



Different Factors Affecting the Preparation of Hexagonal Barium Ferrite and its Evaluation by Radar Wave Absorption

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Abstract: Hexagonal barium ferrites have wide applications as anti radar filler in coatings and other composites. M type barium hexagonal ferrite ($\text{BaFe}_{12}\text{O}_{19}$) has been synthesized by citrate sol gel auto combustion method using barium nitrate and ferric nitrate as sources for cations and citric acid as fuel. The effect of cations to fuel ratio were studied using ratios of (1:1, 1:2, 1:3) with solutions at pH 7 in all cases. The effect of calcination temperature and calcination time were studied in the range $850^{\circ}\text{C} - 1000^{\circ}\text{C}$ and 3 – 6 h respectively. Prepared samples were characterized by FTIR, XRD, TEM and SEM. Reflection losses of the prepared samples in the frequency range X and Ku bands (8-18 GHz) were measured. The results show that cations to fuel ratio of 1:2 show the formation of hexagonal barium ferrite with nano size particles. Calcination temperature of 950°C for 5 h calcination time give the best radar absorption in the X and Ku frequency bands with maximum absorption of 62.17% at 12.1 GHz.

Keywords: Hexagonal barium ferrite, anti radar, radar wave absorption

1. Introduction

An electromagnetic wave is vector in nature and composed of both electric (E) and magnetic (H) fields, which are able to propagate by itself [1]. Radar absorbing materials reduce the energy reflected back to the radar by means of absorption. Radar energy is absorbed through one or more of several loss mechanisms, which may involve the dielectric or magnetic properties of the material. The loss is actually the conversion of radio frequency energy into heat [2].

Magnetic absorbers are based on carbonyl iron and hexaferrites. These materials have absorption in the MHz and GHz ranges [3]. Ferrites are ferrimagnetic substances composed of iron oxides and other metallic oxides. Because they are no conducting, ferrites naturally provide a high packing density of magnetic material. Also, due to the lattice structure and the metallic elements present, the electromagnetic properties of ferrites can be better tailored to meet specific requirements than those of iron or other metallic magnetic substances [1].

Hexaferrites are classified into five types depending on the chemical formula and the crystal structure. These include M-type ($\text{BaFe}_{12}\text{O}_{19}$), W-type ($\text{BaMe}_2\text{Fe}_{16}\text{O}_{27}$), X-type ($\text{Ba}_2\text{Me}_2\text{Fe}_{28}\text{O}_{46}$), Y-type ($\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$) and Z-type ($\text{Ba}_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}$), where Me is a transition cation or a combination of cations as in spinel ferrites [4].

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Barium ferrite with hexagonal molecular structure ($\text{BaFe}_{12}\text{O}_{19}$), a well-known permanent magnetic material with superior chemical stability, anti-erosion properties, magnetocrystalline anisotropy and high curie temperature [5]. It can be used as a good microwave absorber in the frequency range of 1 to more than 20 GHz due to the above reasons and in addition its high saturation magnetization and great coercivity [6].

Synthesis of barium ferrite has been reported by using the sol–gel auto combustion technique [7]. The method uses the energy produced by the exothermic decomposition of a redox mixture of metal nitrates with an organic compound. In the combustion mixture, nitrates and organic compounds behave like conventional oxidants and fuels. Exothermic redox reactions associated with nitrate decomposition and fuel oxidation take place. Gases such as N_2 , H_2O , and CO_2 evolve, favoring the formation of fine particle ashes after only a few minutes [7].

2. Experimental Procedure

2.1 Preparation of Barium Ferrite

For the preparation of barium ferrite nano particles, barium nitrate $\text{Ba}(\text{NO}_3)_2$, ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and citric acid were taken as starting materials. The stoichiometric ratio of Fe/Ba should be 12 for $\text{BaFe}_{12}\text{O}_{19}$. It was reported by D. BAHADUR that a slight excess of barium is needed to ensure the formation of single phase $\text{BaFe}_{12}\text{O}_{19}$ [7]. Hence, the molar ratio of Ba to Fe was fixed at (1: 11.5). The nitrates were dissolved with a minimum amount of de-ionized water to get a clear solution.

