STUDY OF MAGNETIC AND MÖSSBAUER PROPERTIES OF Al^{3+} IONS SUBSTITUTED Mg-Mn-Ni NANOFERRITES

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Abstract: Nanocrystalline Al^{3+} ions doped $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$ compositions, where y=0.0, 0.05 and 0.10 have been synthesized by citrate precursor method. Crystal structure and magnetic properties have been investigated at room temperature by means of X-ray diffraction, TEM and VSM. Particle size decreases as non-magnetic Al content increase. Lattice constant was determined and applicability of Vegard's law has been tested. A decrease in lattice constant and saturation magnetization with an increase in aluminium concentration was attributed to smaller ionic radius and weakening of exchange interaction. Observed features for citrate precursor samples such as co-existence of a paramagnetic doublet and magnetic sextets in the Mössbauer spectra and lower saturation magnetization confirm nanoparticle ferrite behavior. Initial permeability μ_i and magnetic loss decreases with increasing substitution of Al^{3+} ions. Relative loss factor has very low value in range of 10^{-6}- 10^{-5} which is three orders of magnitude lower than samples prepared by conventional method.

Keywords: Initial permeability, Mössbauer spectroscopy, Saturation magnetization.

Introduction: Synthesis of nanometer size particles proved to be one of interesting fields of material science in material processing and technological applications as small size particles have some of interesting properties as compared to bulk particles. Magnetic nanoparticles promise some interesting applications such as in high frequency devices, magnetic fluids, high density magnetic recording and colour imaging etc. In recent times, processing of ferrites by nonconventional solution techniques has gained importance with a view to obtaining high quality and high performance materials for various applications. However, no literature is available for mixed Mg-Mn-Ni ferrites prepared by citrate precursor method. This has motivated us to study the effect of Al^{3+} ions on magnetic and Mössbauer spectral properties of Mg-Mn-Ni ferrite in light of literature and observed results.

Experimental Procedure: The ferrites series with composition $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$ (y=0.0, 0.05 and 0.10) has been prepared using hydrated nitrates of constituent elements by citrate precursor method [1]. Solid state reactions used for preparation of ferrite sample was:

$$0.2[Mg(No_3)_2.6H_2O]+0.5[Mn(No_3)_24H_2O]+0.3[Ni(No_3)_2.6H_2O]+y[Al(No_3)_2.9H_2O]+(2-y)[C_6H_5FeO_7.3H_2O]\rightarrow Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4 \quad (1)$$

Initial permeability was calculated by using relation $\mu_i=L/L_o$ where L is measured inductance of sample and L_o is air core inductance and is expressed as $L_o=4.6N^2d \log (OD/ID) \times 10^{-9}H$. Pellets were coated with silver paste to make electric contact for electrical measurements. Initial permeability and relative loss factor (RLF) were measured using toroids/rings on Agilent Technologies 4285A Precision LCR Meter. X-ray diffraction measurement was taken on XPERT PRO diffractometer using Cu-Kα source. M–H studies were carried out by VSM. ^{57}Fe Mössbauer measurements were carried out in transmission mode with ^{57}Co as radioactive γ-ray source embedded in Rh matrix.

The theoretical or X-ray density of samples was calculated using relation:

$$\rho_{th}=8M/Na^3 gmcm^{-3} \quad (2)$$

Where M is molecular weight of ferrites sample, N is Avogadro's number and 'a' is lattice constant. Experimental density was calculated using Archimedes principle.

Results and Discussion:

Structural characterization: X-ray diffraction pattern of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Fe_2O_4$ ferrite composition is shown in Figure 1. As is evident from figure, sample exhibit all characteristic peaks related to spinel crystal structure. A close examination of XRD pattern reveal that diffraction peaks became broader with increasing aluminum content y, which may be due to distribution of nanocrystallinity. Average crystallite size D was evaluated by measuring FWHM of most intense peak (311) using Scherrer Debye's formula [2]:

$$D=0.9\lambda/\beta\cos\theta \quad (3)$$

Average crystallite size decreases from 102 nm to 41.5 nm when y changes from 0.0 to 0.1. Figure2 exhibits the variation of lattice constant with Al^{3+} ions concentration. Linear decrease in 'a' may be due to substitution of smaller Al^{3+} ions (0.51Å) with larger Fe^{3+} ions (0.64Å) in $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$ ferrite. Since smaller ions are replacing larger ones, a decrease in lattice constant is expected and it obeys Vegard's law [3]. X-ray density decreases i.e. 5.070 g cm^{-3} to 5.014 g cm^{-3} with increasing Al^{3+} ions concentration.

