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EFFECT OF MANGANESE SUBSTITUTION ON Co – Ga AND Co – Tl FERRITE NANOPARTICLES PREPARED BY HYDROTHERMAL ROUTE

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ABSTRACT

Nanoparticles of $CoFe_2O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ ferrites were synthesized by hydrothermal method and the influence of Tl^{3+} and Ga^{3+} doping on the properties of $Co_{0.5}Mn_{0.5}Fe_{2-x}M_xO_4$ (M = Tl and Ga) was studied. X-ray diffraction studies revealed the formation of single phase spinel type cubical structure and the particle sizes of the as- obtained samples were found to be ~65nm. FE-SEM and TEM were used to characterize the microstructure of the samples and particle size determination, which exhibited the formation of spherical nanoparticles. The particle size was found to be in the range of 52 to 63 nm. The variation of saturation magnetization for $Co_{0.5}Mn_{0.5}Fe_2O_4$ nanomaterials could be attributed to the noncolliner magnetic structure of $CoFe_2O_4$ nanoparticles with Tl^{3+} and Ga^{3+} ions consisting of a core with the usual spin arrangement of the nanoparticles.

I INTRODUCTION

Co – Mn are one of the magnetic materials having wide applications in magnetic recording, electrical devices and as photomagnetic materials [1 - 3]. Manganese substituted cobalt ferrites are promising ones for magnetic stress sensors, noncontact torque sensing, magneto - optical, magneto - mechanical, and high magnetostriction applications [4 - 7].The magnetization of Mn- substituted cobalt ferrites depends on the cation distribution of the magnetic Fe^{3+}, Mn^{2+}, Tl^{3+}, Ga^{3+} and Co^{2+} ions among the A and B sites. Substitution of some trivalent nonmagnetic ions such as In^{3+}, Al^{3+}, Tl^{3+}or Ga^{3+} for Fe^{3+} in spinel ferrites is made for special magnetic and electrical function [8]. Although a tremendous work has been reported on manganese substituted cobalt ferrites, the simultaneous investigation of the variation of electrical and magnetic properties of Co–Mn nano ferrites with Tl^{3+} and Ga^{3+} ions has not been reported earlier. Therefore, in the present investigation, an attempt is made to synthesize $Co_{0.5}Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ using the hydrothermal method and study the effects of simultaneous substitution of Mn^{2+} and Tl^{3+} and Ga^{3+} ions on the magnetic properties of cobalt nano ferrites.

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II EXPERIMENTAL DETAILS

All the reagents used were of an analytical grade and used as received without any further purifications. Required quantities of Cobalt Nitrate Co $(NO_3)_2.6H_2O$, Iron nitrate Fe $(NO_3)_2.9H_2O$, Gallium (III) nitrate Ga $(NO_3)_{3.}3H_2O$, Manganese nitrate and Thallium (III) Nitrate were dissolved in deionized water. The mole ratio of $CoFe_2O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$ and $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ were calculated, and the salt solution was prepared. A sodium hydroxide (NaOH) 3 M/liter solution was added and stirred vigorously for another 15 minutes. The mixture was then poured into a Teflon-lined stainless steel autoclave of 250 ml capacity. The autoclave was placed in an electric oven at a temperature of 120 °C for 24 hrs. After 24 hrs, the autoclave was allowed to cool to room temperature. The brown precipitates were then filtered out and washed 4-5 times. The precipitates were then dried at 100 °C over the night to obtain the powder. Prepared samples were grounded and calcinated at 500°C for 6 hours. Then grounded finally, and used for further characterization.

III RESULTS AND DISCUSSION

3.1. Powder X-Ray diffraction (XRD) studies

Fig: 1 represents the XRD patterns of $CoFe_2O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$. The peaks are well indexed with the standard pattern of JCPDS card number: 22-1086 ($CoFe_2O_4$). The presence of manganese, thallium and gallium are seen through the shift in the peaks.

The average size of the nanoparticles estimated by the Sherrer equation, $d = 0.9\lambda/\beta$ (cos θ), which are found to be 42nm, 52nm and63nm for $CoFe_2O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ respectively.

