



RESEARCH ARTICLE

PREPARATION OF BARIUM FERRITE NANO PARTICLES IN ETHANOL/WATER MEDIA AND
STUDY OF ITS PHYSICAL PROPERTIES

¹Tahseen H. Mubarak, ^{*2}Karim H. Hassan and ³Nisreen Zaidan Khalaf

^{1,3}Department of Physics, College of Science, University of Diyala, Diyala, Iraq

²Department of Chemistry, College of Science, University of Diyala, Diyala, Iraq

ARTICLE INFO

Article History:

Received 26th January, 2013
Received in revised form
24th February, 2014
Accepted 10th March, 2014
Published online 23rd April, 2014

Key words:

Nano particles, Barium ferrite, physical properties, Co-precipitation, Synthesis.

Copyright © 2014 Tahseen H. Mubarak et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

ABSTRACT

Barium ferrite nano particles was prepared by co-precipitation route using (ethanol/water) solutions of iron chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and barium chloride $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ with a Fe/Ba molar ratio of 15. the produced powder was dried at 80 °C for 12 h and then calcined at various temperatures for 2 h. Nano particles of barium ferrite with particle size of about 30 and 70 nm were observed from SEM micrographs of the samples synthesized and calcined at 800 °C and 1000 °C for 2 h, respectively.

INTRODUCTION

Ferrites have continued to attract attention over the years. As magnetic materials, ferrites cannot be replaced by any other magnetic material because they are relatively inexpensive, stable and have a wide range of technological applications in transformer core, high quality filters, high and very high frequency circuits and operating devices. The physical properties of ferrites are controlled by the preparation conditions, chemical composition, sintering temperature and time, type and amount of substitutions (Costa *et al.*, 2010). Barium hexaferrite with hexagonal structure ($\text{BaFe}_{12}\text{O}_{19}$) has been recognized as a permanent magnetic material that has high - performance, theoretically it has large crystalline magnetic anisotropy, high coercivity (6700 Oe), high Curie temperature (450 °C), a relatively large magnetization (78 emu/g), and corrosion resistant. In military field barium hexaferrite is used as a radar absorbing material (Hessein *et al.*, 2008). The fabrication of bulk barium ferrite requires powders with outstanding characteristics in terms of particle size, morphology, composition uniformity, purity and magnetic properties (Benito *et al.*, 2001). However, in order to improve the material properties, several non-conventional routes such as co-precipitation (Ataie *et al.*, 2002), hydrothermal (Duong *et al.*, 2007), micro-emulsion (Palla *et al.*, 1999), glass crystallization (Muller *et al.* 1999) and sol-gel methods (Tahseen 2003) have been employed to synthesize barium ferrite. Among these methods, co-precipitation is the most attractive one due to its being simple and easy one.

EXPERIMENTAL DETAILS

Materials

Barium chloride $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium hydroxide NaOH, ethanol all are of analytical grade are used.

Instruments used

1. Powder type X-ray Diffractometer (XRD-6000, Shimadzu, Japanese origin) which uses CuK_α (1.54060Å) as a radiation source operated at 40 kV and 30 mA was used for verification of crystal structure and the average crystallite size of particles.
2. Scanning electron microscope (magnification ranging from 20X to approximately 30, 000X, spatial resolution of 50 to 100 nm), produced by TESCAN, s.r.o., Libušina trída 21. Was used to characterize the particles morphology.
3. LCR meter is Agilent impedance analyzer an American origin, its range of frequency (50Hz-5MHz) was used to measure The electrical properties.

