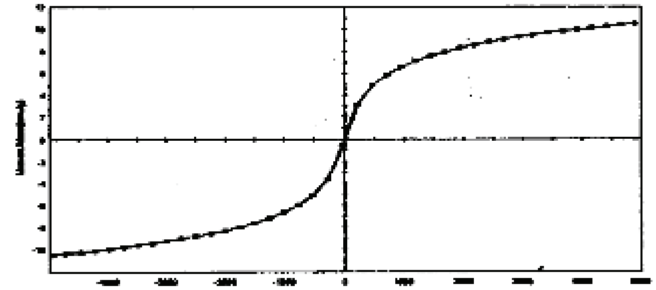
The molecular mass of ferrites MFe_2O_4 (M=Mg, Ca, Cu, Ni) was calculated and it was taken in stoichiometric proportions and the aqueous solution of the above ferrites were prepared, mixed together and stirred at 60ºCto 80º C temperature for two hours. Brown slurry was formed, known as precursor. This precursor was dried in an oven at a temperature of 80º C. This dried material was the citrate precursor. This citrate precursor is annealed at predetermined temperature 450°C in a temperature controlled muffle furnace. These samples, prepared at this temperature, were crushed in a crucible and the powdered sample is stored. After that, this sample was characterized through X-Ray diffraction for its crystalline size and phase determination. Vibrating sample magnetometer (VSM) was used to study the magnetic behaviour of ferrites and Scanning Electron Microscopy (SEM) was used to get the information about the surface formology.

Results and Discussion :

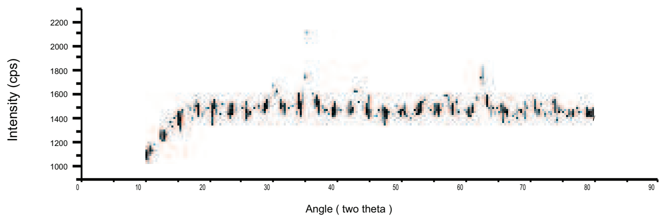
The X-ray diffraction patterns for Mg, Ni , Ca and Cu ferrites are shown in fig 1. The intensity peaks corresponds to ferrite spinel as compared to JCPDS data file (JCPDS 1977). The average crystalline size was calculated using Scherrer formula (Culity 1978; West 2007) and found to be 13 nm, 23nm, 10nm and 43nm . The purity of materials in Ni ferrite is maximum and some poor crystallinity appears in Ca and Cu ferrites. Thus at annealing temp 450°C, different synthesized materials have different particle size, order of crystallinity and position of prominent intensity peaks.



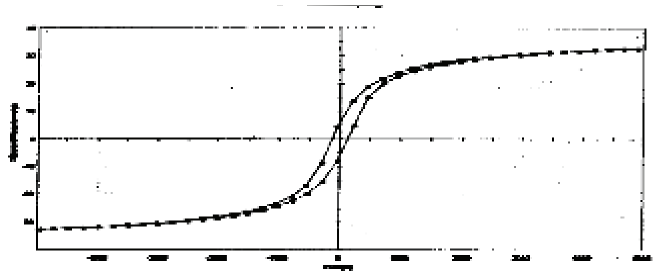
(a) XRD pattern of Nickel ferrite nanoparticles annealed at 450 °C.



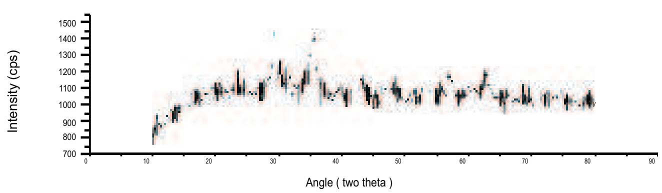
(a) Magnetization curve for Mg Ferrite



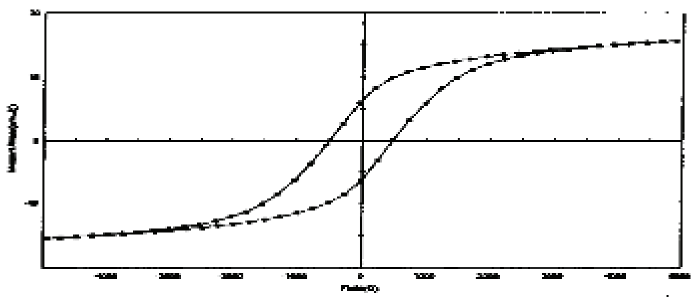
(b) XRD pattern of Magnesium ferrite nanoparticles annealed at 450°C.



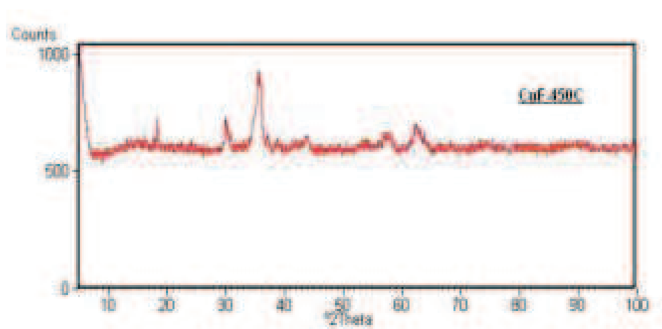
(b) Magnetization curve for Ni Ferrite



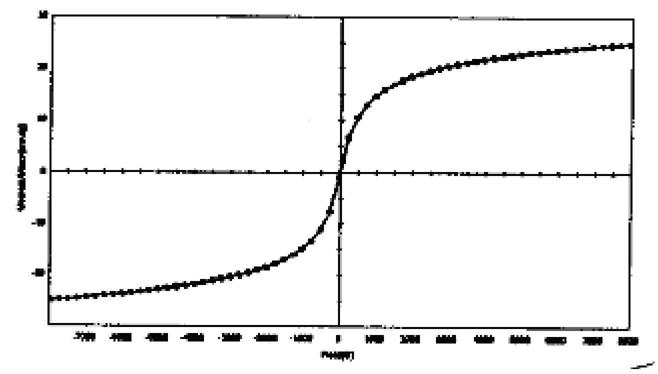
(c) XRD pattern of Calcium ferrite nanoparticles annealed at 450 °C.



