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STUDY OF STRUCTURAL AND MAGNETIC PROPERTIES, TRIVALENT CATION SUBSTITUTION OF COBALT BASE SPINEL FERRITES $CoCr_{0.04}Gd_xFe_{1.96-x}O_4$ ($0 \le x \le 0.12$)

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In the presented work, double substitution ($Cr^{3+}Gd^{3+}$) for $CoCr_{0.04}Gd_xFe_{1.96-x}O_4$ ($0 \le x \le 0.12$) synthesized by co-precipitation method. X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) are employed to confirm the phase identification. The lattice constants calculated lies in the range 8.3169-8.3717Å, while Scherrer formula was used to calculate the average crystallite size 21-106 nm. Morphology of the samples was studied by SEM. M-H-loop showing the effect of Gd^{3+}concentration on intrinsic as well as extrinsic magnetic parameter. It is observed that saturation magnetization of the resulting samples were decreased from 63.5 -53.8 emu/g with the increase in content, while coercivity observed less than 1 KOae

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1. Introduction

Polycrystalline ferrites materials are extensively used in technological applications, it has general formula AB_2O_4, whereas A-site is represented by divalent cations and the B-site is for trivalent cations. The spinel ferrite fcc cubic structure having space group Fd3m. Ferrite of the unit cell, the oxygen is composed of A-site having 64 tetrahedral and B-site contains 32 octahedral interstitial sites. In the inverse spinel type, the ferric ions occupy eight on the tetrahedral site while sixteen ferric ions occupy on octahedral B-sites. It is reported that the material characterization depends upon these factors; synthesis technique, chemical compositions, sintering temperature, sintering time, PH value, the use of additive, and distribution of cations between the A- and B-sites [1]. Ferrite due to the high coercivity, chemical stability, good mechanical properties, and intermediate saturation magnetization are used in many technological applications [2-4]. Ferrites due to their various applications are being used in magnetic resonance imaging, high-density magnetic recording medium, communication signals, and electronics [5-6].The structural and magnetic properties can be modified effectively by using the additives in the composition such as rare-earth elements substitution play vital role in modification of ferrites properties [7]. Toksha *et al*; [8] described the cobalt ferrite structural and magnetic properties are altered by substituted of Cr^{3+} ions which take place of Fe^{3+} at B-site and change the structural and magnetic properties [9-12]. Ferrites characteristics are changing due to the exchanging cations of A- and B-sites via oxygen ions. However, many disadvantages have been discussed in literature about spinel ferrites for low quantity of rare-earth ions such metal monoxides [13-14] as the hematite α-Fe_2O_3 [15-16] and orthoferrites [17]. Another difficulty is to influence the high nucleation rate of crystal size. Kumar *et al*; [20] reported that saturation magnetization reduces with the increase of Gd^{3+}ions

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concentration. Tahar and Kim *et al;* [18] were reported Gd^{3+} substituted for Co-ferrites saturation magnetized increases with the increase of annealing temperature while coercivity observed decreases [19]. Burianova *et al*; [21] investigated that the coercivity of the ferrites samples based on particle size and follows the Brown relation. In this work, the chief aims to study the structure and magnetic properties for substituted (Cr^{3+} Gd^{3+}) $\mathbf{CoCr_{0.04}Gd_xFe_{1.96-x}O_4}$ **ferrites** by using co-precipitation technique

