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Effect of Surfactant and Ph on the Structural and Morphological Properties of $CoFe_2O_4$ Nanoparticles

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Abstract: In this study, structural properties of cobalt ferrite synthesized by sol-gel autocombustion method with hexa-decyl tri-methyl ammonium bromide (HTAB) as a surfactant, at different pH values have been investigated. $CoFe_2O_4$ nanoparticles were synthesized using metal nitrates and urea as precursor materials. The average crystallite size of the synthesized samples was ranging from 20 to 38 nm, which had found to be dependent on both pH value of the reaction and type of surfactant. The presence of surfactant leads to decrease of the size of the formed nanoparticles. Apparently, the heat treatment of the precursor at 600 °C for 2h, results in the formation of pure crystallized $CoFe_2O_4$ nanocrystals. The results demonstrated that sol-gel auto-combustion is a one-step, rapid and cost effective method for the preparation of cubic spinel ferrite. X-Ray Diffraction (XRD), Energy Dispersive X-ray Analysis (EDX) and Scanning Electron Microscopy (SEM) were used to investigate the structural, elemental analysis and morphological properties of nanoparticles.

Key words: $CoFe_2O_4$ % Spinel Structure % HTAB % Sol-Gel Autocombustion Method

INTRODUCTION

Ferrite nanomaterials are among the most widely used electromagnetic materials for a broad category of applications over a wide frequency range due to their peculiar optical and electrical properties. Such nanoparticles can apply as magnetic materials, refractory materials and as catalysts [1].

Spinal ferrites of the type AB_2O_4 such as $ZnFe_2O_4$, $MnFe_2O_4$, $NiFe_2O_4$ and $CoFe_2O_4$ have already numerous applications, including gas sensors, microwave devices, photocatalysis, adsorption technologies and high-frequency transformer technology [2]. Among spinels, $CoFe_2O_4$, finds a wide range of applications based on high density recording, spintronics, Ferro fluids, magnetic resonance imaging and delivery of drugs to specific areas of the body [3-7].

It has been reported that, the properties of ferrite nanoparticles are strongly influenced by its composition and microstructure which are extremely sensitive to the method of preparation. Various methods have been developed to synthesize $CoFe_2O_4$ nanocrystallines, namely, co-precipitation [8-10], polymerized complex [11], hydrothermal [12, 13], microwave [14], sol-gel [15-18], solvothermal [19] and microemulsion techniques [20].

Sol-gel autocombustion have received much attention due to fact that they are highly cost, time and energy effective process. In order to adjust the physical and chemical properties in the nano- regime, many efforts have been made on optimizing the particle size by varying parameters such as temperature, pH, ionic strength imposed by non-complexing salts and surfactant [21, 22].

The formation of nanoparticles in solution in the presence of surfactants leads to a reduction in their average diameter in comparison with the decomposition process in the absence of solvent which is due to the prevention of caking and a more uniform heating of the reaction mixture [23].

The purpose of the present work was to investigate the role of surfactant and pH simultaneously on the crystallization of the mixed oxide $CoFe_2O_4$ obtained by sol-gel autocombustion route.

Experimental

Materials: In the current study, commercially available materials were used without further purification and treatment. Deionized water was used for the preparation of all the samples. Cobalt nitrate hexa hydrate, ferric nitrate nona hydrate, urea, hexa-decyl tri-methyl ammonium bromide (HTAB) and ammonia were all supplied by Merck Company.

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Synthesis of $CoFe_2O_4$ Nanoparticles: Aqueous solutions of Co $(NO_3)_2.6H_2O$ and Fe $(NO_3)_3.9H_2O$ were prepared in a 1:2 molar ratio. Three moles of urea per one mole of metal ions was used for this synthesis. HTAB was then added into the cation mixture to form the mixed normal micelles. The pH of the resulting mixture was then adjusted to 3, 5, 7, 9 and 11, respectively and the mixed solutions were evaporated on a hot plate to a temperature of 60°C for 6 hours. Following the evaporation of water, the obtained brown gel was then ignited and $CoFe_2O_4$ powders were obtained. The precursors were washed 3 times with deionized water and once with absolute ethanol. The washed powders were then dried at 80°C for 4 hours and calcined at 600 °C with a heating rate of 10°C min^{-1}. At the end, nanopowders were sonicated at room temperature for 15 minutes to obtained uniform cobalt ferrite nanoparticles.

The resulting powder was then characterized by the powder X-ray Diffraction (Cu Ká radiation, model STOE).The average particles sizes of the different phases were determined from the line widths of the diffraction peaks using Debye Scherrer equation:

$$D = (0.9)\,\lambda/\beta\cos\theta$$

Where D is the grain diameter, β is half-intensity width of the relevant diffraction; λ is X-ray wavelength and θ the diffraction angle. A Philips XL-30 scanning electron microscope was used to characterization the morphologies and microstructure of the samples. The elemental analysis of the samples was carried out using energy- dispersive X-ray spectroscopy technique.

