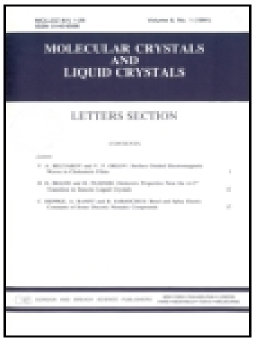
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Structural and magnetic properties of nanometric $Zn_{0.5}Co_{0.5}Fe_2O_4$ prepared by hydrothermal method

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ABSTRACT
The study of the structural, morphology and magnetic properties of $Zn_{0.5}Co_{0.5}Fe_2O_4$ ferrite is the objective of this work. The sample was prepared by hydrothermal method and was characterized by X-ray diffraction (XRD), (SEM) and (TEM) micrographs and magnetization measurements.
The magnetic hysteresis loops, field cooling (FC) and zero field cooling (ZFC) curves, in temperature range (0-400K), were measured using XL-SQUID magnetometer and the values of blocking temperatures (T_B) were determined. The results indicated that $Zn_{0.5}Co_{0.5}Fe_2O_4$ sample were formed in a single spinel phase and gives the value for the lattice parameter (8.3952 Å) and nanosizes of particles (13.8 nm) were compared with these obtained from $ZnFe_2O_4$ sample prepared also by synthesis method (8.4261 Å and 14 nm). Although, the superparamagnetic behaviour for Co-Zn ferrite has observed at 350K with a blocking temperature ($T_B = 300K$), that is maximum at the value obtained in the case of Zn-ferrite ($T_B = 12K$).

KEYWORDS
Spinel ferrites; blocking temperature T_B; superparamagnetism; nanosizes

1. Introduction

The spinel ferrites are subjects of intense theoretical and experimental investigation due to their remarkable magnetic and electric properties [1–3]. Cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material with high coercivity and moderate magnetization. These properties, along with their great physical and chemical stability, make $CoFe_2O_4$ nanoparticles suitable for magnetic recording applications [4]. Many efforts have been made to improve the basic properties of these ferrites by substituting or adding various cations of different valence states depending on the applications of interest. Among spinel ferrites, Zn^{2+} substituted $CoFe_2O_4$ nanoparticles exhibit improved properties such as excellent chemical stability, high corrosion resistivity, magnetocrystalline anisotropy, magnetostriction, and magneto-optical properties [5, 6].

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Various preparation techniques, such as sol–gel pyrolysis method [7, 8], the microwave hydrothermal method [9], template-assisted hydrothermal method [10], and solvothermal technique are used to prepare ferrites nanoparticles [11]. However, the co-precipitation method is considered as an economical way of producing fine particles [12, 13].

In this work, focus was placed on the $Zn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles prepared via hydrothermal method. The dependence of the morphology and magnetic properties with synthesis method of the final ferrite product has identified and discussed.

2. Materials and methods

The $Zn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles were prepared by hydrothermal method in which stoichiometric amounts of iron, zinc and cobalt nitrates were dissolved in distilled water obtaining a homogenous solution. By adding a KOH 2M solution until pH = 11 using a pipette, the iron, zinc and cobalt hydroxides were precipitated. This precipitate was transferred into a Teflon stainless-steel autoclave and heated for different periods of time, ranging from 3 hours to 15 hours at 160°C to obtain (Zn-Co) ferrite. The final product was filtered and washed with distilled water and ground after drying in air and was slowly cooled and between each heat treatment, the powder was ground using an agate mortar. The powder obtained was sintered at temperatures (4, 25, 50, 155, 250 and 350 K) in air atmosphere during 12 h.

The structural phase of the sample were identified by X–ray powder diffraction employing a Siemens/D–5000 X–ray diffractometer over a 2❶ range from 15° to 100° using Cu kα radiation ($\lambda = 1.5481$ Å). Micro-structural characterization was evaluated by transmission electron microscopy (TEM) using a JEOL-2000FX electron microscope working at 200 kV. Scanning electron micrographs (SEM) were taken in a JEOL 6400 electron microscope working at 20 kV. Magnetic susceptibility and magnetization measurements were done in a Quantum Design XL-SQUID magnetometer in the temperature range of 0–400 K at different magnetic fields up to 1000 G. Magnetic susceptibility measurements were performed after the sample was cooled at 4K in zero field cooling (ZFC). In the so called field cooling measurements modality (FC) the sample was cooled in presence of the required magnetic field down to 4K