2. Materials and methods

2.1. Samples preparation and equipment

A series of Gd^{3+} substituted Co-Cr ferrite $\mathbf{CoCr_{0.04}Gd_xFe_{1.96-x}O_4}$ was prepared by using these chemicals with regent grade $Co(NO_3)_2.6H_2O$, $Cr(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, and $Gd(NO_3)_3.6H_2O$. Transparent solution of these compounds was prepared by using the deionized water and continue magnetic stirrer of this solution about 1 h, after this NaOH solution was added drop wise to maintain the pH value 11. The obtained precipitates were put into pre heated water bath for digestion and set at 90°C for 1 h. After completion of digestion process, precipitates was washed three to four times with deionized water and confirm all impurities to be removed. Final product was dried by using electric oven at 95°C for 24 h, then dried powder grinded to homogenize by mortar and pestle about 1 h. The XRD method is considered for microstructure studies. Accordingly, the diffractometer (Xpert Pro PANalytical) with Cu-Kα radiation (λ=1.54056 Å) at 30 mA and 40 kV was applied for each sample characterization. The XRD data was recorded at scanning speed 0.05° /s with an angle of 2θ at 20-70°. Morphology of the synthesized samples were studied by using scanning electron microscope (SEM) of model JSM-6490 JEOL. For the confirmation of functional group and structure of the synthesized material, IR Spectra was scanned in the range 400-4000 cm^{-1} by using Jasco-310 spectrometer. To record the magnetic properties the vibrating sample magnetometer (VSM) was of lake-shore735. The XRD data were used to calculate different physical parameters with the help of these relations [22-23].

$$a = \frac{\lambda}{2Sin\theta}\sqrt{h^2 + k^2 + l^2} \tag{1}$$

$$V_{cell} = a^3 \tag{2}$$

$$D = \frac{k\,\lambda}{B_{(hkl)}\cos\theta} \tag{3}$$

$$\rho_{X-ray} = \frac{Z\,M}{N_A\,V} \tag{4}$$

In ferrites sample, the lattice constant 'a' (Angstrom), the Miller indices represented by (hkl), unit cell volume, Z be a symbol of eight molecules per unit cell, Avogadro's constant (6.02×10^{23} g/mol) is represented by N_A and the molecular weight is written by M. The estimation of crystallite size (D) is in nm, λ is for X-ray source wavelength and θ is Bragg's angle in the Scherer's equation.

3. Results and discussion

3.1 Structural Analysis

Fig 1 Shows Gd Substituted Co-Cr ferrite synthesized by co-precipitation method sintered at 850°C for 8 h, all the prepared samples shows the secondary phase, diffraction pattern confirm cubic structure with space group Fd3m. The Jade 5 software was used to analyze XRD pattern. It is observed that the intensity of the peaks shows the crystallinity of the sample and on broadening of peaks reflect the crystallite size which is measured by using Debye-Scherers Eq.3. The average crystallite size was found in the range (21-106 nm). The Maximum value of crystallite size was found 106 nm, and behavior of the crystal size increased with the increasing of the content. The secondary phase of the samples observed due to high reactivity of rear earth Gd^{3+} ions with Fe^{3+} ions. The lattice parameters of the prepared samples are determined by the Eq.1 and obtained lattice constant values was listed in the Table 1, it is observed that the lattice constant values lies in range 8.3169-8.3668 Å. The different values of the lattice constant observed due to different ionic radii of the substituent such as the Gd^{3+} = 0.938 Å, Fe^{3+}= 0.67Å. As observed in the presented work, the Gd^{3+}=0.938 Å of the ionic radius of the substituted ions is greater than the Fe^{3+}= 0.67Å. Maximum lattice constant found 8.3668 Å at x= 0.12. It is clearly seen in the Table 1, the lattice constant value observed increased with the increasing the Gd^{3+} concentration. Moreover, X-ray density is calculated by the Eq.4 and the obtained value lie in the range 5.31 -5.41 g/cm^3. The variation in the X-ray density due to different molar mass if the constituent such as Gd^{3+} =157.25 g/mol in comparison with the Fe^{3+}= 55.84 g/mol.

