Optical and Magnetic properties of non Stoichiometric Lithium substituted Magnesium ferrite nanoparticles for multifunctional applications.

Nishant Kumar, Rakesh Kr. Singh*and Harendra Kr Satyapal
Aryabhatta Centre for Nanoscience and Nanotechnology, Aryabhatta Knowledge University, Patna, India, 800001
***corresponding author:** rakeshsinghpu@gmail.com(Dr. Rakesh Kr Singh)

Ref-

Journal of Materials Science: Materials in Electronics, DOI 10.1007/s10854-020-03454-z

Optical Measurement

The room temperature UV-Visible-NIR spectrum was obtained using Perkin Scan Lambda 950 UV Visible spectrometer is shown in fig 1. The energy band were calculated to know the effect of lithium ion concentration. The following formula is to used to determine energy band gap using tauc plot

$$\mathbf{Eg} = \frac{hc}{\lambda}$$

Symbols have usual meaning. The direct band gap and indirect band gap were evaluated using formulae

$$\alpha h\nu = (h\nu - \mathrm{Eg})^n$$

Where n= different types of electronic transitions having ½ for direct band gap and 2 for indirect energy band. The sample were characterized in the wavelength range of 200 nm to 1000 nm radiation source at room temperature. The effect of substitution of non-stoichiometric Mg/Li ferrite is studied for optical behaviour of general formulae $Mg_{0.5+x}Li_{1-2x}Fe_2O_4$ with concentration of x in the range of (0, 0.15 and 0.35). The spectral data were analyzed further to study its effect on indirect band energy using tauc plot shown in fig 1.8. Slight decrease in the band gap (2.5 eV), (1.98 eV) and (2.41eV) respectively was found with the decrease in lithium concentration. Several research group reported that Eg values of ferrite materials lies between 1.17eV-2.10 eV . The change in the band gap is related to the crystallite size of the prepared materials and may be explored accordingly Brass effective mass model. According to this model energy band gap can be expressed as function of particle size, which is as follows

$$E_g \cong E_g^{bulk} + \frac{\hbar^2\pi^2}{2er^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r},$$

Where Eg is energy band gap, r is the particle size, me is the effective mass of the electron, mh is the effective mass of the holes ε is the relative permittivity, ε_0 is the permittivity of free space, h is the plank constant and e is the charge on electron. On the other hand The materials have strong absorption in the UV-Vis-NIR(about 300 nm to 900nm) . The sharp absorption band shows the overlap of optical band as mentioned by Beer-Lambert law. The variation of absorption with intensity of different materials like a electronic excitation and this may be also due to changes in their morphologies and microstructure of the materials as shown in the SEM image. This results also reveal that materials are optically active.

Photoluminescence spectra measurement

Fig 3 shows room temperature PL Spectra of $Mg_{0.5+x}Li_{1-2x}Fe_2O_4$ with (x = 0, 0.15 and 0.35) recorded in the (540 to 660) nm wavelength range, using excitation of 200 nm radiation source. It has reported that non-stoichiometric Lithium substituted magnesium ferrite Shows good luminous property as its intensive intensity lies in the orange range (590nm -635 nm). It has been also found that the intensity of the peak is proportional to the amount of lithium ion as it is highest in case of $Mg_{0.5}LiFe_2O_4$ and decreases regularly as the molar concentration of Li^{1+} ions decreases. This decrease in intensity may be due to the oxygen deficiency created by Li^{1+} ion concentration.

The energy values corresponding to intense peaks of materials calculated using formula

$$E = = \frac{hc}{\lambda}$$

and found to be 2.019 eV(615nm), 2.026 eV(613 nm) and 2.027 eV(612nm) $Mg_{0.5+x}Li_{1-2x}Fe_2O_4$ with (x = 0, 0.15 and 0.35). Such observed emission of luminescence of prominent peaks are in visible range. Properties of bright luminescence in visible range with uniform particle size, possesses magnetism may be emerging class of materials for optoelectronics devices and Biomedical sciences. In photoluminiscence emission the yellow-orange region centred at about 650 nm is may be due Fe-Mg phase . According to Fermi-golden rule, the maximum intense peak corresponds to the maximum transition probability.