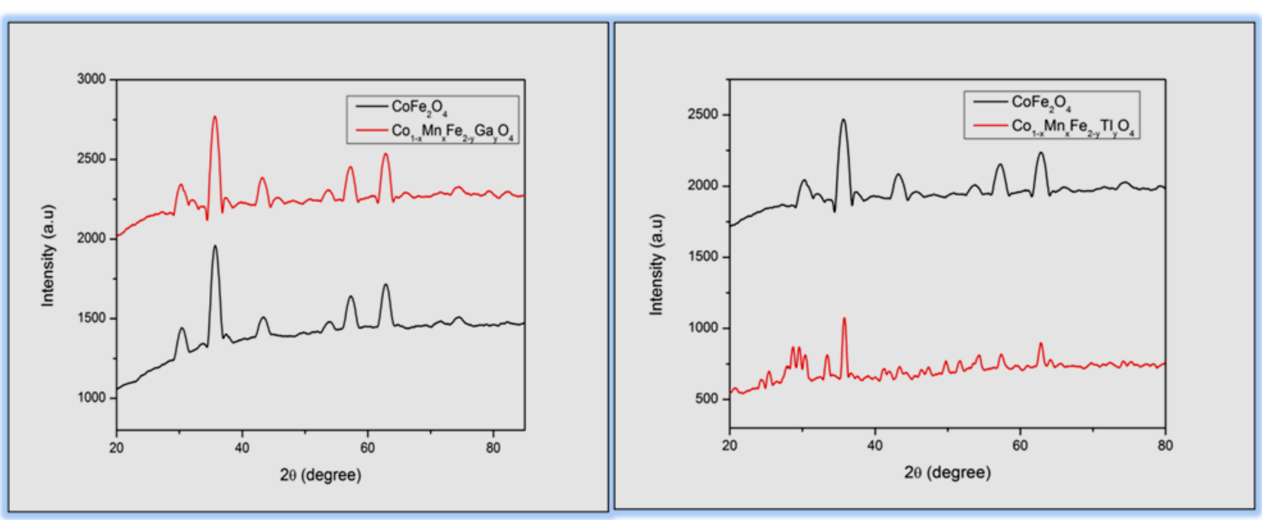

Fig: 1 XRD pattern for $CoFe_2O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$

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3.2. FE-SEM / EDX analysis

Field Emission Scanning Electron Microscope was used to investigate the surface morphology and the elemental composition of the samples. The samples were all coated with carbon prior to SEM analysis. Fig: 2 show that the cobalt ferrite nanoparticle appears in uniform sphere- like shape with a particle size in the range of 52 to 63 nm. In Fig. 2(a) the spherical morphology of particles with very strong agglomeration due to the magnetic characteristic of particles. The EDX spectrum shows no impurity is present in the prepared compound of both $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$ and $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_{4.}$