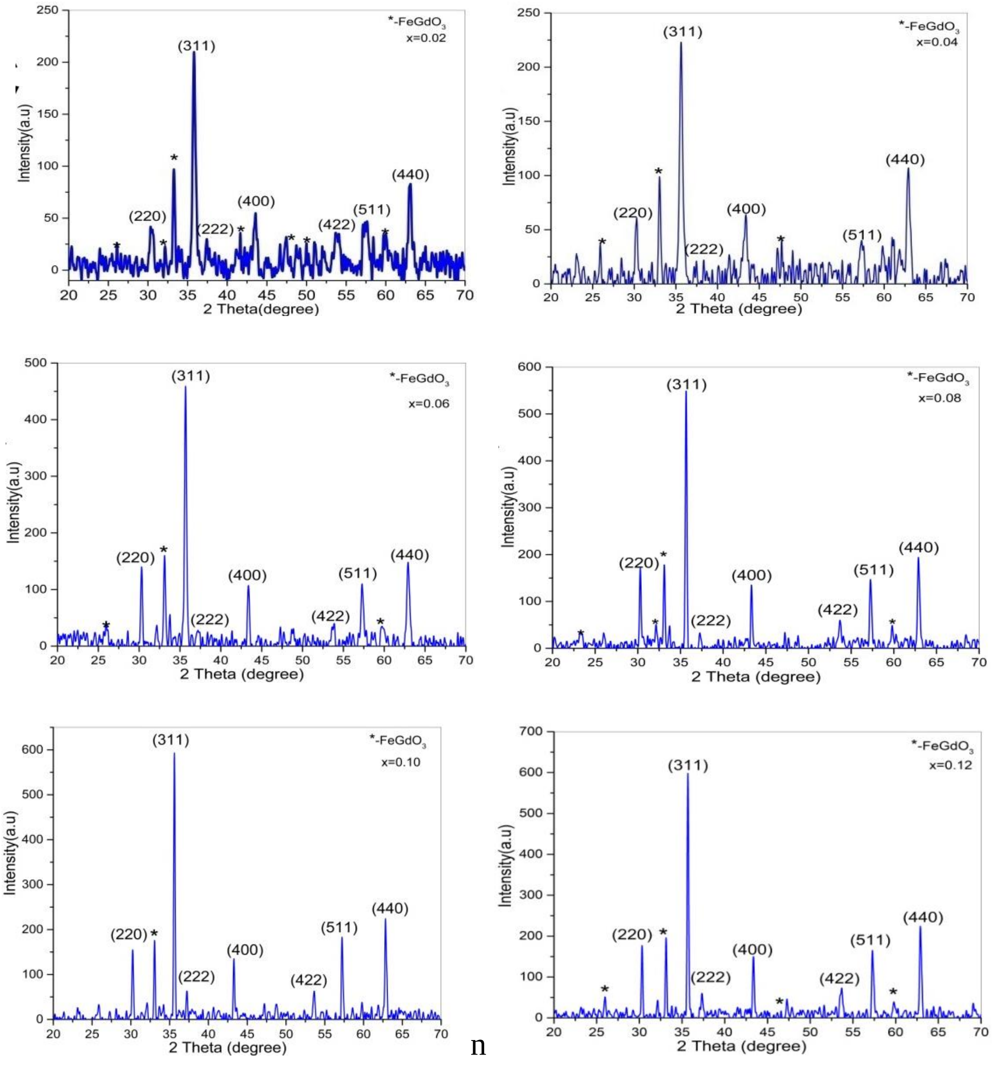


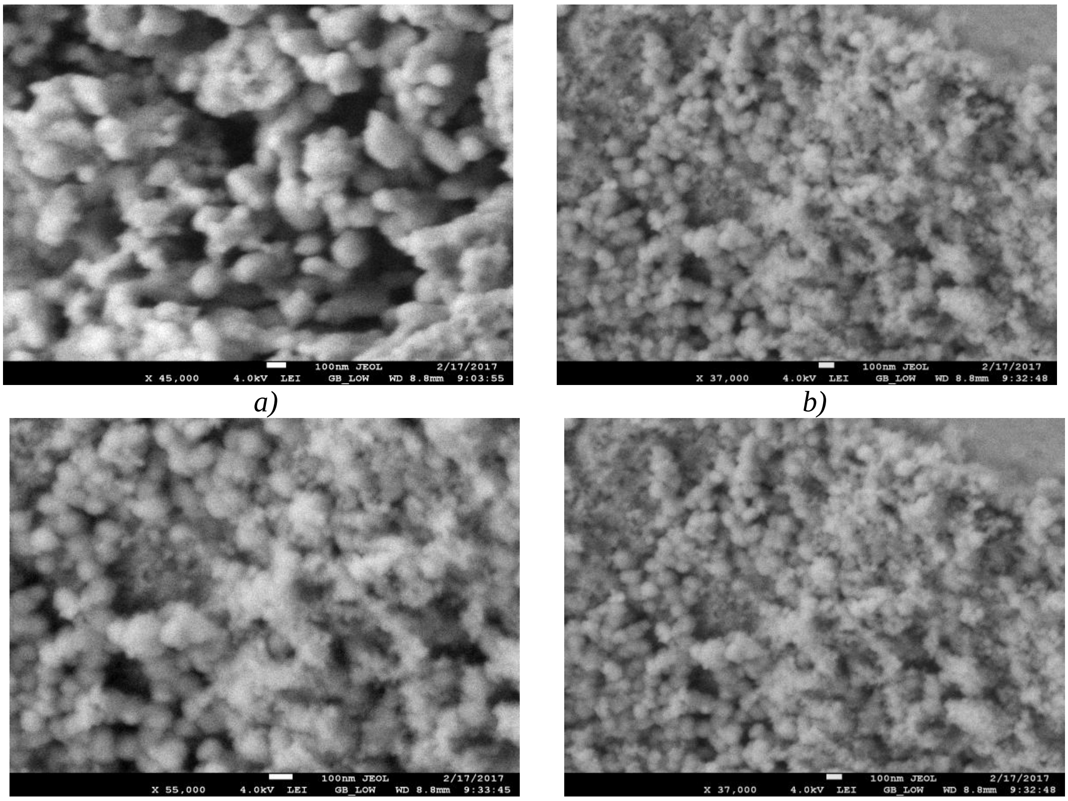
Fig. 1. XRD Patterns of $CoCr_{0.04}Gd_xFe_{1.96-x}O4$ $(0.02 \le x \le 0.12)$ ferrites.

Table 1.Lattice constant, Crystallite size (nm), Unit cell volume and X-ray density $CoCr_{0.04}Gd_xFe_{1.96-x}O_4$ ferrites

Composition	Lattice Constant (Å)	Crystallite Size (nm)	Unit Cell Volume (Å^3)	X-ray density g/cm^3
$CoCr_{0.04}Fe_{1.96}O_4$	8.3717	67	586.7	5.3
$CoCr_{0.04}Gd_{0.02}Fe_{1.94}O_4$	8.3169	21	575.3	5.4
$CoCr_{0.04}Gd_{0.04}Fe_{1.92}O_4$	8.3433	26	580.8	5.3
$CoCr_{0.04}Gd_{0.06}Fe_{1.90}O_4$	8.3467	47	581.5	5.3
$CoCr_{0.04}Gd_{0.08}Fe_{1.88}O_4$	8.3539	47	583.1	5.3
$CoCr_{0.04}Gd_{0.10}Fe_{1.86}O_4$	8.3622	106	584.7	5.3
$CoCr_{0.04}Gd_{0.12}Fe_{1.84}O_4$	8.3668	84	585.7	5.4

3.2. Morphology analysis

Fig.2 (a-d) shows the samples of SEM micrographs. The distribution of the grain size was observed in homogeneous; the shape of the resulting samples observed spherical and the grain size is estimated by the line intercept method, it is also observed that the material of the prepared samples have porous nature [24], it is observed that few agglomeration due to long sintering temperature as well as weak Van-der Waals forces [25-26].



