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Synthesis and Structural Analysis of Nanocrystalline $MnFe_2O_4$

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Abstract

Nanocrystalline form of manganese ferrite ($MnFe_2O_4$) has been synthesized by simple sol-gel auto combustion method using citric acid as chelating agent. The obtained nanocrystalline powders of manganese ferrite were subjected to structural and magnetic measurements. Temperature dependent magnetization was also carried out for the single phase nanocrystalline manganese ferrite and the results have been discussed in detail.

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1. Introduction

The study of fine particle systems has been a subject of continuous interest in physics as well as in other disciplines [1]. In recent years, many studies have been focused on the synthesis of metal oxide nanoparticles because of their exceptional properties. To a greater extent, the increased miniaturization and data-storage density of new devices requires the use of nanosized magnetic particles. Spinel ferrites show interesting electrical, magnetic properties and applications. Manganese ferrite ($MnFe_2O_4$) is one among the compounds originally thought to be an inverse spinel, but later found to be 80% normal and 20% inverse structure. It has received a great attention in microwave electronic storage and magnetic storage device applications. It has high magnetic permeability and electrical

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resistance. To obtain ferrite powders, several synthetic methods have been developed. The other methods have several disadvantages like large and non-uniform particle size and including impurities, which prevent further improvement in the performance of the products [2,3]. In order to overcome these difficulties and to meet the requirements for new applications, some wet chemical processes like sol–gel citrate [4,5], hydrothermal method [6], micro- emulsion process [7], co-precipitation technique [8], solution spray [9] and the detonation of emulsion explosive [10] have been considered for the production of nanoscale ferrites with excellent magnetic properties.

Manganese ferrite ($MnFe_2O_4$) has received increasing attention for their remarkable magnetic properties, (low coercivity, moderate saturation magnetisation), combined with a good chemical stability, high permeability and mechanical hardness [11] The importance of high density manganese ferrites also lie in their technological application such as core materials for coils or transformers, information and communication devices etc [12]. Finally, the present study shows that the properties like particle size and magnetic properties of Mn ferrites are processed by the citrate precursor method. The increase in calcination temperature leads to the increase in the size of crystal. Recently, they are used in compact and lightweight and high efficiency switching power supplies.[13,14].

2. Materials and methods

2.1. Synthesis of $MnFe_2O_4$ nanoparticles

Merck grade manganese (II) nitrate hexahydrate (Mn $(NO_3)_2$ $6H_2O$) and ferric (III) nitrate nanohydrate (Fe $(NO_3)_3$ $9H_2O$) (99%) were used as starting materials. The metal nitrates were dissolved together in a minimum amount of deionised water about 200ml to get a clear solution. The metal nitrates precursor solution was added with citric acid under continuous stirring. The entire reaction was carried out at 80ºC [10]. Condensation reaction occurs between the adjacent metal nitrates and the molecules of citrates yielding a polymer network in colloidal dimensions known as sol. Continuous heating of the sol leads to self combustion until brown agglomerates was observed and thus it leads to the formation of amorphous manganese ferrite powders. The powder was then calcined at different temperatures.

2.2. Apparatus

To identify the structure, powder X-ray diffraction (XRD) patterns of the samples were recorded by RIGAKU-DMAX2500 X-ray diffractometer with Cu Ka radiation (l ¼ 1:54056 A) at a scanning rate of 5/min for 2θ ranging from 10 to 80º. Magnetic measurements were carried out using a superconducting vibration sample magnetometer (Oxford Instruments) with a maximum field of 80 kOe in the temperature ranging from 2K to room temperature. Temperature dependent magnetization was also measured using the same instrument fitted with high temperature (HT) set-up for the samples calcinated at 700 ºC for the maximum applied field of 10 kOe. The particle size and surface morphology were examined through JEOL JEM 2100 High Resolution Transmission Electron Microscope (HRTEM) 200 Kv Japan. FTIR spectrum for the powder sample was recorded in the frequency range from 400 to 4000 cm^{-1} at room temperature using Bruker IFS 66V FTIR spectrometer.

