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The effect of molar ratio on structural and magnetic properties of $BaFe_{12}O_{19}$ nanoparticles prepared by sol-gel auto-combustion method

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ABSTRACT

Nanocrystalline particles of barium hexaferrite has been prepared by the sol–gel auto- combustion method using iron and barium nitrate with a Ba:Fe molar ratio of 1:10. The effect of fuel such as citric acid and aspartic acid was investigated on the structure and magnetic properties of nanoparticles. The results revealed that the formation of barium hexaferrite_fine particles is influenced by molar ratio of metal nitrates to fuel. The formation of pure crystallized $BaFe_{12}O_{19}$ nanoparticles occurred when the precursor was heat-treated at 900°C for 2 h. Nanoparticles of barium hexaferrite with average crystalline size between 60-69 nm has been obtained. X-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) were employed to identify the structural phases, surface morphology and magnetic properties of the prepared nanoparticles, respectively. Magnetic measurements showed that the $BaFe_{12}O_{19}$ nanoparticles exhibited a great coercive field and high saturation magnetization of up to 5100 Oe and 55 emu g^{-1}, respectively.

Keywords: *$BaFe_{12}O_{19}$; Permanent magnets; Hexagonal ferrites; Sol-Gel auto -combustion method.*

INTRODUCTION

Nowadays, nanostructured magnetic materials have been intensively investigated due to their applications in magnetic recording media, sensors and biomolecular separations [1]. Some ferrite ceramics with magnetic properties have been extensively studied for use as permanent magnetic materials, electromagnetic wave absorption materials and for use as advanced recording media. Permanent magnets are characterized by high remanence, coercivity and energy product [2–4]. Ferrimagnetic barium hexaferrite with magnetoplumbite structure, $BaFe_{12}O_{19}$, has been considered as a permanent magnet. Magnetoplumbite are of the type $A^{2+}O{\cdot}6B_2^{3+}O_3$.

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The arrangement of the 12 Fe^{3+} ions in the unit cell is as follows: two ions in the tetrahedral sites (four nearest O^{2-} neighbors), nine ions in the dodecahedral sites (six nearest O^{2-} neighbors) and one ion in the hexagonal site (five nearest O^{2-} neighbors) [5].

$BaFe_{12}O_{19}$, is well-known for its high performance permanent magnetic and good mechanical hardness which has attracted considerable attention in recent years owing to its high coercivity, high curie temperature, relatively large magnetization, and the superior chemical stability and corrosion resistivity. This material has been widely used in high-density magnetic, magneto-optic recording media and traditional permanent magnets. $BaFe_{12}O_{19}$ has been used as microwave absorbing agent in 2–18 GHz to eliminate unwanted electromagnetic signals, which may interfere with electronically controlled systems and be harmful to health [6-9].

In order to achieve highly homogeneous ultrafine particles of barium hexaferrite it is necessary to find the best synthesis conditions. Conventional way of producing these materials is the solid-state reaction method in which the oxides or carbonates of barium and iron are mixed and annealed at high temperatures (≥1200˚C). The solid-state reaction method has some disadvantages such as production of inhomogeneous coarse powders as a consequence of high temperature annealing and introduction of impurities during ball milling [10]. To avoid these detrimental effects seen in conventional solid-state reaction method, various techniques such as chemical coprecipitation [11-13], hydrothermal [14-16], sol–gel [17, 18], micro-emulsion [19], salt-melt [20], mechanical milling [21] and reverse micelle [22] methods have been developed.

The most important feature of these methods is to use liquid media to intimately mix the required metallic constituents on an ionic level, resulting in small particles with uniform compositions and narrow size distribution. [23].

In recent years, mainly because of its inexpensive precursors and relatively simple manipulations, sol-gel auto-combustion synthesis method has attracted considerable attention in fabricating homogeneous and multi-component metal oxide ceramic powders [23, 24].

Sol–gel auto-combustion is a way with a unique combination of the chemical sol–gel process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous and fluffy product with large surface area. This process is less complicated than the others [25, 26].

In this research, the sol–gel auto-combustion method was applied to prepare barium ferrite fine nanoparticles. Incidentally, the effect of fuels such as citric acid and aspartic acid was investigated on the structure, magnetic and morphological properties of barium hexaferrite.