a) *b)*

c) *d)*

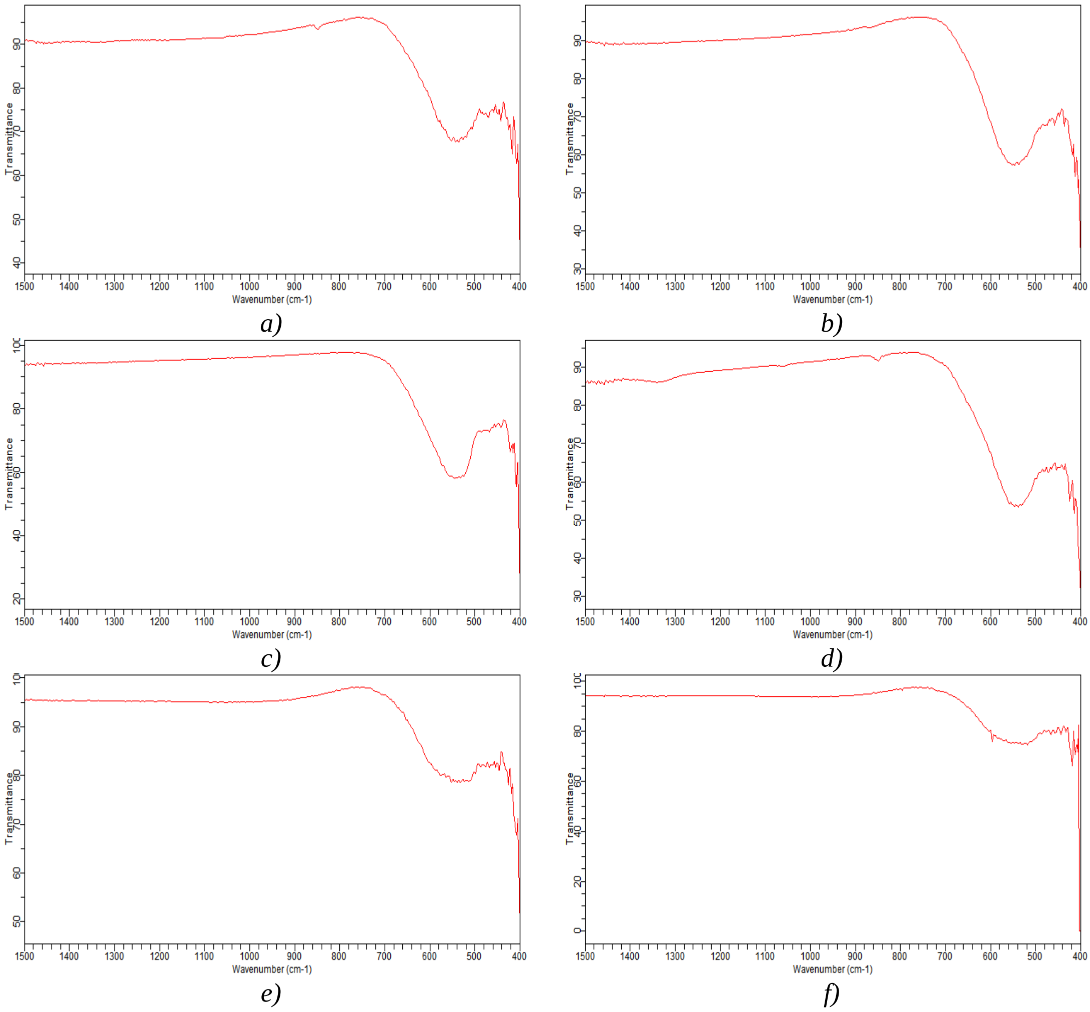
Fig. 2 Micrographs of Co-$Cr_{0.04}Gd_xFe_{1.96-x}O_4$ ferrites (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.06$ and (d) $x = 0.08$.