3. Results and discussion

3.1. X-ray analysis

X-ray diffraction (XRD) pattern for $Zn_{0.5}Co_{0.5}Fe_2O_4$ ferrite prepared by hydrothermal method is presented in Figure 1. At the calcination temperature of 900°C, fully crystallized $Zn_{0,5}Co_{0,5}Fe_2O_4$ has obtained with sharp peaks indexed as (220), (311), (222), (400), (422), (511), (440) planes of spinel structure and the maximum intensity peak in this sample corresponds to (311) plane and no extra peaks were observed. These X–ray diffraction data comparing with the patterns of standard JCPDS card reveal that the ferrite Zn-Co sample obtained by this synthesis method crystallize in a single phase pure with the cubic spinel type structure and space group *Fd*3¯*m*. The $Zn_{0.5}Co_{0.5}Fe_2O_4$ sample prepared has the lowest lattice parameter (a = 8.3952Å) that it was compared with the value (a = 8.4261Å) obtained for $ZnFe_2O_4$ sample prepared by also synthesis method [14].

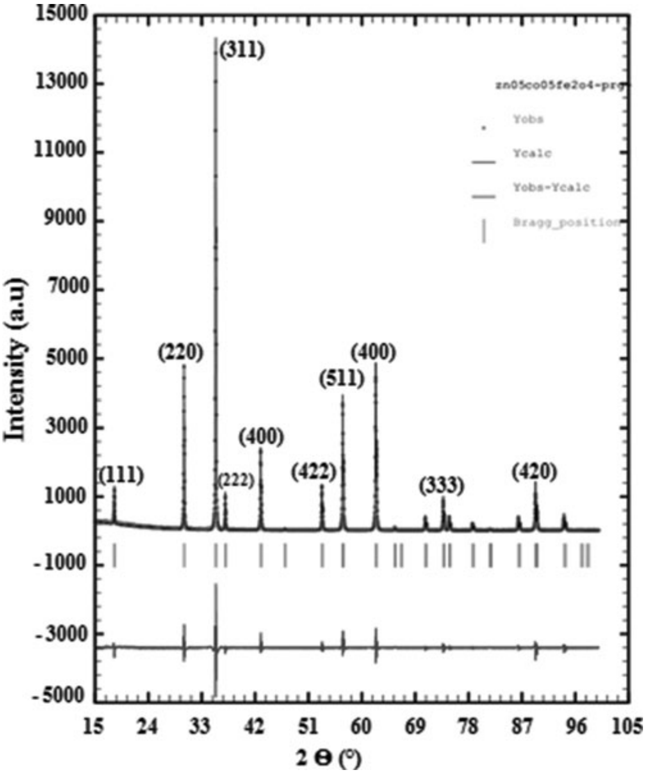

Figure 1. X-ray diffraction diagram of $Zn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles prepared by hydrothermal method.

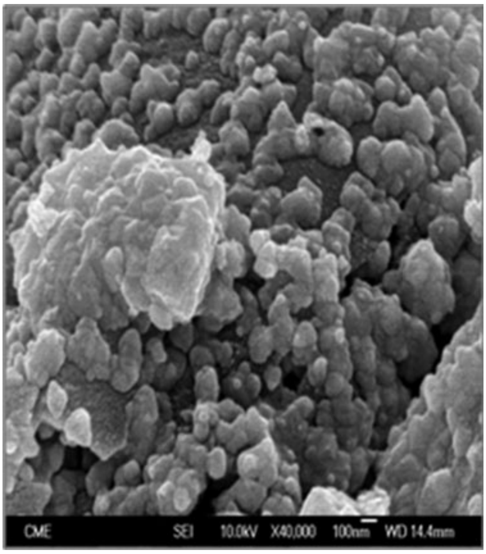

Figure 2. SEM micrograph of $Zn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticules prepared by hydrothermal method at 350K.