3 Result and discussion

3.1 Structural characterization

Fig. 1 presents the XRD patterns of cube, where all the diffraction peaks could be indexed to face-centered cubic according to JCPDS card no.74-2403. The diffraction peak positions and intensity in the XRD patterns match well with standard $MnFe_2O_4$ ferrite crystals. The peaks in the XRD pattern of the product can be perfectly indexed to the (111), (220), (311), (400), (422), (511), and (440) facets of the $MnFe_2O_4$ phase. No characteristic peak for impurities was observed which confirms the purity of $MnFe_2O_4$. In addition, the intensities of diffraction peaks vary directly with the tested amount of $MnFe_2O_4$ samples. The sharp characteristic peaks could demonstrate that $MnFe_2O_4$ ferrite possesses higher crystallinity.

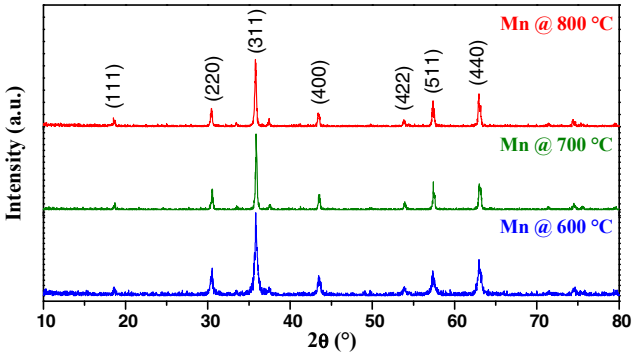

Fig.1 X ray diffraction pattern for the $MnFe_2O_4$ samples calcinated at 600ºC ,700ºC and 800ºC.

3.2 Magnetic characterization

Room temperature magnetic measurements carried out for the $MnFe_2O_4$ samples calcinated at different temperatures 600 ºC, 700 ºC and 800 ºC is given in Table 1. It shows that the sample calcinated at 800 ºC retains higher saturation magnetization. This may be due to the increase in the size of the grains which leads to the enlargement of the magnetic domain area of the polycrystalline samples. The sample calcinated at 700 ºC was then used for temperature dependent magnetic measurement which is shown in the Fig.2. The magnetisation versus temperature M-T curves obtained in the temperature range 300- 650 K, reveals that on heating, the crystallite size found to increase with decrease in corresponding Ms values. The hysteresis loops show high coercivity (H_c), saturation magnetisation (M_s) and remanence ratio (M_r/M_s). From the curve, we analyse that fine particles are easier to be thermally activated to overcome the magnetic anisotropy [3,8]. The inset of the graph depicts the magnetization with respect to the temperature of the samples calcinated at 700 ºC.

Table 1. Magnetic parameters of the samples with different morphologies from hysteresis loops

Sample	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	M_r/M_s
Mn600	56	23	1110	0.4107
Mn700	62	26	1084	0.4194
Mn800	67	29	1030	0.4328

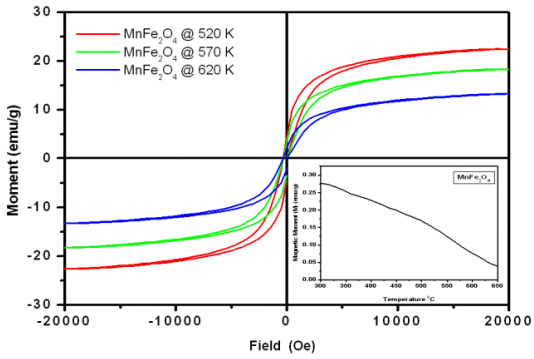

Fig.2 High temperature magnetic measurement of $MnFe_2O_4$ samples calcinated at 700ºC representing hysteresis loop at 520, 570 and 620 K (Inset figure represents the temperature dependent magnetization)

