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Research Paper

Preparation and characterization of $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles synthesized by thermal decomposition of $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$

Chemistry

KEYWORDS : Nanoparticles, TG-DTA, XRD, SEM, HRTEM

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ABSTRACT

Ni-Mn ferrite nanoparticles have been synthesized using carboxylate precursor via thermal decomposition route. The prepared precursor $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$ was characterized by hydrazine, metal analyses, infrared spectral and thermal analyses. Using appropriate annealing conditions, $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles of average size 13 nm were synthesized by thermal treatment of the precursor. The nanoparticles were characterized by using X-ray diffraction (XRD), Scanning Electron Microscope (SEM), High Resolution Transmission Electron Microscope (HRTEM) and Selected Area Electron Diffraction (SAED) techniques. The details of synthesis and characterizations of the nanoparticles are reported in this paper.

INTRODUCTION

Nanotechnology has gained enormous interest in the past 20 years. They are interesting due to their fascinating size-dependent. Transition metal nanoparticles have drawn huge attention due to the unique optical, electronic, magnetic, thermal, mechanical, chemical properties and magnetic properties derived from their nanosizes and uniform size distribution [1]. Magnetic ferrite nanoparticles can be used in heat transfer devices, drug delivery systems and medical diagnostics because of their high electrical resistivity, chemical stability, mechanical hardness and reasonable cost [2-4]. Typically nanosized spinel ferrite particles have attracted considerable interest, and efforts continue to investigate them for their technological applications in the microwave industries, disk recording, refrigeration systems, electrical devices, ferrofluids, etc. [5-7]. Increased application of ferrites has led to the development of many chemical methods which includes ceramic technique [8], coprecipitation [9], microemulsion [10], micelle and hydrothermal methods [11] and sol–gel process [12]. The size and shape of the ferrite particles are dependent on the synthesis process.

The growing interest during the past decade is essentially due to the possibility of reduction in manufacturing cost on account of energy savings, shorter processing times and improved product uniformity and yields. Thermal treatment is an exciting new field with enormous potential for synthesizing new materials and novel nanostructures. Precursor used in the thermal treatment is more important for the synthesis of fine nanoparticles. Hydrazine derivatives of metal carboxylates serve as precursors to produce fine particle oxide materials. Hydrazine is not only used as a fuel, it also supports for combustion in the reduction of particle size [13,14]. Many such thermal decomposition methods are employed for the synthesis of metal and mixed metal oxides using metal carboxylate and carboxylatohydrazinates complexes of oxalate [15], formate [16], acetate and propionate [17] malonate, succinate and itaconates [18,19], maleate and tartrate [20,21], malate [22] and fumarate [23-25] have been studied

Thermal decomposition method is an easy and fast process which yields high-purity, homogenous, crystalline oxides in a short time and with less energy. We deal in this paper with the preparation of Ni-Mn ferrites using the inorganic precursor $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$ and detailed structural characterization of these particles.

Preparation of nickel manganese ferrous phenylacetate hydrazinate $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$

Nickel manganese ferrous phenylacetate hydrazinate was prepared by mixing an aqueous solution containing the requistant quantity of phenylacetic acid and hydrazine hydrate to the solution containing the stoichiometric amount of freshly prepared ferrous sulphate solution mixed with nickel nitrate hexahydrate and manganese acetate tetrahydrate with constant stirring. The complex is precipitated slowly, which is kept for sometime. A yellow coloured precipitate thus obtained was filtered off, washed with ethanol, dried with diethyl ether and then stored in a vacuum desiccator.

Preparation of $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles by thermal decomposition method

The precursor complex $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$ thus prepared was taken in a clean silica crucible and heated gently at the starting and strongly when the decomposition starts. As a result the precursor complex was completely decomposed to ferrite $Ni_{0.8}Mn_{0.2}Fe_2O_4$.

CHARACTERIZATION

All the chemicals used were of pure commercial grade. The hydrazine content in the precursor was determined by volumetric analysis using (0.25M) KIO_3 as the titrant under Andrews' condition [26]. The percentage of nickel, manganese and iron in the precursor was estimated by the standard methods given in the Vogel's textbook [26]. The metal content in the sintered oxide sample were also determined by EDX.

Infrared analysis of the precursor complex $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$ was carried out on a Perkin-Elmer model 597 spectrophotometer using KBr pellets. The thermal measurements (TG- DSC) are performed using a Netzsch SDT Q600 device from RT to 1000°C in nitrogen atmosphere. The crystalline phases are identified by XRD powder methods using a Seifert X-ray diffractometer (CuK_ radiation). The morphology of the as synthesised nano particle was determined by a Scanning Electron Microscope(SEM, Philips XL-30) which is equipped with an Energy-Dispersive X-ray spectrometer (EDX). High Resolution Transmission Electron Microscopy (HR-TEM) images and Selected Area Electron Diffraction Pattern (SAED) were collected using a Jeol Jem 2100 advanced analytical electron microscope to determine the shape and size of the nanoparticles.