Magnetic Measurement

Room temperature Magnetic parameters were evaluated using vibrating sample magnetometer, (Lakeshore ,7400) in the range of (-20k Oe to +20k Oe) magnetic field maintained and is shown in figure 4 . Existing soft materials properties can be expected as it shows narrow loops. It is reported that if the value of M_r / M_s lies in the range of 0 to 1. The interactions are supposed to be magneto static. Also Li^{1+}ion is non magnetic in nature and in our reported research it is being substituted by magnesium ion(magnetic). Earlier reported research work suggested that it will goes in the tetrahedral sites which results into decrease magnetic moment in that site (M_A) .This further effect the octahedral and tetrahedral structure of (A-B) site and presence of α-Fe_2O_3 and ultimately affects saturation magnetization.

But since we are not working on stoichiometry substitution it will not behave as the above discussed parameters . Present research deals with non- stoichiometric concentration of lithium which results in higher concentration of Li^{1+}which accumulate on octahedral site and as a result there will be decline in saturation magnetization. Thus from the table 3, that the least value of magnetization were reported 11.63 emu/g for sample ($Mg_{0.5}LiFe_2O_4$) having the concentration of Li concentration of one mole. But when we slightly decreased the concentration of Li in the sample ($Mg_{0.65}Li_{0.7}Fe_2O_4$) the magnetization value increases from 11.63 emu/gm to 15.51emu/gm . Similar results are obtained for $Mg_{0.85}Li_{0.3}Fe_2O_4$, the magnetization was found to increases from 15.51 emu/g to 16.24 emu/g. The coercivity of the materials increases with decrease in concentration of Li ion with (110.81) Gauss in case of $Mg_{0.5}LiFe_2O_4$ to (139.65) G in $Mg_{0.65}Li_{0.7}Fe_2O_4$ and further increased to (156.67) G for $Mg_{0.85}Li_{0.3}Fe_2O_4$. Anisotropic constant 'K' were obtained using formulae

$$K=\frac{Ms*Hc}{0.96}$$

The value is listed in the table 3 and it also follows a pattern which shows the fact that decrement in $Li^{1+}$the value of 'K' increases as listed in table3 (. 1342.41 to 2650.33). This sort of properties can be used in varieties of application as mentioned by numerous researchers .The most interesting observation is that all the magnetic parameters such as magnetization, retentivity, coercivity and anisotropic constant are found to increases with non-molar ration of x =0, 0.15 and 0.35 in $Mg_{0.5+x}Li_{1-2x}Fe_2O_4$. While all the materials are annealed at single temperature 550^{o}C. The increasing value of coercivity, anisotropic constant (table-1) reveal the characteristics of hard magnetic nanomaterials.

Curie temperature measurement (M-T)

The magnetic property of these synthesized nanomaterials shows asystematic variation in magnetic properties as mentioned in above section. Therefore measurement of magnetic parameter with variation in temperature has been studied. The M-T plots shows the temperature dependent variation of saturation magnetization of lithium substituted magnesium ferrite (non-stoichiometric ratio), shown in figure 5(a-b). The average Curie temperature is evaluated using dM/dT curve which confirms at higher temperature of nearby 479°C (752 K) , the moment value drops to zero value and start showing paramagnetic behavior. This temperature is considered as the Curie temperature. The largest value of Curie temperature reported is 722K for monovalent K substituted magnetium ferrite .

