Preparation of $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowders by using a novel EDTA precursor method and their microstructute, DC resistivity and magnetic properties

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A simple EDTA precursor based chemical method has been reported for preparation of $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowders. The influences of microstructure, composition, and measurement temperature on the DC resistivity of the synthesized nanopowders have been investigated. Room temperature resistivity values (ρ_{RT}) of the as-synthesized samples were in the order of ~10^7 Ωcm, Variation of room temperature magnetic parameters, such as saturation magnetization and coercivity, has also been reported with respect to change in Zn^{2+} concentration.

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1. Introduction

Recently, investigations on Mn-Ni-Zn-ferrites have gained profound interest for their applications in a variety of magnetic devices such as transformer cores, noise filters, recording heads etc. However, Mn-Ni-Zn-ferrites have certain limitations for magnetic applications at high frequencies because of their low electrical resistivity [1]. The properties of ferrites are sensitive to their compositions and microstructure, which largely depend on their preparation methodologies. So to obtain high performance ferrites it is critical to use a specialized preparative route, which is capable of producing compositionally stoichiometric materials. The traditional high temperature solid state method usually suffers from the disadvantages of prolonged high temperature heating schedule and intermittent milling of the oxides for mixing, which sometimes result in non-stoichiometric composition and formation of undesired impurity phases [2]. Co-precipitation and citrate precursor based methods [2,3] have been reported for preparation of $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowders. However, these methods are also associated with some limitations. For example, co-precipitation method requires prolonged sintering schedule (5 h at 500 ^{0}C) and filtering and washing of the precipitates. Washing may cause non-stoichiometry in the final product [3]. In case of citrate route, requirement of high sintering temperature (>1200 ^{0}C) sometimes causes loss of Zn [2]. So, to overcome these limitations there is a need to develop a novel but simple method, which can produce nanosized MnNiZn ferrite powders at a comparatively low temperature.

In this communication, we have reported the synthesis of single-phase $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowders using a novel but simple aqueous solution-based ethylene diamine tetra acetic acid (EDTA)-precursor method. We have investigated the impact of microstructure, composition and measurement temperature on the DC resistivity of the synthesized nanopowders. Variation of room temperature magnetic parameters, such as saturation magnetization and coercivity, has also been studied with respect to change in Zn^{2+} concentration.

2. Experimental details

To prepare $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowders, we have used metal nitrates, such as $Fe(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$, $Mn(NO_3)_2.4H_2O$, $Zn(NO_3)_2$ as starting materials and water as solvent. All the chemicals used were 99.9% pure and procured from Merck, India. Stoichiometric amounts of metal nitrates were dissolved in distilled water according to the molar compositions of $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ (x= 0.2, 0.3 and 0.4). The aqueous solutions of metal nitrates and EDTA were mixed in a molar ratio of 1: 1 and stirred for 1 h at room temperature using a magnetic stirrer. The pH of the reaction mixtures was found to be in the range of 1 to 2, depending upon the composition. Dark brown colored precursors were formed when the reaction mixtures were evaporated to dryness on a hot plate at 125 ^{0}C. Partial decomposition of the precursors was observed during drying. The precursor powders were then calcined in air for 2 h at 525 ^{0}C to obtain Mn-Ni-Zn ferrite nanopowders.

The precursor and calcined powders were characterized by using X-Ray diffractometer (Mini Flex II, Rigaku, Japan), thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) DTG-60 and a

DSC-60 (Shimaduzu, Japan), particle size analyzer (Delsa Nano S, Beckman Coulter, USA) and Scanning Electron Microscope (SEM) (JSM-6360LV, JEOL, Japan).

DC resistivity of the as-synthesized nanopowders and the sintered pellets were measured with respect to temperature (from room temperature to 225 ^{0}C) using a two-probe method with an electrometer (Keithley Electrometer 6517A, USA). Room temperature magnetization with respect to external magnetic field was measured for the synthesized powder (calcined at 525 ^{0}C) by using a vibrating sample magnetometer (EV5, ADE Technology, USA).

3. Results and discussions

Thermo gravimetric analysis (TGA) showed two step decomposition of the precursor powders in air atmosphere in the temperature range from 40 to 600 ^{0}C (Fig. 1): (i) initially, ~10% weight loss occurred in the region of 40 to 200 ^{0}C due to the loss of absorbed moisture from the sample and then (ii) ~60 % weight loss in the temperature range of 200 to 500 ^{0}C. This might be due to the oxidative thermal decomposition of precursor and evolution of CO_2 and NO_x gases. This decomposition was also reflected in DSC thermogram as two exothermic peaks at 450 ^{0}C and 495 ^{0}C. No further weight loss was observed in TGA when the sample was heated beyond 500 ^{0}C. This confirmed the full decomposition of carbonaceous mass of the precursor occurred within 500 ^{0}C.

