Effect of Heat Treatment on Structural and Magnetic Properties of Nanocrystalline SrFe12O19 Hexaferrite Synthesized by Co-Precipitation Method

Ma. Ganjali[a,]*, Mo. Ganjali[a], A. Eskandari[a], M. Aminzare[b]

[a] *Department of Nanotechnology and Advanced Materials, Material and Energy Research Center, karaj, Iran.*
[b] *Department of Materials and Metallurgical Engineering, Iran University of Science and Technology, Tehran, Iran.*

ARTICLE INFO

Article history:

Received 5 Dec 2013
Accepted 18 Dec 2013
Available online 25 Dec. 2013

Keywords:

Hexaferrite
Synthesis
Magnetic properties
Co-precipitation
Nanocrystalline

ABSTRACT

Nanocrystalline strontium hexaferrite ($SrFe_{12}O_{19}$) powders have been successfully synthesized using facile Co-precipitation method. Ferrite precursors were obtained from mixtures of strontium and ferric chloride in an aqueous medium without any surfactant and soft template. The as-received powders were calcined at 800 and 1000 ˚C for 2 hours in air. The final powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET surface area analysis and Vibrating Sample Magnetometer (VSM). The effects of calcination temperature on phase composition, particle size and shape as well as magnetic properties of the products have been investigated. The results indicated that higher calcination temperature (1000 ^{o}C) resulted in higher particle sizes (98.1 nm), maximum saturation magnetization (60.53 emu/g), remanence value (36.23 emu/g) and less surface area (12 m^2g^{-1}). The magnetocrystalline anisotropy constant, K, calculated from the Stoner–Wohlfarth theory, increases by increasing temperature up to 15.1 (HA^2/kg).

1. Introduction

M-type hexaferrites, with chemical formula of $MeFe_{12}O_{19}$, (Me = Ba, Sr and Pb) have been widely used as permanent magnets and their great technical importance has attracted an extensive attention for the last few decades. They are widely used in fabrication of computer data storage, high-density perpendicular magnetic and magneto-optic recording, magnetic fluids and certain microwave devices [1, 2]. M-type hexaferrites are hard magnets with high coercivity which is due to their high magneto-crystalline anisotropy with an easy single magnetization axis [3].

An ultrafine strontium hexaferrite powder has a mean particle size less than 0.1μm and is made of homogeneous particle size distribution[2]. The large surface area often dominates the properties of the powders and significantly enhances mechanical[4, 5], chemical and physical properties[6, 7] of the materials resulting in interesting and sometimes unexpected behavior of nanoparticles. It is difficult to obtain ultrafine and mono-sized particles by the conventional ceramic method

---

Corresponding author:
E-mail address: ganjali.m@gmail.com(Mansoureh Ganjali).

(solid-state reaction) which requires the firing of stoichiometric mixture strontium carbonate and α-iron oxide at high temperatures (about 1300 ˚C)[6, 8-10].

In order to achieve highly homogeneous ultrafine particles of M-type hexaferrite, various chemical techniques were investigated, such as chemical co-precipitation[11], hydrothermal[12] , plasma spraying [1], sol-gel [2] and microemulsion method [13]. Among the chemical routes, co-precipitation is low cost, simplistic and a more reliable method where the stoichiometry can effortlessly be controlled and be easily usable for production of nanocrystalline hexaferrite powder.

The objective of the present work is to investigate the synthesis of nanocrystalline $SrFe_{12}O_{19}$ particles by facile chemical co-precipitation method in aqueous media. Effects of heat treatment, microstructural state and phase composition on magnetic properties of Sr-hexaferrite are also studied.