3.3. FTIR spectroscopy

Fig. 3 (a-f) shows the IR spectra of Gd^{3+}substituted Co-Cr- ferrites samples which have been recorded of 400-4000 cm^{-1}.The common characteristics features of ferrite spectra show absorption peaks at below 600 cm^{-1} that represent metal oxygen (M-O) vibration mode [27]. In IR results, there are two prominent observed peaks at tetrahedral sites. The high frequency peaks appear in the frequency range 600-500 cm^{-1} due to metal-oxygen stretching. The low frequency peaks in the range 430-385 cm^{-1} are corresponding to the appearances of the octahedral sites.

3.4. Magnetic properties

In the present study, Fig.4 exhibits MH loops of synthesized samples at room temperature. The results show soft nature of material. The saturation magnetization lies in the range 63.5 -53.8 emu/g while coercivity 798-763 Oe. Generally, magnetic properties depend on the synthesizing routes along with some specific conditions such as their particle size and distributions of cations on different sites. High saturation magnetization of pure bulk sample cobalt ferrites has been reported [28]. In the present work, the substitution Gd^{3+}ions played a vital role in spin canting at the surface of nanoparticles and moderates overall magnetization due to strong spin-orbit coupling and promote the asymmetrical structure and observed strong interaction at lattice sites. Another reason for the improvement in coercivity can be attributed due to pinning effect of a domain wall and to the microstructure [29].



a) b) c) d) e) f)

Fig.3. FITR pattern $CoCr_{0.04}Gd_xFe_{1.96-x}O_4$ ferrites (a) x = 0.00, (b) x = 0.02, (c) x = 0.04, (d) x = 0.06, (e) x = 0.08 and (f) x = 0.1.

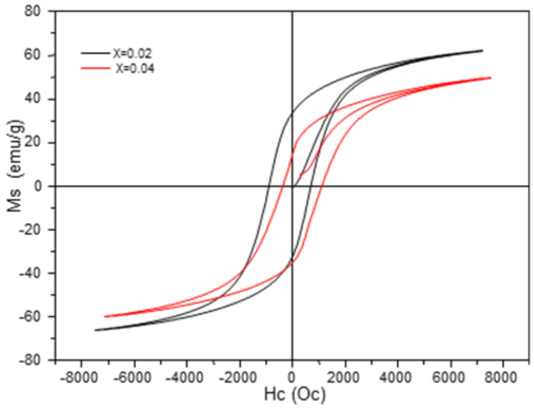


Fig.4. M-H loops of Gd^{3+} substituted Co-Cr ferrites at an applied field of 8kOe.

4. Conclusions

The spinel ferrites, Gd^{3+} substituted $CoCr_{0.04}Gd_xFe_{1.96-x}O_4$ have been synthesized through co-precipitation technique. The structure stability was analyzed by calculating different parameters from XRD data. The average crystallite size determined in the range (21-106 nm) by using the Scherrer's formula, the grain size results were consistent obtained by scanning electron microscopic.The intrinsic magnetic properties revealed that the behavior of saturation magnetization, anisotropy constant decrease by increase Gd^{3+} concentration, also observed low coercivity which is below 1KOe.

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References

[1] A. Goldman, Modern Ferrite Technology, second ed., Springer, New York, 2006.
[2] R. Valenzuela, Magnetic Ceramics, Cambridge University Press, 1994.
[3] J. Smit, Ferrites, Wiley, New York, 1959.
[4] L. Kumar, M. Kar, IEEETrans. Magn. **47**, 3645 (2011).
[5] E.C. Snelling, Soft Ferrites: Properties and Applications, second ed.,Butterworths, London, UK, 1988.
[6] J.L. Dormann, D. Fiorani, Magnetic Properties of Fine Particles, North-Holland, Amsterdam, 1992.
[7] L. Kumar, M. Kar, J. Magn. Magn. Mater. **323**, 2042 (2011).
[8] B.G. Toksha, S.E. Shirsath, M.L. Mane, S.M. Pantage, S.S. Jadjav, K.M. Jadhav,J. Phys. Chem. C **115**,20905 (2011).
[9] M. Anis-ur-Rehman, A. Abdullah, M. Ansari, Zeb-un-Nisa, M.S. Awan, WorldAcad. Sci. Eng. Technol. **76**, (2011) 679.
[10] M. Han, C.R. Vestal, Z.J. Zhang, J. Phys. Chem. B **108**,583 (2004).
[11] S.T. Alone, Sagar E. Shirsath, R.H. Kadam, K.M. Jadhav, J. Alloys Compd. **509**, 5055 (2011).
[12] B.D. Culity, Introduction to Magnetic Materials, Addision-Wesely, 1972.
[13] N. Rezlescu, E. Rezlescu, C. Pasnicu, M.L. Craus, J. Phys.: Condens Matter **6**, 5707 (1994).
[14] K.K. Bharathi, J.A. Chelvane, G. Markandeyulu,J. Magn. Magn. Mater. **321**, 3677 (2009).

