

The Effect of pH in Nickel Ferrite Nanoparticles Synthesis by Hydrothermal Method

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In this study, NiFe₂O₄ nano particles was prepared with aqueous solutions of nickel nitrate and ferric nitrate salts. An appropriate ratio of solutions nickel nitrate and ferric nitrate were dissolved in deionized water and poured into a crucible. Later, polyethylene glycol 600 (PEG 600) was added to this mixture. Samples were adjusted to various pH values. In experiments, samples obtained by hydrothermal method were heat treated at 700 °C for 8 h to enhance their crystallinity and remove the residual organic materials. The structural and morphological properties of NiFe₂O₄ nano particles were determined by X-ray powder diffraction (XRD) and Scanning Electron microscopy (SEM). Results showed that increasing calcination temperature contributed to crystallinity of NiFe₂O₄ nano particles. But also average particle size increased. As a result, average particle size was calculated by using Debye-Scherrer Formula as approximately 30 nm. However, this results was confirmed with SEM analysis.

Keywords: Nanoparticles, Nickel ferrite, Hydrothermal.

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1. INTRODUCTION

Spinel ferrites, MFe₂O₄, are technologically important group of materials due to their enhanced optical, magnetic, and electrical properties. These properties make them very attractive for a variety of applications including but not limited to use as electrodes in energy storage devices, as catalysts, in magnetic storage devices, etc. [1-2-3].

Spinel ferrites have the general formula of AFe₂O₄ (where A²⁺: Fe, Co, Ni, Zn, etc.) and unit cell contains 32 oxygen atoms in cubic close packing with 8 tetrahedral (Td) and 16 octahedral (Oh) occupied sites. By changing type of the divalent cation, it is possible to obtain significantly different physical and magnetic properties in these ferrites [3].

Magnetic ferrites are a group of technologically important magnetic materials. Synthesis of nanocrystalline spinel ferrite has been investigated intensively in recent years due to their potential applications in high-density magnetic recording, microwave devices, and magnetic fluids [4-5]. Nickel ferrite (NiFe₂O₄) is one of the most important spinel ferrites as well as a typical spin soft-magnetic ferrite. It has an inverse spinel structure showing ferrimagnetism that originates from magnetic moment of anti-parallel spins between Fe³⁺ ions at tetrahedral sites and Ni²⁺ ions at octahedral sites [6]. Recently, various methods have been developed to synthesize nanocrystalline NiFe₂O₄ such as mechanical alloying [7], pulsed wire discharge [6], sol-gel method [8], micro-emulsion [9], hydrothermal-microwave [10] and hydrothermal processes [11]. Among these established methods, hydrothermal synthesis has attracted great interest because it offers many advantages, including the enhancement of solubility, diffusion, and crystallization as well as the control of the morphologies, sizes and phase transformation, etc. [12-13].

The hydrothermal process is also a promising method for the synthesis of fine nanosized spinel

oxides. Hydrothermal methods depend on the ability of water to hydrolyze and dehydrate metal salts at elevated pressures and temperatures. The elevated temperatures favor high dehydration rates, as does the high diffusivity of reactants in water at these conditions [15,16]. Very high super saturations can be achieved in this process because of the very low solubility of metal hydroxides and oxides, so that very fine crystals can be obtained [14,15,17]. Parameters such as pressure, temperature, reaction time, and the precursor can be tuned to maintain high nucleation rates and to control the growth [18,19]. The process is environmentally benign and versatile, since it does not involve any organic solvents or post-treatments such as calcination [20]. As a result, high pressure hydrothermal processes have been widely investigated for the synthesis of metal oxides as powders, nanoparticles and single crystals [38,21-24]. As described, already the effect of temperature in the sol-gel process it has been also observed the effect of reaction temperature during hydrothermal synthesis of NiFe₂O₄ nanoparticles. It was observed that [25,26] NiFe₂O₄ nanoparticles synthesized at different temperatures exhibit different magnetic properties. Satyanarayana et al. [27] have also synthesized NiFe₂O₄ nanoparticles at different temperature and investigated the gas sensing properties of the NiFe₂O₄ nanoparticles. They observed that the reaction temperature in the hydrothermal process play a deterministic role in obtaining smaller sized particles and thereby influencing the gas sensing characteristics.

The aim of this study, NiFe₂O₄ nanoparticles are to synthesis by hydrothermal method and this particles are to characterize with X-ray diffraction and Scanning Electron microscopy (SEM). However, in this study, the effect of pH values of solutions was investigated to particle sizes and crystallinity.

