www.amlett.org, www.amlett.com, DOI: 10.5185/amlett.2013.icnano.111

Synthesis and characterization of $Fe_4[Co(CN)_6]_3.16H_2O/SiO_2$ nano-composites by coprecipitation method

Sunil Rohilla[1,*], P. Aghamkar[2], Shyam Sunder[2], Atul Kumar[2] and Bhajan Lal[3]

[1]*Materials Science Lab, Department of Applied Physics, Guru Jambheshwar Univ. of Sc. & Tech., Hisar 125001 and TIT & S Engg. College, Birla Coloney, Bhiwani 127021, India*
[2]*Materials Science Lab, Department of Physics, Chaudhary Devi Lal Univ., Sirsa 125055, India*
[3]*Department of Applied Science, Govt. Polytechnic for Women, Sirsa 125055, India*

[*]Corresponding author. Tel: (+91) 94164-34763, E-mail: rohillasunil2003@yahoo.co.in

ABSTRACT

Nano-dimensional powder of iron cobalt cyanide hydrate in silica matrix (member of Prussian-blue family) was obtained using ferric chloride, cobalt chloride, potassium cyanide and silica in their dilute solution through coprecipitation method. The crystal structures and surface morphology of nanoparticles were characterized by the powder X-Ray diffraction (XRD) and transmission electron microscopy (TEM). The formation of compound $Fe_4\ [Co(CN)_6]_3.16H_2O$ was revealed by Fourier transform infrared (FTIR) spectroscopy. The magnetic properties of prepared samples were measured at room temperature using a Vibrating sample magnetometer (VSM). Effect of the thermal annealing on the phase decomposition and phase evolution of prepared samples for different temperature and time duration has been discussed. The results showed that the structure, phase and shape of the nanocrystallite are strongly influenced by the sintering temperature and time period. Results also showed that direct phase transition from $Fe_4\ [Co\ (CN)_6]_3.16H_2O$ to $CoFe_2O_4$ occurred at temperature 300^0C (2h). The shape of embedded $CoFe_2O_4$ (a final product) in silica matrix is almost spherical and its average size ranges 15-25 nm. Copyright © 2013 VBRI press.

Keywords: Prussian-blue; coprecipitation; thermal treatment; nanocomposites; cobalt ferrite.

Sunil Rohilla born in Rohtak, India has been working as Assistant Professor in Physics at The Technological Institute of Textile and Sciences, Bhiwani, Haryana, India-91-127021,(India). He obtained his M.Sc. (Physics) from GJUS&T, Hisar in 2001 and M.Phil (Physics) from CDLU, Sirsa in 2009 and PhD (Physics) from GJUS&T, Hisar in 2012. He worked as Research Associate in SOTL Ltd. Aurangabad, Maharastra from 2001 to 2004 during this period he has been involved in Installation of MCVD plant and manufacturing of Optical fiber. He also worked on Installation of hydrogen production plant with Scientist and Engineers of STUART Energy, Canada. He joined TIT&S College as lecturer Physics in 2004. He presented his research papers in fifteen International/ National conferences. He has published Ten research papers in reputed International journals. His current areas of interest are Nanoscience and nanotechnology i.e characterization and development of novel nanomaterial and use them for device making.

Praveen Aghamkar born in Bhilai, India and received his Degree in post-graduation (M.Sc.) and Doctoral (Ph. D.) from Pt. Ravi Shankar Shukla University, Raipur and Barkatulla University, Bhopal, respectively. He worked as TRIL (ICTP) fellow in Lecce, Italy. He has established research environment in Physics In the area of Nanomaterials and Nonlinear Optics in Ch. Devi Lal University, Sirsa, India. His current areas of interest are Nanocomposites and Optical Switching/limiting.

