Synthesis and Characterization of $Mn_2[Fe(CN)_6].xH_2O$ Nanocomposites by Coprecipitation Method

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Abstract

Nanocomposites of $Mn_2[Fe(CN)_6]xH_2O$ were achieved by using the materials like manganese chloride, $FeCl_3$, and $K_3FeC_6N_6$ in the form of a dilute solution with the help of a wet chemical Co-precipitation process. The crystal structure of the prepared sample was characterized by using XRD method and the surface morphology of prepared nanoparticles was characterized by FTIR spectroscopy. Quality results suggest that spherical shaped nano-composites of $Mn_2[Fe(CN)_6]xH_2O$ can be obtained. Thermal treatment of these compounds provides manganese ferrite ($MnFe_2O_4$) with defined grain boundaries. The size of the prepared nano-crystallites was 15-25 nm. Here, we observed the thermal change in the phase decomposition and the phase evolution of the ready sample. The outcomes from the characterization showed that the shape, phase and crystal structure of the nano-crystals were strongly changed. Besides, the direct phase transition from Manganese Iron Cyanide Hydrate $Mn_2[Fe(CN)_6]xH_2O$ to $MnFe_2O_4$ occurred at 300°C for 3houres. The overall size of the finally obtained product i.e. $MnFe_2O_4$ (manganese ferrite) is approximately 25 nm.

Keywords— *Nanocomposites, Coprecipitation, Prussian Blue, Manganese Ferrite***.**

INTRODUCTION

$Mn_2[Fe(CN)_6].xH_2O$ is a mixed compound having valance iron(III) hexacyanoferrate(II) which belongs to the Prussian Blue (PB) family. The general Formula of the PB family is $A_n[B(CN)_6]_m.xH_2O$ where A and B represent transition metals. Recently, Prussian Blue (PB) due to its analogous has great interest it is widely used in the area of electrochemistry [1,2], optics [3], hydrogen adsorption [4] molecule-based magnets [5–7], etc. Due to their ideal properties, these nano-sized PBA's with balanced size are used in numerous applications as electrochromic [8], nano-magnetic [9], biomedical [10] devices, and biosensing [11–14], etc. Nanocrystalline Prussian-blue (PB) has been provide various information which synthesized by different methods in which different agents like sol-gel [3], porous alumina [15], sodium hexametaphosphate [16], Nafion [17], Stearylamine [18], anionic surfactant sodium bis(2-Ethylhexyl) sulfosuccinate [19], apoferritin [20], or polyvinyl pyrrolidone [21] were used to stabilize nanoparticles. In general, it is found that these methods are utilized in small space for the growth of PBA's nanoparticles by using changed types of pattern and surfactants. These patterns were found in the sample and reside in the cavities amongst the prepared nanoparticles and respond as nano spaces particles. Therefore, the synthesis of PB nano-composites by these processes is very important which may widen its applications. On using the wet chemical technique i.e. co-precipitation method it was found that the main chances of getting contamination form were negligible [22].

In the present work, it was reported that the powder form of synthesis of Manganese Iron Cyanide Hydrate ($Mn_2[Fe(CN)_6]xH_2O$) nano-composites and effects were observed on heat treatment of the prepared samples with the help of XRD, FTIR analysis. Results of these prepared samples show that the sample of manganese iron cyanide hydrate was in the range of nanometer with good homogeneity. It was also observed that there occurs the transformation of $Mn_2[Fe(CN)_6]xH_2O$ into $MnFe_2O_4$, due to thermal annealing at 300^0C for 3 hours.

EXPERIMENTAL

A. Preparation Of The Sample

The $Mn_2[Fe(CN)_6].xH_2O$ nano-composites has been prepared by wet chemical Coprecipitation method. The purified reagents like $K_3[Fe(CN)_6]$ (Aldrich 99.98%), $MnCl_2$ (Aldrich99.98%), $FeCl_3$ (Aldrich99.98%), and also de-ionized water was used. The suspension for the sample was prepared by the methods given in the literature [22].