An aqueous solution contain 12.5 mole of citric acid was mixed with nitrate solution. After complete dissolution of all starting materials, an appropriate amount of ammonia solution was added dropwise with agitation until the pH of the solution reach's 7 [9]. The resulting solution was then heated at 85°C for 3 h followed by heating at 110°C until the transparent solution turned to viscous foamy gel [7, 9].

The foamy gel was kept on the oven at 150°C till a spontaneous ignition occurred [7]. The combustion reaction was completed within few minutes and brown ash was formed. This ash was crushed manually and ground thoroughly giving very fine powder.

The fine powder was treated by heat (presintered) in a calcination oven at 450°C for 3 h to remove carboneous materials [10, 11]. The temperature then increased to 850°C for 4 h for the final formation of barium ferrite nano particles.

2.2 Effect of Changing Fuel Ratio

When fuel (citric acid) oxidation takes place, gases such as N_2 , H_2O , and CO_2 evolve leading to the formation of fine particle ashes after only a few minutes of heating. The particle size, surface area and porosity of the final powder depend on the method of combustion. Here, an effort has been made to identify the effect of fuel ratios on barium ferrite synthesis at pH value of 7 and their influence on structure, size and microwave absorption.

Three samples of hexagonal barium ferrite were prepared by changing the fuel ratio from (1 -3). The above described procedures were used for this preparation.

2.3 Effect of Changing Calcination Temperature and Calcination Time

Calcination is the final step for the formation of ferrite lattice and it is essentially for the interdiffusing of the substituent oxides into a chemically and crystallographically uniform structure. Here, an effort has been made to identify the effect of changing the calcination temperature and calcination time on the microwave absorption.

Twelve samples with different calcination temperatures and calcination times were prepared by the same procedures mentioned in item (2.1) using cations to fuel ratio (1:2). The calcination temperature is changed from 850°C to 1000°C and calcination time is changed from 3 to 6 h.

The reflection losses of all samples are measured using PR-17 reflectometer by mixing the powders with polyurethane polymer with 10% weight percent ratio. The produced coating was casted on iron sheet using iron die with internal dimensions of (18 cm * 18 cm) and 1.5 mm thickness, followed by drying at 50°C for 3 h and complete the drying at normal temperature for 24 h, giving iron sheet coated with barium ferrite composite with thickness of 1.5 mm.

3. Results and Discussion

FTIR spectra of the produced barium ferrite using cations to fuel ratio from 1:1 to 1:3 qualitatively confirm the formation of barium ferrite. Figure 1 shows strong absorption observed in the three samples between (500-600) cm^{-1} (588.11, 576.46 and 585.27 cm^{-1}) indicates the formation of metal oxide bond (M-O-M) which confirm the formation of the ferrite.

The EDAX analysis (Fig. 2) shows that, the produced barium ferrite elements ratio (Ba : Fe : O) approximately don't change by increasing the cations to fuel ratio from (1:1) to (1:2) but a great change is occurred when the cations to fuel ratio reach (1:3) so that (1:2) ratio are preferred to use instead of (1:1) because increasing citric acid content lead to increasing foaming process lead to decreasing ferrite particle size diameter.