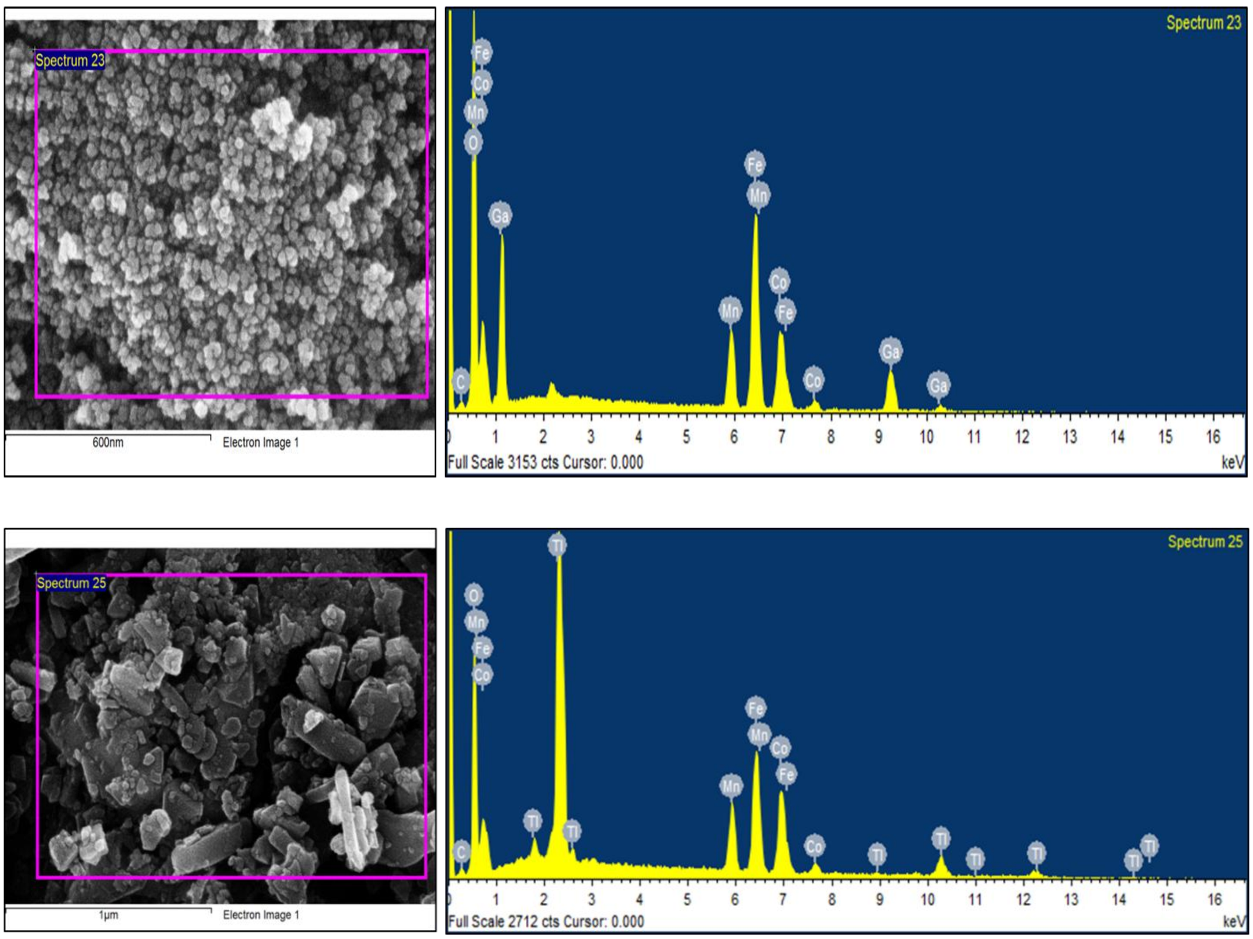

Fig: 2. FE-SEM/EDX images of (a) $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ (b) $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$

3.3. TEM Analysis

The TEM micrographs of $CoFe_2O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ ferrites calcinated at 500°C for 6 hrs are shown in Fig: 3. It indicates that the particles obtained by this method are uniform in both morphology and

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particle size, but they are agglomerated to some extent. The particle sizes are in the range 52 to 65 nm, consistent with the average crystallite size determined from the XRD data. It is evident from the TEM images that the Tl^{3+} ions are having a rod-like a shape in Cobalt ferrite compound while Ga^{3+} ions have a spherical shape as seen in FE-SEM images Fig: 2.

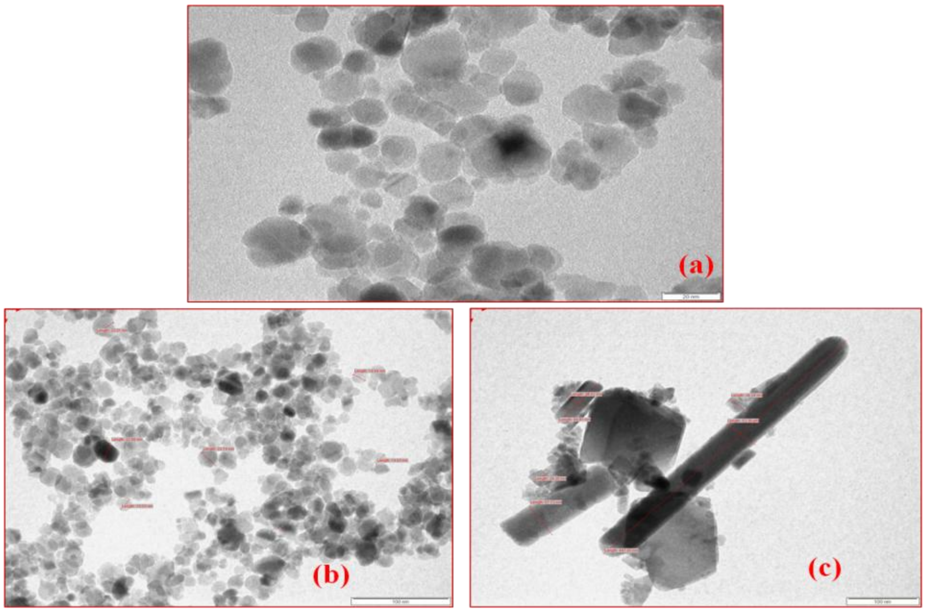

Fig: 3 TEM images of (a) $CoFe_2O_4$ (b) $Co_{0.5}Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ (c) $Co_{0.5}Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$

3.4. Magnetic Studies

Hysteresis loops for the samples of $CoFe_2O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ are shown in Fig: 4. Room temperature magnetic properties of Co–Mn with Tl and Ga spinel ferrite nanoparticles were obtained. Using M–H plots (Fig. 4) the saturation magnetization (Ms), Remanence magnetization (Mr) and coercivity (Hc) were determined for each sample. Magnetic properties of ferrites dependents on the structure, composition, defects, and internal stress. The value of coercivity (H_c), the remanent magnetization (M_r), saturation magnetization (M_s) is shown in table I, which shows the effects of Mn substitution on the magnetic properties of $Co_{0.5}Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ nano ferrites. The saturation magnetization increases with the increase in the content of doping material. The Ms of $CoFe_2O_4$ nanoparticles calcined at 500 °C is 1.992 emu/g, which is still lower than the bulk value [9].It was well known that the magnetic properties depend on the properties of nanoparticles and the interaction among them. The variation of saturation magnetization for $Co_{0.5}Mn_{0.5}Fe_2O_4$ nanoparticles could be attributed to noncolliner magnetic structure of $CoFe_2O_4$ nanoparticles with Tl^{3+} and Ga^{3+} ions consisting of a core with the usual spin arrangement and a boundary surface layer with disordered atomic moments [10].

