

Lead adsorption study on combustion derived γ -Fe₂O₃ surface

ARUNKUMAR LAGASHETTY*, H VIJAYANAND, S BASAVARAJA[†],
N N MALLIKARJUNA^{††} and A VENKATARAMAN[†]

Appa Institute of Engineering and Technology, Gulbarga 585 102, India

[†]Department of Materials Science, Gulbarga University, Gulbarga 585 106, India

^{††}Centre of Excellence in Polymer Science, Karnatak University, Dharwad 580 003, India

MS received 14 October 2008

Abstract. New combustion synthetic route for the synthesis of nanosized γ -Fe₂O₃ by microwave-assisted route is reported. X-ray density, tap density and powder density of prepared γ -Fe₂O₃ are calculated. Adsorption study of Pb²⁺ on combustion derived nanosized γ -Fe₂O₃ is studied by dynamic method. The γ -Fe₂O₃ structure and lead adsorbed γ -Fe₂O₃ (Pb- γ -Fe₂O₃) are studied by X-ray diffraction (XRD). Additional lead peaks in Pb- γ -Fe₂O₃ sample pattern confirm the lead adsorption. Morphology of as prepared γ -Fe₂O₃ and Pb- γ -Fe₂O₃ is studied by scanning electron micrograph (SEM) technique. Varied morphology for Pb- γ -Fe₂O₃ compared to its γ -Fe₂O₃ is observed. Variation of bonding in Pb- γ -Fe₂O₃ sample due to lead adsorption is viewed by infrared spectroscopic (IR) technique. Energy dispersive X-ray microanalysis (EDX) is scanned for the lead adsorbed γ -Fe₂O₃ to know the presence of lead on γ -Fe₂O₃ surface. The eluent lead solution is characterized by atomic absorption spectroscopy (AAS) and solution conductivity (SC). Reduction in the concentration and increase in conductance of eluent lead solution is observed. The potential use of solid adsorbents for the adsorption of heavy metal pollutants is envisaged in the present work.

Keywords. γ -Fe₂O₃; microwave assisted; adsorption; lead; structure.

1. Introduction

Ferrite nanoparticles have been of interest due to their applications in the preparation of high-density ferrite cores, as suspension materials in ferromagnetic liquid, and as catalysts. Among these, iron oxides, in particular, are technologically useful as pigment semiconductors and also for their magnetic property (Mallinson 1987; Rao and Ramesh 1995; Patil *et al* 1997; Everhard *et al* 1998). The stability and semiconductor properties of α -Fe₂O₃ allow it to be used as a photocatalyst (Yang and Kang 1982), while the magnetic properties of γ -Fe₂O₃ make it a common action compartment of high-density recording media (Rao and Ramesh 1995). Semiconducting thick film of γ -Fe₂O₃ as sensors for CH₄, H₂, NH₄, and alcohols are extensively employed (Reddy *et al* 2000). Ultrafine oxides possess high surface area and hence have formed applications as adsorbent for many metal ions and phosphates (Mallikarjuna and Venkataraman 2003; Lagashetty and Venkataraman 2004). It was observed that γ -Al₂O₃ with fully occupied octahedral sites and randomly distributed tetrahedral sites show excellent adsorption behaviour (Rao 1994). The adsorption behaviour of metal ions

on γ -Al₂O₃ is well reported (Rao 1994). This present work is a continuation of our study using ferrites, ferrite–thiourea composites and ferrite–rubber composites as adsorbents (Lagashetty *et al* 2003; Mallikarjuna and Venkataraman 2003; Vijayanand *et al* 2003). In the present case, the ferrous benzoate dihydrate precursor was used for the synthesis of γ -Fe₂O₃. The γ -Fe₂O₃ has similar structure as γ -Al₂O₃, however, both the tetrahedral sites and octahedral sites are occupied by Fe⁺³ ions and the 1/8th vacancies are present in the octahedral sites. The molecular formula of γ -Fe₂O₃ is given as Fe⁺³₈[Fe⁺³_{40/3}□_{1/8}]₃₂O₃₂, where □ indicates vacancy sites. This inverse spinel ferrite can be doped with ions of similar size (as Fe⁺³) to get a monophasic-doped γ -Fe₂O₃. When ions with higher ionic radii are employed these ions get adsorbed on γ -Fe₂O₃ surface. The ionic sizes of Fe⁺³ and Pb²⁺ are 55 ppm and 119 ppm, respectively and hence it was felt that Pb²⁺ ions could adsorb on γ -Fe₂O₃ surface and get reduced as Pb⁰ under suitable conditions.