B. Characterization Of The Sample

The structure and phase of prepared samples were characterized by using XRD, FTIR, VSM, Rietveld Refinement techniques. The XRD patterns of prepared samples were recorded PW/1710. At potential 50 KV and current 40 mA the Ni filter and monochromatic Cu Kα radiation found wavelength 1.5418 Å. The XRD data were recorded in the range of 2θ ranging from 10 to 70 degrees. Infrared spectra were recorded by Fourier Transform Infrared (FTIR) Spectrometer found in the range of 2500-400cm^{-1}.

RESULT AND DISCUSSION

C. FTIR

The FTIR spectrum of the prepared sample shown in Fig. 1. From this spectra, it is observed that the characteristics of prepared sample is flexible vibration of OH [23] in the absorption band from 3500 to 2350cm^{-1} in the presence of water in the prepared sample. The peaks at 586cm^{-1} appropriate to Fe-CN-Mn banding mode [23]. The absorption peak around 2080cm^{-1} shows the strongest peak of the flexible mode of the Cyanide group. [24]

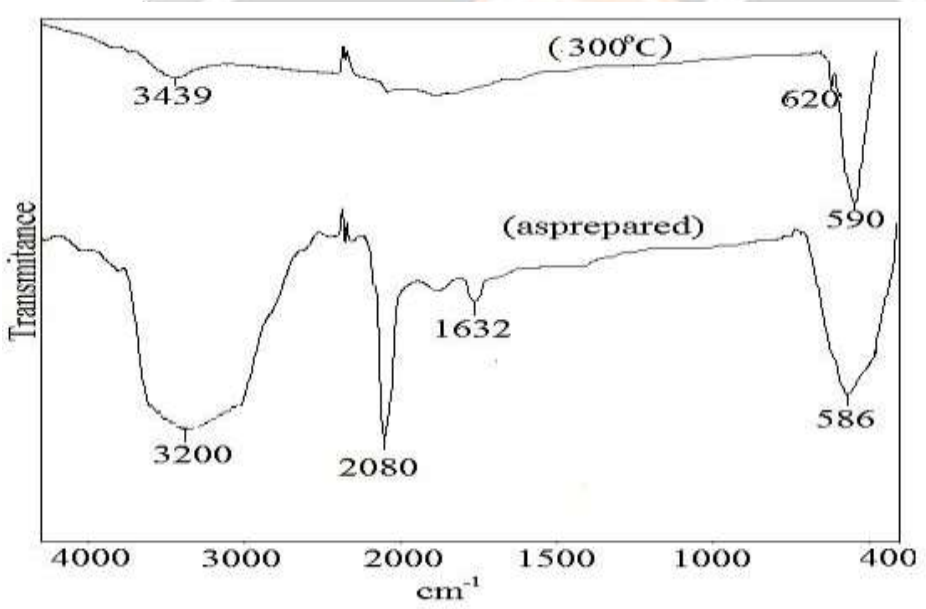

Figure 1 FTIR spectra of manganese iron cyanide hydrate

The occurrence of Green Bluish prepared precipitate with a 2080cm^{-1} peak of FTIR spectra approves the formation of manganese iron cyanide hydrate. When the prepared sample was heat-treated under the temperature of 300°C, the absorption band at 2080cm^{-1} was disappeared completely and shows the formation of nanocrystals of $MnFe_2O_4$. The band that occurs at 590cm^{-1} was attributed to lexible O-Fe at the shape tetrahedral site shows the presence of manganese ferrite [26].