Preparation procedure

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ with a Fe/ Ba molar ratio of 15 were dissolved in ethanol/water with a volume ratio of 3:1. Two prepared solutions were co-precipitated by the addition of NaOH with OH^-/Cl^- molar ratio of 2 at room temperature. The samples obtained were washed by ethanol/water solution with a volume ratio 2:1, and dried at 80 °C for 12 h, then the dried powder was calcined at 800 and 1000 °C for 2 h in air to

*Corresponding author: Karim H. Hassan,

Department of Chemistry, College of Science, University of Diyala, Diyala, Iraq

obtain barium ferrite. The schematic representation of the main steps employed in the preparation is shown in Figure (1)

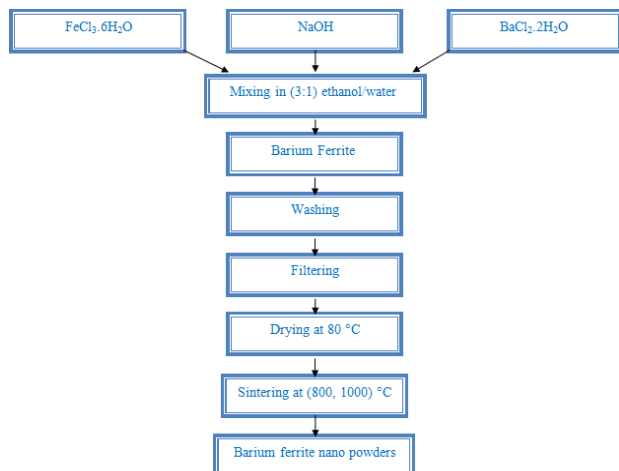


Figure 1. Preparation steps of barium ferrite nano particles

The mean particle size of $\text{BaFe}_{12}\text{O}_{19}$ powders was calculated from the X-ray of the more intense peak using and Scherrer equation:

$$D = 0.9\lambda / \beta \cos\theta$$

Where:

D is the mean particle size

λ is the X-ray wavelength;

β is the line broadening at half the maximum intensity (FWHM),

θ is the Bragg angle.

RESULTS AND DISCUSSION

XRD analysis and particle size calculation

The XRD patterns of the samples synthesized in ethanol/water and calcined at 800°C is shown in Figure (2).

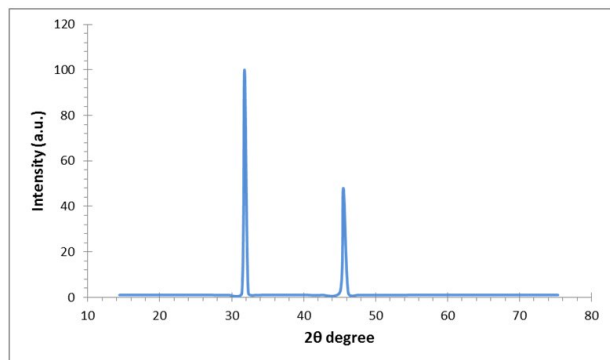


Figure 2. XRD pattern of the barium ferrite was calcined at 800°C

It seem from the Figure 2. That barium ferrite is the major phase, although some unreacted intermediate phases like barium monoferrite and hematite were still observed. The remaining of impurities phase at 800°C indicates the poor

reactivity of agglomerated precursor co-precipitated from the ethanol/water solution, which retarded the diffusion of Ba^{2+} and hence formation of barium ferrite.

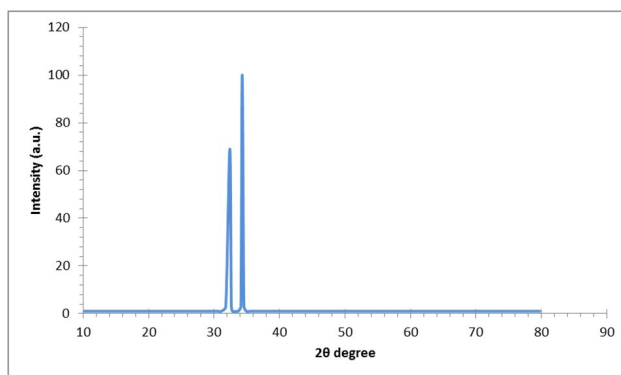


Figure 3. XRD pattern of the barium ferrite which was prepared at 1000°C

Figure (3) shown a full growth of barium ferrites phases, by comparing the charts with ASTM card it is noticed that both are identical, as it observed two strongest sharp peaks, which mean that FWHM is very small causing a good crystallinity which will be proved by calculation. The detailed analysis of the XRD and the assignments of various reflections peaks are given in Tables (1) and (2).