2. Experimental

The synthesis was performed using strontium chloride ($SrCl_2.6H_2O$) (MERCK, purity> 99.99%) and ferric chloride ($FeCl_3$) (MERCK, purity> 99.99%) as precursors. Stoichiometric amount of these materials were put into 100 ml water and mixed to give a homogeneous aqueous solution. The sodium hydroxide solution (NaOH, 10 M) was added drop wise to the solution contacting Sr and Fe cations in order to co-precipitate a brown gel-like cake. The precipitation was performed at pH value of 12.6 and room temperature. The precipitate was washed for several times with a mixture of distilled water and ethanol (1:1), dried at 100 °C and subsequently heated to 800 and 1000 ˚C.

Hexaferrite powders were characterized by X-ray diffraction (XRD) method. XRD was carried out by German Unisantis (XMD-300) using Cu Kα (1.5418˚A) radiation. Hexaferrite crystallite sizes were determined by well-known Scherrer's equation[8]:

$$D = 0.9 \Big/ \left[(\beta - \beta_1).\cos\theta \right] \qquad [1]$$

where D is the crystallite size, λ is the wavelength of the X-ray radiation, β is the full width at half maximum (FWHM) of the relevant diffraction peak, β_1 represents the FWHM due to instrumental broadening.

The BET surface area was determined by a multipoint BET method (BET, BEL Japan Inc.) using the adsorption data in the relative pressure (P/P0) range of 0.05–0.3. A desorption isotherm was used to determine the pore size distribution by the Barrett–Joyner–Halender (BJH) method, assuming a cylindrical pore model. The nitrogen adsorption volume at the P/P0 of 0.994 was used to determine the pore volume and the average pore size.

The particle size and morphology of the samples were determined by scanning electron microscopy (SEM-Tescan) and transmission electron microscopy (TEM, Philips, 200kV).

Magnetic measurements were carried out using vibrating sample magnetometer (VSM, VSM-5, TOEI Industry Co.), with a maximum applied field of ±20 kOe at room temperature.

3. Results and Discussion

The main reactions proposed for preparation of nanocrystalline SrFe12O19 Hexaferrite is:

$$12FeCI_3 + SrCI_2 + 38NaOH \rightarrow 38NaCI + SrFe_{12}O_{19} + 19H_2O \qquad [2]$$

Fig.1 shows the XRD patterns of $SrFe_{12}O_{19}$ Hexaferrite powders before and after calcinations at different temperatures for 2 h. It can be seen that there are not any distinguished peaks for as-synthesis powders. Further observation shows that with increasing calcination temperature form 800°C to 1000°C, crystallization process occurs and the characteristic peaks can be observed. By heating the samples at 800 ^{o}C, besides the Sr-hexaferrite phase, two other phases can be detected. XRD peaks of $Fe(OH)_2$ and γ -Fe_2O_3 were indexed for the samples heated at 800 ^{o}C for 2h at2θ values of 20.65,21,2, 26.2 and 29.1, 45.16, respectively. However, their intensities then completely disappeared after heating at 1000 ^{o}C, indicating that the aforementioned reaction was completed. It is demonstrated that

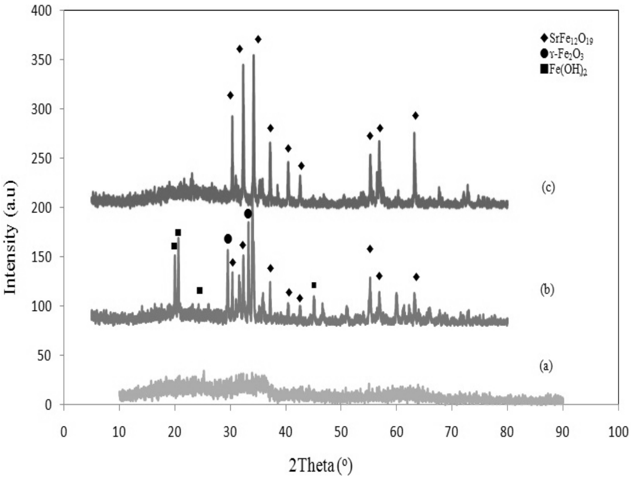

Fig. 1. XRD patterns of $SrFe_{12}O_{19}$nanopowder synthesized via co-precipitation method before (a) and after calcination at 800ºC (b), 1000ºC (c), for 2 h.