Introduction

$Fe_4[Co(CN)_6]_3.16H_2O$ is a mixed-valance Iron(III) hexacyanoferrate(II) compound that belongs to the Prussian-blue (PB) family (General formula of PB family is $A_n[B(CN)_6]_m.xH_2O$ where A and B are transition metals). PB and its analogues have attracted renewed and growing interest in the field of molecule based magnets **[1–3]**, electrochemistry **[4, 5]**, hydrogen adsorption **[6]** and optics **[7]** owing to their unique properties. Nano-dimensional PB analogues with controllable size and properties are highly desirable for various applications such as nanomagnetic **[8]**, biosensing **[9–12]**, electrochromic **[13]**, and biomedical **[14]** devices. Nanocrystalline PB has been reported to be synthesized by various methods in which various agents, such as anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate**[15]**, polyvinylpyrrolidone **[16]**, sol–gel **[7]**, sodium hexametaphosphate **[17]**, apoferritin [**18**], porous alumina **[19]**, stearylamine **[20]** or nafion **[21]**, were used to stabilize nanoparticles. In general, these methods utilize a spatial confinement in the growth of Prussian blue nanoparticles using various kinds of templates/surfactants. The templates occupy the cavities between the nanoparticles or act as nanospaces containing particles.

In the light of above facts, in the present work the coprecipitation method is used in which chances of getting contamination from outside are negligible as well as it provides monitoring of a good control on particles size, shape and their uniform dispersion in a matrix. Silica matrix allows growth control and provides chemical anchoring for the molecule based magnetic nanoparticles. In addition, binary systems containing molecule based magnets in nonmagnetic (SiO_2) matrix are important in various fields of technology, including magnetic switches, optical and photomagnetic devices, etc. It is found that the composites $Fe_4[Co(CN)_6]_3.16H_2O/SiO_2$ on heat treatment transformed into nano dimensional $CoFe_2O_4/SiO_2$ spinel ferrite at a temperature 300^0C (2h). Such nanocomposites have been utilized in modifying the properties of materials like catalytic **[22]**, magnetic **[23]**, magneto-optic **[24]** and mechanical properties **[25]**. Coprecipitation process has been proved to be one of the efficient methods to prepare ultra-fine particles and their uniform dispersion in different matrices **[26]**. Using this method, a control over the surface morphology, structure and chemical composition can be attained by carefully monitoring the preparation parameters.

In the present work, using coprecipitation method $Fe_4[Co\ (CN)_6]_3.16H_2O$ and $CoFe_2O_4$ were prepared and embedded in silica matrix. The authors optimized the annealing temperature as well as annealing time to obtain single domain nano-dimensional cobalt ferrite in silica matrix. The XRD, FTIR, TEM and VSM studies of the prepared samples were carried out.

Experimental

Synthesis of $Fe_4[Co(CN)_6]_3.16H_2O$ nanosuspension

The iron cobalt cyanide hydrate $Fe_4[Co(CN)_6]_3.16H_2O$ nanosuspension was prepared by co-precipitation technique. The high purity reagents: Potassium ferry cyanide ($K_3[Fe(CN)_6]$); Aldrich 99.99%), cobalt chloride ($CoCl_2$; Aldrich 99.99%)and de-ionized water were used. The suspension is prepared by the method given in literature **[27]**.

Synthesis of amorphous SiO_2 nanosuspension

In this step, suspension of amorphous SiO_2 was prepared by adding 50ml 0.3M SiO_2 (AR grade; Aldrich 99.99%) aqueous solution in 50ml 0.6M NaOH (Aldrich 99.99%) using the technique **[28]**.

Synthesis of ($Fe_4[Co(CN)_6]_3.16H_2O/SiO_2$) nanocomposites

With an objective to prepare nanocomposites resultant suspensions of step-I was doped in to step-II suspensions and was mixed smoothly with stirring for 6h at a speed of 8000 rpm. The temperature of the system was kept constant at 60^0C in a water jacketed reaction vessel using circulating thermostatic bath. The resultant solution was then filtered and washed many times; and then filtrate was dried at 80^0C in a vacuum oven at a pressure of 100mmHg for 6 hours. The samples were ground to very fine powder. The powdered material so obtained was sintered in muffle furnace (KSL 1600X, MTI) in air at temperature of 300^0C with uniform heating rate of 2^0C/minutes for different time durations.