A detailed study on the use of solid adsorbents for γ -Fe₂O₃ is not reported in the literature. However, some important work on the physical surface-complexation models for sorption at mineral water interface is reported (Sverjensky 2003). The other reports on solid adsorbents include adsorption of cobalt (III) on gamma alumina-water surface *in situ* (Chisholm-Brause *et al* 1989) and surface passivation of magnetite by reaction with aqueous

*Author for correspondence (arun_lagashetty@yahoo.com)

Cr(VI) employing EXAFS and TEM studies (Peterson *et al* 1997).

Current investigation is a new synthetic route using ferrous benzoate precursors for the synthesis of γ -Fe₂O₃ employing microwave assisted route. This work is an extension of our earlier work (Lagashetty *et al* 2007) on synthesis of metal oxides by different precursors employing microwave assisted route. Polyvinyl alcohol was used as a fuel for the precursor. The feasibility of the conversion of the precursor (as mentioned above) to γ -Fe₂O₃ through microwave-assisted route is reported. In search of a suitable economic fuel, our use of polyvinyl alcohol has given promising results in the conversion of precursor into γ -Fe₂O₃. This paper also represents the adsorption study of Pb⁺² ions on the as prepared γ -Fe₂O₃ surface.

The characterization study of as prepared γ -Fe₂O₃ and adsorbent γ -Fe₂O₃ was undertaken by employing XRD, IR, SEM and TEM. EDAX is scanned for Pb⁺² adsorbed γ -Fe₂O₃ to know the adsorbed Pb⁺². Solution conductivity and atomic absorption spectroscopy for the eluent lead solution is taken to know the presence of adsorbed lead.

2. Experimental

2.1 Materials and methods

Ferrous sulphate, benzoic acid and lead acetate used were AR grade chemicals. Polyvinyl alcohol of molecular weight 10,000 was obtained commercially (Marketed by Mrs Hi-media chemicals, Mumbai). The cold double distilled water was used for preparation of solution.

The methods used for the synthesis of γ -Fe₂O₃ were by thermal decomposition of ferrous benzoate precursors using microwave-assisted route. The polyvinyl alcohol was used as a fuel for the combustion reaction. Adsorption study of lead ions on as synthesized γ -Fe₂O₃ was carried out by dynamic method.

2.2 Preparation of ferrous benzoate

The γ -Fe₂O₃ was synthesized through microwave-assisted route, employing ferrous benzoate dihydrate as precursor. This precursor was prepared by dissolving equimolar quantity of ferrous sulphate heptahydrate and benzoic acid in minimum amount of water. This mixture was well stirred in a three-necked flask. The yellow precipitate of ferrous benzoate dihydrate obtained was filtered through sintered glass funnel and washed with double distilled water. Finally it was washed with dry acetone and dried under vacuum.

2.3 Synthesis of γ -Fe₂O₃

Thermal decomposition of benzoate precursor with a fuel leads to the formation of high surface area γ -Fe₂O₃. The

above prepared ferrous benzoate was mixed with polyvinyl alcohol (PVA) in the weight ratio 1 : 5 (Vijay 2000; Mallikarjuna *et al* 2003) and ground well in a pestle and mortar. The resultant solid was placed in a crucible and heated on a electrical oven in an open air atmosphere. Initially it burned with evolution of large volume of white fumes. After completion of the fumes, the sample was placed in a domestic microwave oven (2.45 GHz) at 90% heating rate. This sample produced golden yellow coloured light in the oven which was due to the presence of iron metal. The reaction completed within five minutes to form well-dispersed surface modified γ -Fe₂O₃ particles.