As shown in fig which is referred for the sample $Mg_{0.5}LiFe_2O_4$,the M-T plot suggests that at initial temperature it follows a stable pattern and as the temperature were increased to around 479°C, it magnetization drops drastically showing that its curie temperature lies around 479°C . Such sharp drop in magnetization with temperature reveal that synthesized materials possess good homogeneity in sol gel method . Similar results were also obtained as in earlier reported work on lithium ferrites . The effect of non-stoichiometric substitution of $Li^{1+}$with concentration of sample ($Mg_{0.65}Li_{0.7}Fe_2O_4$) related M-T plot is shown in 5(a-b). As Lithium ion concentration is reduced the Curie point significantly decreases to 454°C. Thus one can concluded from above reported work that Li^{1+} ion may be the reason for the enhancement in Curie temperature. This might be occurred due to the geometry, cation redistribution and A-B interactions fluctuation due to oxygen deficient or excess of metal molar concentration. This occurred as a result of tetrahedral and octahedral region which ultimately may causes the oxygen scarcity in prepared sample. Systematic variation in magnetic behavior in ferrite materials in low temperature range was also reported .This property of high Curie temperature is applicable in various industrial applications such as in memory component, Circulator, Isolator, microwave devices etc.

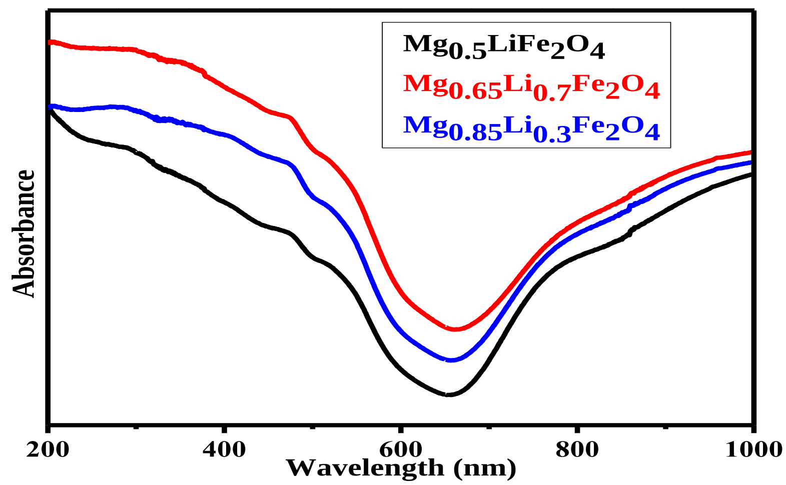

Fig.1.UV spectra of $Mg_{0.5+x}Li_{1-2x}Fe_2O_4$different concentration having $0 \leq x \leq 0.35$