EXPERIMENTAL

Synthesis of $BaFe_{12}O_{19}$ Nanoparticles

The starting materials were barium nitrate, iron (III) nitrate, citric acid, aspartic acid and ammonia, all of analytic purity. Reactants were supplied from Merck Company and used without purification. Deionized water was used for the preparation of all the samples. $Ba(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$ in the molar ratio of 1:10 were dissolved in minimum amount of deionized water. Fuel (citric acid or aspartic acid) was then added into the prepared aqueous solution to chelate Ba^{2+} and Fe^{3+}. Table.1 showed the characteristic of samples which were prepared with different amount of fuels.

The mixed solution was neutralized to pH 7 by adding ammonia and then stirred continuously at 60˚C until a viscose brown gel was obtained. The obtained gels were ignited until all gels are completely burnt out to form a loose powder. Finally, powders were calcined at 900˚C for 2 hours with a heating rate of 10 ˚C min^{-1} to obtained barium hexaferrite phase.

Table. 1. Feature samples

Samples	Fuel	Metals:Fuel
S_1	Citric acid	1:1
S_2	Citric acid	1:2
S_3	Citric acid	1:3
S_4	Aspartic acid	1:1
S_5	Aspartic acid	1:2
S_6	Aspartic acid	1:3

Materials Characterization

The X-ray diffraction was carried out to check the phase purity with an STOE X-ray powder diffractometer using Cu K_α radiation. The particles size 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 magnetic properties of the ferrites were measured at room temperature using a vibrating sample magnetometer in a maximum applied field of 10 kOe. From the obtained hysteresis loops, the saturation magnetization, M_s, remnant magnetization, M_r and coercivity, H_c were determined.

RESULTS AND DISCUSSION

X-Ray Analysis

The X-ray diffraction patterns of samples which prepared with various amounts of citric acid is shown in Figure 1(a-c).The results revealed the formation of barium hexagonal phase with space group, p63/mmc [194], in the all samples, but the well-crystalline samples were formed at 1:2 and 1:3 molar ratios. It seems that in the case of sample which prepared with 1:1 molar ratio, the amount of citric acid was not sufficient for the formation of hexaferrite phase. The presence of sub-phases such as FeO and $BaFe_2O_4$ in this sample confirms that the amount of fuel is not suitable for the chelation of Ba^{2+} and Fe^{3+} ions and the reaction is not complete. The average crystalline size of these samples is shown in Table 2.