D. XRD Analysis

The peaks in X-ray diffraction (XRD) patterns and annealed powder samples of prepared sample were shown in Fig 2. The XRD pattern of prepared sample results diffraction peak at 2θ~17.3° (200), 25.5° (220), 30.12° (311), 35.10° (400), 38.10° (331), 40.12° (420), 44.20° (422) and 56.8 (620) and matched with JCPDS file No. 46-0910. The space group for manganese iron cyanide hydrate ($Mn_2[Fe(CN)_6]xH_2O$) was obtained as F43m (216). The crystal structure of $Mn_2[Fe(CN)_6]$ x H_2O was face centered cubic (FCC) and the lattice parameter was 10.06 Å. These observations and calculations approach the FTIR data. The prepared sample in powder form calcined at 300°C for 2 hours, results in diffraction peaks at 2θ ~ 28.60° (220), 34.92° (311),

42.48° (400), 56.52° (511), and 61.15° (440). These peaks show that the prepared samples were of manganese ferrite and matched with JCPDS file No. 73-1964. The space group and crystal structure of the obtained data are found to be of Fd3m (227) and FCC respectively. For obtain the average size of Manganese Iron Cyanide Hydrate ($Mn_2[Fe(CN)_6]xH_2O$) and Manganese Ferrite, by Debye-Scherer formula was obtained in size ~ 15 and 25 nm respectively.

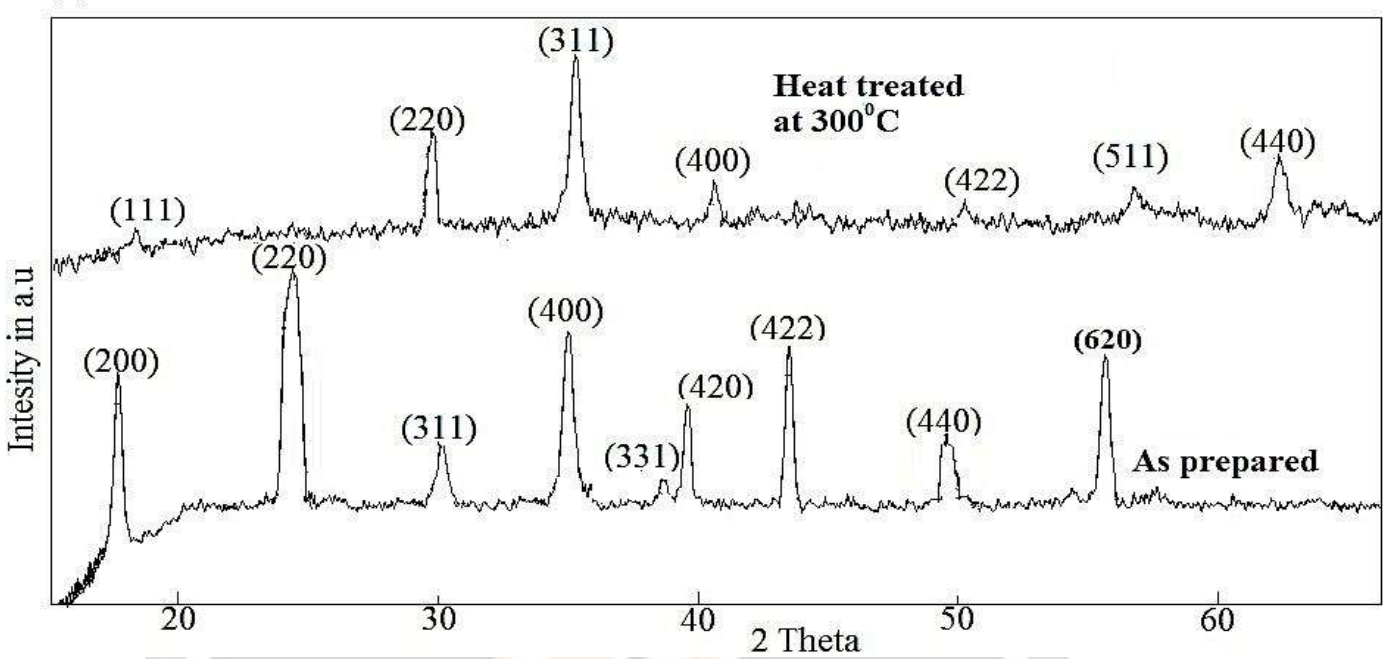

Figure 2 XRD patterns of $Mn_2[Fe(CN)_6]xH_2O$ and $MnFe_2O_4$.