Table 1. Strongest three peaks of ferrite calcined at 800°C

| No | Peak No | 2θ (degree) | d(Å) | FWHM (degree) | Intensity I/I ₁ | hkl | Card NO |
|----|---------|-------------|---------|---------------|----------------------------|-------|---------|
| 1 | 12 | 31.7775 | 2.81367 | 0.16990 | 100 | [110] | 200127 |
| 2 | 29 | 45.5109 | 1.99148 | 0.15200 | 48 | [200] | 200127 |
| 3 | 15 | 34.1412 | 2.62409 | 0.19500 | 31 | [441] | 290172 |

Table 2. Strongest three peaks of ferrite calcined at 1000°C

| No | Peak No | 2θ (degree) | d(Å) | FWHM (degree) | Intensity I/I ₁ | hkl | Card NO |
|----|---------|-------------|---------|---------------|----------------------------|-------|---------|
| 1 | 63 | 34.3009 | 2.61223 | 0.22190 | 100 | [114] | 430002 |
| 2 | 57 | 32.4098 | 2.76021 | 0.12140 | 69 | | 280144 |
| 3 | 53 | 29.7811 | 2.99759 | 0.09500 | 54 | | 280144 |

Particle size calculated using Scherrer equation for sample being calcined at

800°C is:

$$D = 48.63 \text{ nm}$$

and for sample calcined at 1000°C :

$$D = 35.81 \text{ nm}$$

Scanning electron microscope

Figures (4), and (5), demonstrate SEM micrograph structure of the barium ferrite calcined at 1000°C .

The grains are more or less spherical in shape and there is grain size distribution over different samples prepared. The rate of grain growth and the resultant microstructure depend in a complex way on many factors, such as the sintering temperature, preparation method and stoichiometry.