3.2. SEM and TEM

The TEM and SEM images of the $Zn_{0.5}Co_{0.5}Fe_2O_4$ prepared by hydrothermal method at 350 K are shown in figure 2 and 3. It is observed, that the prepared powder sample was in nanosize with sizes less than 40 nm (10 $\sim$ 40 nm) that they are similar for the Zn-ferrite particles

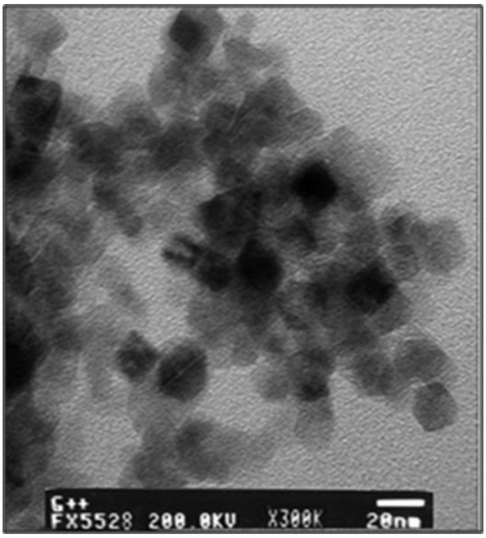

Figure 3. TEM micrograph of $Zn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles prepared by hydrothermal method at 350K.

prepared by also elaboration method [14]. We observe a more homogenous particle size presented in TEM micrograph of figure 3. The average size estimated from the image of about 50 particles of this sample was 14 nm.

The average particle size has been calculated using the well-known Scherrer's formula ($d = 0.9\ \lambda/\beta\ \cos\theta$), where d is the crystalline size, λ the wavelength (Cu Kα), θ the Bragg angle and β the full width to half maximum of the (311) reflection on the $Zn_{0.5}Co_{0.5}Fe_2O_4$ cell. The results indicated that the hydrothermal method give the smallest nanosize of particles (13.8 nm) that it is near of the nanosize of $ZnFe_2O_4$ (14 nm) obtained with also synthesis method [14].

In this preparation method of Zn-Co ferrite, the particle size is in good agreement with the values obtained from the X-ray powder data and this prepared sample present a best homogenous particle size distributions.

On the other hand, there nanosizes of $Zn_{0.5}Co_{0.5}Fe_2O_4$ prepared by hydrothermal method were compared with these obtained by metallo-organic decomposition method (95 ∼ 142 nm) [15], sol-gel (16 ∼ 22 nm) [16], co-precipitation (18 ∼ 24 nm) [17] and by citrate precursor (21 ∼ 28 nm) [18]. This comparison we suggest that the hydrothermal method is better than the other synthesis methods for obtaining an especially fine nanoparticle dimensions (in close of 14 nm).

3.3. Magnetic properties

3.3.1. M-H loops

Room temperature M-H loops for $Zn_{0.5}Co_{0.5}Fe_2O_4$ sample treated at different temperatures are shown in figure 4. The superparamagnetic behaviour was detected for the prepared sample for all thermal treatments (at 4 K, 25 K, 50 K, 155 K, 250 K, and 350 K) due to the small size of the formed particles of this sample. The values of saturation magnetization M_S (emu/g) are determined by the extrapolation of magnetization curves with the magnetizing field H(T). Inset of figure 4 displays the variation of M_S with the thermal treatment. M_S shows slight decreases with thermal treatment tell 50K and sharp rise to temperature 350K. This behavior could be explained according to the movement of Co^{2+} ions with ($3\mu_B$) to B-site and Fe^{3+} ions