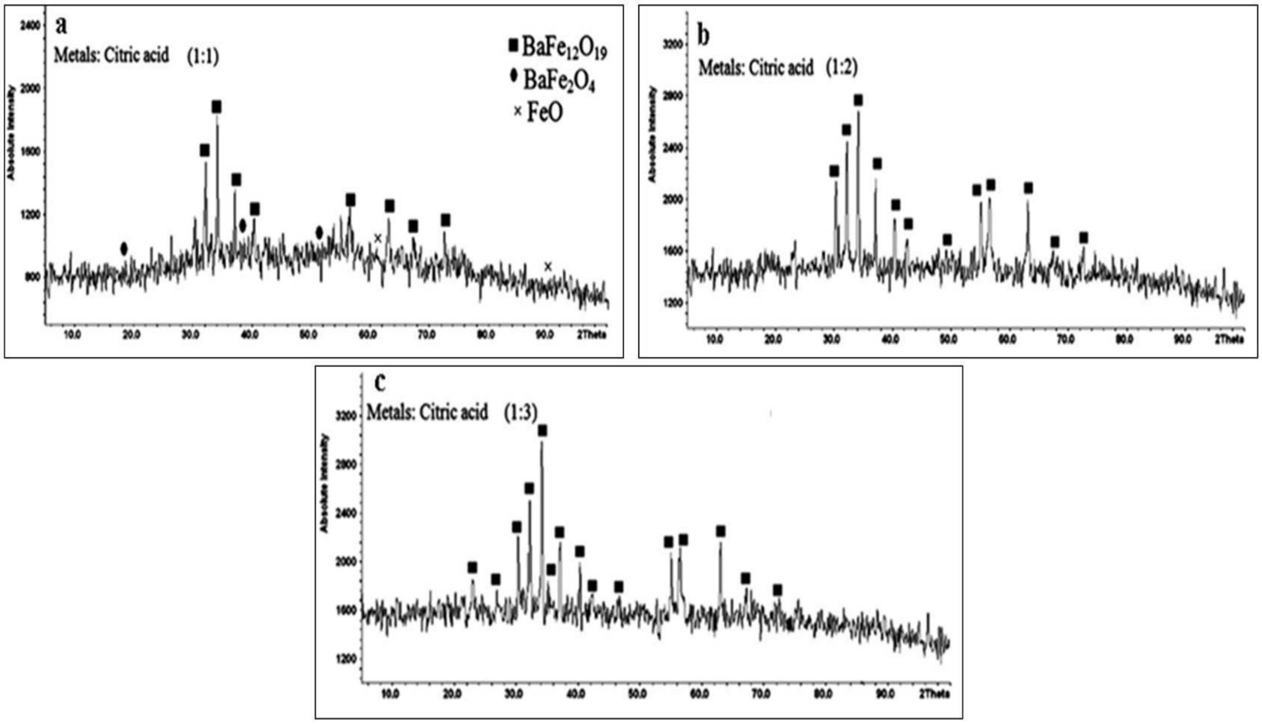

Fig.1. X-ray diffraction patterns of three samples prepared with different molar ratios of metal nitrates to citric acid at pH=7 and calcined at 900˚C.

Table 2. Average size of samples prepared with different amount of citric acid.

Samples	Metals: fuel	Average size (nm)
S_1	1:1	65
S_2	1:2	63
S_3	1:3	60

Figure 2(a-c) show XRD patterns of three samples which were treated with various amounts of aspartic acid. The results confirmed the formation of single-phase hexagonal ferrite in the all samples. The average crystalline size calculated from Sherrer equation of these samples is shown in Table 3.