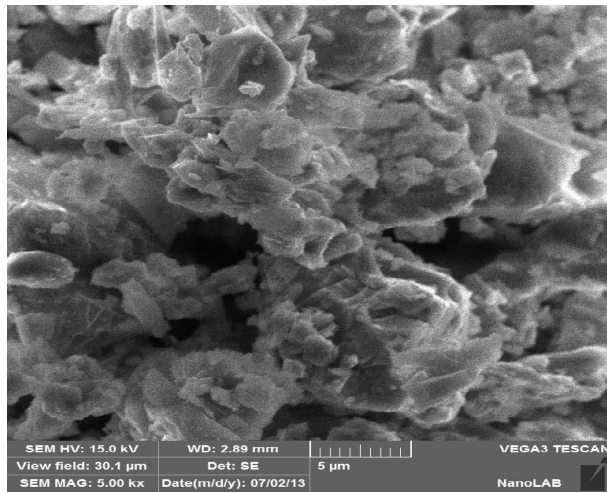


Figure 4. SEM images for barium ferrite calcined at 1000 °C with 5kx

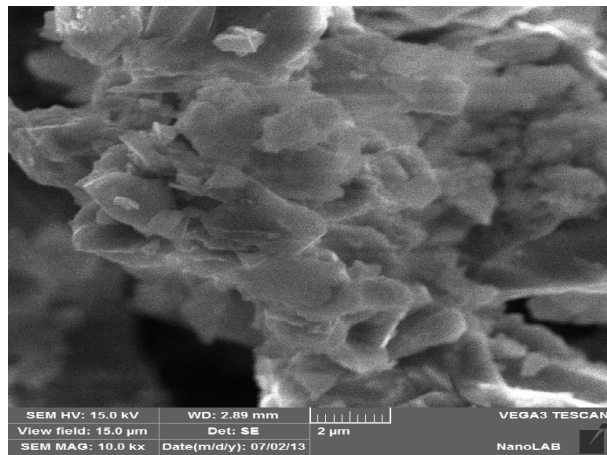


Figure 5. SEM images for barium ferrite prepared at 1000 °C with 10kx

From the SEM images, it observed the formation of soft agglomerates with irregular morphology constituting the quite fine particles. The study of SEM micrographs reveals a less number of pores with smaller lump size, and a homogeneous system with agglomerates of submicronic particles. Since the ceramic method involves sintering of the stoichiometric mixtures at high temperatures, the crystallites are in order of micrometer with relatively smooth surface. The aggregate of crystallites of various sizes indicates a size distribution in the micrographs. The variation in size of the particles among the different samples is due to the difference in processing temperatures. When the ferrite powders with more crystalline content are used for samples sintered at high temperatures, the local shrinkage speed is much higher than the densification speed of the ceramics, and also its shows a homogeneous system with agglomerates of submicronic particles. SEM images of $BaFe_{12}O_{19}$ also reveal a great decrease of particle size, and a loss of the original morphology of the particles. It also reveals a decrease in calcinations temperature resulting to particles being finer and more uniform as we observe in figure (4), (5). The resulting powder consists of small irregularly shaped agglomerates.

Electrical measurements

It is necessary to control the stages of preparation of the barium ferrite to obtain the desired microstructure compositions containing high density and regular granular sizes, this lead to the preparation of ferrites showing a wide variety in the electrical characteristics. The electrical properties of ferrite were affected also by the borders between granules of product composition and density. But in order to indicate the extent of appropriate the ferrite report for the practical application, some important electrical tests were conducted which includes measuring electrical resistivity of the samples as well as the dielectric constant, and electrical loss tangent by using LCR meter at range of frequencies [50 Hz- 5 MHz]. In order to find the best ferrite maintains high values for electrical insulation and the electric loss tangent a low within the frequency specific at which being the measurement.

Measurements of electrical resistivity (ρ) and electrical conductivity (σ)

Electrical resistivity (ρ) was measured at different sintering temperatures. The following figures (6), (7) show the resistivity as a function of frequency for the two samples:

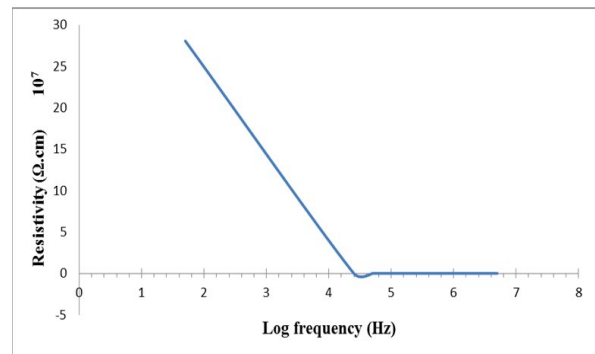


Figure 6. Resistivity as a function of frequency for barium ferrite calcined at 800 °C

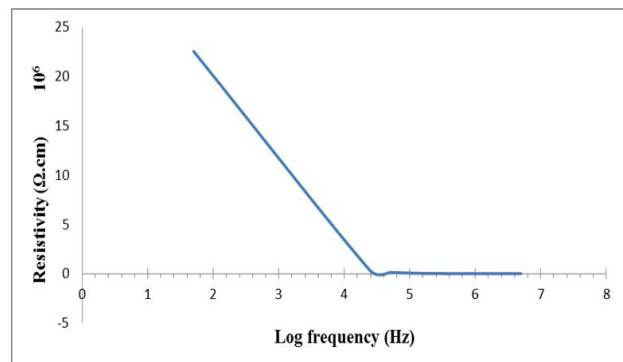


Figure 7. Resistivity as a function of frequency for barium ferrite calcined at 1000 °C

The figures showed that electrical resistivity values are decreases when the frequency increased and then settled at a value of (4.5 Hz) frequency. It also showed that the resistivity of the ferrites is decrease with increasing of the sintering

temperature, there is some factors other than those considered above which are also important in determining the resistivity of ferrites.

