

## Preface

Transition metal oxides in nano dimension have wide technological applications for the unusual structural features and their properties. Some of the essential applications of these materials are in magnetic memory devices, colour imaging, magnetic refrigeration, medical imaging, controlled drug delivery, ferrofluids, catalysis and sensors. The single domain magnetic nanoparticles show many unusual phenomena such as superparamagnetism, giant coercivity, enhanced remanence and quantum tunneling of magnetization.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, the ferrimagnetic cubic form of iron oxide is one of the widely used magnetic materials. It is well known that the size, shape and the capping agent present on these nanoparticle surface, control the properties of these materials. Thus proper variation of these parameters with development of new synthetic methods to modulate the properties of the nanoparticles is a flourishing contemporary research in nanoscience.

In the present work various diols have been used for the synthesis of transition metal oxide nanoparticles. Investigations have also been carried out to develop a method for a one step synthesis of in situ capped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The nanoparticles are systematically characterised and the effect of capping on the nanoparticle surface was studied by Raman spectroscopy and magnetic measurement techniques.

**Chapter-1** deals with a general introduction of nanomaterials, discussing the structural, electronic, optical, catalytic and magnetic properties of materials in the nanometer length scale with special emphasis on transition metal oxides. The basic features of commonly used solution phase bottom-up methods for the synthesis of nanocrystalline oxides, such as coprecipitation, sol-gel, microemulsions, hydrothermal/solvothermal and nonhydrolytic methods and their development are discussed. An introduction to characterization of nanomaterials by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscope (TEM) and Mössbauer

spectroscopy, investigation of surface capping by thermal analysis and FTIR spectroscopy are given. A brief overview of different kind of magnetisms exhibited by materials with emphasis on Ferrimagnetism and superparamagnetism are also given. This chapter also deals with a review of the published work on synthesis and properties of some of the iron oxide nanocrystals and aim and scope of the present work.

**Chapter-2** deals with the synthesis of nanocrystalline oxide samples in various diols i.e. ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol and 1,5-pentanediol. The description of instrument specifications and techniques used for the characterization and study of samples by X-ray diffraction, FTIR spectroscopy, Raman spectroscopy, thermal analysis, TEM, Mössbauer spectroscopy and AC susceptibility are given.

**Chapter-3** deals with the results of nanocrystalline oxide samples prepared by polyol method. Characterization of the samples is done by XRD, FTIR spectroscopy, Raman spectroscopy, thermal analysis and TEM. XRD patterns show that lepidocrocite is formed on refluxing the solution of ferric nitrate in ethylene glycol or 1,3-propanediol, at 453K. On annealing lepidocrocite samples at 573K in argon atmosphere XRD patterns show a cubic spinel phase and the broad lines in the XRD patterns suggest that the samples are nanocrystalline in nature. FTIR spectra of the samples show that the diol moiety is attached to the lepidocrocite and on annealing at 573K a strong band at  $560\text{cm}^{-1}$  due to the spinel phase appears with a decrease in intensity of the bands pertaining to the diol moiety.

On refluxing the solution of ferric nitrate in 1,2-propanediol at 403K, nitrous fumes evolved and a precipitate is formed. XRD pattern of the precipitate show a strong low angle reflection similar to the layered alkoxides. The XRD patterns of the samples formed on annealing the alkoxide in argon atmosphere at 573K, 673K and 773K show a single phase cubic spinel structure. FTIR spectrum of the precipitate shows bands due to the diol moiety and also due to the M-O bond. On annealing the sample at higher

temperatures diol moiety is gradually removed and a strong band at  $560\text{cm}^{-1}$  due to the spinel structure appeared.

The XRD patterns of the samples formed by refluxing the solution of ferric nitrate in 1,4-butanediol and 1,5-pentanediol at 483K and 513K respectively correspond to a single phase cubic spinel structure and broad lines suggest that the samples are nanocrystalline in nature. FTIR spectra of the samples show a strong band at  $560\text{cm}^{-1}$  due to the spinel phase and bands in the higher wavenumber region due to the diol moiety. The XRD patterns of the precipitates formed on refluxing the solution of cobalt nitrate, copper nitrate and  $\text{KMnO}_4$  in 1,4-butanediol at 403, 433 and 483K respectively, match with that of  $\text{Co}_3\text{O}_4$ ,  $\text{Cu}_2\text{O}$  and  $\text{Mn}_3\text{O}_4$  (Hausmannite).

Thermal analysis (TG, DTG & DTA) of the samples prepared in ethylene glycol and 1,2-propanediol at 453K and 403K respectively show a one step weight loss but samples prepared in 1,3-propanediol at 453K, 1,4-butanediol at 483K and 1,5-pentanediol at 513K show a two step weight loss with corresponding peaks in DTA and DTG curves. The results of the FTIR studies of these samples annealed at different temperatures are also reported.

Raman spectra of all the nanocrystalline spinel phase iron oxide samples at low laser power show characteristic bands for  $\gamma\text{-Fe}_2\text{O}_3$ . TEM micrographs show that the particle size of all the  $\gamma\text{-Fe}_2\text{O}_3$  samples are between 6 to 15nm. The TEM micrograph of samples prepared in ethylene glycol and 1,2-propanediol show that the particles are agglomerated but that of samples prepared in 1,3-propanediol, 1,4-butanediol and 1,5-pentanediol are well dispersed.