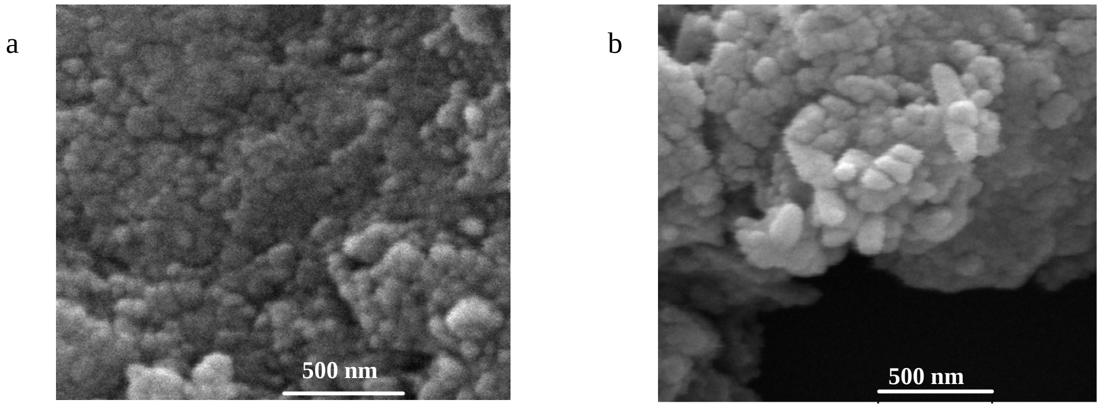

Fig. 2. SEM images of the $SrFe_{12}O_{19}$ nanopowder after calcination at 800ºC (a), 1000ºC (b), for 2h.

Fe_2O_3 crystals as an intermediate structure, playa significant role in formation of hexaferrite phase. In fact, the two structures of Fe_2O_3 have controversial effect on formation of hexaferrite. It is well known that γ-Fe_2O_3 is a cubic spinel, whose chemical formula is Fe[Fe5/3y1/3]O4, where (y) stands for a cation hole. In Contrast, α-Fe_2O_3 as an orthorhombic hexahedron crystal hinders the transformation of Iron oxide to hexaferrite phase[14]. As it was mentioned in Fig.1, γ-Fe_2O_3 peaks were detected; therefore, γ-Fe_2O_3 can be easily converted into $SrFe_{12}O_{19}$ phase. According to the JCPDS card No. 00-024-1207, characteristic peaks of hexaferrite can be observed at 2θ values of 30.3◦, 32.3◦, 34.1◦, 56.8◦ , 63.2◦ corresponding to the crystal planes of (1 1 0), (1 0 7), (1 1 4), (2 0 11), (2 2 0). It can also be seen that no impurity phases have been detected. From equation (1), the crystallite size of hexaferrite sample which had been calcined at 800˚C, is determined to be about 38nm. The result of X-ray diffraction pattern of the sample calcined at 1000 ˚C shows a single hexaferrite phase with crystallite size of 57 nm. According to XRD result, it was found that the crystallite size increases drastically with increasing the calcinations temperature. The increase in average crystallite size is due to the tendency of atoms to move. In other words, the increase in crystallite size may be attributed to the increase of the crystal growth rate at higher temperatures.

Morphology and size of the samples were examined by SEM. Fig. 2 shows the general morphology of the product calcined at 800 ^{o}C and 1000 ^{o}C. It reveals that the co-precipitated hexaferrite nanopowders are relatively uniform spherical shape with diameters of ~80 nm.

