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Optical Investigation in Visible Region of IOUP below Single Domain

Nishant T. Tayade
Ph.D. Student, Department of Physics, Govt. Institute of Science
R.T. Road, Civil Line, Nagpur, Maharashtra, India
Dr. Purushottam R. Arjunwadkar
Associate Professor, Department of Physics, Govt. Institute of Science
R.T. Road, Civil Line, Nagpur, Maharashtra, India

Abstract:
Iron Oxide Ultrafine Particles (IOUP), having Magnetite phase, 18nm size, a high saturation magnetization, below the single domain magnetic behavior, were synthesized successfully by the chemical route co-precipitation. Optical characterization in visible range was carried out to analyze its interaction with nearly superparamagnetic IOUP and study the nature of below single domain particles. Optical energy band gap was found to be at 2.4eV without exciton-phonon interaction. Systematic investigation confirmed the IOUP's behavioral significance in the visible region.

Keywords: *Iron Oxide, IOUP, magnetite, superparamagnetic nanoparticles, single domain, spectroscopy,*

1. Introduction
Iron Oxide Ultrafine particles (IOUP) exhibit a size effect. Their magnetic properties change with their critical size in nano dimension. Below a particular size the domain theory is became no more significant. For IOUP below a single domain size, super-paramagnetic phenomenon appears. Such a IOUP are required for the diverse area of applications like memory, printing inks [1], biomedical devices [2], magnetic refrigerator [3], ferofluid [4], catalyst [5], drugs [6] etc. In the applications like catalyst, it is necessary to have an information about the behavior of IOUP for photon energy in a visible region.
In a photo catalyst application, IOUP can be recollected using magnet after its use [5]. According to Chang-Ning Shauo et. al. magnetic film exhibit good transmittance in the visible region and excellent UVB absorption [7]. Therefore, it is assumed that the black color lustrous IOUP does not have any absorption peak in a visible range however good absorption within a range. It is also well known that as a size decreases, the change in optical properties occurs. El Ghandoor et. al.' have observed 'the presence of both direct and indirect transition' and semiconductor nature of the sample for size less than 20nm [8]. This is an interesting and novel result and the Urbach energy and the Fermi energy have been used to support the result [8]. According to Huan Qin et al., light shows very small effect on an oxidation process [9]. In this paper, optical behavior of IOUP (strictly) in a visible region of photon energies has been examined and exploring their behavior significance.

2. Materials and Methods
A. R. Grade Ferric Chloride Hex hydrated ($FeCl_3.6H_2O$) for Fe^{+2} and Ferrous Sulphate Hydrated ($FeSO_4.7H_2O$) for Fe^{+3}, extra pure NH_3 from Merck (India) and the double distilled water were used. Wet chemical route co-precipitation technique is used to synthesize the IOUP for the formation of Fe_3O_4 phase without surfactants. Precursors $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$ in the proportion of 2:1 with 0.25 molarities were mixed in a reactor chamber using fifteen-minute stirring and then increase its temperature to 333K. NH_3H_2O was prepared by adding double distilled water to Ammonium solution which was added to reactor chamber quickly and increases its temperature. Black particles were precipitated out. Temperature was kept constant at 363K for one hour under the high stirring rate. The precipitate solution was cooled down to room temperature with high speed stirring. Precipitate was decanted using strong magnet and washed twice by hot water and then dispersed in the mixture of Acetone and Hexane. Sample is dried for few hours and later kept in vacuum for 48 hours. For spectroscopy IOUP which were dispersed in a double distilled water and ultrasonicated.
The X-ray diffraction (XRD) was carried out on a Philips X-Ray Diffractometer using Cu-Kα radiation of wavelength (λ) approximately 1.54 Å, range 20-80 degree with a step size 0.02 degree to investigate structure, phase, size etc. for the confirmation of required IOUP (particularly the magnetite phase) is whether formed or not. The PC based pulsed M-H loop tracer system with the range of field between -6 KOe to 6KOe was used for magnetic study at the room temperature 294K which was calibrated by standard Nickel crystal before use. For optical study were carried out using double beam ELCO SL159 Visible spectrometer and the data was recorded at 294K.

