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Research Article

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Microwave sintering of Ni-Co doped barium strontium hexaferrite synthesized via sol-gel method

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ABSTRACT

Microwave energy is highly efficient for heating and processing ceramic materials. Microwave sintering of doped barium strontium ceramics led to higher densification and the fine microstructure and improved magnetic properties. Effects of the substituted amount of Ni^{2+} *and* Co^{2+} *on structure and magnetic properties of* $Ba_{0.5}Sr_{0.5}Fe_{12-x}Ni_xCo_xO_{19}$ *compounds have been systematically investigated by X-ray diffraction (XRD), high resolution scanning microscope (HR-SEM) and vibrating sample magnetometer (VSM). In our results, the suitable amount of* Ni^{2+}–Co^{2+} *substitution slight decreased saturation magnetization. For Substitution of Ni-Co content of* $x \leq 0.4$ *the saturation magnetization varied from a range of 60.58 to 63.59* Am^2/kg *and while coercivity decreased from 805.37 to 280.28 Gauss respectively.*

Keywords: Ceramics; X-ray diffraction; microstructure; magnetic properties

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INTRODUCTION

Hexagonal ferrites, the prototype of which is represented by $MeFe_{12}O_{19}$ (M= Ba, Sr or Pb) belongs to a class of ferrimagnetic oxides. They have interesting applications not only as microwave devices but also as traditional permanent magnets, potential magneto optical devices,

High density magnetic recording media and compacts (submicron powders) for high-frequency devices. The following are considered to be important: 1) differences in samples resulting either from different compositions, different synthesis conditions or both and 2) differences in methods of sintering. Thus, cobalt doping in particular has been the subject of many such investigations [1–3]. The magnetic properties of a hexagonal ferrite depend on the intrinsic magnetic properties of the M-type phase. The M-type ferrite crystallizes in a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites. The 24 Fe^{3+} atoms are distributed over five distinct sites: three octahedral sites (12k, 2a and 4f2), one tetrahedral (4f1) site and one bipyramidal site (2b). The magnetic structure given by the Gorter model is ferromagnetic with five different sub lattices, three parallel (12k, 2a and 2b) and two anti parallel (4f1 and 4f2) which are coupled by super exchange interactions through the O^{2+} ions [4]. Several cation combinations such as La^{3+}–Co^{2+}, Gd^{3+}–Co^{2+}, Nb^{4+}–Zn^{2+}, Ir^{4+}–Zn^{2+}, Sm^{3+}–Co^{2+}, Ti^{4+}–Mn^{2+}, Ti^{4+}–Ni^{2+} and Ti^{4+}–Co^{2+} have been attempted by several researchers [5–10]. The reason for Ni^{2+} substitution is an attempt to increase the saturation magnetization as guided by references such as [11, 12]. Since coercivity is dependent on the anisotropy constant, k1. The reason for Co^{2+} substitution is simply our attempt to control the coercivity to achieve values appropriate for recording materials [13]. We Note that the k1 of Co^{2+} containing ferrite is generally positive and much higher than most of the negative k1 of the other ferrites, for example K1 of $CoFe_2O_4$ is +2000 ergs/cm^3. Hence positive k1 and negative k1 values partially cancel each other to give the desired values. As regards, the required charge neutrality it would occur by the system adjusting itself, involving formation of vacancies [14]. In order to increase saturation magnetization M_s and decrease intrinsic coercivity (H_c) of anisotropic Sr ferrite magnets have been carried out concerning cationic substitution [15].

Microwave heating and sintering are fundamentally different from conventional sintering. Microwave heating involves conversion of electromagnetic energy into thermal energy. The advantages of this mechanism are rapid and highly efficient heating, time and energy saving, and a high temperature reached short time. Microwave heating has been widely used as an alternative to conventional resistance heating and gas fired heating to sinter ceramic materials for the advantage of very high efficiencies, rapid heating, significant reduction in manufacturing costs due to energy saving and shorter processing times [16-22]. In the present study, Ni-Co substituted barium Strontium hexaferrites were prepared by sol-gel method. The influence of Ni-Co ions substitution on the structure and magnetic properties was discussed.

