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Structural, spectral, dielectric and photocatalytic studies of Zr-Ni doped $MnFe_2O_4$ co-precipitated nanoparticles

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ABSTRACT

In this study the $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles fabricated by co-precipitation technique were investigated. Thermo-gravimetric analysis (TGA) exhibited the annealing temperature of the nanoparticles ~990 °C. Cubic spinel structure of $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles was confirmed by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analysis. Crystallite size was calculated by XRD data and found in the range of 32–58 nm. Photocatalytic activity of $Mn_{0.92}Zr_{0.04}Fe_{1.88}Ni_{0.12}O_4$/graphene nanocomposites was tested by degrading methylene blue (MB) under visible light irradiation. The MB was almost completely degraded in the presence of $Mn_{0.92}Zr_{0.04}Fe_{1.88}Ni_{0.12}O_4$-graphene nanocomposites under visible light irradiation. Dielectric parameters were also investigated in the frequency range 1×10^6–3×10^9 Hz. An overall decrease in the values of dielectric constant, dielectric loss and tangent loss was observed on account of the substitution of Zr and Ni with Mn and Fe cations.

1. Introduction

In recent years, nano-ferrites have been paid significant attention by the researchers due to their diverse physical and chemical properties [1]. Nano-ferrites play vital role in modern industrial era with wide range of advanced technological applications [2]. Spinel or soft manganese ferrites with chemical formulation $MnFe_2O_4$ have extensive range of potential applications and can be used in microwave devices, electronic devices, information storage, drug delivery, water treatment and gas sensing etc. [3]. Photocatalytic activity of ferrites is also of special interest as the ferrite exhibit the absorption spectrum in visible range and can be separated and recycled due to their inherent magnetic characteristics [4]. Various structural, electrical and magnetic properties can be affected by synthetic methods, nature of substituent (s) and composition of fabricated particles because they are directly reliant on the microstructure and composition of the materials [5]. Several methods have been reported in the literature such as sol-gel, co-precipitation, citrate precursor, microwave assisted hydrothermal, auto combustion, reverse micelle etc. for the fabrication of nanomaterials [6]. These different synthesis methods serve as an effective means to control the crystallite sizes, surface morphology and composition of the nanomaterials [2]. A careful literature analysis exhibited that many researchers throughout the world are making efforts to develop the simple and cost effective methods to prepare nanocrystallite with narrow size distribution [2]. They are interested to modify and enhance the structural, magnetic and dielectric properties of manganese ferrites by substituted them with metal cations like Co^{+2}, Zn^{+2}, Zr^{+4} etc. [7]. From carful investigation of spinel ferrites it has been observed that tetrahedral and octahedral sites distribution are tend to form by the presence of cations with variable oxidation states. Structurally spinel ferrites posses cubic close packing which contains 32 oxygen atoms with 8 tetrahedral and 16 octahedral sites [1].

The purpose of the present investigation is to study the simultaneous effects of Ni and Zr cations substitution on of manganese ferrites. In the present work, we have discussed the synthesis of $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles via cheap wet chemical route (co-precipitation) for evaluation of structural, dielectric and photocatalytic behavior.

2. Materials and method

$Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles were prepared by using following chemicals: zirconium (IV) oxychloride octahydrate (Sigma-

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Aldrich, 98%), manganese (II) chloride tetrahydrate (Beijing Chemical Works, 98%), nickel (II) chloride hexahydrate (BDH, England, 98%), iron (III) nitrate nonahydrate (Merck, 98%), aqueous ammonia (BDH, 35 wt%) and deionized water (conductivity ~2–4 S). Aqueous solutions of metal salts of required molarities were prepared in deionized water. The metal salt solutions were mixed in required stoichiometric ratio and subjected for stirring at 60 °C to get homogenous solution. The pH of all the reaction mixtures was raised to about 10–11 by dropwise addition of freshly prepared 2 M aqueous ammonia solution. Resultant reaction mixtures were further stirred for 6 h at room temperature and were left covered overnight. All the precipitates were washed several times with deionised water to reduce the pH to ~7. Drying was carried out in oven at 100 °C. Further these precipitates were grinded and then annealed at 990 °C using controlled Muffle Furnace Vulcan A-550.

The reduced graphene oxide (rGO) was prepared by following the literature procedure [8,9]. $Mn_{0.92}Zr_{0.04}Fe_{1.88}Ni_{0.12}O_4$-rGO nanocomposites were prepared by ultra-sonication method. Typically 0.10 g $Mn_{0.92}Zr_{0.04}Fe_{1.88}Ni_{0.12}O_4$ nanoparticles were mixed with rGO 15 mg. The mixture was dispersed with 150 cm^3 deionised water. The obtained dispersion was ultrasonicated for ~2 h. The obtained black colored suspension was filtered followed by washing several times with deionised water. The drying was carried out at 110 °C for 10 h vacuum oven. The as-synthesized $Mn_{0.92}Zr_{0.04}Fe_{1.88}Ni_{0.12}O_4$/rGO nanocomposite was utilized for photocatalytic investigations.

XRD analysis was performed of all samples was done by using Philips X-Pert PRO 3040/60 diffractrometer. FTIR spectra were recorded by SHMADZU FTIR spectrometer. The dielectric measurements were carried out at 300 K on Wayne Ker WK6500B precision equipment in the range of 1 MHz–3 GHz. TGA was done using thermal analyzer (SDT Q600 V8.2 Build 100). All UV-Visible measurements were performed at Cary 60, dual beam spectrophotometer in the range of 400–800 nm.