Initial permeability: Initial permeability μ_i is an

important magnetic parameter which decides the suitability of a ferrite for particular application. Figure 3 shows the variation of initial permeability μ_i with Al^{3+} ions concentration at different frequency which can be explained from following dependence of initial permeability according to the relation [4]:

$$\mu_i = M_s^2 D_m / K_1 \quad (4)$$

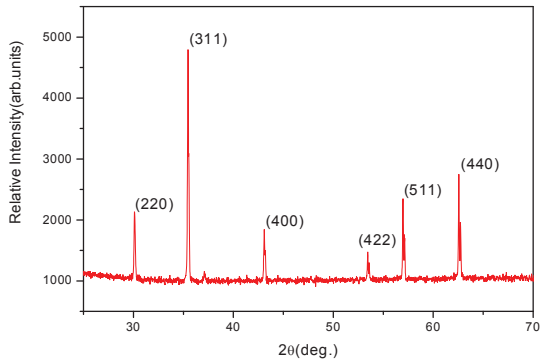

Figure1.XRD pattern of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Fe_2O_4$ ferrite.

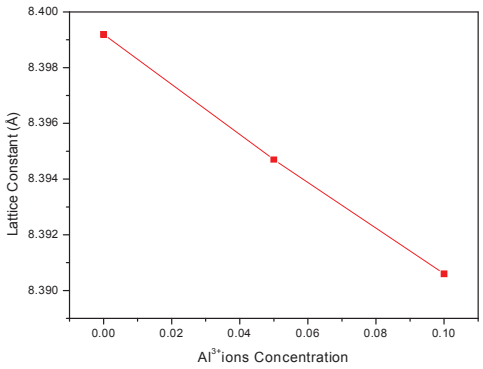

Figure 2. Variation of lattice constant with Al^{3+} ions concentration.

Where D_m is average grain diameter, K_1 is magneto crystalline anisotropy constant and M_S is saturation magnetization. Initial permeability decreases continuously with increasing Al^{3+} ions concentration.

Variation of initial permeability with frequency at different temperatures of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Fe_2O_4$ ferrite is shown in Figure 4. When temperature increases there is increase in density of ferrite sample which helps in movement of spins as number of pores which block wall motion are reduced [5]. Further with increase in temperature as grain size increases number of domain walls in each grain also increases and since μ_i depends on movement of domain walls, initial permeability increases with increase in number of domain walls and its movement. Initial permeability which depends on domain walls displacement remains constant as long as there is no phase lag between applied field and domain wall displacement. Constant value of initial permeability over wide frequency range indicate compositional stability and quality of ferrites samples prepared by citrate precursor method which is desirable characteristic for various applications. Resonance appears when frequency of applied magnetic field match Larmor precession of electron spins and so energy is transferred from field to system to rotate magnetic dipoles. Since resonance occurs at higher frequencies for Mg-Mn-Ni-Al ferrites it shows its utility at higher frequency for various applications. Resonance peaks shifts towards the lower frequency side as temperature increases. As temperature increases magnetic anisotropy decreases which lower magnetic field experienced by precessing spins so frequency of Larmor precession decreases and results in resonance to occur at lower frequencies. This is in accordance with Globus model i.e.

relaxation character can be expressed as:
$(\mu_i\text{-}1)^2 f_r$=constant (5)

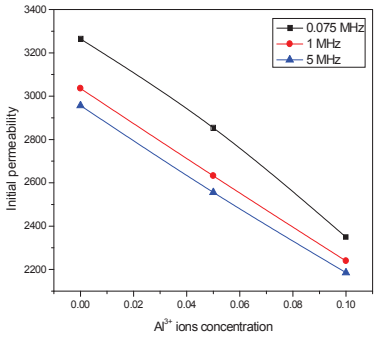

Figure 3. Variation of initial permeability with Al^{3+} ions concentration.