(c) Magnetization curve for Cu Ferrite



d) XRD pattern of Cu ferrite Nanoparticles annealed at 450°C



(d) Magnetization curve for Ca Ferrite

Fig 1. X-ray diffraction patterns for Mg, Ni, Ca and Cu ferrite

Fig 2. Magnetization curve for ferrites MFe_2O_4 (M=Mg, Ca, Cu, Ni)

This result shows that crystal field stabilization energy is not same for these synthesized nanocrystalline ferrite materials. Many researchers have observed that $450^{\circ}C$ temperature is optimum for ferrite synthesis and after this temperature new reaction starts and property gets changed in citrate precursor method (Singh et al 2010). On the other hand we observed very small shift in prominent peak positions and interplanner distances (Table 1). The magnetic properties were calculated using Vibrating sample magnetometer (VSM) hysteresis curves are shown in Fig. 2 whereas tabulated magnetic parameters are in Table 1.

Table 1. Data observed from XRD and VSM

Prominent peak Positions (Degree)	Interplanner distances- d-in (A°)	Ferrite Sample	Particle size (Nm)	Magne-tization (emu/g)	Coercivity (G)	Retentivity (emu/g)
35.355	2.536	$MgFe_2O_4$	13	10.486	13.382	0.108
35.647	2.516	$NiFe_2O_4$	23	32.727	125.89	6.173
35.697	2.513	$CaFe_2O_4$	10	25.008	18.555	0.408
35.975	2494	$CuFe_2O_4$	43	15.536	481.56	6.283

Thus we observed differences in Crystalline size and Magnetic parameters at same annealing temperature $450^{\circ}C$. In these materials only divalent metal and ionic radius is different. Only Ni divalent ions have site preference for octahedral and rest of them have tetrahedral sites (Wohlfarth1982). Mg and Ca belong in the same group of periodic table. Among these ferrite materials, only Cu ferrite shows broad hysteresis loop where as Ca ferrite shows small hysteresis loop having small particle size (10nm) i.e tending to superparamagnetic behaviour. The SEM image of calcium ferrite nanoparticles is shown in Fig 3.

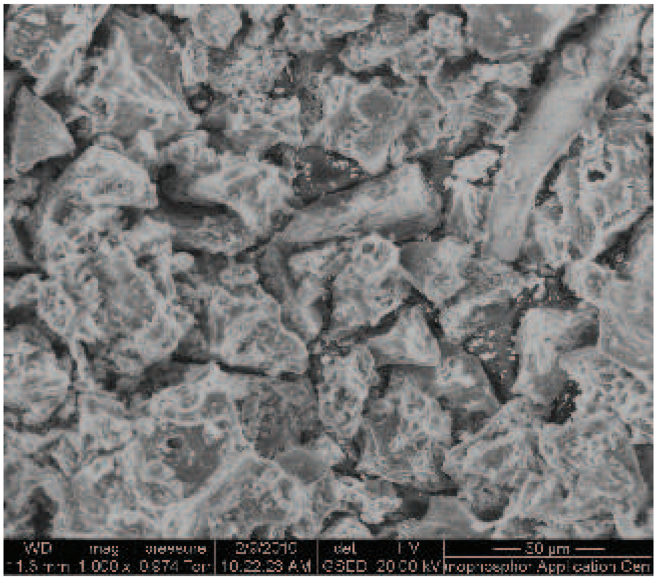


Fig 3. Scanning Electron Microscopy Image of Ca-ferrite Nanoparticles annealed at 450C.

The properties of ferrites depend on superexchange interaction, method of synthesis, crystalline size and site preference of ions, together with crystal field stabilization energy (Mohamed et al 2010, Kumar et al 2008; Singh et al 2010). In all these samples only Cu ferrite shows maximum coercivity and retenvity with broad hysteresis loop and large particle size. Cu Ferrite is a tetragonal spinel ferrite, which is ferromagnetic at room temperature and the tetragonal distortions in Cu Ferrite is a function of Cu^{2+} ion concentration and temperature dependent (Roy and Ghosh 2000) while Ca ferrite also shows small retentivity with small particle size (10nm).

Conclusion :

Ferrite nanoparticles, MFe_2o_4 (M=Mg, Ni, Cu and Ca) were successfully synthesized using chemical based Citrate precursor method annealed at a single temperature $450^{\circ}C$. The average particle size was found 13 nm, 23 nm, 10 nm and 43 nm for $MgFe_2o_4$, $NiFe_2O_4$, $CaFe_2O_4$, $CuFe_2O_4$ respectively and the prominent peak position for each ferrite was observed at 35.355° 35.645° , 35.697° and 35.975° respectively. The height of the intensity peak position was largest (2700 cps) for Nickel ferrite and lowest for Cu- ferrite (880 cps). At the same annealing temperature 450°C, $CuFe_2o_4$ was found to have large particle size with large coercivity (481.56G) and retentivity (6.283 emu/g) where as $CaFe_2O_4$ has low value of retentivity (0.408 emu/g) and coercivity (18.555 G) with small particle size-10nm. Cations distributions and crystal field stabilization energy affect crystal growth, structural and magnetic properties.

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