EXPERIMENTAL SECTION

The starting reagents $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and D-Fructose were of analytical grade. Metal nitrates and D-Fructose in the molar ratio of 1:1 were dissolved in distilled water to form aqueous solutions using magnetic stirrer. The resultant solution was continuous stirring and heated up to 80°C to get a sticky liquid gel. The gel was heated in hot air oven for two days to get precursor. The calcined powder was uniaxially pressed into pellets using a hydraulic press and polyvinyl alcohol (PVA) as a binder. Microwave sintering was completed by using a VBCC 2-magnetron microwave heating furnace in which the compacted samples were sintered at 1150°C at a rate of 50°C/min and soaked for 10 min followed by fast cooling to room temperature at a rate of 20°C/min. The sintering temperature was measured with a pyrometer and it was standardized with reference to a thermocouple and the emissivity was measured to be between 0.90 and 0.98 for the different samples of strontium hexaferrite. The microwave output power level was about 2.2KW with 2.45GHz frequency and it was controlled by a Eurotherm PID controller.

The pressed pellets were for 10 minutes. The Powder X-ray diffraction [23] patterns were collected on a (PANalytical X'pert pro) CuKα radiation at 45kV and 40 mA (λ = 0.15406 nm) in a wide range of 2θ (20°<2θ<80°). The microstructure [24] observation of the specimens was performed in FEI Quanta FEG 200-High Resolution Scanning Electron Microscope (HR-SEM). Hysteresis loops were measured at room temperature using by Vibrating Sample Magnetometer (Lakeshore 7304).

RESULTS AND DISCUSSION

Structural Analysis

The XRD patterns of microwave sintered $Ba_{0.5}Sr_{0.5}Fe_{12-2x}Ni_xCo_xO_{19}$ samples with x = 0.0–0.8 mol% are shown in Fig. 1. Clearly, all of these possess a magnetoplumbite single phase (JCPDS-51-1879). The main peaks are matched with barium strontium hexaferrite and extra secondary Alpha-Fe_2O_3 phase is observed around 33~34 deg. All diffraction peaks of the Ni-Co substituted samples (0.2~0.8 mol%) are shifted toward a higher angle in comparison with these of non-doped sample (0 mol%). In general the shift toword higher 2 theta values indicate a slight reduction in the d-spacing values. This is to be expected since Fe^{3+} ionic radius differs slightly from Ni^{2+} and Co^{2+} ionic radii and slight lattice distortion could occur due to vacancy formation for charge-neutrality adjustment mentioned before.

The lattice parameters 'a' and 'c' show that the values of 'a' remain almost constant but the values of 'c' increase by increasing the Ni–Cr content, x, as shown in Table 1. It indicates that change of easy magnetized c-axis is larger than a-axis with Ni^{4+} and Co^{2+} ions substitution. This is due to the fact that the ionic radii of Ni^{2+} (0.69A°) and Co^{4+} (0.745A°) are larger than that of Fe^{3+} (0.645A°) [25]. The change in lattice constants also varies with the distance between magnetic ions resulting in change of exchange interaction and thus magnetic properties are altered with substitution [26].