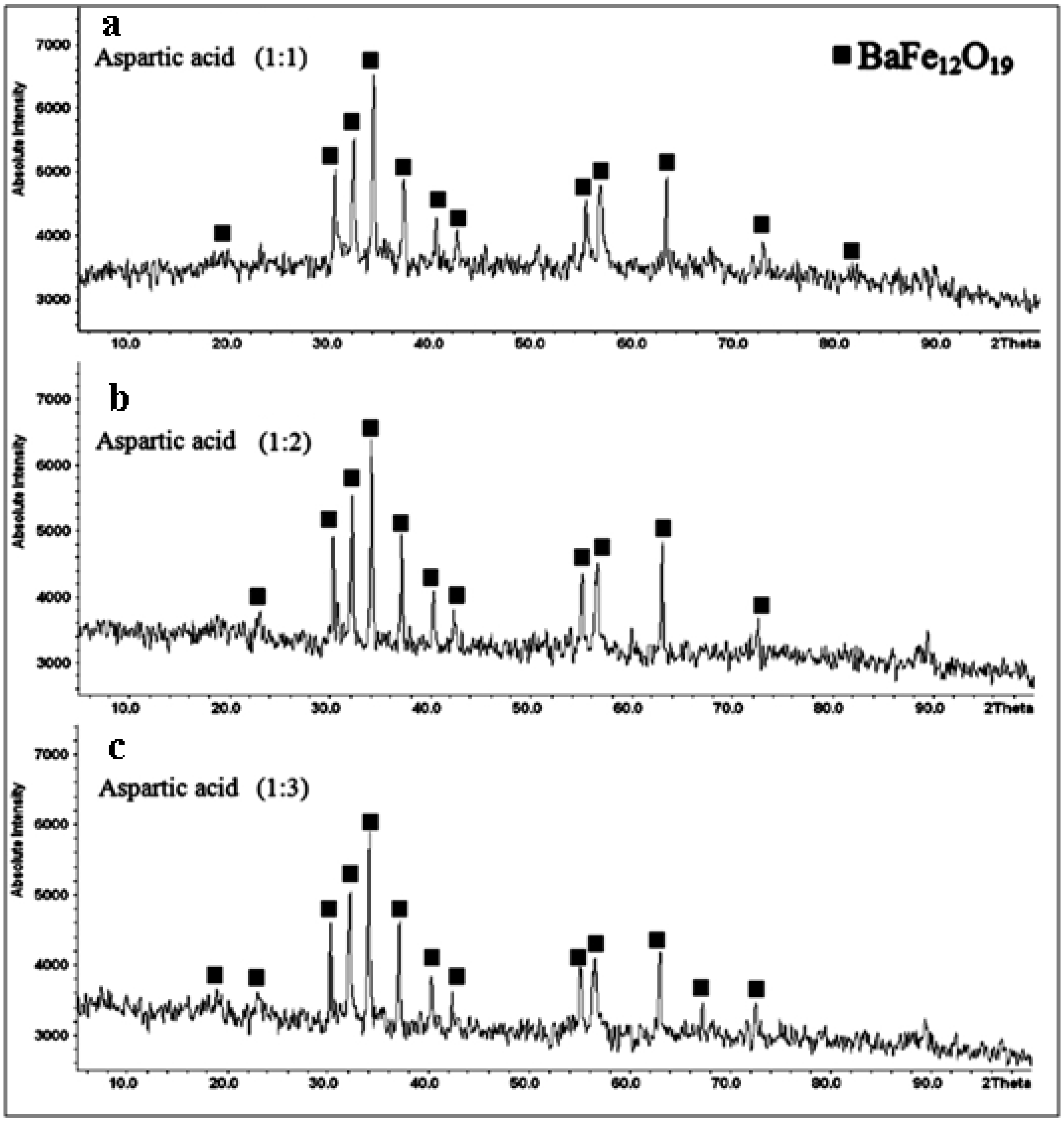

Fig. 2. X-ray diffraction patterns of three samples prepared with different molar ratios of metal nitrates to aspartic acid at pH=7 and calcined at 900˚C.

Table 3. Average size of samples prepared with different amount of aspartic acid

Samples	Metals: fuel	Average size (nm)
S_4	1:1	69
S_5	1:2	67
S_6	1:3	63

As a result, by using an aspartic acid as a fuel, possibility of the sub-phase formation decreased in compared with citric acid, but the average size of nanoparticles were relatively greater than those were prepared with citric acid.

SEM Images

Figure 3(a-c) give the SEM images of samples were obtained by citric acid.

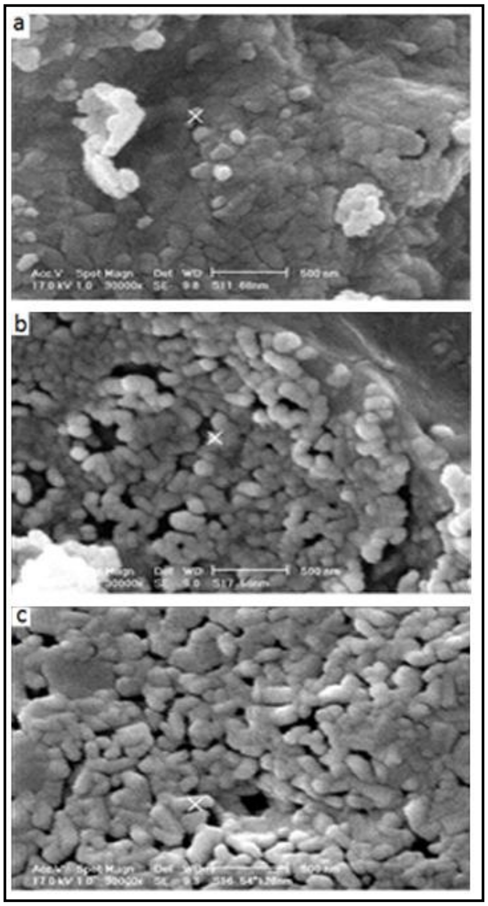

Fig. 3. SEM images of three samples prepared with different molar ratios of metal nitrates to citric acid a) S_1, b) S_2 and c) S_3.

It can be clearly noted that the powders are composed of many tiny crystallites, but the average particles size dramatically increase by decreasing the citric acid content from 1:3 to 1:1 molar ratios. The mean particle size estimated for S_2 was about 58 nm and the particles were spherical in morphology. Where as, the rod-shape structures were found in S_3 with size of about 54×128 nm. It is also found that some irregular aggregations formed in S_1 and the average size was increased to 68 nm.

It is expected that the combustion synthesis were completed with the excess amount of citric acid as it is considered before in some paper [25, 26]. These SEM results are in according with the calculation of average size from Scherrer's equation.

SEM images of the samples were obtained with aspartic acid is shown in Figure 4(a-c). As the pictures show, the average size of S_4 and S_6 were 68 nm and 34 nm, respectively with particles in spherical shape. In the case of S_5 nano-rods with size of 34×187 nm have been observed.