[15] E.E. Sileo, R. Rotelo, S.E. Jacobo, Physica B **320**, 257 (2002).
[16] S.E. Jacobo, W.G. Fano, A.C. Razzitte, Physica B **320**, 261 (2002).
[17] E.E. Sileo, S.E. Jacobo, Physica B **354**, 241 (2004).
[18] W.C. Kim, S.J. Kim, J.C. Sur, C.S.Kim, J.Magn.Magn. Mater.**242**, 197 (2002).
[19]L.B. Tahar, M. Artus, S. Ammar, L.S. Smiri, F. Herbst, M.J. Vaulay, V.Richard, J.M.Greneche, F.Villian, F. Fievet, J. Magn. Magn. Mater. **320**, 3242 (2008).
[20] P. Kumar, S.K.Sharma, M. Knobel, M.Singh,J. Alloy Compd.**508**, 115 (2010).
[21] S. Burianova, J.P. Vejpravova, P. Holec, J. Plocek, D. Niznansky, J. Appl. Phys. **110**, 073902 (2011).
[22] M. Azam, M. A. Chaudhry, N. Amin, M. I. Arshad, M. U. Islam,S. Nosheen, M. Ahmad, H. Anwar, M. Waseem ,G. Mustafa, Digest Journal of Nanomaterials and Biostructures Vol. 11, No. 3, July-September 2016, p. 953-962.
[23] I. Ali, N. Amin, A. Rehman, M. Akhtar, M. Fatima, K.Mahmood, A. Ali, G. Mustafa, M. S. Hasan, A. Bibi, M. Z. Iqbal, F. Iqbal, A. Aslam, K. Mehmood, Z. Latif, K. Hussain,Z. H. Nawaz, S. Sharif, M. Jilani, U. Danish, I. Yaseen, A.Dilbar, N. Tahir, M. Bilal, A. Amin, M. I. Arshad, Digest Journal of Nanomaterials and Biostructures Vol. 15, No. 1, January-March 2020, p. 67-73
[24] G.Mustafa, M. U. Islam, H. Anwar, M. Asif, M. I. Arshad, N. Sabar,M. R. Ahmad, G. urtaza, M. A. Bashart, A. Ali, M. R. Saleem,H. Akhtar, Journal of Ovonic Research Vol. 14, No. 4, July-August 2018, p. 261-267
[25] J. Feng, Li-Qin Guo, X. Xu, S.Y. Qi, Mi-Lin Zhang, PhysicaB: Condensed Matter **394**, 100 (2007).
[26] J. Wang, C. Zeng, Z.M. Peng, Q.W. Chen, Condensed Matter**349**, 124 (2004).
[27] T. George, A. T. Sunny, T. Varghese, IOP Conference Series: Materials Science and Engineering **73**,012050 (2015).
[28] M.A. John Jacob, Khadar, J. Appl. Phys. **107**, 114310 (2010).
[29] F.X. Cheng, J.T. Jia, Z.G. Xu, B. Zhou, C.S. Liao, C.H. Yan, L.Y. Chen, H.B. Zhao, Journal of applied physics **86**, 2727 (1999).