Sample characterization

Complementary methods were used to characterize the structure and phase of heat treated samples. XRD of samples were recorded by a Philips X-ray diffractometer PW/1710 having GIXRD geometry; with Ni filter, using monochromatic CuKα radiation of wavelength 1.5418 Å at 50 KV and 40 mA, in the range, 2θ~ $10\text{-}70^0$. The analysis of size, shape and particle distribution of the samples was carried out using Transmission electron microscope (Hitachi-H7500) at 100 KV. For this purpose, dispersions of sample nanoparticles were pipetted onto carbon-coated copper grids. Infrared spectra were recorded by using Fourier transform infrared spectrometer (Perkin Elmer 1600) ranging 2500-400 cm^{-1}, on the pellets obtained by dispersing the samples in KBr. Magnetization data were recorded by Vibrating sample magnetometer VSM, P525, QD6000, with a maximum field of 60 kOe, in a temperature range 10 to 300 K.

Results and discussion

FTIR

The FTIR spectrum of the as-prepared sample is shown in **Fig. 1(a).** In this spectrum, absorption band from 3500 cm^{-1} to 2350 cm^{-1} is the characteristics of stretching vibration of OH which shows the presence of water in the sample. Further, strong absorption bands at 790, 1080, 1414 cm^{-1} and 1632 cm^{-1} which may be assigned vibration mode of ring structure of SiO_2tetrahedra **[33]**, TO mode of Si-O-Si asymmetric bond stretching vibration **[34]**, O-H banding mode **[29]** and bending vibration modes of H-O-H absorbed in silica **[35]** respectively. The peak at 586 cm^{-1} may be assigned to Fe-CN-Co banding mode **[30]**. The absorption around 2080 cm^{-1} which is the most strong peak of FTIR spectrum shows the stretching mode of CN **[32]** for the PB like compounds $[M_K{}^A[M^B(CN)_6]_L.xH_2O$ {(K, L) = (1,1) (4,3) (3,2) (2,1)} in which cyanide forms bridges between M^A and M^Bcations**[32]**. The presence of bluish green precipitate (on dissolving $K_3\ [Fe(CN)_6]$ with dilute mineral acid $CoCl_2$) along with 2080 cm^{-1} peak of FTIR spectrum confirms the formation of cobalt iron cyanide hydrate. The characteristic absorption bands at 1080, 790cm^{-1} indicate the formation of silica network **[36]**.

Fig 1(b) depicts shifting of absorption band towards higher wave number (i.e. blue shift) which suggests rearrangement of silica matrix network **[37]**. The shoulder around 620 cm^{-1} was probably due to the contribution from Co-O vibrations and band centered at 590 cm^{-1} may be attributed to the presence of cobalt ferrite **[37]**. This figure also reveals the elimination of water molecules, Si-OH and volatiles in the samples and as a result densification of $CoFe_2O_4/SiO_2$ was observed.

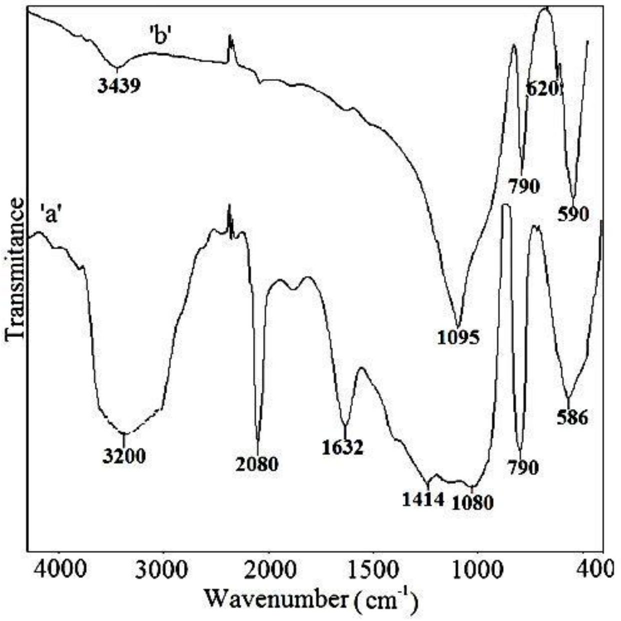

Fig. 1. FTIR spectra of Iron Cobalt Cyanide hydrate/Silicananocomposites: As-prepared ('a') and heat treated at 300^{0}C for 2h ('b').