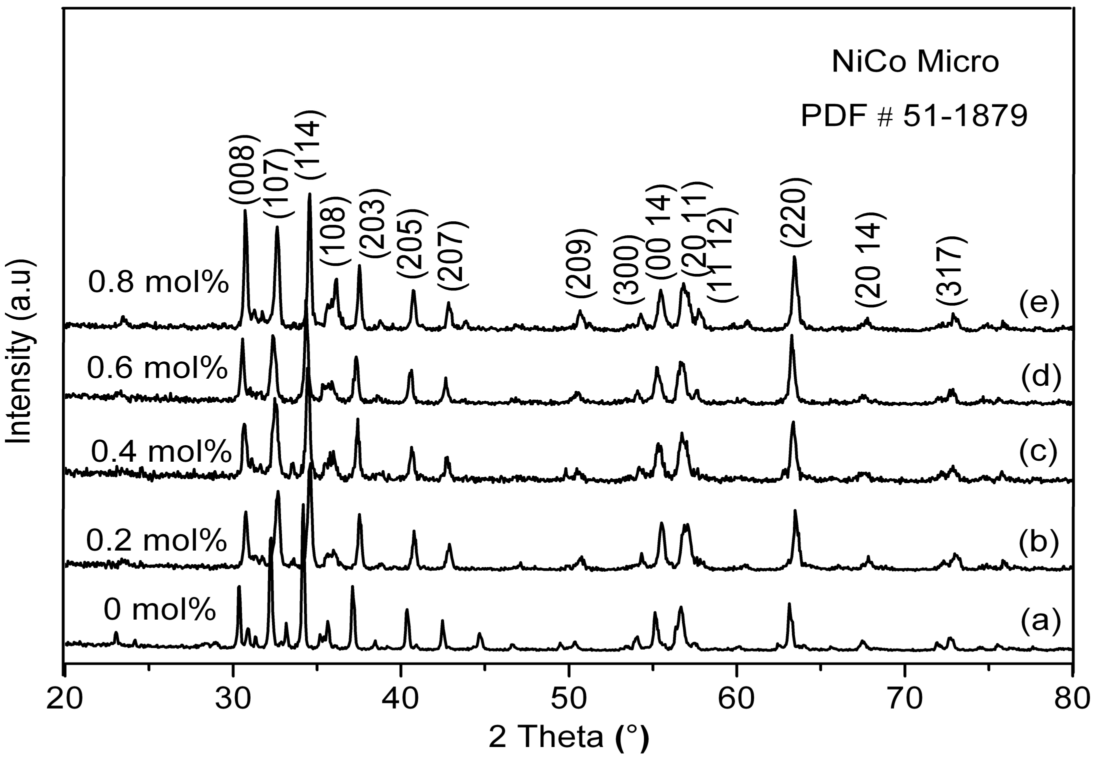

Fig. 1 pattern of microwave sintered $Ba_{0.5}Sr_{0.5}Fe_{12-2x}Ni_xCo_xO_{19}$ with different doping concentration

Table 1 Variation of lattice parameters with Ni-Co substitution

S. No	Hexaferrites (1150C)	Lattice Parameters a=b	Lattice Parameters c	System
1	$Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$	5.886	23.13	
2	$Ba_{0.5}Sr_{0.5}Fe_{11.6}Ni_{0.2}Co_{0.2}O_{19}$	5.891	23.14	
3	$Ba_{0.5}Sr_{0.5}Fe_{11.2}Ni_{0.4}Co_{0.4}O_{19}$	5.892	23.16	Hexagonal
4	$Ba_{0.5}Sr_{0.5}Fe_{10.8}Ni_{0.6}Co_{0.6}O_{19}$	5.897	23.19	
5	$Ba_{0.5}Sr_{0.5}Fe_{10.4}Ni_{0.8}Co_{0.8}O_{19}$	5.90	23.21	

Surface Morphological Analysis

The FE-SEM images of microwave sintered of Ni-Co substituted samples (x = 0.2, and 0.8 mol%) are presented in Fig. 2. The sintered samples exhibit hexagonal platelets structure and grain sizes increased with increasing substitution level to 0.8 mol%. Addition of Ni-Co level is increased to 0.8 mol% increases the grain size and also forming dense microstructure. This suggests that Ni-Co substitutions encourage the grain growth. Energy dispersive X-ray (EDX) analysis of $Ba_{0.5}Sr_{0.5}Fe_{12-x}Ni_xCo_xO_{19}$ (x = 0.8 mol%) sample shows the evidence for the presence of Zn-Nb in Fig. 2b (inset).

Magnetic Analysis

Fig. 3 clearly shows that the value of saturation magnetization (M_s) first increases for lower a substitution (0.2%) and then decreases slightly on higher Ni–Co substitution. This variation in the value of magnetization with substitution (Ni-Co) is related to the distribution of Ni–Co ions on the five Fe sites. In M-type hexagonal ferrite, Fe^{3+} ions occupy seven octahedral sites 12k and 2a, trigonal site 2b with spins in one direction, two octahedral sites 4fI and two tetrahedral sites 4fII with spins in opposite direction. Magnetization variation is related to distribution of substituents on five crystallographic sites, i.e. 12k–2a–2b (spin-up) and 4fI–4fII (spin-down). The doping of Fe3+ ions in spin up state reduces magnetization and it increases with substitution on spin-down state [27].