3. Result and Discussion

Indexing of peak profile from intensities versus scattering angles (fig.1) is very close to JCPDS 65-3107 with a single phase magnetite (Fe_3O_4) [10]. Structure is inverse spinal. Broadening of peaks indicate the presence of nanocrystallites. The size of crystallite is estimated as 18nm by Debye-Scherrer's formula used for (311) peak after elimination of instrumental broadening error. The IOUP are found crystalline at ambient room temperature.

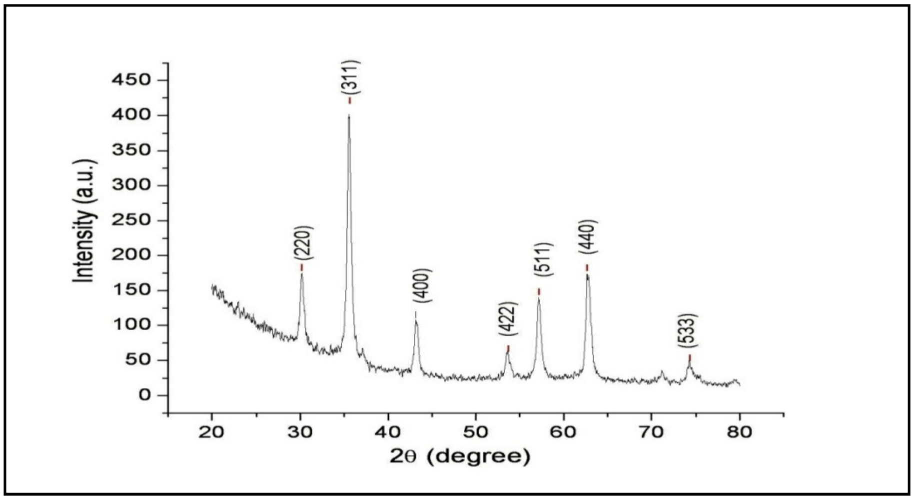

Figure 1: X ray diffraction of IOUP

M-H loop shows small coercivity (Mc) i.e. 78 Oe, low retentivity (Mr) and small squareness factor at room temperature is illustrated in fig. 2. The remanance ratio Mr/Mc was found less than 0.5 that has been aspect for the single domain and nearly non-interacting randomly oriented particles. Magnetic saturation is started at lower field and it is high and still have not achieved for 6kOe field. The behavior looks like approaching toward an-hysteresis nature. Small area of hysteresis indicates formation of the soft magnetic material. This suggests particles are close to the super-paramagnetic nature and structure below single domain has been formed at a room temperature. Small Magnetic Anisotropy is present.