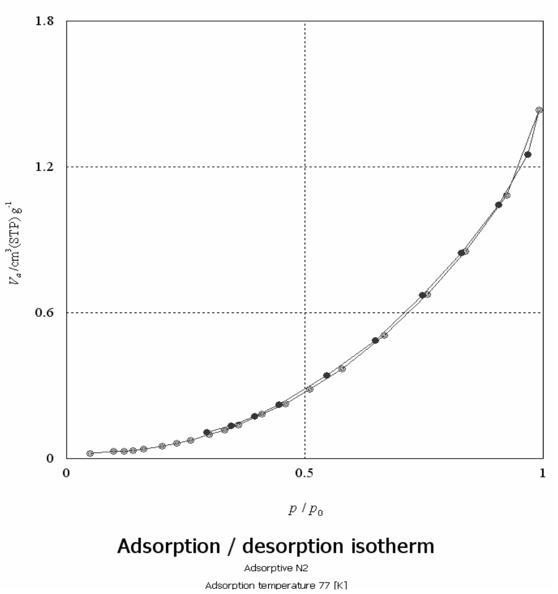

Fig. 3. N_2 adsorption/desorption isotherm at 77K of $SrFe_{12}O_{19}$ nanopowder calcined at 1000˚C.

From this figure, higher calcination temperature resulted in higher particle size. In other words, further calcination temperature (1000 ˚C) leads to crystal growth and average particle sizes increase up to ~ 120 nm.

The nitrogen sorption isotherms of the Sr-Hexaferritenanopowders were measured to gain the information about the specific surface area and the pore sizes for samples heat treated at 1000 °C. Surface area analysis indicates that synthesized nanoparticles have mesoporous surfaces [7]. These pores may have been formed during calcination when OH- groups come out of the precursors. As a result, these pores influence the crystallinity and magnetic properties of the samples. Particle size estimated from BET is given by equation[15] (Fig. 3):

$$D = 6/a_{s,BET} \times \rho \qquad [3]$$

Where ρ is theoretical density of strontium hexaferrite (5.18 m^2g^{-1}) and $a_{S,BET}$ corresponds to surface area calculated from BET analysis (16 m^2g^{-1} and 12 m^2g^{-1} for 800 ˚C and 1000 ˚C respectively). According to BET results, with increasing the temperature from 800 to 1000˚C, the particle size increases from 62 to 98 nm.

To give further insight into the morphology and structure of hexaferritenano powders, transmission electron microscopy was performed. TEM images of the samples calcined at different temperatures (800˚C and 1000°C) are shown in Fig.4 (a, b). It is clear from the figures that the mean particle sizes increase from 80 to ~95 nm. It is also observed that at lower calcination temperature, the product consists of varied size of ultra fine particles while the heat treated samples at 1000 °C have more uniformity in size and shape. The results of measuring particle size from the TEM images are in well agreement with the BET result. It is notable that the mean particle size of nanopowders is almost 2 times greater than the crystallite size obtained by x-ray diffraction pattern. It can be concluded that each nano particle consists of two crystallites.

To study the magnetic properties, the hysteresis loop of hexaferrite synthesized by co-precipitation method was analyzed. Fig. 5 shows the magnetic hysteresis loop, M (H) of $SrFe_{12}O_{19}$ nanopowders at 300 K. The saturation magnetizations (Ms) are found to be 28.34 and 60.53 emu/g for the samples calcined at 800 ˚C and 1000 ˚C, respectively. These results are smaller than the theoretically predicted value (67.70 emu/g), but agree well with other experimental values obtained from different preparation methods [8]. One reason for increasing MS at higher temperatures maybe owing to the more degree of crystallinity, increasing crystallite size and growth of magnetic domains of the sample at evaluated temperature [16, 17].The remanence (Mr) and coercivity (Hc) values also increase by increasing the temperature (Table 1). Based on Stoner–Wohlfarth theory, the coercivity of nano particles is determined by magnetocrystalline anisotropy constant (K) and saturation magnetization (Ms) according to the following equation [17]:

$$Hc = \frac{2K}{\mu . \times MS} \qquad [4]$$

where μ_0 is the universal constant of permeability in free space, H/m. The magneto crystalline anisotropy constant (K) can be calculated by using equation (4). In this regard, the magnetocrystalline anisotropy constant increases by increasing temperature from 6.9 to 15.1 (HA^2/kg). This issue is in well agreement with increasing the crystallinity of nanopowders by increase of the heating temperature. Kanagesan et al. [16] reported that