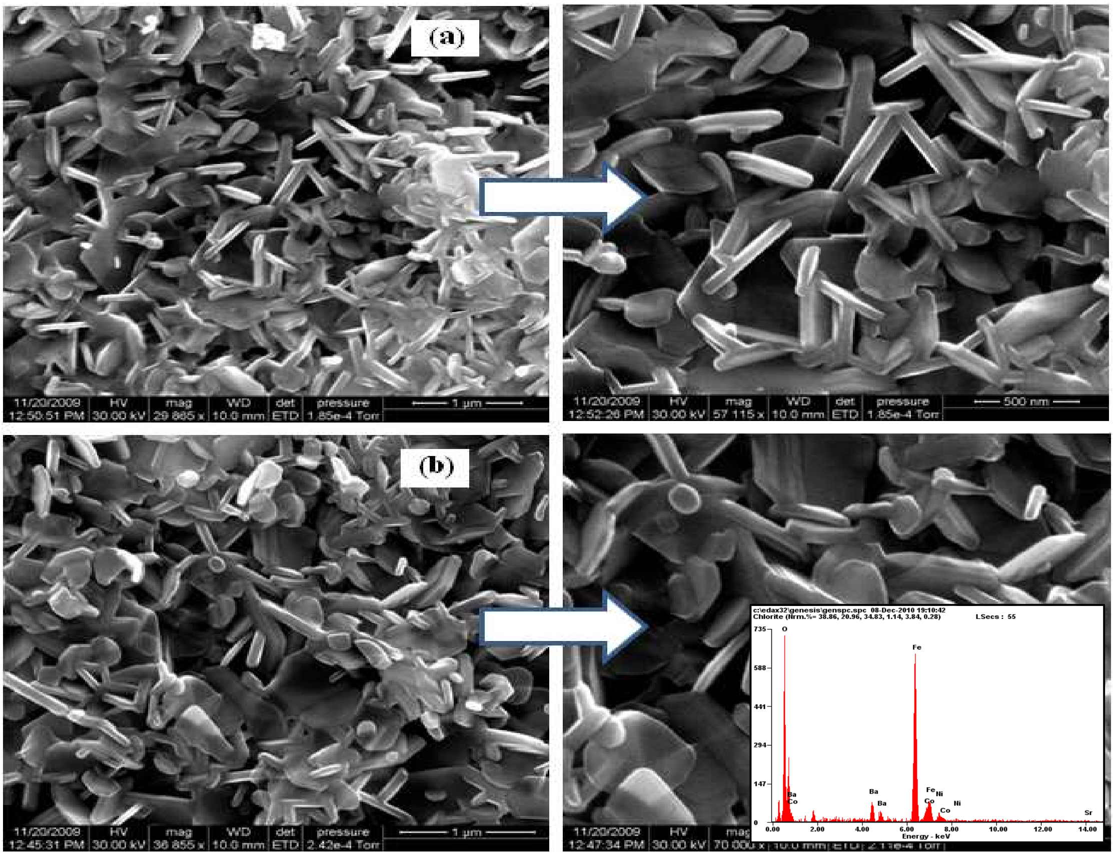

Fig. 2 FE-SEM image of $Ba_{0.5}Sr_{0.5}Fe_{12-2x}Ni_xCo_xO_{19}$ (x = 0.2, 0.8 mol%) microwave sintered at 1150°C for 10 minutes