3. Results and discussion

3.1. Thermogravimetric analysis

The thermal decomposition processes of $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ powders were characterized by thermal gravimetric analysis. The typical TGA graph of $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles is shown in Fig. 1. The main purpose of the TGA was to know the annealing temperature for all compositions of $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles. The TGA graph showed the 23% total weight loss. This total weight loss could be divided into more than one step. The weight losses in first two steps are due to the presence of moisture contents and water molecules inside the pores of the prepared nanoparticles. The weight loss in remaining two steps is due to formation of metal hydroxides and conversion of these hydroxides into corresponding oxide nanoparticles. The annealing temperature identified from the TGA graph was 990 °C. The TGA data of $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles is similar to that of already reported reports in the literature for similar compounds / metal oxide nanoparticles [10].

3.2. Scanning Electron Microscopy

Scanning electron microscopic (SEM) analysis was performed to investigate the surface morphology and grain size of the prepared nanoparticles. Fig. 2 depicts the typical cross sectional SEM image of the $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles. The grain size of $Mn_1Zr_0Fe_2Ni_0O_4$ nanoparticles was estimated by SEM image. The average grain size was < 100 nm.

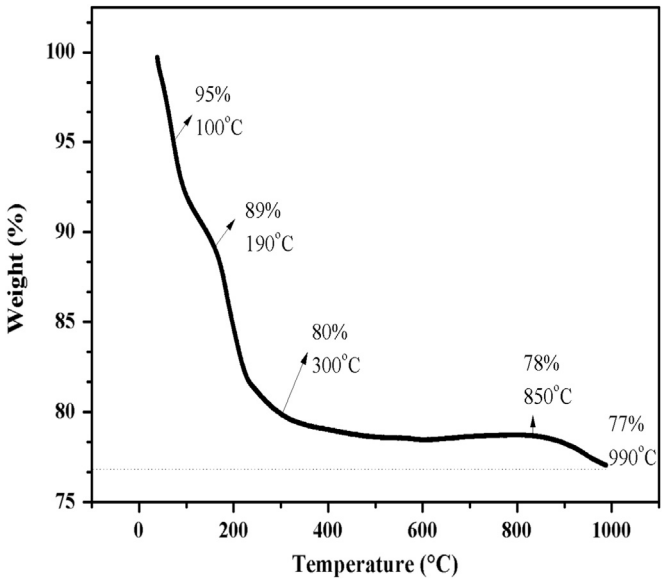

Fig. 1. TGA for $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles.

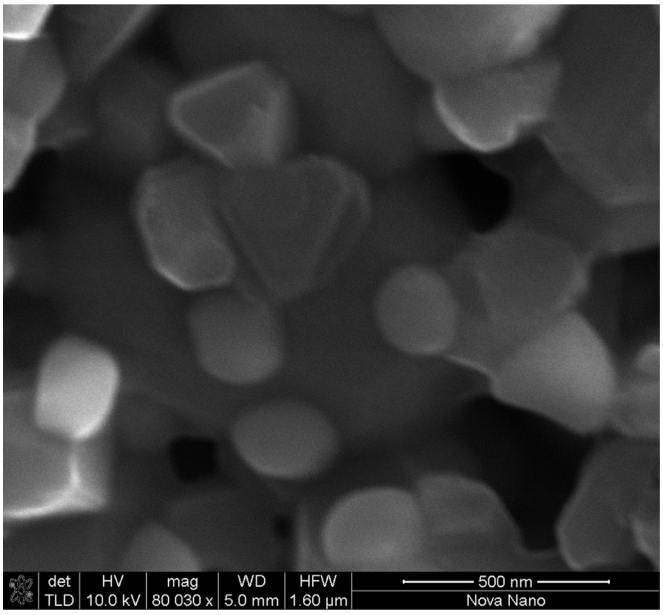

Fig. 2. SEM image of $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles.

3.3. X-ray diffraction analysis

The phase identification for all compositions of $Mn_{1-2x}Zr_xFe_{2-y}Ni_yO_4$ nanoparticles i.e. $MnFe_2O_4$, $Mn_{0.96}Zr_{0.02}Fe_{1.94}Ni_{0.6}O_4$, $Mn_{0.92}Zr_{0.04}Fe_{1.88}Ni_{0.12}O_4$, $Mn_{0.88}Zr_{0.06}Fe_{1.82}Ni_{0.18}O_4$, $Mn_{0.84}Zr_{0.08}Fe_{1.76}Ni_{0.24}O_4$, $Mn_{0.80}Zr_{0.10}Fe_{1.70}Ni_{1.30}O_4$ was carried out using XRD analysis. The XRD patterns of all these samples are shown in Fig. 3. All obtained diffraction patterns were matched with data card 01-074-2403 [11]. All diffraction patterns showed the characteristic features of the spinel ferrite materials and confirmed the formation of the cubic spinel structure of synthesized nanoparticles. The crystallite size was determined by using Sherrer's formula with the most intense peak at $2\theta = 35°$ labeled with hkl (311). The estimated crystallite size of prepared nanoparticles was 32–58 nm annealed at 990 °C. Lattice parameter *a* for all samples were calculated using cell software. The obtained values were found similar to those reported in the data card 01–074-2403 [11]. The following diffraction planes (220), (311), (222), (400), (422), (511), (531), (442) were found in great synchronization with standard $MnFe_2O_4$ cubic structure [12]. The