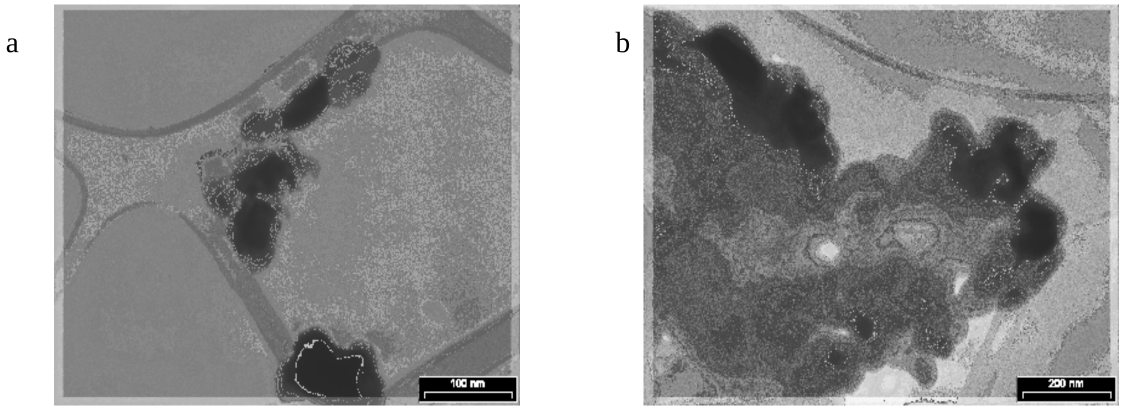

Fig. 4. TEM image of the hexaferrite nanopowder calcined at 800°C (a) and 1000˚C (b).for 2 h.

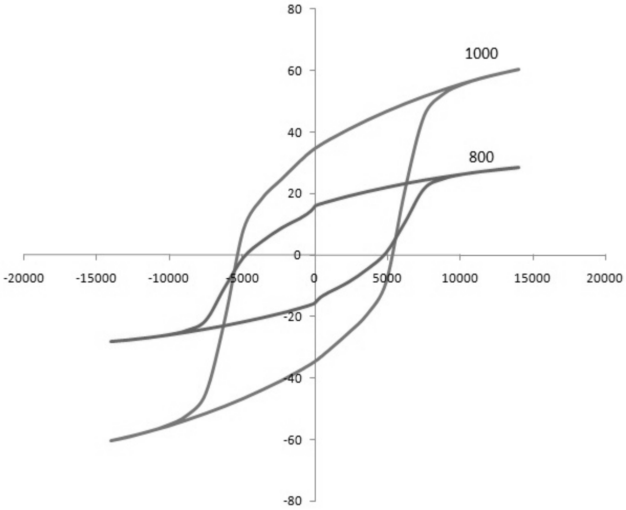

Fig. 5. Hysteresis loops of hexaferrite nanopowders calcined at 800˚C and 1000˚C for 2h.

Table 1. Physical properties of Sr-hexaferrite synthesized by co-precipitation

Temperature (^oC)	Ms (emu/g)	Mr (emu/g)	Hc (kOe)	Magnetocrystalline anisotropy constant (HA^2/kg).	Particle size (nm)	Surface area (m^2g^{-1})
800	28.34	16.65	4.9	6.9	80	19
1000	60.53	36.23	5	15.1	120	12

the variation of the coercivity is mainly related to the raise of the magneto crystalline anisotropy of the magnetic phase, which increases the coercivity. These values are, however, much more than those previously reported in the literatures. Zi et al. [11] reported that by using the precipitation method, the coercivity for hexaferrite samples was obtained ~1.06 kOe. Also, M. Jean et al. synthesized the $SrFe_{12}O_{19}$ hexaferrites particles in an alkaline medium using a hydrothermal process at 180 °C, and claimed that the coercivity was around the 3.5 kOe [12]. For better comparison of Sr-hexaferrite which is synthesized in this article, magnetic properties of some researches [6, 9, 12, 18-20] are listed in Table 2. Accordingly, the outstanding magnetization saturation and coercivity of nanostructured hexaferrite can be seen in this table which can be used in hard magnetic devices and microwave absorption applications.