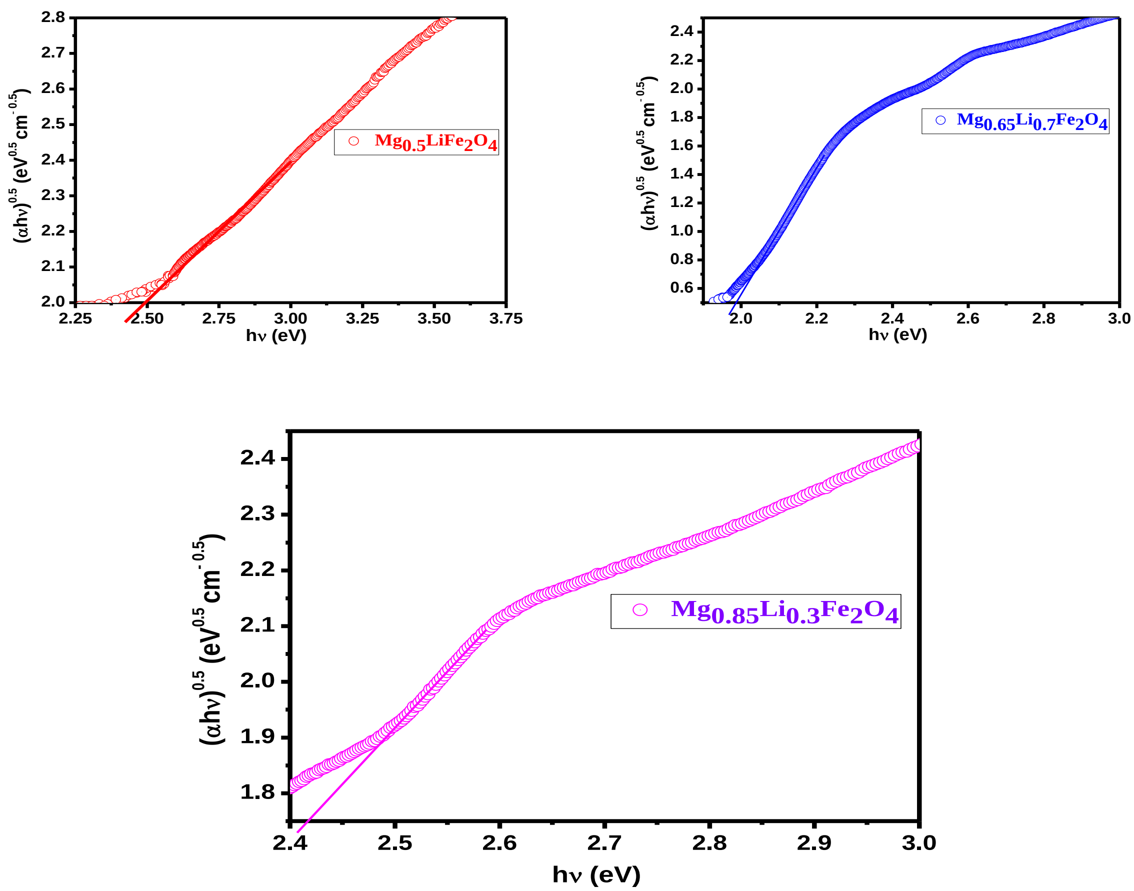

Fig.2 Tauc plot of $Mg_{0.5+x}Li_{1-2x}Fe_2O_4$different concentration having $0 \leq x \leq 0.35$.