XRD

Fig. 2 shows the X-ray diffraction patterns of as-prepared and annealed powder samples, both the spectrum shows a hump around 23^0 which corresponds to the amorphous matrix of SiO_2. Peaks in diffractograms were indexed by comparing the interplaner distances with JCPDS data. Fig. 2(a) illustrates the crystal structure revealed by XRD pattern of the as-prepared sample. This figure shows a very strong diffraction peak at 2θ~ 17.2^0 (200), three strong peaks at 24.4^0 (220), 34.8^0 (400), 39.1^0 (420) and a weak peak centered at 49.8^0 (440) and these peaks can be readily indexed to a face–centered-cubic phase (space group Fm3m) of iron cobalt cyanide hydrate with a lattice parameter of 10.308A^0 [JCPDS file No. 83-2293]. These XRD data support the FTIR data. The powder sample calcined at 300^{0}C for 2h, Fig. 2(b), shows diffraction peaks at 2θ~30.08^0 (220), 35.06^0 (311), 43.08^0 (400), 56.96^0 (511) and 62.5^0 (440). These diffraction peaks may be assigned to spinel face centered cubic cobalt ferrite [JCPDS File No. 22-1086], which confirms the formation of $CoFe_2O_4$ nanocrystallites. In order to obtain the average size of cobalt iron cyanide hydrate and cobalt ferrite, well known Debye-Scherer formula ($t = k\lambda/\beta \text{Cos}\theta$, here λ is the wavelength of radiation, k=0.9 (for spherical particle), $\beta=(B^2 - b^2)^{½}$ is the full width at half maximum(FWHM), where B and b represents FWHM of diffraction peak of prepared samples and standard material, respectively) is employed. It is worth mentioning that the Debye-Scherrer formula provides a lower bound on the particle size. The reason for this is that a variety of factors can contribute to the width of a diffraction peak; besides crystallite size, the most important of these are usually inhomogeneous strain and instrumental effects. If other contributions to the peak width are negligible, then the peak width would be determined solely by the crystallite size and the Debye-Scherrer formula would apply. In the present work, the contribution of line width of standard material is taken into consideration and the size is found to be in the range 15- 25 nm. It is also noticed that the crystallite size of cobalt ferrite increases with increasing calcination temperature because of the coalescence of nanoparticles, which is in agreement with reported results **[32]**.

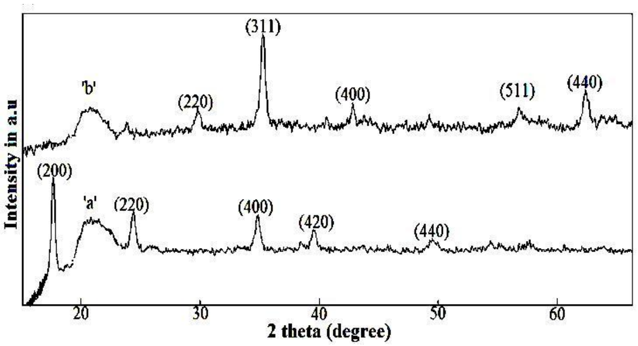

Fig. 2. XRD of Iron Cobalt Cyanide hydrate/Silica nanocomposites: As-prepared ('a') and heat treated at 300^{0}C for 2h ('b').

TEM analysis

The morphology and microstructure of the as-prepared (Fig. 3(a)) sample, was investigated by TEM. **Fig. 3(a)** depicts a homogeneous distribution of well crystallized and nearly spherical iron cobalt cyanide hydrate nanoparticles in silica host matrix. The rings of the **Fig 3(a^1)** are assigned to iron cobalt cyanide hydrate and are well resolved at (200), (220), (400) and (420) reflections in XRD. The average particle size estimated by a statistical method is approximately 17 and 28 nm, respectively, which is in accordance with the values calculated by XRD.