3.3 Nanostructured analysis

The morphology and the particle size of the Mn ferrites ($MnFe_2O_4$) was determined by TEM technique. The TEM micrographs of the sample calcinated 700 ºC is shown in Fig.3, showing almost homogeneous and uniform distribution of these particles in the powder samples. The particles consist of some regular and irregular cubic structure with mean sizes of about 45 nm, much smaller than the sizes obtained from the XRD measurements

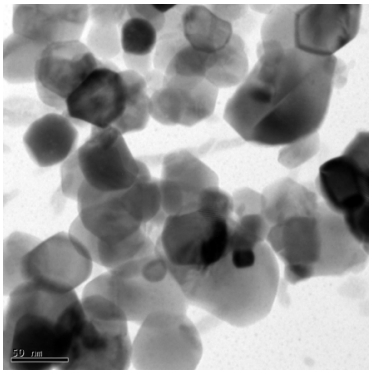

Fig.3. TEM Micrograph of nanocrystalline $MnFe_2O_4$ samples calcinated at 700 ºC

3.4 FTIR Analysis

The vibrational spectroscopy is considered to be a very useful technique for detection of chemical and structural changes. Fig. 4 displays the FTIR spectra of nanocrystalline $MnFe_2O_4$ calcinated at 700 ° C temperature. Fig.4 shows the characteristic bands for symmetric and asymmetric O–C–O stretching modes which appear at (1327 and 1370 cm^{-1}) and (1635 cm^{-1}), respectively. Also identified as O–H stretching and bending modes of vibration was revealed by the characteristic bands appeared at 3421 and 1632 cm^{-1} and are attributed to the adsorption of water molecules by ultra-fine granules of a- Fe2O3. With progressive increase in the calcination temperature, the resolution and sharpness of the bands increase. This can be ascribed to better crystallinity. The appearance of the bands at 532, 460 and 350 cm^{-1} indicated that iron (III) oxide crystallinity was improved and it was reported that the characteristic infrared bands for well crystallized α-Fe2O3 at 540, 470, 345 and 308 cm^{-1} [15]. The small shift in the locations of these characteristic bands obtained can be attributed to the presence of foreign ions (manganese ions) in the a-Fe2O3 structure.

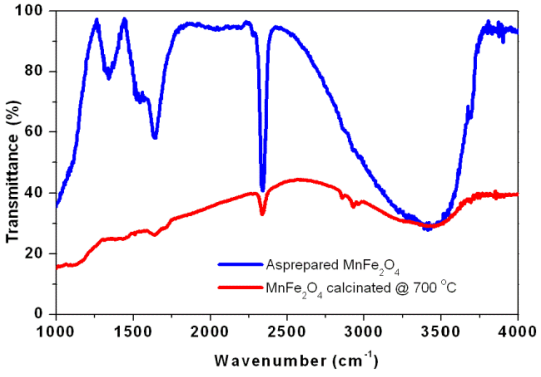

Fig.4. FTIR Spectra of nanocrystalline $MnFe_2O_4$ samples calcinated at 700 ºC

4 Conclusion

Nanostructured manganese ferrite ($MnFe_2O_4$) was prepared by combustion synthesis method. It is found that the combustion of manganese nitrate and iron nitrate with citric acid results in a series of mixtures of new phases, which convert to $MnFe_2O_4$ spinel phase during subsequent heat treatment at 700ºC The results also show that combustion synthesis of $MnFe_2O_4$ can efficiently induce a redistribution of divalent and trivalent ions in the A and B sites. $MnFe_2O_4$ ferrite was synthesized by calcinations at various temperatures. The manganese ferrite formed in the cubic spinel structure has been confirmed by XRD and TEM. Magnetization, remanence and coercivity increased with the increase of the calcined temperature. It is expected that $MnFe_2O_4$ ferrite produced by auto combustion method can be used as magnetic materials for magnetic recording device, magneto-optical recording and electronic devices.

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