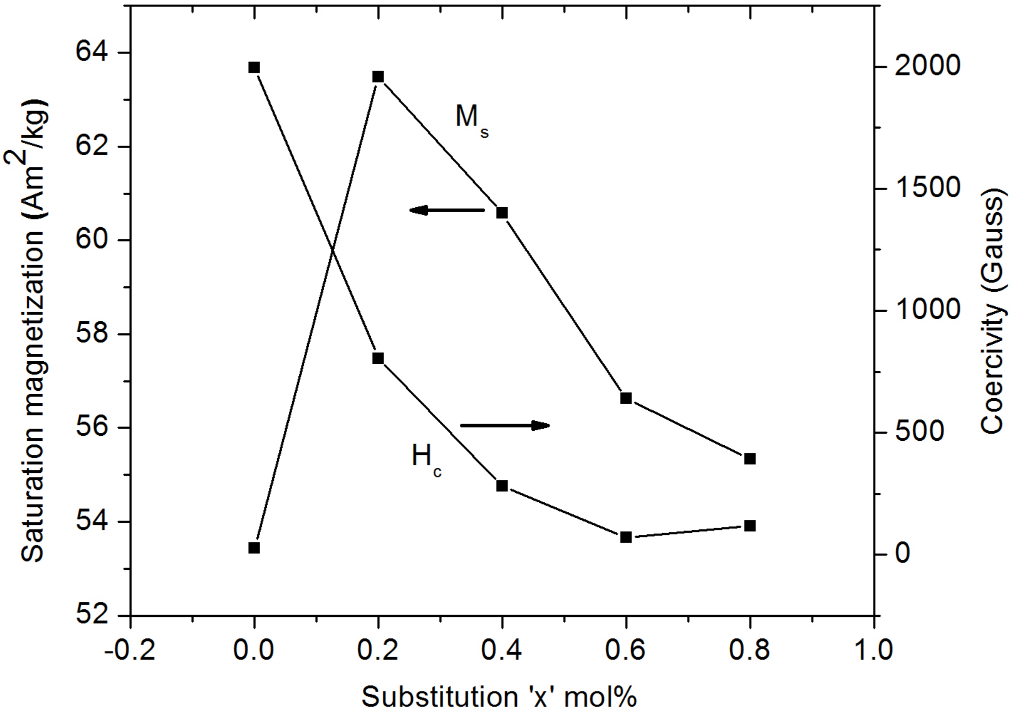

Fig. 3 The specific saturation magnetization (M_s) and the coercivity (H_c) of microwave sintered $Ba_{0.5}Sr_{0.5}Fe_{12-2x}Ni_xCo_xO_{19}$ as a function of substitution content 'x' mol% at room temperature

Teh et al., reported [28] Co^{2+} has a preference to occupy tetrahedral sites preferentially (4f1) and Belous et al. also reported [29] larger Co^{2+} ions occupy the larger octahedral 2a position. The gradual decrease of saturation magnetization was explained on the Kikuchi et al and Rane et al reports [30, 31]. This change mainly attributed to the decrease in molar magnetic moment caused by doping of Co^{2+} (~4 µB) for Fe^{3+} (~5 µB). However, this decrease of Ms is larger than the expected degree according to the decrease in molar magnetic moment. Increase of M_s with lower substitution (0.2%) is due to the Ni^{2+} ions replacing Fe^{3+} ions at the 4f2 site for x ~ 0.1, and at the 12k site for larger values of doping [31]. The steep fall in coercivity translates hard ferrite to soft ferrite. The decrease of coercivity may be one of the reason, related to the increase of grain size conformed from HR-SEM results. Similar trend has also been observed by Charanjeet Singh et al., in Co-Ru substituted hexagonal ferrite [32].

CONCLUSION

Single-phase nominal composition of $Sr_{0.5}Ba_{0.5}Fe_{12-2x}Ni_xCo_xO_{19}$ (x = 0.2, 0.4, 0.6, 0.8mol %) were successfully synthesized by sol-gel method. XRD data of the synthesized samples point to the formation of single magneto plumbite phase structures. The variation in magnetic parameters is described in terms of preferential site occupancy of the substituted cations. The lattice parameters and magnetic properties are found to be affected, hense controllable, by doping with nickel and cobalt. The transition from hard phase to soft phase results in reduction of hysteresis loss area per cycle. The microwave method is found to be simple, fast and quite general for the preparation of technologically important electro ceramics. Fine microstructure and better densification are the main advantages of the microwave sintering in this study.