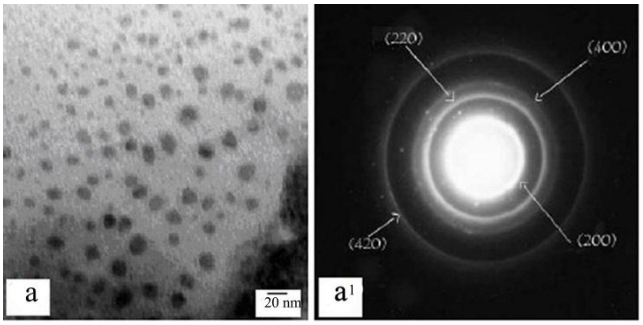

Fig. 3. TEM micrographs of Iron Cobalt Cyanide hydrate/Silica nanocomposites: The morphology micrograph (a); and The selected area electron diffraction pattern (a^1).

Magnetization studies

In order to investigate the magnetic properties of the prepared powder samples, the magnetization characteristics as a function of the applied magnetic field were carried out at room temperature using vibrating sample magnetometer

(VSM). The magnetization behavior of as-prepared (say ‘a’) and samples annealed at temperatures 200^{0}C and 300^{0}C (say ‘b’)is shown in **Fig 4**. For the sample ‘a’ superparamagnetic behavior under an external magnetic field with negligible remanent magnetization (M_r) and coercivity (H_c) at room temperature was observed. Superparamagnetism (SPM) is the property of single domain magnetic nanoparticles in which particles get magnetized swiftly with an external magnetic field and also return back to their nonmagnetized state when the external magnetic field is removed. It has been noticed that the concentration of dispersed magnetic nanoparticles in insulating matrix is large enough that both dipolar and exchange interactions are minimal. Under such conditions the magnetic properties of nanocomposites depends on the effects of anisotropy. Besides, the room temperature coercivity is very low and remains constant up to when average anisotropy field in the system is larger than the interaction field **[38]**. The magnetization for the heat treated samples (‘b’) is higher than the magnetization of as prepared sample. Furthermore one may observe that saturation in magnetization occurs at a high field. As we have noticed in FTIR, XRD pattern and TEM, with increasing annealing temperature crystallinity and densification of nanocomposites increases. The XRD peaks infer single crystal structure of spinel $CoFe_2O_4$ and which is a hard magnetic ferrite. In such type of ferrites, domain rotation predominates over domain wall motion, due to this the change in magnetization with respect to applied magnetic field is relatively very small, after knee magnetization, and finally the magnetization saturates at high magnetic field **[39]**.

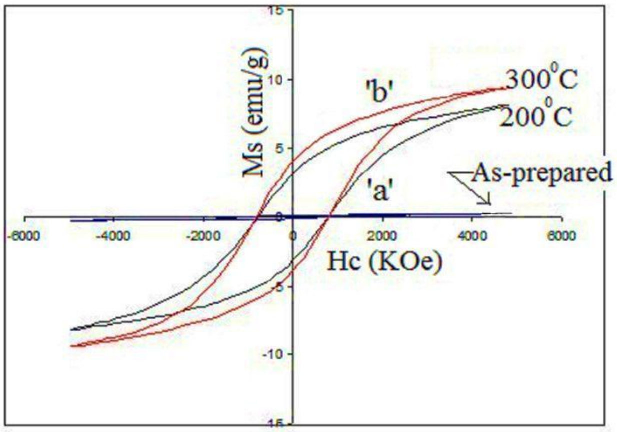

Fig. 4. Magnetization curve of Iron Cobalt Cyanide hydrate/Silica nanocomposites: As-prepared (‘a’) and heat treated at 200 and 300^{0}C for 2h (‘b’).