4. Conclusions

In this study, $SrFe_{12}O_{19}$ hexaferrite nanoparticles were successfully synthesized via co-precipitation method in an aqueous solution.

Table 2. Comparison of magnetic characteristics and particle size of Sr-Hexaferrite with literature.

Saturation magnetization (emu/g)	Remanence (emu/g)	Intrinsic coercivity(kOe)	Synthesis route	Calcination temperature (^oC)	Particle size (nm)	Ref
50.15	25.18	2.64	Combustion synthesis	1000	52	[20]
47.5	24.3	1.64	Microwave induced combustion process	1000	70-90	[18]
54.80	29.52	5.261	Microwave assisted chemical synthesis	850	100	[19]
60.53	36.23	5	Co-Precipitation	1000	120	This work
47.5	26.44	5.45	Co-Precipitation	900	230	[9]
49	35	3.7	Molten flux	1050	800	[6]
39		2.4	Hydrothermal	1000	2000	[12]

Hexaferrite nanopowders were formed after annealing at 800 ˚C for 2h with the average crystallite size of around 38 nm. Increasing the calcination temperature resulted in grain growth and the crystallite size was obtained around 57 nm by calcination at 1000 ˚C. The maximum value of the saturation magnetization (Ms) and coercivity come out to be 60.53 emu/g and 5 kOe from the samples calcined at 1000 ˚C. The magnetocrystalline value also increases at higher temperature.

5. Acknowledgment

This work has been supported by the Materials and Energy Research Center (MERC), Nanotechnology and Advanced Materials Department in the framework of Project Number 728811.

References

1. S. P. Gubin, Yu. A. Koksharov, G B. Khomutov, G. Yuyurkov, "Magnetic nanoparticles: preparation, structure and properties",.Russ. Chem. Rev. Vol. 74, 2005, pp. 489 - 520.
2. M. G.Hasab, S. S. A. Ebrahimi, A. Badiei, “An investigation on physical properties of strontium hexaferrite nanopowder synthesized by a sol–gel auto-combustion process with addition of cationic surfactant”, J. Eur. Ceram. Soc., Vol. 27, 2007, pp. 3637–3640.
3. C. A. Stergiou, G. Litsardakis, “Electromagnetic properties of Ni and La doped strontium hexaferrites in the microwave region”, J. Alloys Compd., Vol. 509, 2011, pp. 6609-6615.
4. A. Eskandari, M. Aminzare, H. Hassani, H. Barounian, S. Hesaraki, S. K. Sadrnezhaad, “Densification Behavior and Mechanical Properties of Biomimetic Apatite Nano-crystals”, Curr. Nanosci, Vol. 7, 2011, pp. 776-780.
5. A. Eskandari, M. Aminzare, Z. Razavi Hesabi, S. H. Aboutalebi, S.K. Sadrnezhaad, “Effect of high energy ball milling on compressibility and sintering behavior of alumina nanoparticles”. Ceram. Int., Vol. 38, 2012, pp. 2627-2632.
6. S. Dursun, R. Topkaya, N. Akdoğan, S.Alkoy, “Comparison of the structural and magnetic properties of submicron barium hexaferrite powders prepared by molten salt and solid state calcination routes”, Ceram. Int., Vol. 38, 2012, pp. 3801-3806.
7. L. Hongbing., W. Shimin., L. Zhao, L. Jinchai, D. Binghai, X. Zuxun, “Hierarchical ZnO microarchitectures assembled by ultrathin nanosheets: hydrothermal synthesis and enhanced photocatalytic activity”, J. Mater. Chem., Vol. 21, 2011, pp. 4228–4234.
8. D. Primc,M.Drofenik, D.Makovec, “Low-Temperature Hydrothermal Synthesis of Ultrafine Strontium Hexaferrite Nanoparticles”, Eur. J. Inorg. Chem., Vol. 2011, 2011, pp. 3802-3809.
9. A. Ataie, S.Heshmati-Manesh, “Synthesis of ultra-fine particles of strontium hexaferrite by a modified co-precipitation method”, J. Eur. Ceram. Soc., Vol. 21, 2001, pp. 1951–1955.
10. Yi, Yang., B. Zhang, W. Xu, Shi, N. Zhou, H. Lu, “Microwave absorption studies of