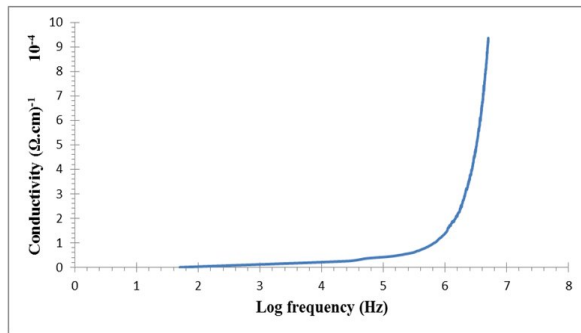


Figure 8. Conductivity as a function of frequency for barium ferrite calcined at 800 °C

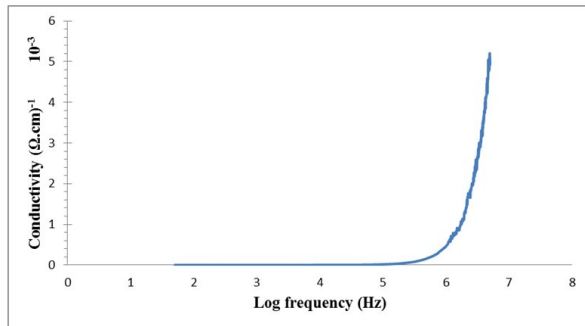


Figure 9. Conductivity as a function of frequency for barium ferrite calcined at 1000 °C

The conductivity is also dependent upon the purity of the starting materials, the preparation details such as sintering temperature and the influential frequency that's mean when the frequency increased conductivity increase; the following charts (8) and (9) show this dependence.

Measurements Dielectric constant (ϵ_r) and electrical loss tangent ($\tan \delta$)

The dielectric constant (ϵ_r) shows a change in the dielectric constant as a function of applied frequency as in figure (10) and (11). Absence of the ions movement, polarization orientation and the decrease in dielectric constant mainly cause the movement of polar groups under the influence of an electric field.

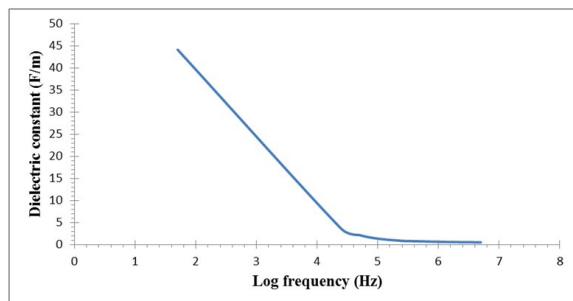


Figure 10. Dielectric constant as a function of frequency for barium ferrite calcined at 800 °C

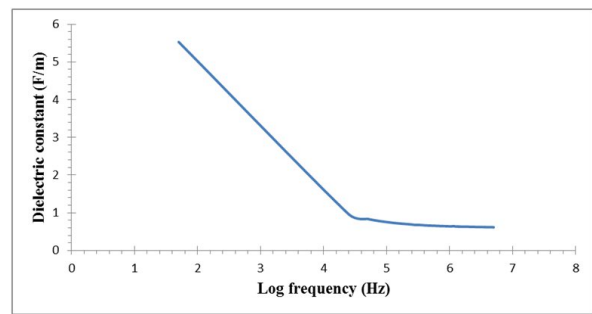


Figure 11. Dielectric constant as a function of frequency for barium ferrite calcined at 1000 °C

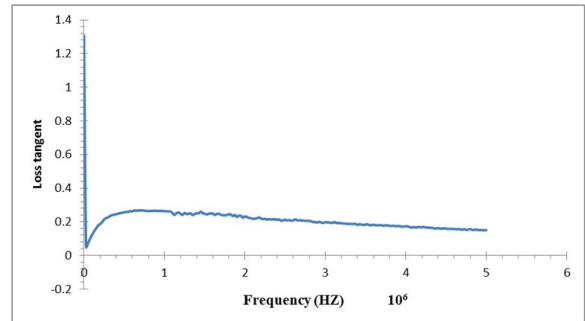


Figure 12. The variation of loss tangent with frequency for barium ferrite calcined at 800 °C

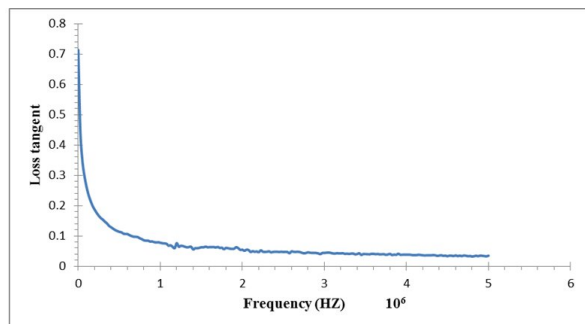


Figure 13. The variation of loss tangent with frequency for barium ferrite calcined at 800 °C