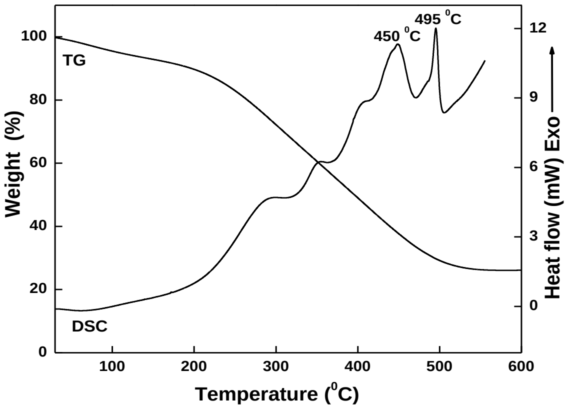

Fig. 1. TGA-DSC thermograms of $Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$ precursor

Room temperature powder XRD spectra for the precursor and calcined powders are shown in Fig. 2, which indicate the formation of pure $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ due to calcinations of precursor. All the diffraction peaks can be indexed to single phase $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ [1,2,3,5]. The notable feature was that, the formation of $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ phase was observed in precursor, which did not undergo any calcination. To the best of our knowledge, precursor containing $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ phase has not yet been reported for any other precursor-based method. Formation of any other impurity phases, such as Fe_2O_3, Fe_3O_4, NiO, MnO, $NiFe_2O_4$ etc was not observed at any stage of calcination. Crystallite size of the calcined powders was calculated using Scherrer's equation, and they were within a narrow range of 16- 19 nm. The lattice constant value (a=b=c) of the synthesized $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowders was found to be in the range of 8.39 to 8.41 Å depending upon the composition and is similar to the reported value [2].

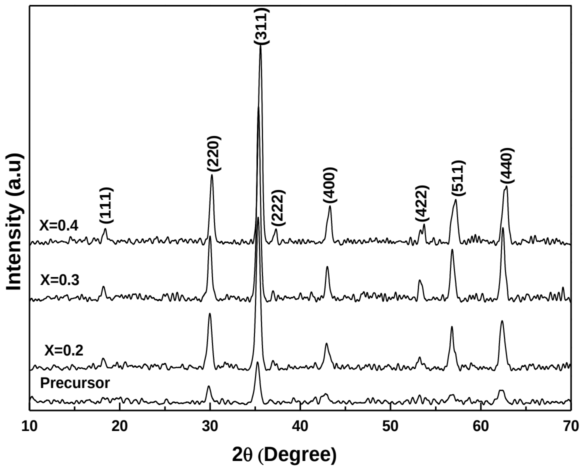

Fig. 2. XRD patterns of precursor and the powders obtained by calcining the precursor at 525 ^{0}C for 2h for the series of composition $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$.

The intensity -weighted particle size distribution of the as-synthesized $Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$ nanopowders, obtained from DLS study at 25 °C, showed a single modal distribution with main peak average around 10.2±8.6 nm. The cumulant mean diameter of the particles was 19.4 nm with a polydispersity index of 0.146.

SEM was used to investigate the change in microstructures of the synthesized $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowders with changing sintering temperature and composition. For this purpose, three pellets were prepared by using 525 ^{0}C calcined powders; (i) one pellet was kept unsintered to investigate the original microstructure of the as synthesized nanopowders. (ii)The other two pellets were sintered at 1000 and 1200 ^{0}C for 2 hrs. SEM micrographs of the as- synthesized samples exhibited uniform, almost spherical shaped and loosely agglomerated particles of Mn-Ni-Zn ferrite powders (Fig. 3a).

When sintering was performed at 1000 ^{0}C, the grains grew to micron-size but retained their spherical shape. The particles were also found to be agglomerated and exhibited intragranular porosity (Fig. 3b). Sintering at 1200 ^{0}C resulted in formation of well defined, bigger grain sizes (~3 microns) with reduction in porosity (Fig. 3c). Inhomogeneity or partial precipitation of any impurity phase was not observed for any of these samples. It should be noted that, though sintering temperature was reasonably high (1200 ^{0}C), Zn loss was not observed in our samples.

In case of citrate- precursor method Verma et. al. have observed through SEM micrographs formation of intergranular pores in the samples due to Zn loss at this high temperature [2].