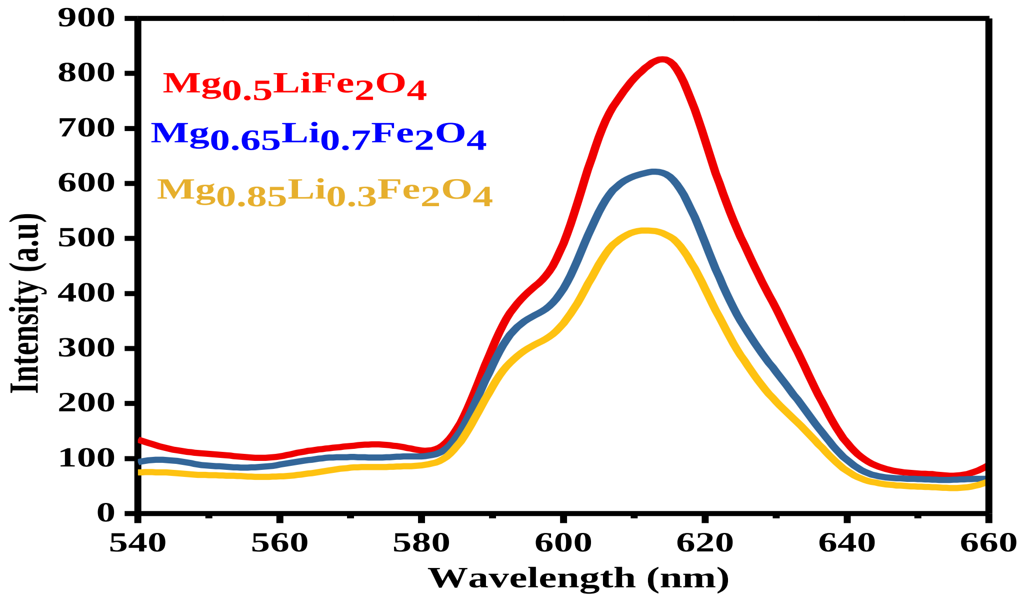

Fig 3.Photoluminescence spectra(PL) of Lithium substituted magnesium ferrite

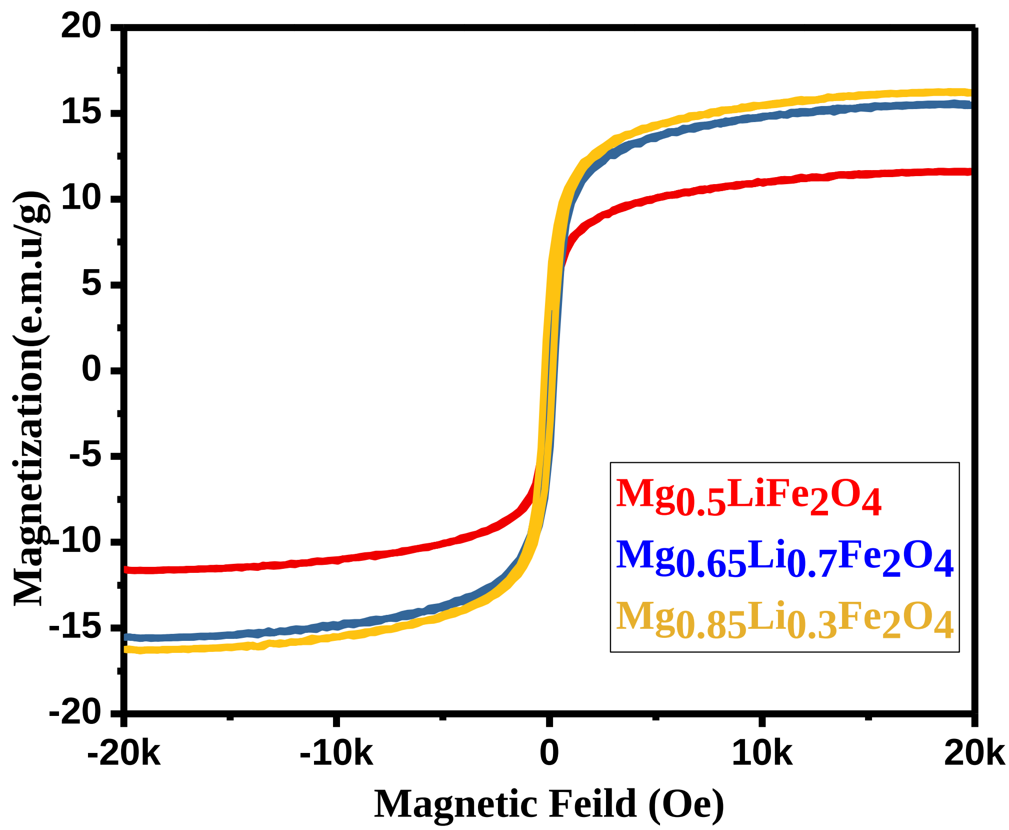

Fig 4. Room temperature Magnetization Versus Applied field curve

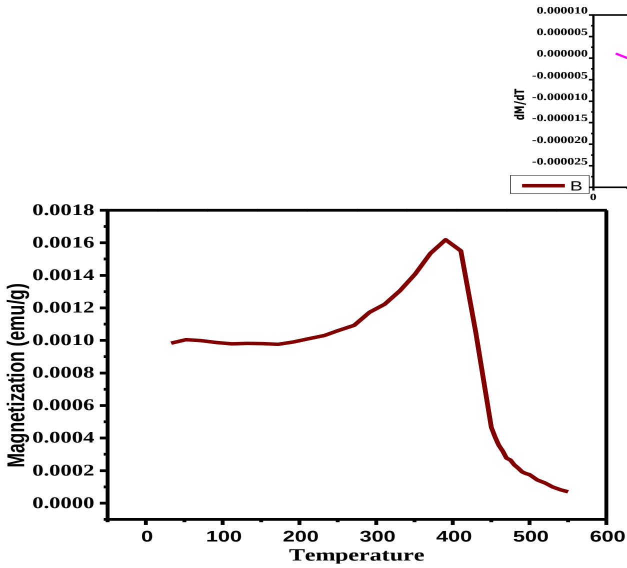

Fig. 5(a) Magnetization-Temperature curve for $Mg_{0.5}LiFe_2O_4$

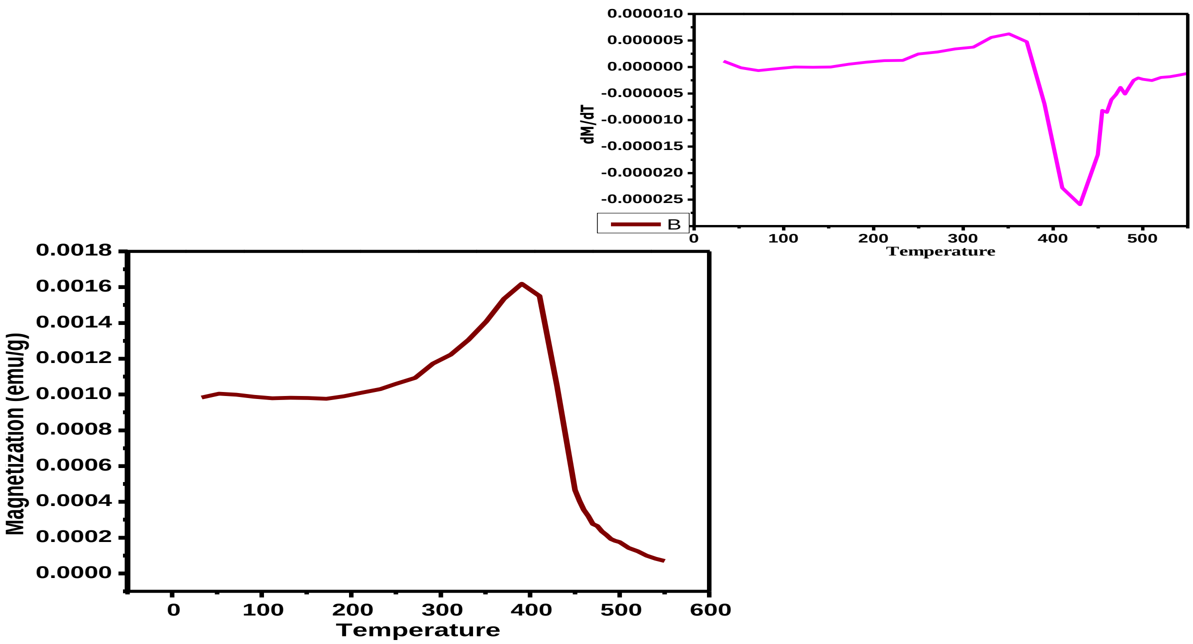

Fig. 5(b) Magnetization -Temperature curve for $Mg_{0.65}Li_{0.7}Fe_2O_4$

Table:1. Magnetic measurements

Magnetic Parameter	At x=0	At x= 0.15	At x= 0.35
Coercivity (Hc)/Oe	110.81	139.65	156.67
Magnetization (Ms)(emu/gm)	11.63	15.51	16.24
Retentivity (Mr)(emu/gm)	2.028	3.103	3.48
Squareness Ratio (Mr/Ms)	0.174	0.2	0.214
Magnetic momentηB (μB)	0.405	0.545	0.576
Anisotropy Constant(erg/Oe)	1342.41	2257.67	2650.334