A high value of (ϵ_r) is observed at lower frequencies which later falls down rapidly with frequency increase. The trend can be explained on the basis that at lower frequencies there is four different types of polarization exist (i.e. electronic, ionic, dipolar and space charge) contributions take a part in the dielectric constant, but at higher frequencies some of polarization contributions relax out, result in the lowering of dielectric constant (ϵ_r). The frequency of electron hopping between the Fe^{+2} and Fe^{+3} ions at octahedral sites is higher as compared to the applied AC field and thus can interact with the applied field easily, resulting in a higher value of dielectric constant at lower frequencies. Contrary to it, at higher frequency the hopping electron cannot follow the frequency of the applied electric field, resulting in lowering of dielectric constant. Consequently, the electron exchange between Fe^{+2} and Fe^{+3} is perturbed at high frequencies, which explains the slower decrease of dielectric constant (ϵ_r) at high frequency.

It observed the influence of the pores shrinking that cause density increase and better homogeneity of the mixture on the dielectric constant of the prepared ferrite which increases at low values of frequencies and then start sliding downward within the frequency range (50Hz – 25KHz). The different values of the constants of the insulating material leads to the possession of a different resonant frequency, at a certain frequency the movement of electric dipole become in the case of resonance then the ferrite block absorbing ability of the influential electric field, But at high frequencies, it cannot be polar electric diodes follow the effective electric field leads to a decline in the values of the dielectric constant of the material. The values of the dielectric constant are within the range 10^{13} at the low frequency to reach 10^{11} at highest frequency of measurement was conducted.

Then the values of loss tangent of dielectric constant ($\tan \delta$) it has ranged between (0.25 – 0) at frequencies within the range (50Hz – 25KHz) respectively, Suddenly decreasing after this level to low values with increasing frequency The values of magnetic loss tangent represents the ratio between the dissipated energy to stored energy, Figures (12) and (13) show that the values of loss tangent is high at low frequency (50Hz-1KHz), then begin to decline at the frequency (1KHZ-1MHZ). It varying from one compound to another depending on the type of ferrite mixture and so it's less of prepared ferrite at high degrees of sintering. The high values of the magnetic loss tangent at sintering temperature of 800°C it result to the presence of pores and small grain size, and possibly micro cracks that stop the movement of the wall of the magnetic field and leads these things combined to decreasing the magnetic permeability (Tahseen 2003).

REFERENCES

- Ataie A., S. Heshmati-Manesh and H. Kazempour: *J. Mater. Sci.*, 37, 2125, 2002.
- Benito G., M.P. Morales, J. Requena, V. Raposo, M. Vazquez and J.S. Moya: *J. Magn. Magn. Mater.*, Vol. 234, 65, 2001.
- Duong G.V., R.S. Turtelli, B.D. Thuan, D.V. Linh, N. Hanh and R. Groessinger: *J. Non-Cryst. Solids*, 353, 811, 2007.
- Hessein, M.M., Rashad, M.M., El-Barawy. K., “Controlling the composition and magnetic properties of strontium hexaferrite synthesized by co-precipitation method”. *Journal of Magnetism and Magnetic Materials* Vol. 320, pp. 336–343, 2008.
- M.M. Costa, G.F.M. Pires Junior, A.S.B. Sombra, “Dielectric and impedance properties’ Studies of the lead doped (PbO)-Co₂Y type hexaferrite (Ba₂Co₂Fe₁₂O₂₂ (Co₂Y))”, *International Journal of Materials Chemistry and Physics*, Vol. 123, pp. 35–39, 2010.
- Muller R., C. Ulbrich, W. Schuppel, H. Steinmetz and E. Steinbei: *J. Eur. Ceram. Soc.*, 19, 1547, 1999.
- Palla J., D.O. Shah, P.G. Casillas and J.M. Aquino: *J. Nanopart. Res.*, 1, 215, 1999.
- Tahseen H. Mubarak, Ph. D thesis, University of Technology, 2003.