RESULTS AND DISCUSSION

Characterization of precursor complex $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$ spectral and structural study

The observed percentage of hydrazine(21.43), nickel(20.95), manganese(4.68) and iron(47.07) are very well in agreement with the calculated values of 21.72, 20.00, 4.70 and 47.80 respectively. From the above data the chemical formula for the precursor complex is tentatively assigned as

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$Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$.

The infra-red spectrum of the precursor complex shows three bands in the range of 3181 cm^{-1}- 3295 cm^{-1} due to N-H stretching frequencies. The separation of asymmetric and symmetric (υ_{asymm} - υ_{sym}) carboxylate stretching of 205 cm^{-1} indicates the unidentate coordination [27] of carboxylate ions. The N-N stretching frequency of hydrazine moieties was observed at 977 cm^{-1} indicating their bidentate bridging nature [28]. The IR data thus reveals that the nickel manganese ferrous phenylacetate hydrazinate complex is formed.

Thermal analysis

The nickel manganese ferrous complex shows a multistep decomposition in nitrogen atmosphere (Fig. 1). Initially it lost two hydrazine molecules exothermally in the temperature range from room temperature to 158 °C, and then it eliminates three hydrazine molecules exothermally in the temperature from 158 – 182 °C. TG curve from 182 - 545 °C can be attributed to the decarboxylation of the dehydrazinated precursor. DTA curve showed exothermic peak in this region 499 °C is due to decarboxylation. $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$ precursor loss thermo gravimetrically from room temperature to 700 °C to yield $Ni_{0.8}Mn_{0.2}Fe_2O_4$ as the final product.

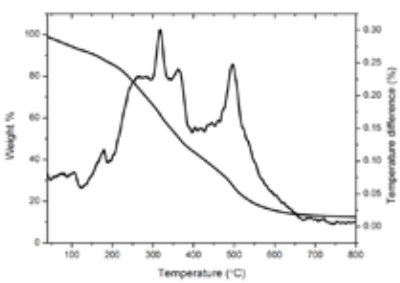

Fig.1 TG-DTA of the precursor
Characterization of $Ni_{0.8}Mn_{0.2}Fe_2O_4$ Nanoparticles

Phase analysis

The phase and its purity were confirmed by powder X-ray diffraction (XRD). Fig. 2 shows the peak position and the relative intensity of all the diffraction peaks which well matched with standard powder diffraction data. No impurity peak was observed, indicating the formation of high purity crystalline $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles. All the peaks coincident with a typical single-phase cubic spinel structure. The broadening nature of the XRD peaks indicates that the crystallite size of the as-prepared sample is within nanometer scale. Considering the more intense peak, the average crystallite size was calculated by Scherrer formula [29,30], $D = (0.94\lambda)/B\cos(\theta)$, where, λ—Wave length of X-rays, B—Full width at half maximum, θ—The diffraction angle.

The Scherrer formula analysis shows that the average diameter of the grain sizes of $Ni_{0.8}Mn_{0.2}Fe_2O_4$ is 13 nm. The X-ray diffraction data such as d-values and lattice parameter of 'as synthesized' $Ni_{0.8}Mn_{0.2}Fe_2O_4$ was found to match closely with the reported values [31,32].

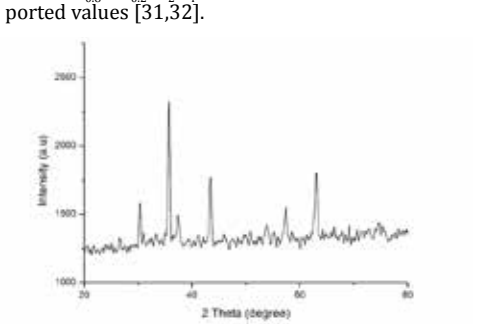

Fig.2 XRD pattern of the as-synthesized $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles

Morphology analysis

The microstructure plays an important role in realizing many application-oriented ferrite properties. Fig. 3a at higher magnification provides immense evidence for the presence of agglomerated worms like nanosized particles with a narrow distribution.

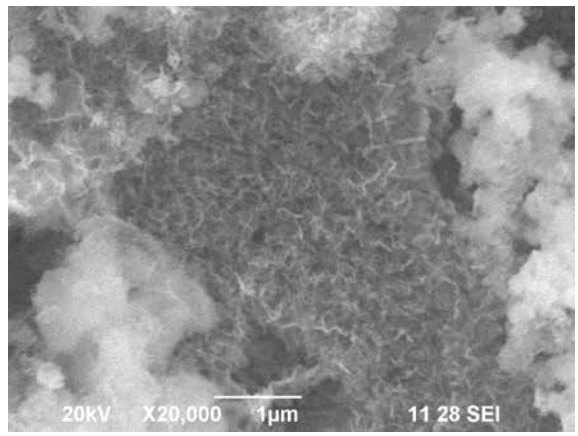

Fig.3a SEM image of the as-synthesized $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles

In order to confirm the chemical composition, EDX analysis was carried out and is shown in fig. 3b. This compositional analysis method results comply with what is expected from the synthesis. The result from EDX spectram shows that the as-prepared $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanospheres contain Ni, Mn, Fe and O, and no contamination element was detected, indicating that the chemical formula of the as-prepared sample is consistent with the experimental stoichiometry.