2.4 Adsorption study on γ -Fe₂O₃ surface

One gram of as synthesized γ -Fe₂O₃ was taken in a 250 ml clean and dried conical flask. Known volume of 50 ml of known concentration (0.1 N) of lead acetate solution was added in the same conical flask. This flask was placed on a mechanical shaker at 150 rpm rate for adsorption of lead ions on γ -Fe₂O₃ particles. After 12 h the solution was eluted using Whatman filter paper no. 41 and preserved for atomic absorption spectroscopy study, meanwhile solution conductivity of eluent was also noted. The solid product i.e. adsorbent, was washed with water and air-dried. The solid was characterized by employing XRD, SEM and FT-IR techniques.

2.5 Characterization

The X-ray diffraction patterns were obtained employing a Geol JDX-8p spectrometer using CuK α radiation. The X-ray generator was operated at 30 kV and 20 mA. The scanning range, $2\theta/\theta$ was selected. The scanning speed = 1° min⁻¹ was employed for precise lattice parameter determination. High purity silicon powder was used as an internal standard.

The shape, size and distribution of the powder, as prepared iron oxide sample, and microstructure of the sample were examined using a Leica-440 Cambridge Stereoscan, scanning electron microscope image. The SEM was operated at 20 kV. The samples were made conducting by the sputtering of gold using a Polaron DC 'sputtering unit' operated at 1.4 kV and 18–20 mA.

The Fourier transform infrared spectra (FT-IR) of iron oxide were recorded on a Perkin-Elmer FT-IR spectrophotometer [Model 1000] in the range 300–4000 cm⁻¹.

The solution conductivity gives the information about the conducting nature of the solution. The conductance of eluent solution of lead before and after adsorption of lead was taken by employing Elico 8 2T Conductivity Bridge.

The concentration of lead solution before and after adsorption of lead on the synthesized γ -Fe₂O₃ was understood by atomic absorption spectroscopy (AAS). The

AAS of lead solution was recorded on a Smith-Hieftji, 1000 automated AA/AE spectrometer.

2.6 Density measurement

2.6a *Density evaluation from X-ray data:* The X-ray density of the samples have been computed from the values of lattice parameters using the formula (Smith *et al* 1959; Venkataraman *et al* 2001).

$$d = \frac{8M}{Na^3},$$

where 8 represents the number of molecules in a unit cell of a spinel lattice, M the molecular weight of the sample, N the Avogadro's number, and a the lattice parameter of the sample.

The lattice constant for the cubic was calculated using the equation

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}.$$

2.6b *Tap density:* The as prepared $\gamma\text{-Fe}_2\text{O}_3$ was crushed in an agate mortar using a pestle and a mortar. A

known amount of this powder was filled into a graduated cylinder of 25 ml capacity. The cylinder was tapped until the powder level remained unchanged. The volume occupied by the powder was noted. The ratio between the weight of the substance and the volume gave tap density (Kinsman 1978).

2.6c *Powder density:* The powder densities were measured using Archimedes principle (Klug and Alexander 1962) with a pycnometer and xylene as a liquid medium. The pycnometer of volume 25 ml was used. The following weights were taken and used in the density calculation.

Weight of the bottle = W_1 g,

Weight of the bottle + substance = W_2 g,

Weight of the bottle + substance + xylene = W_3 g,

Weight of the bottle + xylene = W_4 g,

Density of xylene = ρ_{sol} .

$$\rho_{\text{sample}} = \frac{(W_2 - W_1)\rho_{\text{sol}}}{(W_4 - W_3) + (W_2 - W_1)}.$$

Density of sample = ρ_{sample} .