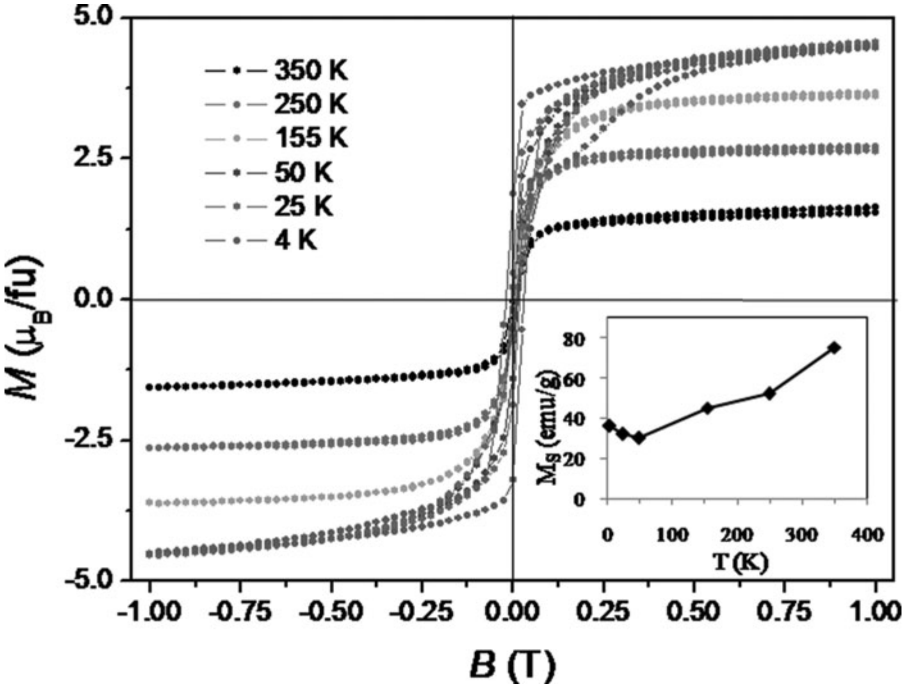

Figure 4. M-H loops of $Zn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles prepared by hydrothermal method at different temperatures. Inset is saturation magnetization as a function of temperature treatment.

with ($5\mu_B$) to A-site. Taking into account that the magnetization of spinel ferrites is given by $M = M_B$-M_A, where M_A and M_B are the magnetization of A and B sites respectively [19]. On the other hand, magnetization and crystallization are enhanced as the particle size increases [20]. Therefore, for higher thermal treatment ($T > 350$ K) where the particle size considerably increases, the effect of particle size dominates the relocation of Co^{2+} ions.

3.3.2. Temperature dependence of magnetic suceptibility

Figure 5 shows the curves of temperature dependence of magnetic susceptibility in the ZFC and FC processes with an applied field H = 100 G and the ZFC at 1000 G for the $Zn_{0.5}Co_{0.5}Fe_2O_4$ spinel prepared by hydrothermal method in the temperature range from 0 to 400K. The $\chi_M = f(T)$ curves (100 G) has a peak value of magnetization commonly refers to the blocking temperature ($T_B = 300$ K) in superparamagnetism. Such a phenomenon is often observed in nanoparticles, each of them is considered as a single magnetic domain. The thermal energy at $T > T_B$ is sufficient to induce fluctuations in the magnetization direction. Consequently, the expected magnetic-ordered behaviour would not prevail even below the Curie temperature. On the other hand, the blocking temperature decreases ($T_B = 120$ K) with increasing of an applied field 1000 G. The inverse molar magnetic susceptibility as a function of the temperature of $Zn_{0.5}Co_{0.5}Fe_2O_4$ prepared by hydrothermal method shown in the figure 6. It reveals two regimes of the Curie-Weiss behavior of $\chi = C/(T—$❶$)$ over a very narrow temperature range (300–350 K) and a positive value of the Weiss temperature as high as 325 K for this sample. This result combined with the values of the magnetization obtained at different temperatures (figure 4) is consistent with the presence of a ferrimagnetic behaviour arising from the partially inverse character of this $Zn_{0.5}Co_{0.5}Fe_2O_4$ spinel.

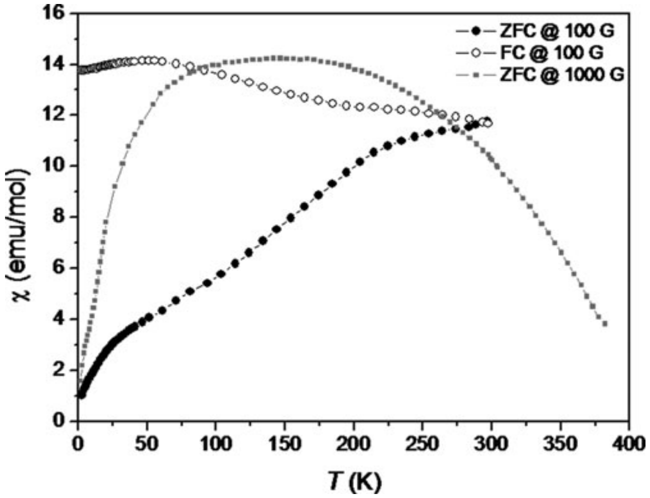

Figure 5. The temperature dependence of molar magnetic susceptibility in the ZFC and FC of $Zn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles prepared by hydrothermal method.