RESULT AND DISCUSSION

The XRD patterns of the synthesized powders at different pH in the presence of HTAB as surfactant are compared in Figure 1. As a result, a single phase spinel ferrite is obtained by the sol-gel autocombustion method in the presence of HTAB in all pH values. We concluded that, the average particle size was decreased as the pH was increased. An increasing in the average particle size observed only in the samples which were prepared at pH=9. The average crystalline size and crystallity percent are summarized in Table 1. As it can be observed from the presented results, the values of crystallity percent are higher than 70% in all samples.

Table 1: The effect of different pH values on the average particle size and crystallity percent of the $CoFe_2O_4$ nanoparticles

Sample	pH	Average size	Crystallity percent
1	3	38	73.24
2	5	30	71.96
3	7	22	75.05
4	9	29	70.58
5	11	20	73.12

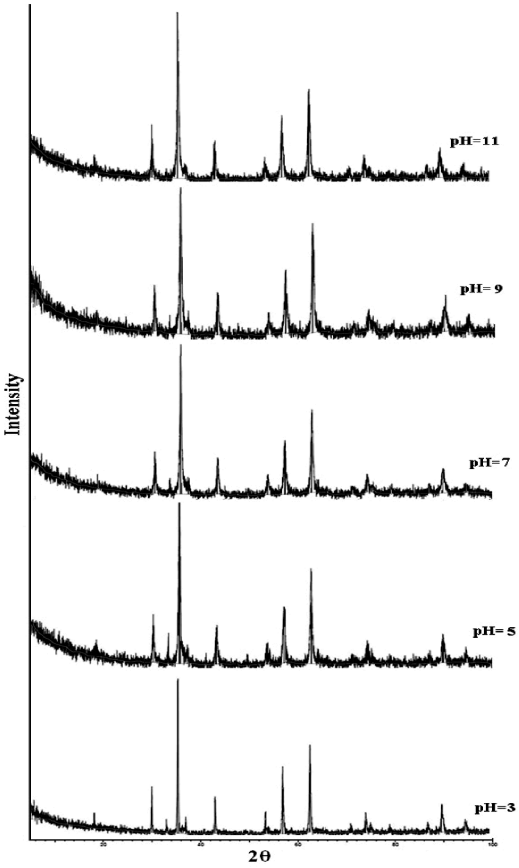

Fig. 1: X-ray diffraction patterns of samples prepared at different pH in presence of HTAB and calcined at 600°C.

The obtained peaks in the patterns of samples at higher PH were broader, in comparison to those which were synthesized under the same condition, with lower PH, which indicated that that peaks became sharper by decreasing the PH value.

The compositional analysis of the samples was determined by EDAX is shown in Figure 2 (a-c). From the EDAX quantification of the samples, the atomic fraction of Fe:Co, was determined. The Fe:Co atomic ratio of the sample is 2.19, which is approximately consistent with the stoichiometric ratio of the cobalt ferrite.