For the mechanistic study of the reaction of ferric nitrate in 1,4-butanediol, intermediates formed were separated and characterized by XRD, FTIR and thermal analysis. The XRD pattern of the intermediate formed at 403K matches with the pattern of 6-line ferrihydrite prepared by standard method. DTA curve of the intermediate show

two exothermic peaks, the first peak at 573K is accompanied with weight loss but the second exothermic peak at 750K is not accompanied with any weight loss. On heating the intermediate 6-line ferrihydrite in air and also in a reducing solvent e.g. tetraline,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is formed.

The stability of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles prepared in different diols, to Raman laser was studied by taking the Raman spectra of the samples at various laser powers and acquisition time. On increasing the laser power and/or acquisition time the spectral pattern changes and new bands appear characteristic of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase.

The room temperature Mössbauer spectra of the samples show a paramagnetic doublet and at lower temperatures magnetic sextet pattern gradually appears. The 20K spectrum, of the sample prepared in 1,4-butanediol by a single step was fitted with two sextets and the 20K spectrum of the annealed (573K) sample was fitted with 3 sextets. The thermal variation of AC susceptibility curve for the sample prepared in 1,4-butanediol show a maximum in the susceptibility curve around 218K. The susceptibility curve of the sample prepared in 1,2-propanediol does not show any maximum.

**Chapter-4** deals with the discussion of the results of the oxide samples. X-ray diffraction analyses show that lepidocrocite is formed on refluxing the solution of ferric nitrate in ethylene glycol and 1,3-propanediol at 453K. On annealing the lepidocrocite at 573K in argon atmosphere spinel phase of iron oxide is formed. The reaction of ferric nitrate with 1,2-propanediol at 403K produces a precipitate of layered iron alkoxide precipitate. On annealing the precipitate at 563K, spinel phase of iron oxide is formed and on increasing the annealing temperature to 673K and 773K the line width of the XRD peaks decreases due to increase in crystallite size from 9nm to 48nm. On refluxing the solution of ferric nitrate in 1,4-butanediol and 1,5-pentanediol at 483K and 513K respectively, spinel phase of iron oxide is formed in a single step without any annealing. On refluxing the solution of cobalt nitrate and copper nitrate in 1,4-butanediol at 403K

and 433K respectively  $\text{Co}_3\text{O}_4$  and  $\text{Cu}_2\text{O}$  are formed. FTIR spectra of the samples show that diol moiety is capped on the surface of the sample.

Raman spectra of all the synthesised iron oxide samples at low laser power confirm that the spinel oxide samples synthesized by the polyol method are  $\gamma\text{-Fe}_2\text{O}_3$ . FTIR spectra and thermal analysis of the samples show that the  $\gamma\text{-Fe}_2\text{O}_3$  samples synthesised in 1,3-propanediol, 1,4-butanediol and 1,5-pentanediol are capped with the diol moiety and the  $\gamma\text{-Fe}_2\text{O}_3$  samples synthesized in ethylene glycol and 1,2-propanediol followed by annealing are not capped. On annealing the capped samples diol moiety is gradually removed and complete removal occurs above 873K. The capped samples form stable dispersions in the respective diols. TEM micrographs of the samples show that the nanoparticles capped with the diol moiety are well dispersed and the uncapped nanoparticles are agglomerated. Histograms drawn by measuring the particle size from the TEM micrographs of the capped samples show a narrow particle size distribution.

The mechanistic study of the reaction of ferric nitrate in 1,4-butanediol reveals that on refluxing the solution at 403K, alongwith the liberation of nitrous fumes, a 6-line ferrihydrite is formed which remains stable in the diol solution upto 473K. On increasing the refluxing temperature to 483K, 6-line ferrihydrite transforms to  $\gamma\text{-Fe}_2\text{O}_3$  by a dissolution reprecipitation mechanism.

Raman spectra taken at various laser powers, of the  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles synthesized in different diols show that at higher laser powers  $\gamma\text{-Fe}_2\text{O}_3$  changes to  $\alpha\text{-Fe}_2\text{O}_3$ . The nanoparticles capped with the diol moiety show higher stability to laser induced degradation than the uncapped samples. The stability of the nanoparticles to laser power also increases with increase in particle size.

Mössbauer spectra taken in the temperature range 20-298K, of the samples prepared in 1,4-butanediol show that the samples are superparamagnetic. The blocking temperature of the sample prepared in 1,4-butanediol by a single step was found to be

~225K and the sample prepared by annealing was found to be 250K. The isomer shift and quadrupole splitting values derived from the 20K spectra of the samples again confirm that the samples are  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The 20K spectrum of the capped sample was fitted with two sextets corresponding to the Fe<sup>3+</sup> on A and B site of the spinel lattice. The 20K spectrum of the uncapped sample was fitted with 3 hyperfine patterns and the 3rd sextet is accounted for the Fe<sup>3+</sup> present on the surface of the nanoparticles. Therefore M $\ddot{o}$ ssbauer spectra can be used to ascertain the capping of the sample. The temperature dependant AC susceptibility plot of the samples show that the blocking temperature of the capped sample is more than the uncapped sample. In the uncapped samples with large particle size distribution the maximum in the susceptibility curve is not well defined.