This behavior for sample prepared by hydrothermal method is confirmed from the magnetization curve obtained a 350 K (figure 4) where the coercive field and remanence have a small value. This indicates that Zn-Co ferrite nanoparticles synthesized by hydrothermal method behave as superparamagnetic at 350 K. This observed magnetization would depend on the measurement time tm relative to the relaxation time ✍ of thermal fluctuations. The relaxation time ✍ for a single particle (equation 1) is given by Hamdeh et al [21],

$$\tau = \tau_0 \cdot \exp\left[\frac{K_{eff} \times V}{k_B \times T}\right] \tag{1}$$

where a characteristic time ✍$_o$ is typically 10^{-9} s, and $k_B \times T$, K_{eff}, and V are, respectively, the thermal energy, the effective magnetic anisotropy constant and the particle volume.

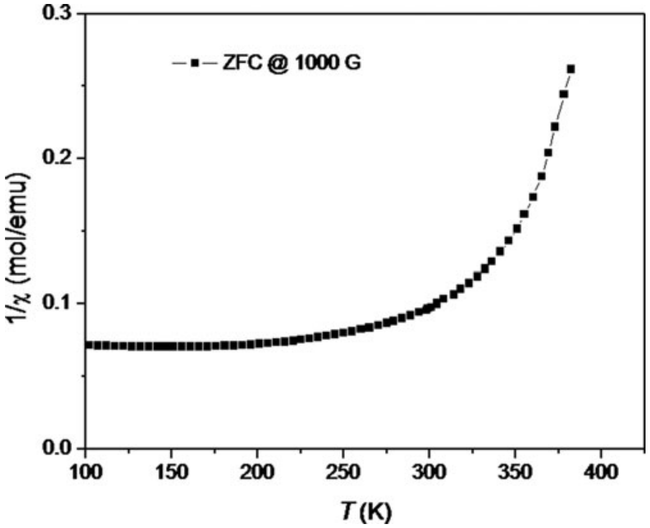

Figure 6. The reciprocal molar magnetic susceptibility as a function with an applied field H = 100 G of the temperature of $Zn_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles prepared by hydrothermal method.

The order temperature for Curie-Weiss behavior T_C is the same that the blocking temperature T_B in superparamagnetic regime. The well known Néel-Brown [22] expression establishes the relation

$$T_B = \frac{K_{eff} \times V}{\left[k_B \times Ln\left(\frac{t_m}{\tau_0}\right)\right]} \tag{2}$$

between anisotropy barrier $K_{eff} \times T$ and T_B.

For ZFC/FC measurement, with the measuring time $t_m =$ ✍ and by assuming $t_m/$✍$_o = 10^{11}$ in a typical magnetization measurement, it is usually assumed that [23],

$$T_B = \frac{K_{eff} \times V}{25 \times k_B} \tag{3}$$

Moreover, a further contribution to the effective magnetic anisotropy can be given by presence of dipolar and/or exchange interactions among the particles [23].

The figure 5 represents the temperature dependence of magnetic susceptibility ② in the ZFC-FC processes with an applied field of 100 G and 1000 G for the $Zn_{0.5}Co_{0.5}Fe_2O_4$ prepared by hydrothermal method. The temperature T_B reaches its minimum at 350 K where K_{eff} (derived using equation 3) reduced dramatically with annealing temperatures. Since Co^{2+} ions migrate from A-sites with small radius to B-sites with larger radius, both the internal stress and effective anisotropy constant is reduced. This leads to reduction of T_B at 120 K as the effect of particle size in this range is not considerable. The enhancement of T_B values at annealing temperatures ($T > 350$ K) indicates that; the effect of particle size enlargement overcomes decreasing the value of K_{eff} with increasing the annealing temperature. When the temperature exceeded T_B, the value of magnetization approaches zero approximately at 350 K for all samples (figure 4). This behavior reveals that the Curie temperature T_C for all samples is almost constant. According to ion pair model, the main factor affects the value of T_C is the A-B interaction [25]. The common value of T_C, especially for the samples which are annealed above 350 K, could be attributed to the struggle between two factors; the relocation of Fe^{3+} ions as discussed before, leads to amplify Fe-Fe interaction in A and B-sites and hence increasing the value of T_C. On the other hand, the moments separated by large distances due to the enhancement of the lattice parameter then the A-B interaction get weaker and hence reduce the value of T_C.

4. Conclusions

Nanoparticules of $Zn_{0.5}Co_{0.5}Fe_2O_4$ ferrite has been prepared by hydrothermal method as a single phase with cubic structure belonging to the fcc system. This wet chemical method is gaining prominence for the preparation of homogeneous and compositionally stoichiometric ferrites.