Conclusion

Using co-precipitation technique almost spherical shaped nano-dimensional iron cobalt cyanide hydrate ($Fe_4[Co(CN)_6]_3.16H_2O$) (a member of Prussian-blue (PB) family) were successfully dispersed in a silica matrix that too uniformly. Upon thermal heat treatment at 300^{0}C (2h) in air ($Fe_4[Co(CN)_6]_3.16H_2O$)/SiO_2 transformed into nano composites of cobalt ferrite($CoFe_2O_4$) in silica matrix. It has been found that with increasing annealing temperature size, crystallinity and densification of nano composites increases. The results of characterization techniques show that $CoFe_2O_4$ has a spinel single domain structure. The magnetization of the sample annealed (300^{0}C, 2h) saturates at ~ 9.44 emu/gm for an applied magnetic field of 4418 kOe. The results of FTIR, XRD, TEM and VSM are in are compatible with each other. A detailed study of ($Fe_4[Co(CN)_6]_3.16H_2O$)/ SiO_2 and $CoFe_2O_4$/ SiO_2 nano composites with Rietveld refinement shall be the subject of future communication.

Reference

1. Ferlay, S.; Mallah, T.; Quahès, R.; Veillet, P.; Verdaguer, M.;, Nature **1995**, 378, 701. **DOI:**10.1038/378701a0
2. Sato, O.; Lyoda,T.; Fujishima, A.; Hashimoto, K.; Science**1996**, 272, 704. **DOI:**10.1126/science.272.5262.704
3. Kahn, O.; Nature **1995**, 378, 667. DOI:10.1038/378667a0
4. Dunbar, K. R.; Heintz, R. A.; Prog. Inorg. Chem. **1997,** 45, 283. **DOI:** 10.1002/9780470166468.ch4
5. Pyrasch,M.; Toutianoush, A.; Jin, W.; Schnepf, J.; Tieke, B.; Chem. Mater. **2003,** 15, 245. **DOI:** 10.1021/cm021230a
6. Kaye, S.S.; Long, J.R.; Catal. Today **2007,** 120, 311. **DOI:**10.1016/j.cattod.2006.09.018
7. Moore, J. G.; Lochner, E. J.; Ramsey, C.; Dalal, N. S;. Stiegman, A. E.; Angew. Chem. Int. Ed. **2003,** 42, 2741. **DOI:** 10.1002/anie.200250409
8. Catala, L.; Gloter, A.; Stephan, O.; Rogez, G.; Mallah, T.; Chem. Commun. **2006,** 1018. **DOI:**10.1039/B516425G
9. Qiu, J. D.; Peng, H. Z.; Liang, R. P.; Li, J.; Xia, X. H.; Langmuir **2007,** 23, 2133. **DOI:** 10.1021/la062788q
10. Kumar, S. S.; Joseph, J. K.; Phani, L.; Chem. Mater. **2007**, 19, 4722. **DOI:** 10.1021/cm0711820
11. Zhao, G.; Feng, J. J.; Zhang, Q. L.; Li, S. P.; Chen, H. Y.; Chem. Mater. **2005**, 17, 3154. **DOI:** 10.1021/cm048078s
12. Zhao, W.; Xu, J. J.; Shi, C. G.; Chen, H. Y.; Langmuir **2005**, 21, 9630. **DOI:** 10.1021/la051370+
13. Baioni, A. P.; Vidotti, M.; Fiorito, P. A.; Ponzio, E. A.; Cordoba de Torresi, S. I.; Langmuir **2007**, 23, 6796. DOI: 10.1021/la070161h
14. DeLongchamp, D. M.; Hammond, P. T.; Adv. Funct. Mater. **2004,** 14, 224. **DOI:** 10.1002/adfm.200304507
15. Vaucher, S.; Li, M.; Mann, S.; Angew. Chem. Int. Ed. **2000**,39,1793. **DOI:** 10.1002/(SICI)1521-3773(20000515)
16. Uemura, T.; Kitagawa, S.; J Am. Chem. Soc. **2003**, 125, 7814. **DOI**: 10.1021/ja0356582.
17. Bagkar, N.; Ganguly, R.; Choudhury, S.; Hassan, P. A.; Sawanta, S.; Yakhmi, J. V.; J. Mater. Chem. **2004,** 14, 1430. **DOI:** 10.1039/B315866G
18. Dominguez-Vera, J. M.; Colacio, E.; Inorg. Chem**2003**, 42, 6983. **DOI:** 10.1021/ic034783b
19. Zhou, P.; Xue, D.; Luo, H.; Chen, X.; Nano Lett. **2002,** 2, 845. **DOI:** 10.1021/nl0256154
20. Yamada, M.; Arai, M.; Kurihara, M.; Sakamoto, M.; Miyake, M.; J Am. Chem. Soc. **2004**,126, 9482. **DOI:** 10.1021/ja0476866
21. Kosaka, W.; Tozawa, M;. Hashimoto, K.; Ohkoshi, S. I.; Inorg. Chem. Commun. **2006,** 9, 920. **DOI:**10.1016/j.inoche.2006.05.032
22. Guerrero, H.; Rosa, G.; Morales, M. P.; Monte, F.; Moreno, E. M.; Levy, D.; Pèrez del Real, R.; Belenguer, T.; Serna, C. J.; Appl. Phys. Lett. **1997**, 71, 2698. **DOI:**10.1063/1.120181
23. Chakraborty, D.; Bull. Mater. Sci. 1992, 15, 411.