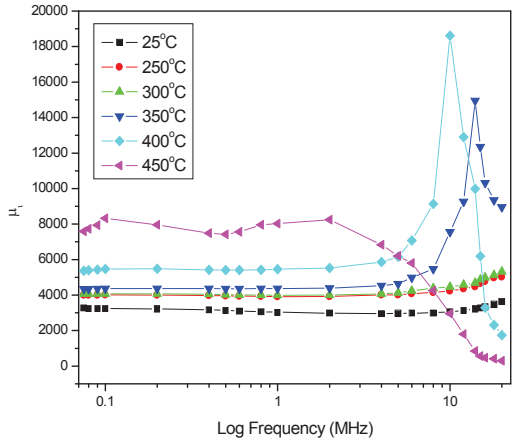

Figure 4. Variation of initial permeability with frequency of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Fe_2O_4$.

Where, μ_i is initial permeability and f_r is relaxation frequency. Transformation of magnetic spectra from relaxation character to resonance character changes eq:(5):
$(\mu_i\text{-}1)^{1/2} f_r$=constant (6)
This equation shows that dispersion frequency decreases with increase in μ_i.

Relative loss factor: Variation of relative loss factor ($\tan\delta/\mu_i$) with frequency at different temperatures of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$ is shown in Figure 5. High initial permeability and low RLF for ferrites are very important for high frequency magnetic applications. RLF tends to increase with increase in temperature which is attributed to thermal randomization of the domains. This loss is attributed to lag of domain wall with respect to applied alternating field and occur due to imperfections in lattice. Value of RLF in present work is of order of 10^{-6}-10^{-5} which is three orders of magnitude lower than reported earlier. Threshold frequency, frequency where RLF is minimum is observed to shift towards lower frequencies with increase in temperature. Since resonance frequency of domain wall oscillations is inversely proportional to grain size, threshold frequency is expected to shift towards lower frequencies with increase in temperature.

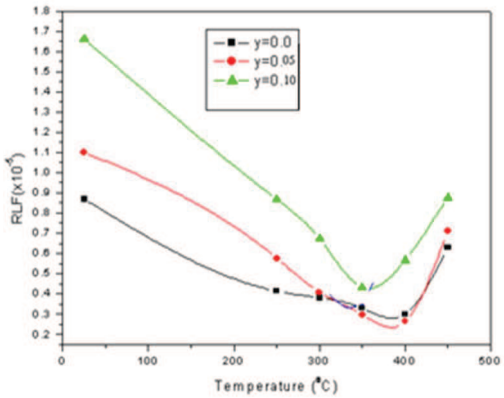

Figure 5. Variation of RLF with temperature of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$

Initial permeability and RLF depends on porosity, grain size, magneto-crystalline anisotropy and Fe^{2+} ions concentration.

Saturation magnetization: Magnetic hysteresis loop of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Fe_2O_4$ ferrite at room temperature is shown in figure 6. It helps in understanding magnetic response of material and provides information about magnetic parameters such as magnetization (M_S), coercivity (H_C), remanance magnetization (M_r) and remanent ratio (R). Decrease in saturation magnetization with increasing Al^{3+} content can be explained on the basis of changes in magnetization M_A and M_B of tetrahedral and octahedral sub lattices, respectively. Al^{3+} ions prefer to occupy B-site where already present Fe^{3+} ions are replaced and pushed to A-site. Removal of magnetic Fe^{3+} ion from magnetic sublattice and substitution of non-magnetic Al^{3+} ion in its place weakens superexchange interaction.

When Al-content increase, M_S decreases because it decreases Fe^{3+}(B)/Fe^{3+}(A) ratio. As aluminum content increases, measured magnetic hysteresis curves became more and more narrow. There are more evidences of change in magnetization with change of nanoparticles size with a general conclusion that in smaller particles reduction of magnetization is more pronounced.