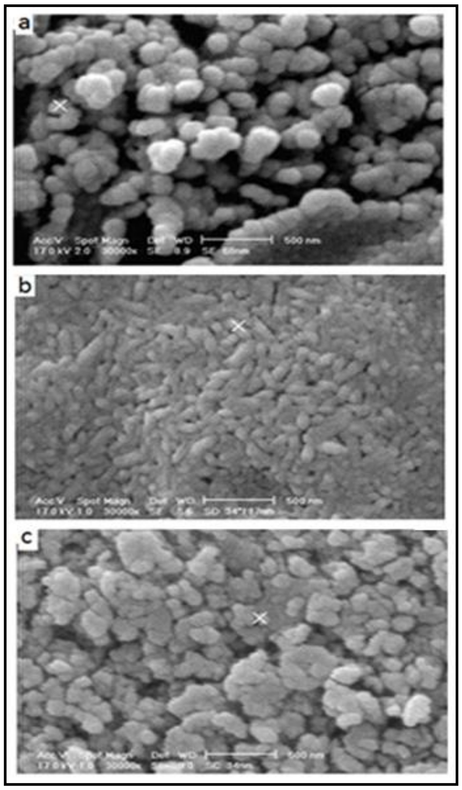

Fig. 4. SEM images of three samples prepared with different molar ratios of metal nitrates to aspartic acid a) S_4, b) S_5 and c) S_6.

In both cases, citric acid and aspartic acid, by choosing 1:1 molar ratio of metal nitrates to fuel, the final products were agglomerated in compared with other products. Based on these results the particles size can be controlled by adjusting the fuel content.

Hysteresis loops

Magnetization versus the applied field plots at room temperature for samples S_2 and S_5 is shown in Figure 5(a ,b).

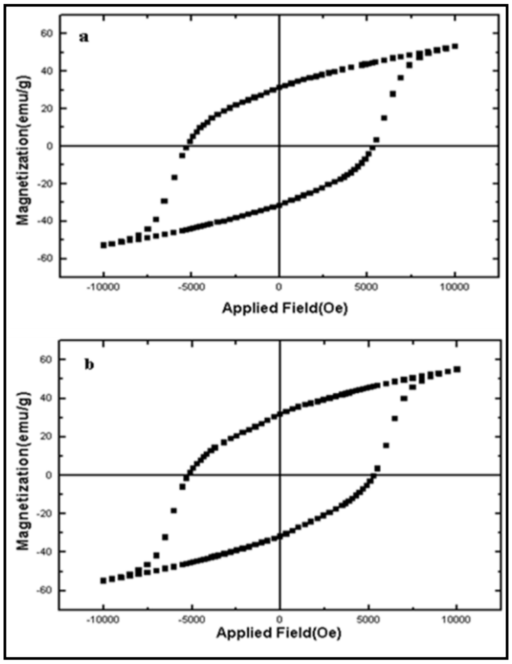

Fig. 5. Magnetization vs. applied magnetic field curves of sample a) S_2, b) S_5 at room temperature in a maximum applied field of 10 kOe.

Sample S_2 showed a saturation magnetization, M_s, 55.9 emu g^{-1} and remnant magnetization, M_r, 31.0 emu g^{-1}. The saturation and remnant magnetization for the sample S_5 were 55.1 emu g^{-1} and 31.84 emu g^{-1}. A coercive force, H_c, was 5100 Oe for two samples. Magnetic properties of the samples were closed together.

CONCLUSIONS

Nanosized particles of barium hexaferrite have been synthesized with sol-gel auto-combustion method. This simple technique is cost effective and highly time and energy efficient process. The combustion reaction can be considered as a thermally induced anionic redox reaction of the gel wherein the fuels act as reductant and NO_3^- ions act as oxidant. In the auto-combustion process a lot of gases such as CO, CO_2 and NH_3 were released. It is also found that, when as-burnt powders were annealed at 900˚C, the excess amount of fuels released more gases, which led the heat to be removed from the system. So, low temperature of the system prevented particles from growing. This fact acts as an important role to reduce the growth rate of particles. Barium hexaferrite was obtained by using two fuels, but the results suggested that applying aspartic acid as a fuel leads to formation of $BaFe_{12}O_{19}$ single-phase in comparison with citric acid. Images showed that the formation of long rod-shape structures changes with the type of fuel. By using aspartic acid as fuel with the molar ratio of 1:2, the length of these structures are higher than the sample was prepared with the same conditions by using citric acid as fuel. Comparing the results of this study with similar studies conducted on the synthesis of $BaFe_{12}O_{19}$ show that the reaction was carried out at lower temperature and the hexagonal phases was obtained. The results indicate that the fuel content play a very important role in developing the hexagonal phase. So, it is necessary to adjust appropriate amount of molar ratio to produce pure barium hexaferrite in the sol-gel auto-combustion method. This technique has proven to produce pure barium ferrite powders with maximum saturation magnetization value of, 55 emu g^{-1}, and coercivity force value of, 5100 Oe.

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