24. Yang, B. L.; Hong, F.; Kung, H. H.; J. Phys. Chem. **1984**, 88, 2351. **DOI:** 10.1021/j150656a020
25. Suryanarayana, C.; Bull. Mater. Sci. **1994,** 17, 307.
26. Wanger, J.; Authenrieth, T.; Hempelmann, R.; J. Magn. Magn. Mater. **2002,** 252, 4. **DOI:**10.1016/j.jmmm.2010.11.001
27. Rohilla, S.; Lal, B.; Aghamkar, P.; S.; Bansal, S.; Agarwal, A.; Kumar, S.; Acta PhysicaPolonica A **2010**,118, 696.DOI: przyrbwn.icm.edu.pl/APP/PDF/**118**/a**118**z4p30.pdf
28. Rohilla, S.; Kumar, S.; Aghamkar, P.; Bansal, S.; Agarwal, A.; JMMM **2011**, 323, 897. **DOI:**10.1016/j.jmmm.2010.11.001
29. Balasubramaniam, R.; Ramesh Kumar, A. V.; Corrosion Sc. **2000**, 42, 2085.
30. Nyquist, R. A.; Kagel, R. A.; IR Spectra of Inorganic Compounds, (Eds.), Academic Press, New York, **1971**.
31. Balasubramaniam, R.; Ramesh Kumar, A. V.; Dillman, P.; Current Sc. **2003**, 85, 1546.
32. Ayers, Ji B.; Waggoner, W. H.; J. Inorg. Nucl. Chem. **1971**, 33, 721. **DOI:**10.1016/0022-1902(71)80470-0
33. Battisha, I. K.; Indian J. Pure Appl. Phys. **2002,** 40,122.
34. Ono, H.; Katsumata, T.; Appl. Phys. Lett. **2001**, 78**,** 1832. **DOI:**10.1063/1.1357445
35. Maniar, P. D.; Navrotsky, A.; Rabinovich, E. M.; Ying, J. Y.; Benziger, J. B.; J. Non-Cryst. Solids **1990,** 124, 101. **DOI:**10.1016/0022-3093(90)91086-7
36. Rao, A. V.; Wagh, P. B.; Haranath, D.; Risbud, P. P.; Kumbhare, S. D.; Ceram. Int. **1999**, 25, 505. **DOI:**10.1016/S0272-8842(97)00085-0
37. Garcia Cerda, L. A.; Montemayor, S. M.; J. Magn. Magn. Mater. **2005,** 294, e43. **DOI:**10.1016/j.jmmm.2005.03.051
38. Sharma, R.; Malik, R.; Lamba S.; S Annapoorni.; Bull. Mater. Sci. **2008**, 31, 409.
39. Cullity B.D. and Graham C.D.; Introduction to Magnetic Materials, IEEE Press, John Wiley, **2009**, Chap. 9.