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2. EXPERIMENTAL

Analytical grade nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Poly ethylene glycol 600 (PEG 600) were purchased from Sigma- Aldrich and used without further purification. NiFe_2O_4 composite powders were prepared according to the hydrothermal method.

A mixed solution of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were prepared in deionized water with vigorous stirring at room temperature. A specific volume of polyethylene glycol 600 (PEG 600) was added to the above mixed solution. After, the solution of NaOH was added until pH values reached 9,10,11,12, respectively. The pH of solution is one of the main factors on which the final composition of the product depends, which can be varied to get the desired final product. The solution was vigorously stirred for 2 h to ensure the proper mixing of the components and the subsequently transferred into the Teflon lined stainless steel autoclave. The temperature of the autoclave was raised slowly up to 200 °C and kept the whole system at this temperature for 24 h. Once the reaction time was completed, the autoclave was cooled to room temperature and the resulting brown precipitate had been washed several times with ethanol and deionized water. The obtained precipitate was dried in a vacuum oven at 105 °C. In the samples obtained from experiments was made X-ray powder diffraction analysis (XRD) and Scanning Electron Microscopy analysis (SEM).

3. RESULTS

3.1 Characterization

An experiment was made as appropriate to experimental procedure given up. The sample was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD pattern for the investigated sample is presented in Fig.1. Average particle size was calculated by using Debye-Scherrer Formula as approximately 30 nm.

Solid phase obtained from the first experiment were examined by Scanning Electron Microscopy (SEM) under appropriate conditions. SEM images of this example are shown in Fig 2. Result of this analysis showed that examples was not washing well by ethanol and distille water. Because, the around of particles was coated with a layer of hydrocarbon.

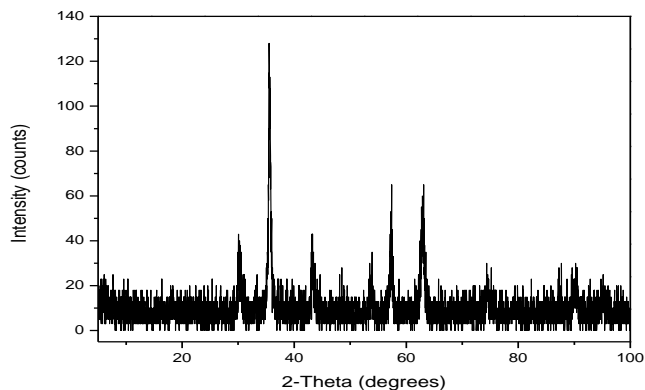


Fig. 1 – X-ray diffraction patterns of samples obtained before calcination at pH ~11

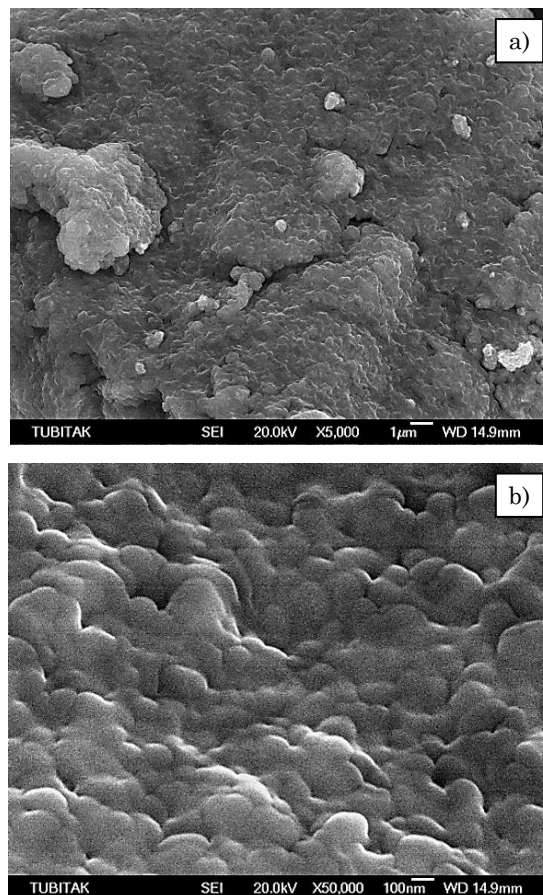


Fig. 2 – SEM images of sample obtained before calcination for pH ~ 11

For the removal of these hydrocarbon layer has been decided to the burning of the samples at high temperatures. Accordingly, this samples was calcined in high temperatures. Calcination experiments were made at 700 °C for 8 h. Samples obtained from all pH experiments were calcined under these conditions. After calcination, XRD analysis was performed in the samples obtained from this experiments. Fig. 3. shows the powder XRD patterns of the samples prepared at various pH values. All the reflection peaks can be