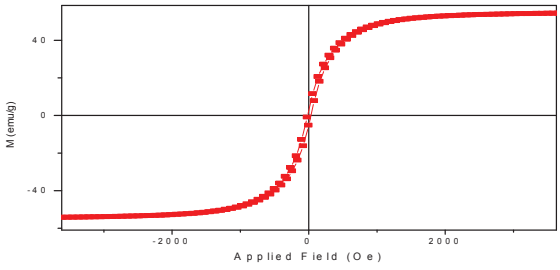

Figure 6. Variation of magnetization with applied field of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Fe_2O_4$.

Mössbauer spectroscopy: The ^{57}Fe Mössbauer spectra in transmission mode recorded at 300K of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_{0.10}Fe_{1.90}O_4$ sample is shown in Figure 7. It shows well defined sextets with small superparamagnetic doublet. Doublet can only be observed when superparamagnetic doublet relaxation occurs at rate higher than the Mössbauer measurement time, giving a time average zero magnetization. For un-doped Mg-Mn-Ni ferrite sample the experimental data was fitted with two normal Zeeman split sextet, one due to the A-site Fe^{3+} ions and other due to B-site

Fe^{3+} ions which indicates ferrimagnetic behavior of the samples. The observed Mössbauer spectrum for un-doped sample shows strong hyperfine magnetic field at both sites (H_A = 47.19 T at tetrahedral A-site and H_B = 50.19 T at octahedral B-site). B-site hyperfine field is more than that of A-site, which is due to dipolar field resulting due to deviation from cubic symmetry and covalent nature of tetrahedral bonds. Hyperfine magnetic field at A-site and B-site decreases gradually with increasing Al^{3+} ions concentration and with deceasing particle size.

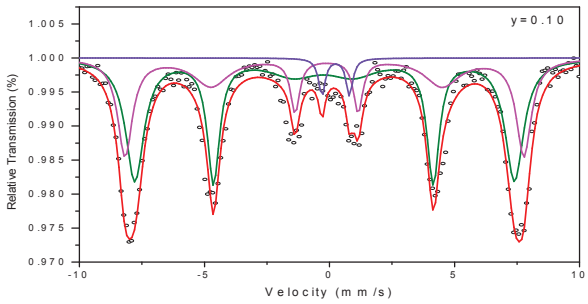

Figure 7. Mössbauer spectra of $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_{0.10}Fe_{1.90}O_4$ sample.

From the Mössbauer spectra, it is found that there is no change in isomer shift corresponding to Fe^{3+} ions at A-site and B-site with increase in Al^{3+} ions concentration. It implies that s-electron charge density around Fe^{3+} nuclei at both sites is not influenced by increased concentration of aluminum ions. A small paramagnetic doublet appearing in the nano samples of y= 0.05 and 0.10 on magnetic sextet show that isomer shift values are consistent with Fe^{3+} valence state. The quadrupole splitting are found to be negligibly small which are attributed to the fact that overall cubic symmetry is maintained between Fe^{3+} ions and their surroundings.

Conclusion: Highly homogeneous Mg-Mn-Ni-Al ferrites were prepared by citrate precursor method. Lattice constant and crystallite size decrease linearly with Al^{3+} ions concentration. Initial permeability and RLF decreases with Al content. RLF have very low values in range of 10^{-6}-10^{-5} which is three orders of magnitude lower than conventional prepared samples. MÖSSBAUER measurements show dependence of Zeeman spectral lines on smaller particle size which is indicative of their superparamagnetic nature.

References:

1. Satish Verma, Jagdish Chand, M. Singh, J. Alloys. Compd. **587** (2014) p 763.
2. B. D. Cullity,"Elements of X-ray Diffraction" Addison-Wesley Publishing Co. Inc. U.S.A. (1972). C.G.Whinfrey, D. W. Eckort. A. Tauber, J. American. Chem. Soc. **82** (1982) p 2695.
3. A.Globus, P. Duplex, M. Guyot, IEEE .Trans. Magn. **7** (1971) p 617.
4. T. Nakamura, Y. Okaro, J. Appl. Phys.**79** (1996) p 7129

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