E. ***Rietveld Refinement***

The Rietveld Refinement of the heat-treated sample has been shown in fig 3. The Rietveld Refinement is done with the help of the Fullprof Suite Software. From the result of Rietveld Refinement, we can see that the profiles of observed and calculated data are fully matched with each other.

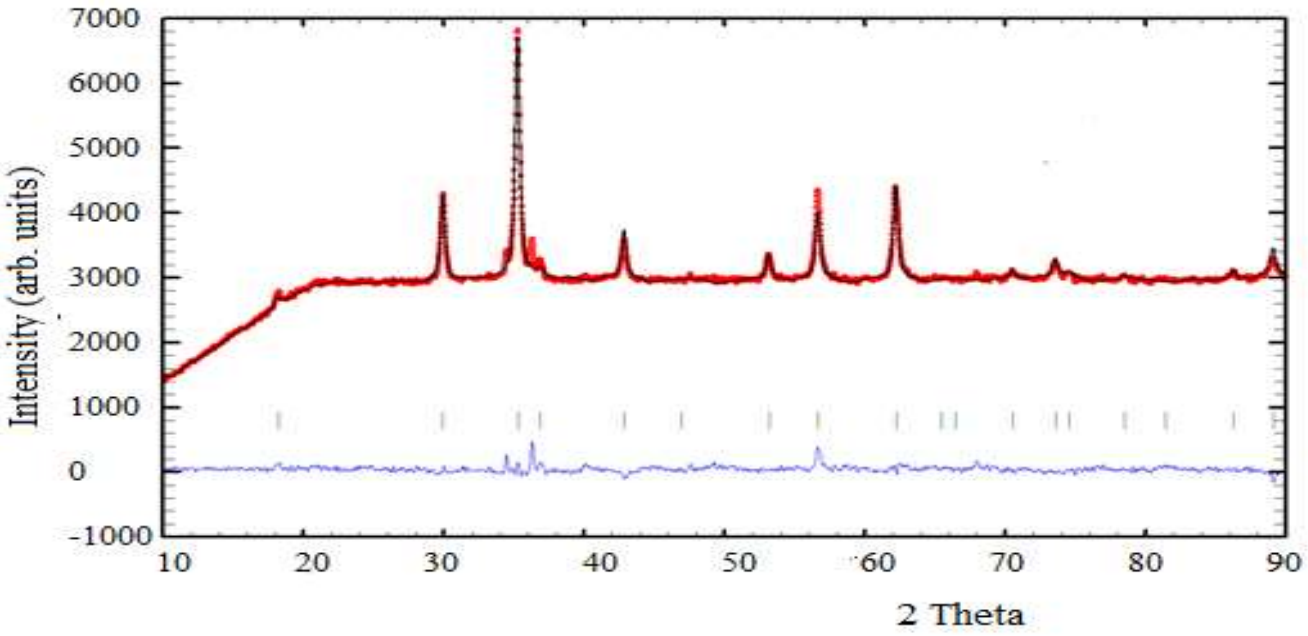

Figure 3 Rietveld Refinement of $MnFe_2O_4$ Nanocomposites

The isothermal parameters and atomic parameters of the heat-treated sample obtained from Rietveld refinement were shown in table I. The Refined factor obtained from the heat-treated sample i.e. $MnFe_2O_4$ was shown in Table II.