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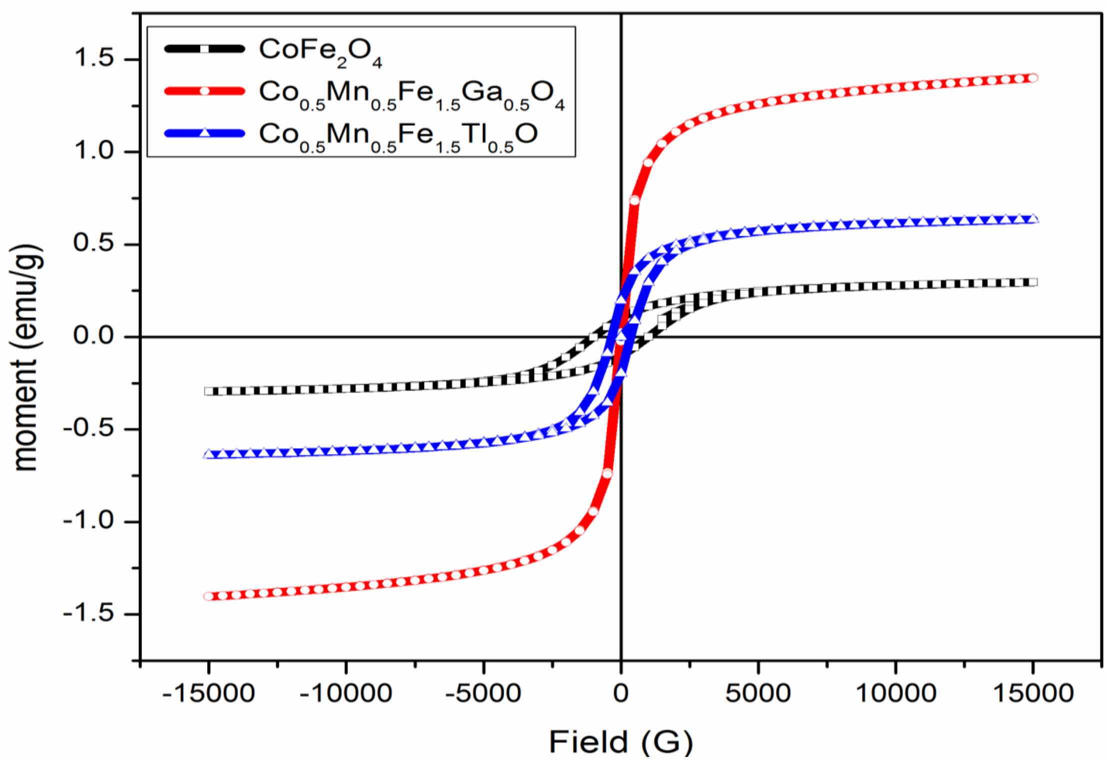

Fig: 4 Hysteresis loop of (a) $CoFe_2O_4$ (b) $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$ (c) $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$

Parameter	**$CoFe_2O_4$**	**$Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$**	**$Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$**
M_s (emu/g)	**1.992**	**2.862**	**1.7676**
M_r (emu/g)	**5.009**	**5.0951**	**5.4477**
H_c (Oe)	**809.49**	**16.517**	**3.452**

Table I: Saturation magnetization (Ms), Remanence magnetization (Mr), Coercivity (Hc) of $CoFe_2O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$, $Co_{0.5}$ $Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ System.

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IV CONCLUSION

The nanoparticles of $CoFe_2O_4$, $Co_{0.5}Mn_{0.5}Fe_{1.5}Tl_{0.5}O_4$ and $Co_{0.5}Mn_{0.5}Fe_{1.5}Ga_{0.5}O_4$ were synthesized by hydrothermal method and sintered at 500°C respectively. The size of the nanoparticles is in the range of 52-65 nm that is in good agreement with the values obtained by XRD, FE-SEM and TEM indicating that there is no agglomeration. The saturation magnetization (Ms), coercivity (Hc) value changes due to the substitution of manganese to the $CoFe_{1.5}Tl_{0.5}O_4$ and $CoFe_{1.5}Ga_{0.5}O_4$, which suppress the ferromagnetic nature of cobalt ferrite. The magnetic studies demonstrated that manganese nanoparticles displayed ferromagnetic behaviors with Tl^{3+} and Ga^{3+} ions nanoparticles with very low saturation magnetization and coercivity value which makes these materials suitable for the application in transformer cores.

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