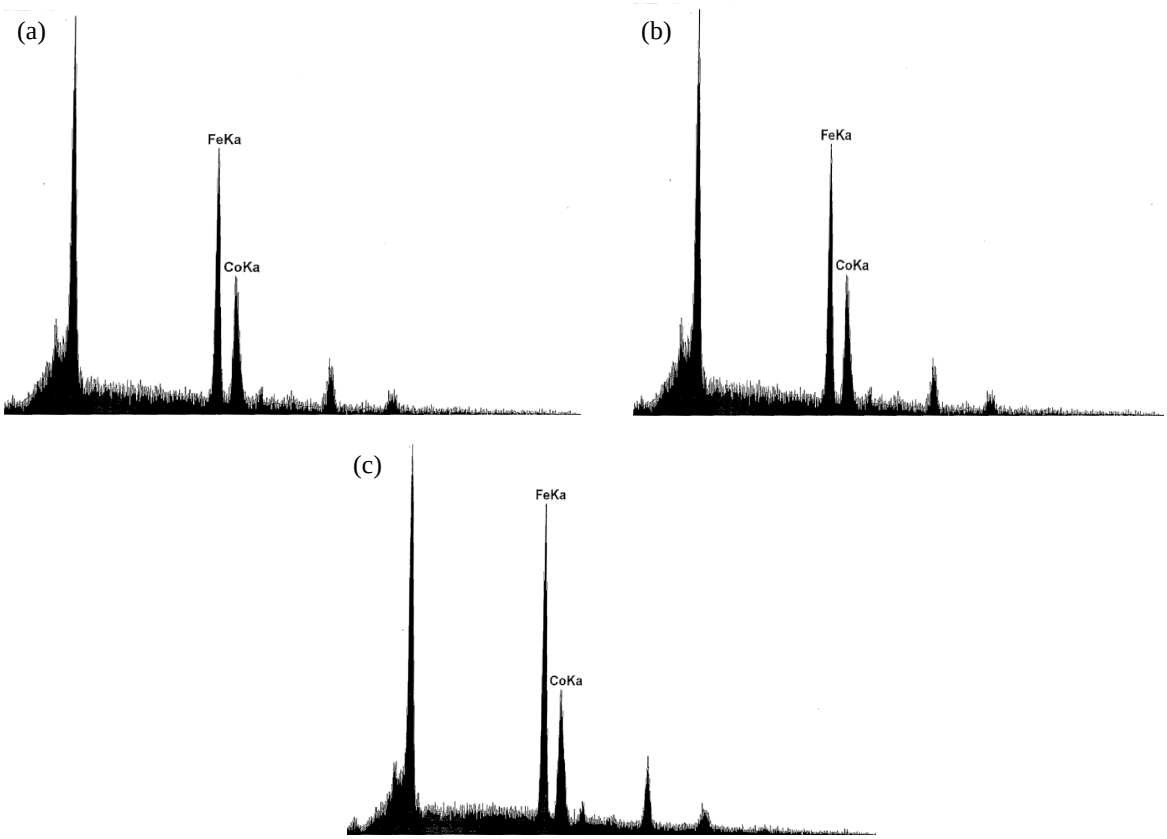

Fig. 2: EDAX analysis of samples prepared at pH a) 3, b) 7 and c) 11
In the presence of HTAB and calcined at 600°C

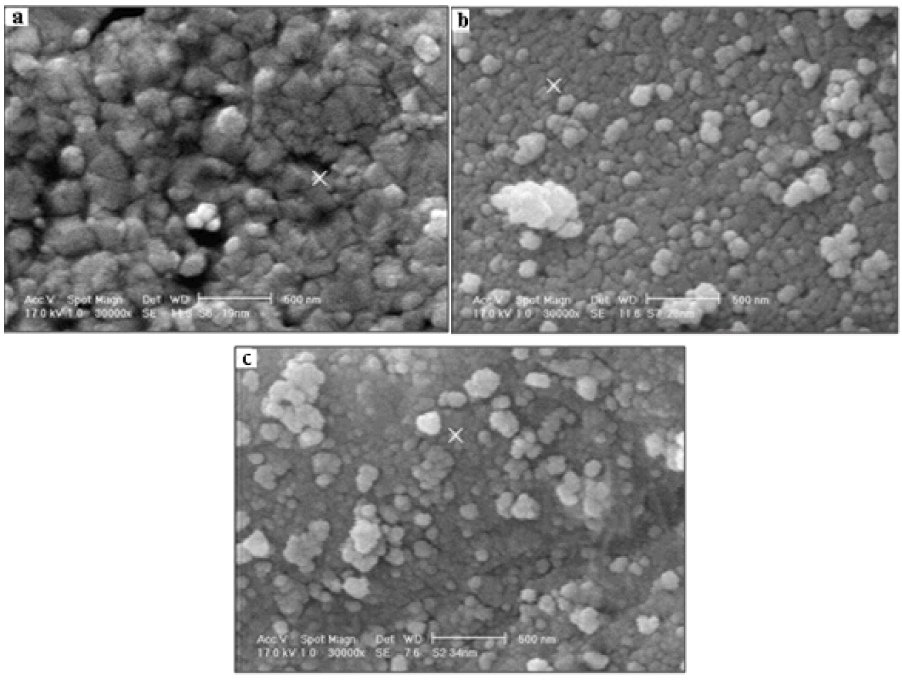

Fig. 3: SEM images of samples prepared at pH a) 3, b) 7 and c) 11
In the presence of HTAB and calcined at 600°C.

As shown in Figure 3(a-c), the SEM images of samples were obtained at different pH values in the presence of HTAB. $CoFe_2O_4$ nanoparticles were contained spherical particles. Also, it is found that some irregular aggregations formed in the sample which was owing to the acidic solution (Fig. 3a). The surfactant plays a fundamental role. Therefore, it could be taken as the ideal template for preparing nanoparticles with spherical shapes in microemulsion due to the enclosed micelles providing a space for inorganic crystal growth.

CONCLUSION

In the current paper, the HTAB-assisted sol-gel autocombustion method, a simple synthesis route, has been used to produce $CoFe_2O_4$ nanoparticles with average size ranging from 20 to 38 nm and crystallity above 70%. All samples contain $CoFe_2O_4$ nanoparticles with cubic spinel structure. As a result, variation in the number of phase, crystallity, size and morphology of synthesized nanoparticles was dependent on the value of pH and type of the surfactant. Also, it was observed that comparing to the other samples, crystallity precent, in pH=7, was at it's highest level.

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