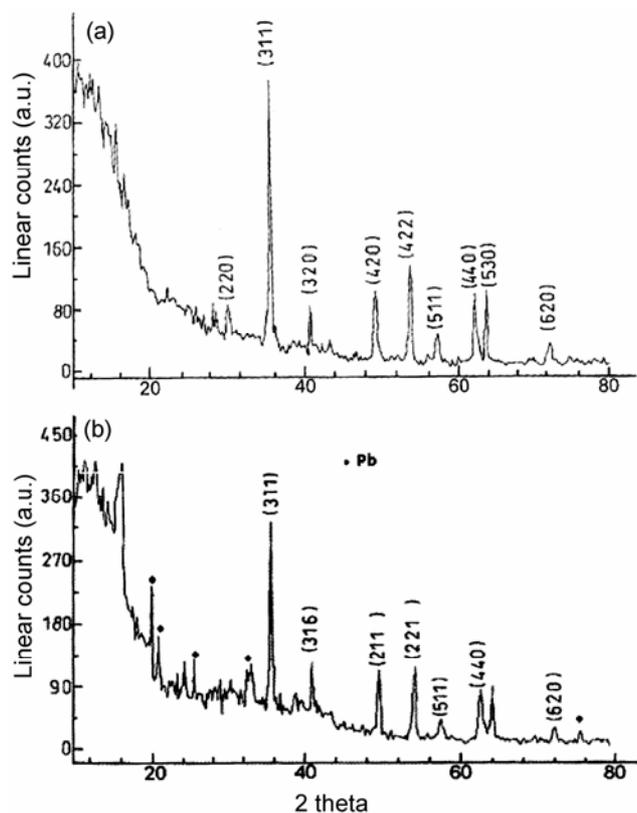


Figure 1 XRD patterns of (a) as prepared $\gamma\text{-Fe}_2\text{O}_3$ and (b) lead adsorbed $\gamma\text{-Fe}_2\text{O}_3$.

3. Results and discussion

3.1 X-ray diffraction study

Figure 1(a) shows the X-ray diffraction pattern of as synthesized $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. Observed Bragg's reflections (Peaks indexed in the pattern) are well in agreement with JCPDS file 4-755. It reveals a good crystalline cubic structure. Figure 1(b) shows XRD pattern of Pb- $\gamma\text{-Fe}_2\text{O}_3$ particles. This pattern shows some additional reflections



Figure 2. SEM image of as $\gamma\text{-Fe}_2\text{O}_3$ at low resolution.

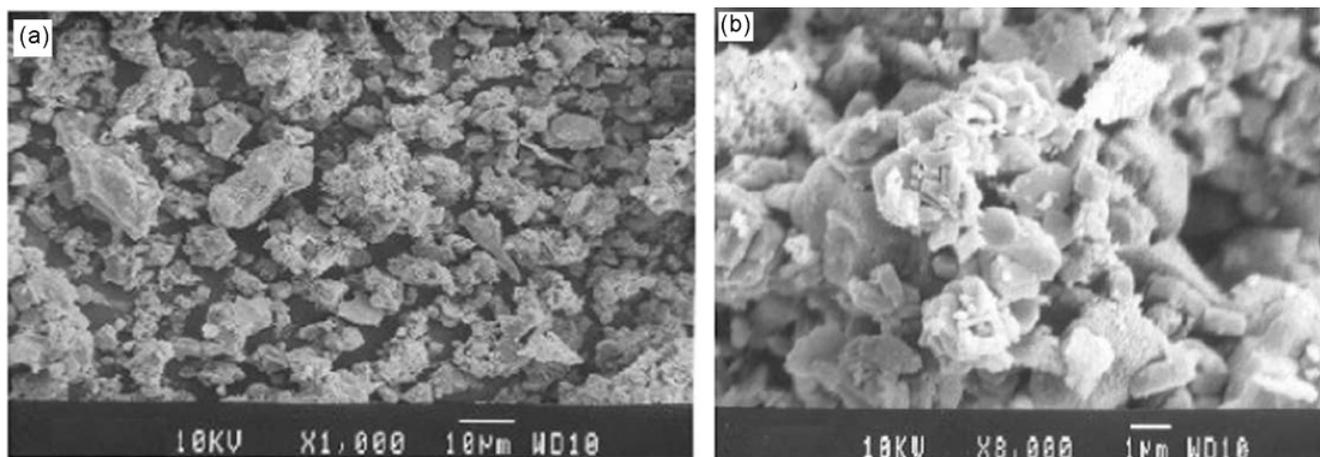


Figure 3. SEM image of lead adsorbed $\gamma\text{-Fe}_2\text{O}_3$ at (a) low resolution and (b) high resolution.