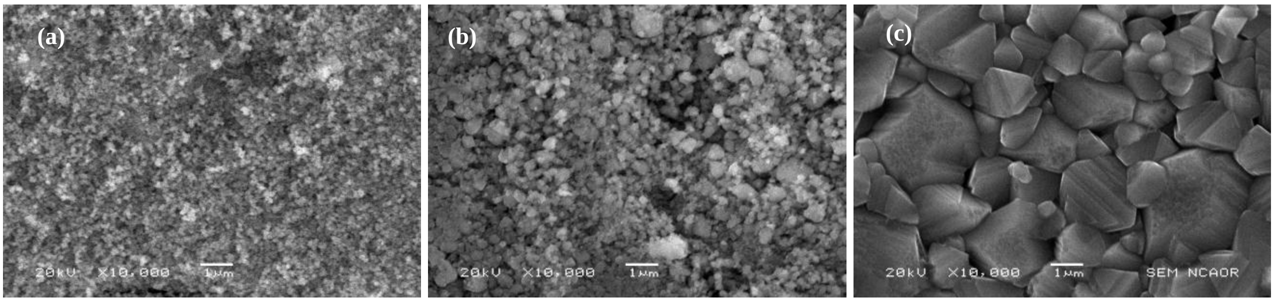

Fig. 3. SEM micrograph of (a) as synthesized $Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$ and sintered at (b) 1000^0C, and (c) 1200 ^0C for 2h.

DC resistivity:

We have recorded the DC resistivity of all compositions for the unsintered pellets (nanopowders) and pellets (micron-sized powders) sintered at 1000, 1200 ^0C. The values of room temperature DC resistivity for the series of compositions for unsintered and sintered samples are listed in Table 1. Resistivity of the unsintered nanopowders and sintered powders at different sintering temperatures for $Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$ is shown in Fig. 4.

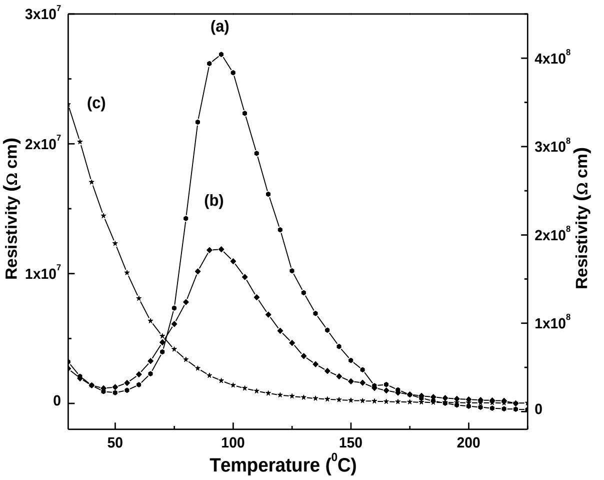

Fig. 4. Variation of the DC resistivity with temperature of $Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$ for (a) unsintered and pellets sintered at (b) 1000 ^0C and (c) 1200 ^0C. Left Y-axis shows the scale for (b) and (c) and right Y-axis shows the scale for (a).

With increasing zinc concentration in the composition of $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ an initial increase in resistivity followed by a decrease was observed. The observed values were in the range of 10^6-10^8 Ωcm. It is known that zinc and nickel ions occupy tetrahedral

(A-sites) and octahedral (B-sites) positions, respectively, while iron and manganese ions occupy both A and B-sites of $Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$ [4]. However, the probability of finding iron and manganese ions is more at B and A-sites, respectively. Although, manganese, nickel and iron ions are known to exist in both +2 and +3 states, manganese and nickel primarily exist in +2 state whereas iron in +3 state. The conduction in ferrites occurs mainly due to the hopping of electrons between ions of the same element but of different valence state present at equivalent sites. Production of ions in more than one valence state depends on the preparation conditions, composition and sintering temperature [1].

It was observed that the room temperature resistivity values (ρ_{RT}) of the unsintered samples were in the order of ~10^7 Ωcm, which are higher than those of reported values of MnZn ferrite (10^2 Ωcm) and NiZn ferrite (10^6 Ωcm) and MnNiZn ferrite (10^4 Ωcm) [5]. With the increase of measurement temperature, the resistivity increased and a maximum resistivity was recorded in the temperature range of 90-100 ^0C. This behavior might be attributed to the presence of open porosity, loose agglomeration of ultrafine powders and entrapped moisture inside the pores of the powders [6- 9,10] (humidity recorded in our lab was ~90% at room temperature). Increasing the temperature up to ~100 ^0C caused the evaporation of moisture from the samples and therefore, maximum resistivity in the order of ~10^8 Ωcm was attained (Fig 4a). After ~100 ^0C, the samples exhibit typical negative temperature coefficient of resistance (NTCR) behavior of ferrites and highest resistivity value of unsintered nanopowders, is ~10^7-10^8 Ωcm. Such high resistivities can be explained by understanding the fact that nanosized grains would offer greater resistance to electron path.