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REFERENCES

[1] R Carey; PA Gago-Sandval; DM Newman; BWJ. Thomas. *J. Appl. Phys*., **1991**, 75, 6789-6791.
[2] X Batlle; X Obradors; J Rodriguez-Carvajal; M Pernet; MV Cabanas; M Vallet. *J. Appl. Phys*., **1991**, 70, 1614-6123.
[3] X Batlle; M Garcia del Muro; J Tejada; H Pfeiffer; P Gornert; E Sinn. *J. Appl. Phys*., **1993**, 74, 3333-3340.
[4] JF Wang; CB Ponton; IR Harris. *J. Magn. Magn. Mater*., **2006**, 298, 122–131.
[5] QQ Fang; H Cheng; K Huang; J Wang; R Li; Y Jiao. *J. Magn. Magn. Mater.*, **2005**, 294, 281–286.
[6] N Shirtcliffe; S Thompson; ESO Keefe; S Appleton; CC Perry. *Mater. Res. Bull*., **2007**, 42, 281–287.
[7] S Thompson; N Shirtcliffe; ESO Keefe; S Appleton; CC Perry. J. *Magn. Magn. Mater*., **2005**, 292, 100–107.
[8] QQ Fang; H Bao; D Fang; J Wang. *J. Appl. Phys*., **2004**, 95, 6360–6363.
[9] H Takaoka; H Suito; *J. Cryst. Growth*., **1994**, 137, 493–498.
[10] GK Thompson; BJ Evans. *J. Appl. Phys*., **1994**, 75, 6643–6645.
[11] M J Iqbal; M N Ashiq; P Hernandez-Gomez; J M Munoz. *Scripta Materialia*., **2007**, 57, 1093–1096.
[12] MV Rane; D Bahadur; AK Nigam; CM Srivastava. *J. Magn. Magn. Mater.,* **1999**, 192, 288.
[13] K K Mallick; P Shepherd; R J Green*; J. Magn. Magn. Mater*., **2007**, 312, 418.
[14] AJ Moulson; JM Herbert. Electroceramics-Materials.properties.applications, Chapman & Hall, 2-6 Boundry Row, London SEI 8HN, Page no 23.
[15] Y Ogata; Y Kubota; T Takami; M Tokunaga; T Shinohara. *IEEE Trans. Magn*., **1999**, 35, 3334-3336.
[16] NJP Subhashini; J Amanaganti; L Boddu; P Acharya Nagarjuna., *Journal of Chemical and Pharmaceutical Research.,* **2013**, 5(1), 140-147.
[17] Fatih Islamoglu, Emre Mentese, Musa Ozil, Emine Akyuz Turumtay, Bahittin Kahveci, *Journal of Chemical and Pharmaceutical Research*, **2013**, 5(1):91-98.
[18] WH Sutton. *Ceramic Bulletin*., **1989**, 68, 376-386.
[19] Y Cheng; Y Wu; W Zhu; J Chen; X Qiao; *Journal of Materials Science Letters*., **1999**, 18, 1933-1935.
[20] IN. Lin, WC Lee; KS Liu; HF Cheng, MW Wu. *J. Europ. Ceramic Soc*., **2001**, 21, 2085–2088.
[21] M Penneerselvam; A Agrawal; KJ Rao. *Mat. Sci. Eng. A.,* **2003**, 356, 267–273.
[22] CY Tsay; KS Liu; IN Lin. *J. Europ. Ceram. Soc*., **2001**, 21, 1937-1940.
[23] D Santhosh Shanthakumar; BN Sivasankar. *Journal of Chemical and Pharmaceutical Research*., **2013**, 5(12), 1017-1023.
[24] S. S. Rahangdale. *Journal of Chemical and Pharmaceutical Research*., **2013**, 5(1):45-48.

[25] TM. Meaz; CB Koch. *Hyp. Interact*., **2004**, 156/157, 341-346.
[26] C Singh; S Bindra Narang; IS Hudiara; Y Bai. *Mater. Res. Bull*., **2008**, 43, 176.
[27] C Singh; S Bindra-Narang; IS Hudiaraa; Y Bai. *Journal of Alloys and Compounds*., **2008**, 464, 429–433.
[28] G B. Teh; N Saravanan; DA Jefferson. *Mater. Chem. Phys*., **2007**, 105, 253-259.
[29] AG Belous, OI Vyunov, EV Pashkova, VP Ivanitskii; ON Gavrilenko. *J. Phys. Chem. B.,* **2006**, 110, 26477-26481.
[30] T Kikuchi; T Nakamura; T Yamasaki; M Nakanishi; T Fujii; J Takada; Y Ikeda. *J. Magn. Magn. Mater*., **2010**, 322, 2381–2385.
[31] MV Rane; D Bahadur; AK Nigam; CM Srivastava. *J. Magn. Magn. Mater*., **1999**, 192, 288-296.
[32] C Singh; S Bindra Narang; IS Hudiara, Y Bai. *Mater. Res. Bull*., **2008**, 43, 176-184.