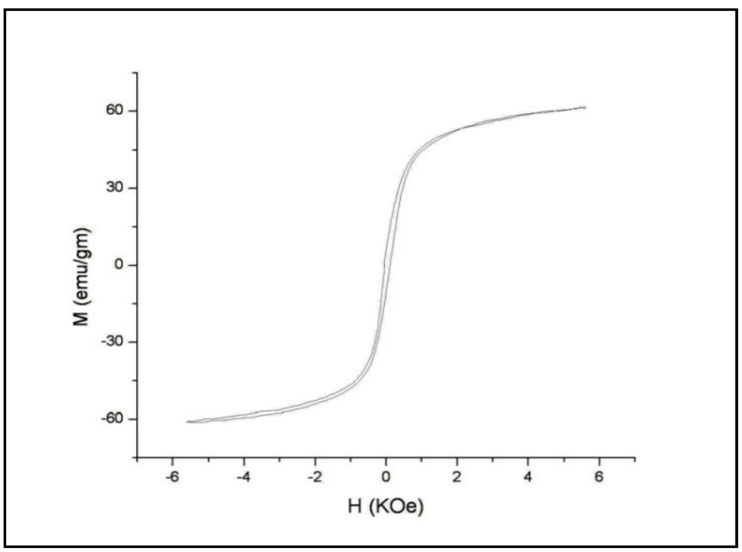

Figure 2: Hysteresis of the IOUP at room temperature

In Fig. 3 (a) shows less absorbance for higher wavelength in visible region and it increases toward the lower wavelength. (Small peak around 680nm is due to the instrumental error. This peak was found for all recorded samples characterized by spectrometer in our laboratory.) For the wavelength less than 400nm due to few data points there is possibility of presence of peak in below lower cut off region of visible spectrum. Transmittance as a function of wavelength and it increases with it as shown in fig.3(b).

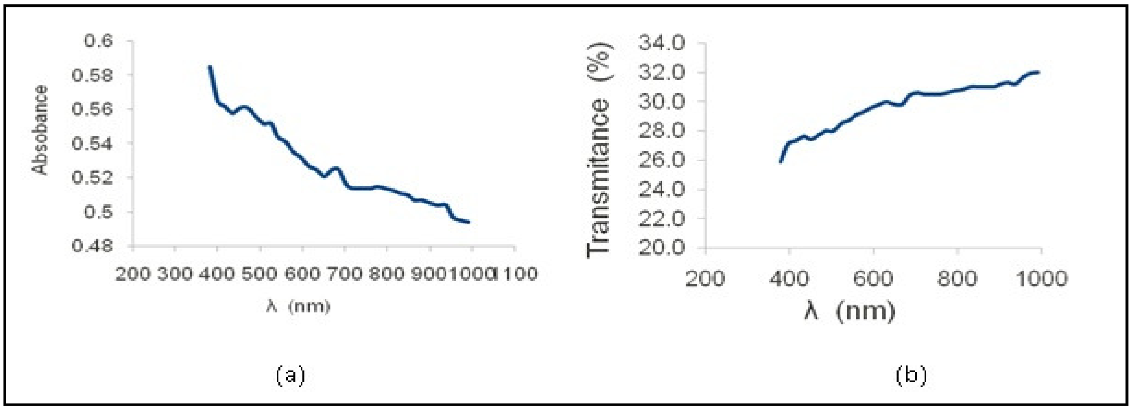

Figure 3: (a) Absorbance as a function of wavelength, (b) Transmittance as a function of wavelength

Absorption coefficient verses $1/\lambda^{-4}$ is illustrated in a fig.4(a) to study possibility of scattering. From 20 to 40 (in unit of 10^{24} m^{-4}) on $1/\lambda^{-4}$ a linear region was fitted by a straight line. Extrapolation on a y-axis gave the coefficient of absorption with considering scattering effect. It is found 0.55 in two significant Figures. Further to know the behavior of IOUP regarding direct and indirect transitions, Touc plot is illustrated in fig.4(b) and fig.4(c) which were plotted between $(ahv)^m$ and photon energy, where 'a' is coefficient of absorption, 'h' is Plank's constant, 'v' is the frequency of light photon and 'm' is a number indicates type of allowed transition. For direct allowed transition m = 2 and for the indirect allowed transition m=1/2. From $(ahv)^2$ versus photon energy (fig. 4(b)), extrapolating tail's linear region illustrated by the blue dotted line on the photon energy axis gives direct allowed band gap 2.4eV in two significant figures. Due to less data at the tail end, another red color dashed line employed to extrapolate for another linear region and band gap was found as 1.4eV. It is confirmed that the band gap is not less than 1.4eV in the direct allowed transition. Both of these are in the range of semiconductors. H. El Ghandoor found 2.87eV means our sample is more conducting as they have mentioned in the result published in their references [9]. However, in our study 2.4eV is found an optical energy band gap. For the indirect allowed band gap, the $(ahv)^{1/2}$ versus photon energy in fig. 4(c) shows the extrapolation on the photon energy axis goes to negative side. Therefore, the exiton-phonon interaction must not occur and indirect band gap is not present. This is the evidence of absence of lattice vibrations, noise, losses during the interaction. From fig.4(d), the Urbach energy was calculated by taking reciprocal of the slope of linear region of the lower photon energy which is found 1.2eV. It is double with compare to found in a literature [9] implies the prepared IOUP below single domain are more conducting.