corresponding to lead, which is adsorbed on the surface of $\gamma\text{-Fe}_2\text{O}_3$ particles. The lead peaks in the pattern are identified by JCPDS file no. 44-0872. Presence of lead peaks along with $\gamma\text{-Fe}_2\text{O}_3$ peaks in $\text{Pb-}\gamma\text{-Fe}_2\text{O}_3$ shows adsorption of Pb^{2+} ions on $\gamma\text{-Fe}_2\text{O}_3$ surface. This is again confirmation with IR and EDX studies, where additional frequencies are observed in IR spectrum and both lead and iron peaks are observed in EDX pattern.

3.2 Scanning electron micrograph study

Morphology of both $\gamma\text{-Fe}_2\text{O}_3$ and $\text{Pb-}\gamma\text{-Fe}_2\text{O}_3$ was studied by scanning electron microscope (SEM) tool. Figure 2(a–b) shows the particle morphology of $\gamma\text{-Fe}_2\text{O}_3$ at low and high resolutions. The particles are mostly irregular in shape with a nanosize range. Some particles are found as agglomerates. Flakes of agglomerates of $\gamma\text{-Fe}_2\text{O}_3$ shaped blocks are of submicron dimensions. Figure 3(a–b) shows the SEM of $\text{Pb-}\gamma\text{-Fe}_2\text{O}_3$ at low and high magnifications. The adsorbed images show fine nanosized lead grains on $\gamma\text{-Fe}_2\text{O}_3$ indicating nucleating growth of lead particles on the $\gamma\text{-Fe}_2\text{O}_3$ surface. However, on high magnification, small hexagonal lead particles on the $\gamma\text{-Fe}_2\text{O}_3$ surface are observed.

3.3 Fourier transform infrared study

Metal oxides give absorption bands below 1000 cm^{-1} arising from interatomic vibrations (Rao 1963). The FT-IR (Fourier transformation infrared spectroscopy) spectrum of $\gamma\text{-Fe}_2\text{O}_3$ sample is given in figure 4(a). The sample shows the absorption in the region 3100 , 1080 , 550 and 450 cm^{-1} . The peak at 3100 cm^{-1} corresponds to water of hydration and the peak at 1080 cm^{-1} is due to the presence of some overtones. The peaks at 550 and 450 cm^{-1} corresponds to the metal–oxygen (Fe–O) vibrational modes of the spinel compound, also these two

peaks are characteristics of spinel compounds. These two bands are sharp and are of strong intensity. Figure 4(b) shows the FT-IR of lead adsorbed $\gamma\text{-Fe}_2\text{O}_3$. The additional bands and variation in vibrational frequencies indicates the presence of adsorption of lead on $\gamma\text{-Fe}_2\text{O}_3$ surface. Additional bands and variation in vibrational frequencies in the adsorbed sample confirms the adsorption of lead on $\gamma\text{-Fe}_2\text{O}_3$ surface.

3.4 Density measurement and crystallite size

Density evaluation from X-ray data, tap density and bulk density of as synthesized $\gamma\text{-Fe}_2\text{O}_3$ are given in table 1. The density values evaluated from different methods are approximately same. The calculated crystallite size of the as synthesized $\gamma\text{-Fe}_2\text{O}_3$ is 25.8 nm .

3.5 Energy dispersive X-ray microanalysis studies (EDX)

The energy dispersive X-ray microanalysis was carried out to know the presence of adsorbed lead on the $\gamma\text{-Fe}_2\text{O}_3$ surface. Figure 5 shows the EDX pattern of lead adsorbed $\gamma\text{-Fe}_2\text{O}_3$ sample. This pattern shows the presence of both lead and iron peaks, confirms the lead adsorption on $\gamma\text{-Fe}_2\text{O}_3$ surface.