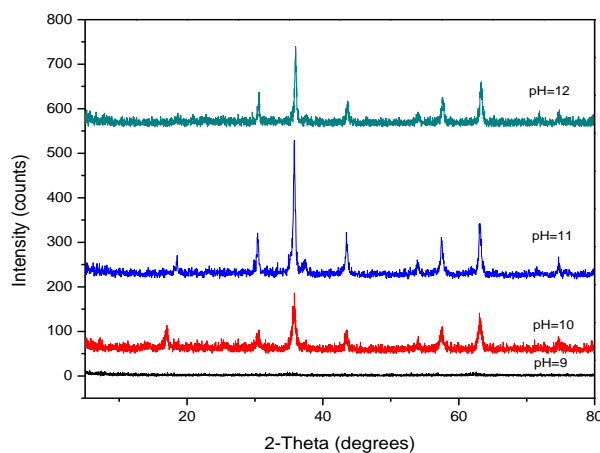


Fig. 3 – XRD patterns of the samples prepared at various pH values after calcined at 700 °C

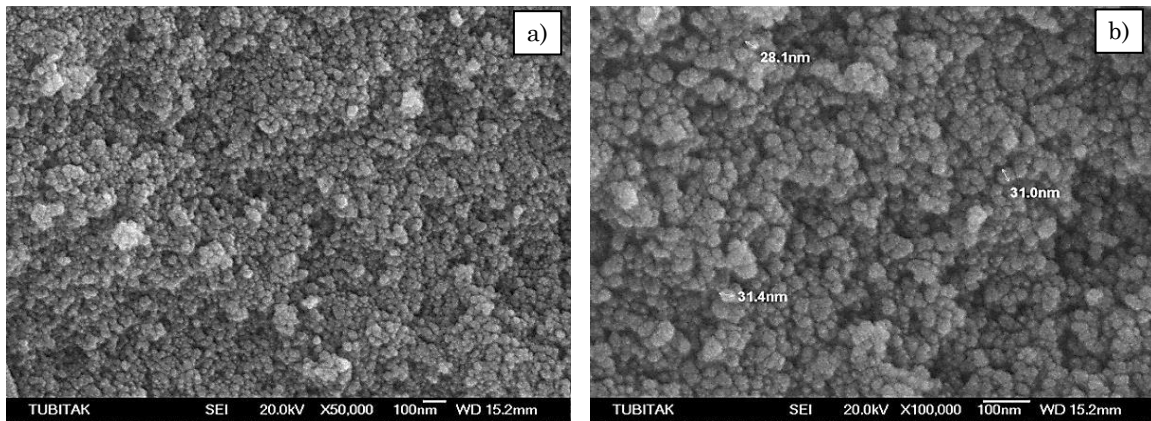


Fig. 4 – SEM images of sample obtained after calcination for pH ~ 9

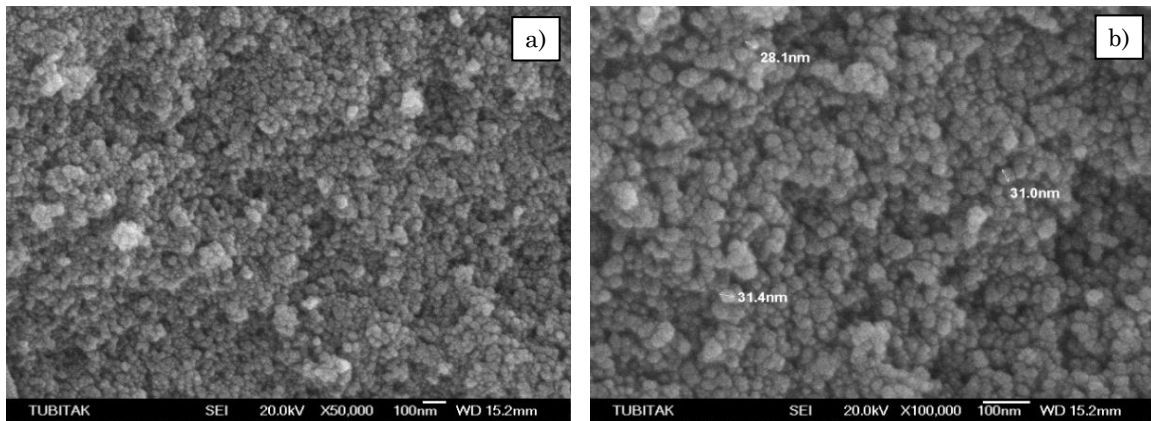


Fig. 5 – SEM images of sample obtained after calcination for pH ~ 10

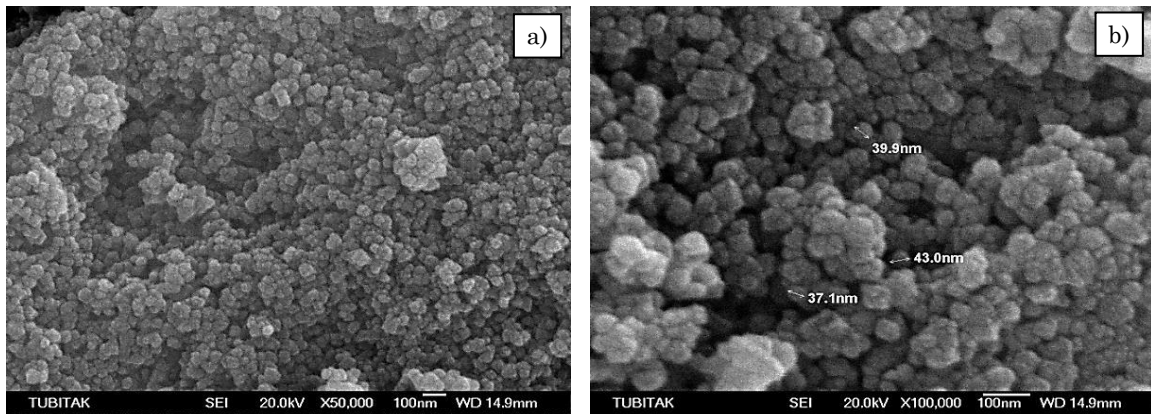


Fig. 6 – SEM images of sample obtained after calcination for pH ~ 11

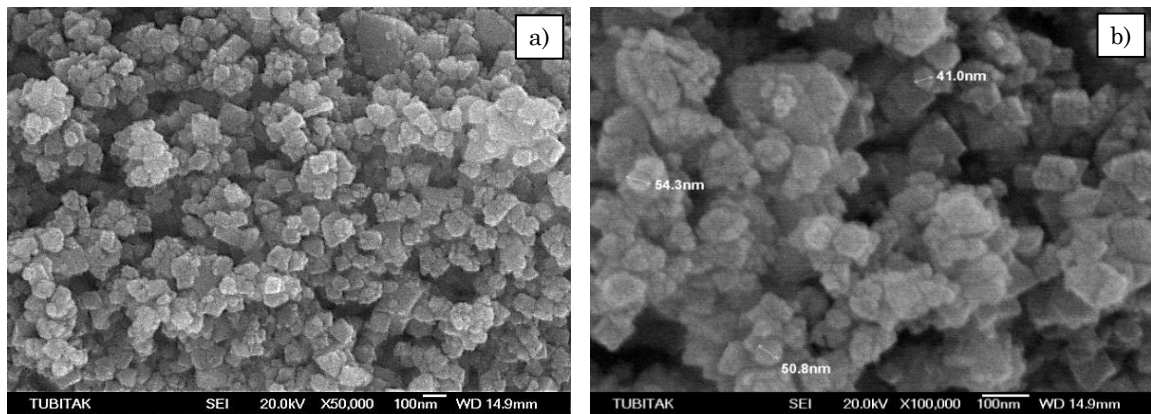


Fig. 7 – SEM images of sample obtained after calcination for pH ~ 12

readily indexed to the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction data for NiFe₂O₄ (#10-0325).

SEM images of samples obtained after calcination are shown below. Accordingly, SEM images of these samples, in Fig 4. for pH 9 value, in Fig 5. for pH 10 value, Fig 6. for pH 11 value and, in Fig 4. for pH 12 value are shown.

4. CONCLUSION

Before from calcining, the around of particles in SEM images of samples was observed to covered by layer of hydrocarbon. Result of this analysis showed that examples was not washing well by ethanol and distille water. Thus, samples were heat treated at 700 °C for 8 h to enhance their crystallinity and remove

the residual organic materials. As a result, around of the samples wasn't observed to hydrocarbon layer after from calcining. Results showed that increasing pH values contributed to cyristallinity of NiFe₂O₄ nanoparticles. However, conditions of experiment made at pH 11 value was accepted as optimum conditions for synthesis of NiFe₂O₄ nano particles by hydrothermal method. Under these conditions, the average particle size and crystal structure was confirmed by XRD and SEM-analysis.

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