TABLE I. ISOTHERMAL PARAMETERS AND ATOMIC PARAMETERS OF HEAT TREATED SAMPLE

Atoms	Wyck.	x/a	y/b	z/c
Fe	16c	1/8	1/8	1/8
Mn	16c	1/8	1/8	1/8
Fe	8b	1/2	1/2	1/2
Mn	8b	1/2	1/2	1/2
O	32e	0.25	0.25	0.25

TABLE II. RESULTS OF THE REFINED FACTOR FOR $MnFe_2O_4$ STRUCTURE

1.	χ^2	**0.8**
2.	R_p	45.4
3.	R_{WP}	22.6
4.	R_E	25.4
5.	R_F -Factor	21.0
6.	Bragg R-Factor	16.1

F. VSM Studies

A VSM result of the annealed powder sample is shown in Fig.3. magnetic hysteresis curve of the prepared sample observes at normal room temperature. The hysteresis loop of prepared sample shows ferromagnetic behavior, saturation magnetization(Ms), coercivity(Hc) and remanent magnetization (Mr) values of about 67emu/g, 520 Oe and 26emu/g, respectively and these values are different from those reported for $MnFe_2O_4$ nanorods (Ms=68.02emu/g, Mr=14emu/g, Hc=361 Oe) [27] and nanoparticles (Ms= 70emu/g, Mr= 18emu/g, Hc= 200 Oe) [28]. The meticulous reasons are not clear and may be concerned with the size effect and the morphology of prepared nanocrystals samples.

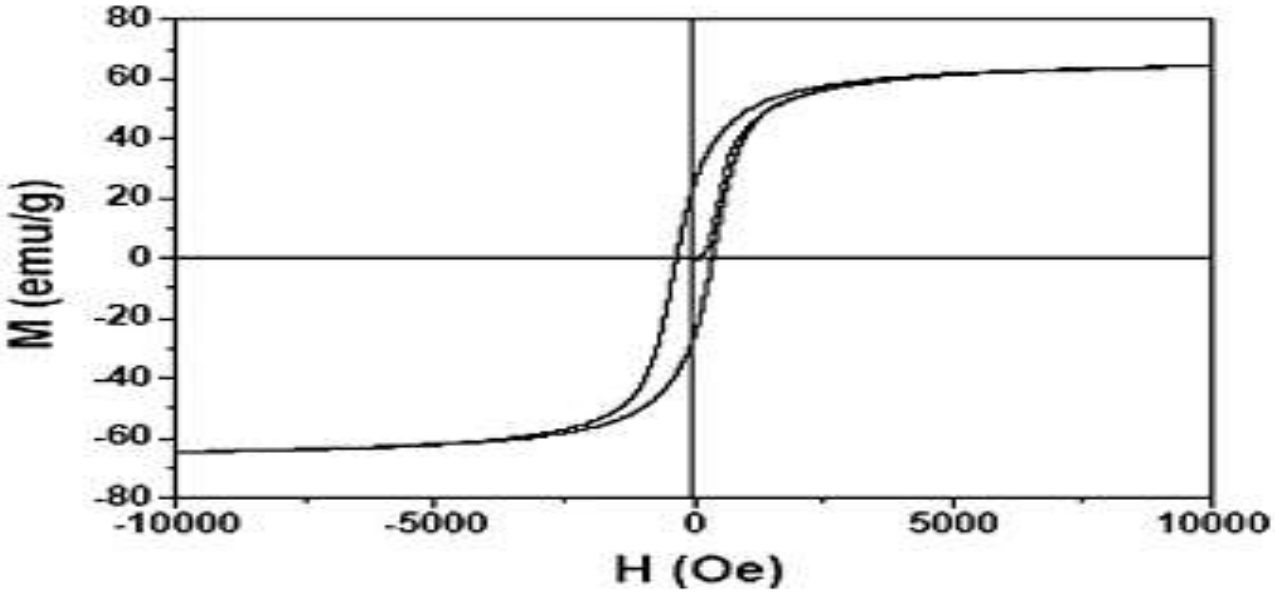

Figure 4 VSM of manganese ferrite nano-crystallites

CONCLUSION

The Coprecipitation method is used to synthesize the nanocomposite of $Mn_2[Fe(CN)_6]xH_2O$. The average size of Manganese Iron Cyanide Hydrate and Manganese Ferrite is obtained as 15nm and 25 nm respectively. We obtained small values of all Rietveld Refined parameters. Hence, there occurs good agreement between the calculated and observed data.

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