3.6 Atomic absorption spectroscopy (AAS) and solution conductivity

Atomic absorption spectroscopic characterization and solution conductivity studies were carried out for the blank lead solution and the eluent lead solution (solution after adsorption). Table 2 gives the atomic absorption spectroscopy and solution conductivity results of blank and eluent lead solution. An atomic absorption result

shows the initial concentration of lead acetate solution to be 280 ppm, whereas after adsorption the concentration of lead solution decreases to 170 ppm. This decrease in the results indicates the absence of some lead ions in the eluent lead solution. Solution conductance gives the information about the conductance of pure lead acetate as well as eluent lead acetate solution. As the concentration decreases the conductance increases because of rapid moment of the metal ions. The conductance of pure lead

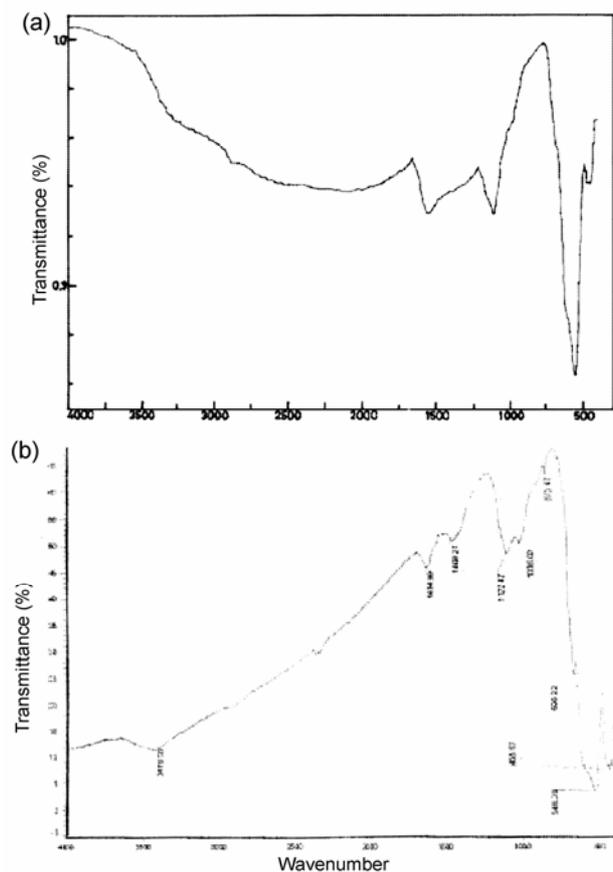


Figure 4. FT-IR spectrum of (a) as prepared $\gamma\text{-Fe}_2\text{O}_3$ and (b) lead adsorbed $\gamma\text{-Fe}_2\text{O}_3$.

Table 1. Densities of $\gamma\text{-Fe}_2\text{O}_3$ in kg/m^3 .

Sample	Density from XRD	Tap density	Bulk density
$\gamma\text{-Fe}_2\text{O}_3$	4920	4980	3620

Table 2. Solution conductivity and AAS result of lead solution and eluent lead solution.

Property	Lead solution	Eluent lead solution
Conductance (mho^{-1})	3×10^{-5}	6.2×10^{-5}
Atomic absorption (ppm)	280	170

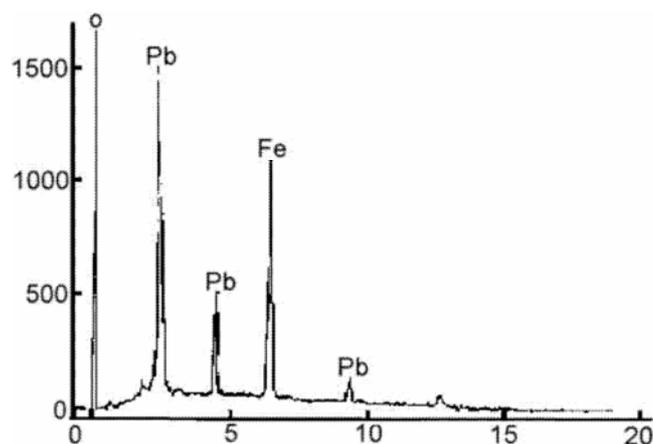


Figure 5. EDX pattern of lead adsorbed $\gamma\text{-Fe}_2\text{O}_3$.

acetate solution is $3 \times 10^{-5} \text{ mho}^{-1}$ and that of eluent solution is $4.5 \times 10^{-5} \text{ mho}^{-1}$. This increase in conductance indicates the absence of some lead ions in the eluent lead solution which matches well with atomic absorption results. These two studies confirm the adsorption of lead ions on the as prepared $\gamma\text{-Fe}_2\text{O}_3$ surface.