When the samples were sintered at 1000 ^0C, the grains grew in micron size and also the porosity was reduced (SEM micrograph Fig. 3b). Therefore, the impact of adsorbed moisture on DC resistivity of 1000 ^0C sintered sample was less pronounced compared to unsintered sample (Fig. 4a, b). The absence of any intragranular porosity was observed for the samples, sintered at 1200 ^0C. Therefore, these sintered samples exhibited typical NTCR behavior of ferrites from room temperature to 225 ^0C (Fig. 4c). The sintered samples possessed comparatively lower resistivities of ~10^6-10^7 Ωcm as compared to the as-synthesized nanopowders (10^7-10^8

Ωcm). This might be due to larger grain size and reduced number of porosity (as seen in SEM micrographs Fig. 3c) in the sintered samples.

Table 1. Room temperature DC resistivity for series of composition $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$.nanopowders.

	Room temperature resistivity (Ωcm)		
Composition	Sintering Condition (^{0}C)		
$Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$	Unsintered	1000	1200
x = 0.2	9.4×10^6	3.6×10^6	1.0×10^7
x = 0.3	6.9×10^7	4.6×10^7	2.4×10^7
x = 0.4	5.1×10^7	8.7×10^6	1.9×10^7

Magnetic measurement:

Room temperature magnetization of the as synthesized $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanoparticles was measured using VSM with an applied field of 2000 Oe and shown in Fig. 5.

All samples showed ferromagnetic behavior and the compositional study of the series showed a decrease in the saturation magnetization (M_s) from 39.1 to 16.3 emu/ g with increasing Zn^{2+} concentration (Table 2).

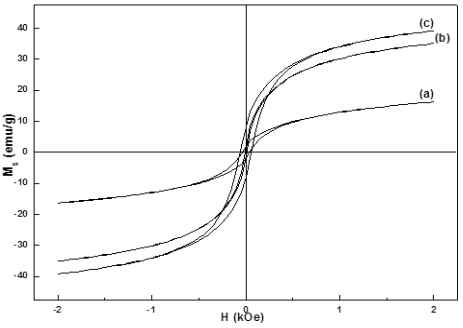

Fig. 5. Room temperature magnetic hysteresis loop for a series of composition $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowder (a) x=0.2, (b) x=0.3 and (c) x=0.4.

$Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$ exhibited super paramagnetic behavior with almost immeasurable coercivity and absence of hysteresis loop. M_s Values of the synthesized nanopowders were found to be less than those of reported multidomain bulk values of $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ [1,2], Ni-Zn ferrite (70 emu/g), Zn-Mn ferrite (45 emu/g) and Ni-Mn ferrite(50 emu/g). Several factors such as size and shape anisotropy, random distribution of nanoparticles, spin disorder in the surface of nanoparticle due to large surface/volume ratio, canting effect, antiferromagnetic exchange interaction etc. play critical role in determining the magnetic properties of the synthesized nanoparticles [1,11- 13].

Table 2. Variation of room temperature saturation magnetization (M_s) and coercivity(H_c) for the series of $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$.nanopowders.

Composition	Magnetic Values	
$Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$	M_s (emu/g)	H_c (Oe)
x = 0.2	16.3	38.9
x = 0.3	35.1	8.6
x = 0.4	39.1	61.1

4. Conclusions

In this communication, we have reported the synthesis of single phase $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanoparticles by using an EDTA-precursor based method. Calcination of the precursor results in formation of pure single phase $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ nanopowders. The calcinations condition required for this method i.e. 525 ^{0}C for 2h, is lower than that of some of the reported methods. Moreover, this method does not require any organic solvent or corrosive reagent like NaOH and any elaborate experimental setup. The starting materials are cheap. The synthesis of precursor can be carried out in open atmospheric condition in aqueous medium. Any impurity phase was not detected in the final product.

The novelty of this EDTA precursor based method lies in its simplicity, cost-effectiveness and requirement of comparatively lower calcination temperature as compared to the traditional methods and capability of producing pure single phase nanosized $Mn_{0.2}Ni_xZn_{(0.8-x)}Fe_2O_4$ powders. This method has also proved to be a convenient method for preparation of variety of ferrite nanopowders such as $Ni_{(1-x)}Zn_xFe_2O_4$ [6], α-Fe_2O_3 [7], $CoFe_2O_4$ [8], $BaFe_{12}O_{19}$ [9], $NiFe_2O_4$ [10].

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