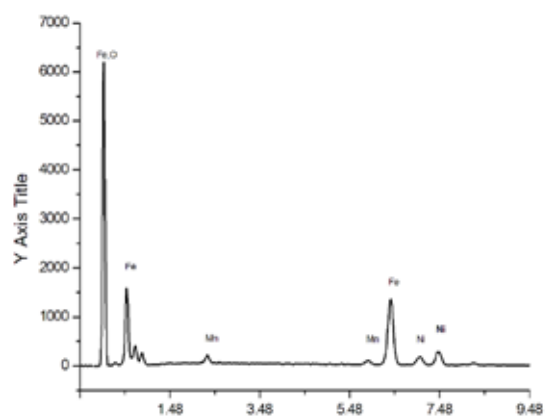

Fig.3b SEM EDX of as-synthesized $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles

Structural analysis

The size and morphology of the as-produced sample in detail were investigated by HRTEM. High resolution transmission electron microscopy (HRTEM) images (Fig. 4(a&b)) of $Ni_{0.8}Mn_{0.2}Fe_2O_4$ shows that the obtained nano particles were almost spherical, ultrafine and homogenously dispersed with agglomeration. From fig.4b the crystallographic orientation of the $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles was investigated and the prominence of the lattice fringes was found to agree well with the separation between the lattice planes. The particle size calculated by HRTEM micrography was in the range of 9–17 nm, which is in agreement with that calculated using the Debye-Scherrer formula.

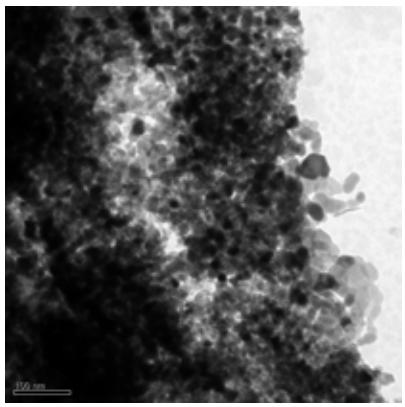

Fig.4a Tem image of as synthesised $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles

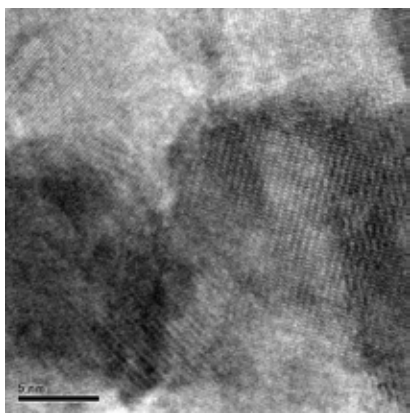

Fig.4b Tem image of as synthesised $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles

The electron diffraction pattern from the HRTEM image (Fig. 5) shows multiple diffraction rings, indicating crystalline structure formation. A careful analysis of the SAED pattern reveals that besides the diffraction rings of $Ni_{0.8}Mn_{0.2}Fe_2O_4$, no additional rings were observed. The bright electron diffraction rings for $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles showed that the particles are fine nanocrystalline and are around 13 nm size.

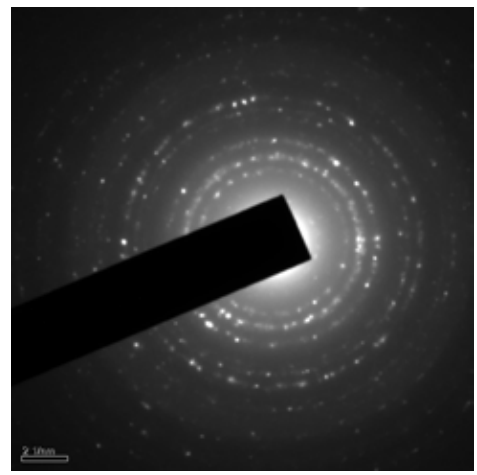

Fig.5 SAED pattern of the as-synthesized $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles

CONCLUSION

In summary, $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles were synthesised by thermal decomposition of the precursor complex $Ni_{0.8}Mn_{0.2}Fe_2(PhAc)_3(N_2H_4)_5$ at room temperature. The unidentate coordination nature of the carboxylate ions and the bidentate coordination behaviour of hydrazine moieties were confirmed by the υ_{asymm} - υ_{symm} value of 205 cm^{-1} and N-N stretching frequency at 977 cm^{-1} respectively. Thermal studies of the precursor complex showed a multi step degradation to form the corresponding oxide nanoparticles, the cubic spinel structure of which is confirmed by XRD studies. The average particle size of 13 nm determined by HRTEM is in agreement with that calculated using the Debye-Scherrer formula.

Thus, this novel route gives an efficient method of preparation of $Ni_{0.8}Mn_{0.2}Fe_2O_4$ nanoparticles, involving low cost, low energy, high purity, high nanocrystallinity and eco friendliness.

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