4. Conclusions

(I) Microwave assisted synthetic route is employed for synthesis of $\gamma\text{-Fe}_2\text{O}_3$, because of its simplicity and easy scale up. This synthetic route may be used for the synthesis of other metal oxides.

(II) Adsorption study explains that, the $\gamma\text{-Fe}_2\text{O}_3$ can be efficiently used as a solid adsorbent for other heavy metal ions. This study also reveals that the other metal oxides may be used as solid adsorbents.

(III) Morphological study envisaged that adsorbed lead ions disturb the morphology of $\gamma\text{-Fe}_2\text{O}_3$.

(IV) The detailed understanding about the quantitative aspects and the structural transformations is the future direction of our work.

Acknowledgements

The authors are thankful to the UGC, New Delhi, for financial assistance. One of the authors (AL) thanks President and Principal, Appa Institute of Engineering & Technology, Gulbarga, for providing laboratory facilities.

References

- Chisholm-Brause C J, Brown G E and Parks Jr G A 1989 *Physica* **B158** 646
- Everhard K, Thomas C A, Denis M C and Eric D D 1998 *Magnetic recording handbook technology and applications* (New York: McGraw Hill Co.) p. 101

- Kinsman S 1978 *Systematic materials analysis* (eds) T H Richardson and R V Peterson (New York: Academic Press) **Vol. 4**, p. 200
- Klug H P and Alexander L 1962 *X-ray diffraction procedure* (New York: John Wiley)
- Lagashetty Arunkumar and Venkataraman A 2004 *Bull. Mater. Sci.* **27** 491
- Lagashetty Arunkumar, Mallikarjuna N N and Venkataraman A 2003 *Indian J. Chem. Technol.* **10** 63
- Lagashetty Arunkumar, Vijayanand Havanoor, Basavaraja S, Balaji S D and Venkataraman A 2007 *Sci. Technol. Adv. Mater.* **8** 484
- Mallikarjuna N N and Venkataraman A 2003 *Talanta* **60** 147
- Mallikarjuna N N, Govindraj B, Lagashetty Arunkumar and Venkataraman A 2003 *J. Therm. Anal. Cal.* **71** 915
- Mallinson J C 1987 *The foundations of magnetic recording* (San Diego: Academic Press)
- Patil K C, Aruna S T and Ekambaran S 1997 *Curr. Opp. Solid State Mater. Sci.* **2** 158
- Peterson M L, White A F, Brown G E and Parks Jr G A 1997 *Env. Sci. Technol.* **31** 1573
- Rao C N R 1963 *Chemical applications of infrared spectroscopy* (New York & London: Academic Press)
- Rao C N R 1994 *Chemical approaches to the synthesis of inorganic materials* (New Delhi: Wiley Eastern Ltd.)
- Rao K J and Ramesh P D 1995 *Bull. Mater. Sci.* **18** 447
- Reddy Gopal G V, Sheela Kalyana and Manorama S V 2000 *Int. J. Inorg. Mater.* **2** 301
- Smith J, Wijn H P T, Phillips N N and Gloeilampenjabricken Eindhoven 1959 *Ferrites (Holland)* 144A
- Sverjensky D A 2003 *Nature* **364** 776
- Venkataraman A, Hiremath V A, Date S K and Kulkarni S M 2001 *Bull. Mater. Sci.* **24** 101
- Vijayanand H, Lagashetty Arunkumar, Mallikarjuna N N and Venkataraman A 2003 *Asian J. Chem.* **15** 79
- Vijay A H 2000 *Synthesis and studies of gamma ferric oxide*, Ph.D. Thesis, Gulbarga University, Gulbarga
- Yang B L and Kang H H 1982 *J. Catal.* **77** 410