W-hexaferrite prepared by co-precipitation/mechanical milling", J. Magn. Magn. Mater., Vol. 265, 2003**,** pp. 119-122.

11. Z. F. Zi, Y. P. Sun, X. B. Zhu, Z. R. Yang, J. M. Dai, W. H. Song, "Structural and magnetic properties of SrFe12O19 hexaferrite synthesized by a modified chemical co-precipitation method", J. Magn. Magn. Mater., Vol. 320, 2008, pp. 2742-2746.
12. M. Jean, V. Nachbaur, J. Bran, J. Le Breton, "Synthesis and characterization of SrFe12O19 powder obtained by hydrothermal Process", J. Alloys Compd., Vol. 496, 2010, pp. 306-312.
13. J. Fang, J. Wang, L. Gan, S. Ng, J. Ding, X.Liu, "Fine Strontium Ferrite Powders from an Ethanol-Based Microemulsion", J. Am. Ceram. Soc.,Vol. 83, 2000, pp. 1049–1055.
14. H. Shang, J. Wang, Q. Liu,"Synthesis and characterization of nanocrystalline BaFe12O19 obtained by using glucose as a fuel". Mater. Sci. Eng., A, Vol. 456, 2007**,** pp. 30–132.
15. J. Becker, K. R. Raghupathi, J. St.Pierre, D. Zhao, and R. T. Koodali, "Tuning of the Crystallite and Particle Sizes of ZnO Nanocrystalline Materials in Solvothermal Synthesis and Their Photocatalytic Activity for Dye Degradation", J. Phys. Chem. C, Vol. 115, 2011**,** pp. 13844–13850.
16. S. Kanagesan, S. Jesurani, R. Velmurugan, T.Kalaivani, "Preparation and magnetic properties of Ni–Zr doped barium strontium hexaferrite", J Mater Sci: Mater Electron, Vol. 23, 2012, pp. 952–955.
17. Y. Li, Q. Wang, and H. Yang, "Synthesis,characterization and magnetic properties on nanocrystalline BaFe12O19 ferrite", Curr. Appl Phys., Vol. 9, 2009, pp. 1375-1380.
18. Y. Fu, Ch-H Lin, "Fe/Sr ratio effect on magnetic properties of strontium ferrite powders synthesized by microwave-induced combustion process", J. Alloys Compd., Vol. 386, 2005**,** pp.222–227.
19. W. Zhanyong, Z. Liuming, L. Jieli, Q. Huichun, Z. Yuli, F. Yongzheng, J. Minglin, X. Jiayue, "Microwave-assisted synthesis of SrFe12O19 hexaferrites", J. Magn. Magn. Mater., Vol. 322, 2010, pp.2782–2785.
20. Ch-Sh. Lin, Ch-Ch. Hwang, T-H. Huang, G-P. Wang, Ch-H. Peng, "Fine powders of SrFe12O19 with SrTiO3 additive prepared via a quasi-dry combustion synthesis route". Mater. Sci. Eng., B, Vol. 139, 2007, pp. 24–36.