The particle size, lattice parameter, magnetic behaviour and blocking temperature depend on the thermal treatment of this preparation method. The hydrothermal method we suggest is better than the other methods and allows obtaining a very fine nanoparticle dimensions (average size of 14 nm) and more homogenous size. The small and homogenous particles obtained by hydrothermal method lead to a perfectly superparamagnetic behavior and a lowest lattice parameter (8.3952 Å).

We conclude that the physical properties of nanoparticles ferrite are of current interest due to the size dependent behavior observed in the nano scale and high crystallinity.

References

[1] El-Shabasy, M. (1997). *J. Magn. Magn. Mater.*, *172*, 188.
[2] Rosales, M. I., Amano, E. & Valenzuela, R. (1997). *J. Mat. Scien. Engin., B.*, *49*, 221.
[3] Mahmud, S. T. & Akther Hossain, A. K. (2006). *J. Magn. Magn. Mater.*, *305*, 269–274.
[4] Skomski, R. (2003). *J. Phys. Condens. Matter.*, *15*, R1–R56.
[5] Vaidyanathan, G. & Sendhilnathan, S. (2008). *J. Physica B.*, *403*, 13–16, 2157–2167.
[6] Akther Hossain, A. K. M. & Kawai, T. (2008). *J. Magn. Magn. Mater.*, *320*, 1157–1162.
[7] Lee, J. G., Minlee, H. & Kim, C. S. (1998). *J. Magn. Magn. Mater.*, *90*, 177.
[8] Singhal, S., Barthwalb, S. K. & Chandra, K. (2006). *J. Magn. Magn. Mater.*, *306*, 233–240.
[9] Kim, C. K., Lee, J. H. & Katoh, S. (2001). *J. Mater. Res. Bull.*, *36*, 12, 2241–2250.
[10] He, H. Y. (2011). *J. Nanotechnology*, Article ID 182543.
[11] Gutierrez, V. B., C. Pascual, E., & Fernandez, M. J. T. (2011). *J. Solid State Chem.*, *184*, 1608–1613.
[12] Urcia-Romero, S. & Pérez, O. P. (2011). *J. Appl. Physics.*, *109*, 7, 07B512-07B512-3.
[13] Veverka, M., Jirák, Z. & Kaman, O. (2011). *J. Nanotechnology.*, *22*(34), 345701.
[14] Benkhouja, K., Lemdek, E. M., Jaafari, K., Bettach, M., Touaiher, M., Sbiaai, K., Boughaleb, Y., Touhtouh, S., Hajjaji, A. & Puche, R. S. (2013). *J. Optoelectonics and Advanced Materials.*, *15*, 5–6, 410–416.
[15] Sharma, A. & Parmar, K. (2012). *J. Adv. Eng. Tech.*, *2231*, 1963.
[16] Mubarak, T. H., Ali, S. M. & Mahmood, L. S. (2013). *J. Diyala. Pure Sci.*, *9*(1), 2222–8373.
[17] El-Saacy, A. S. & Badawi, A. (2014). *J. Appl. Chem.*, *7*, 11, 2278–5736.
[18] Vinuthna, Ch., Ravinder, D. & Raju, R. M. (2013). *J. Eng. Rech. App.*, *3*, 6, 2248–9622.
[19] Sattar, A. A., El-Sayed, H. M. & El-Shokrofy, K. M. (2005). *J. Appl. Sci.*, *5*, (1), 162–168.
[20] Maaz, K., Mumtaz, A. & Hasan, S. K. (2007). *J. Magn. Magn. Materials.*, *308*(2), 289–295.
[21] Hamdeh, H. H., Hikal, W. M. & Taher, S. M. (2005). *J. Appl. Phys.*, *97*, 064310.
[22] Brown, W. F. (1963). *J. Phys. Rev.*, *130*, 1677–1686.
[23] Kneller, E. F. & Luborsky, F. E. (1963). *J. Appl. Phys.*, *34*, 656.
[24] Otero, J. G., Porto, M. & Bunde, A. (2000). *J. Phys. Rev. Lett.*, *83*, 63.
[25] Eltabey, M. M. & El-Shokrofy, K. M. (2011). *J. Alloys and Comp.*, *509*, 2473–2477.