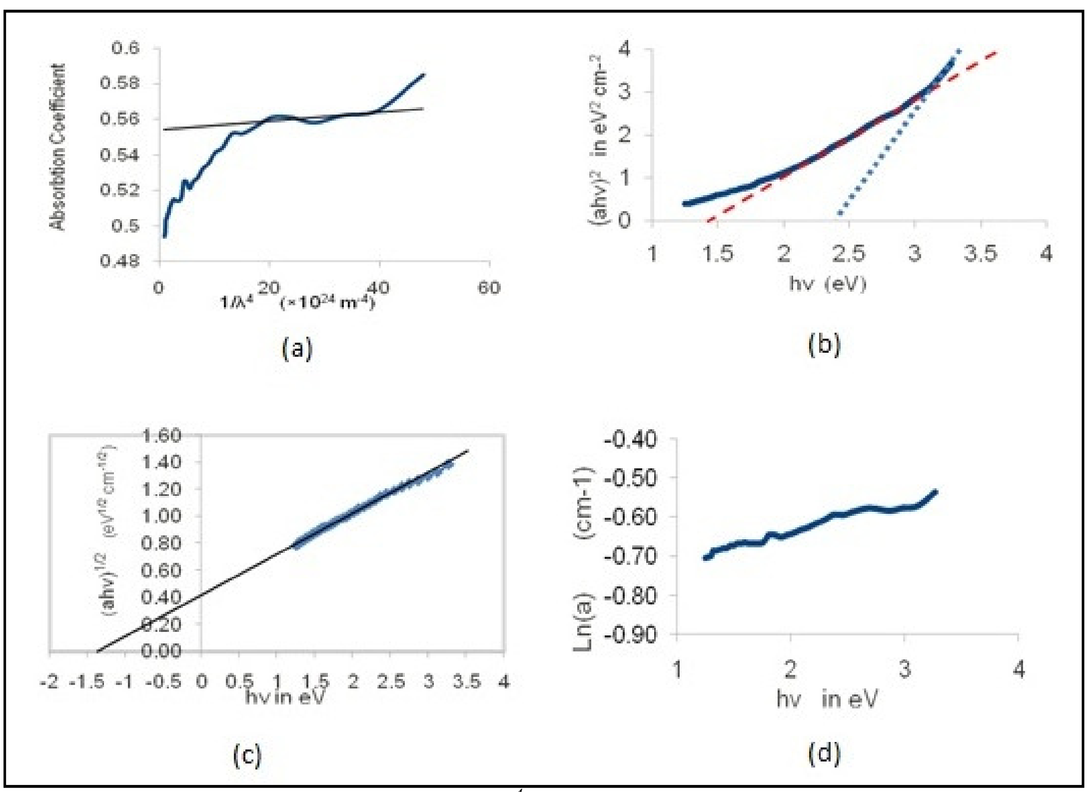

Figure 4: Absorption coefficient against $1/\lambda^4$ (b) shows (ahv)2 against photon energy (c) shows $(ahv)^{1/2}$ against photon energy (d) shows Ln(a) against photon energy.

4. Conclusion

Nearly super paramagnetic IOUP of magnetite phase below single domain was successfully synthesized by chemical route co-precipitation method which has nano dimension, inverse spinal structure and soft magnetic properties. Spectroscopic investigation reveal that the IOUP is a semiconducting nature and its direct optical energy band gap is 2.4eV. Simultaneously It is confirmed the absences of the exiton-phonon interaction. The lattice vibration due to photon energy in a visible range is therefore absent. Urbach energy also confirm better conductivity below single domain IOUP. This study indicates optical behavior is significant for below the single domain IOUP.

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