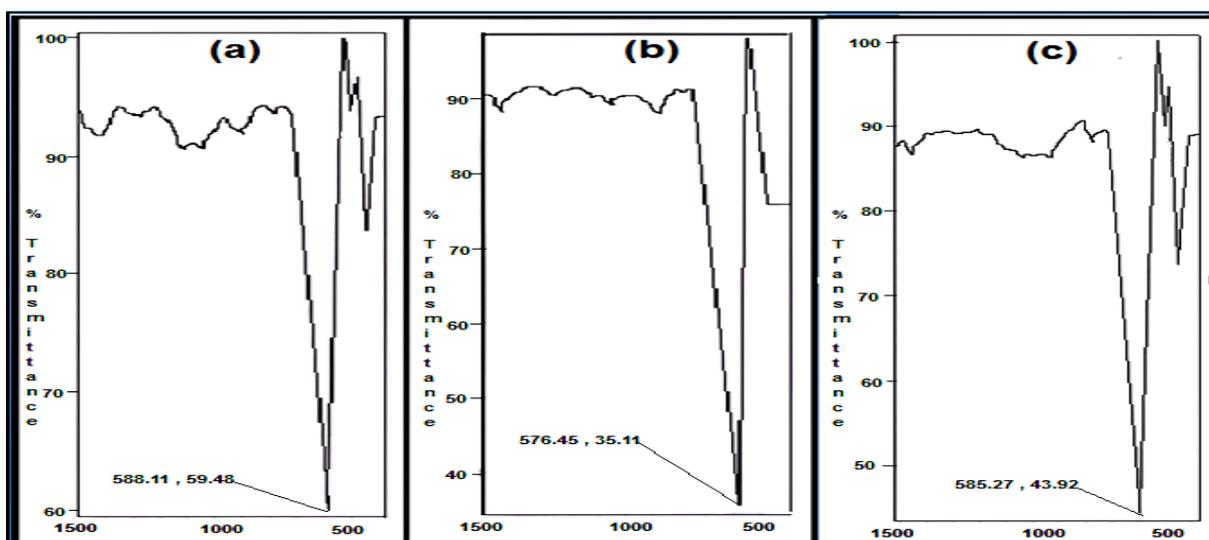


Fig. 1 FTIR Spectra of the Prepared Barium Ferrite Samples with Cations to Fuel ratio (a) 1:1 (b) 1:2 (c) 1:3 respectively

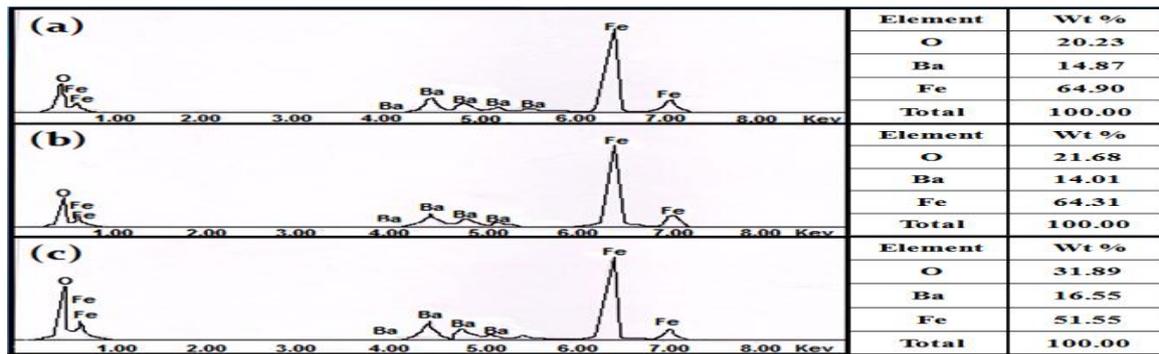


Fig. 2 EDAX Analysis of the Prepared Barium Ferrite Samples with Cations to Fuel Ratio (a) 1:1 (b) 1:2 (c) 1:3 Respectively

The XRD pattern of the prepared sample using cations to fuel ratio (1:2) (Fig. 3 (a)) shows the formation of hexagonal barium ferrite with 92.7 % weight percent and 7.3 % some other phases (BaFe_2O_4 (cubic phase), BaO and Fe_2O_3). The XRD pattern of prepared sample using cations to fuel ratio (1:3) (fig.3 (b)) shows the formation of hexagonal barium ferrite with 81 % weight percent and 19 % some other phases (BaFe_2O_4 (cubic phase), BaO and Fe_2O_3).

This result agrees with the conclusion obtained from EDAX study which shows that (1:2) is best fuel ratio.

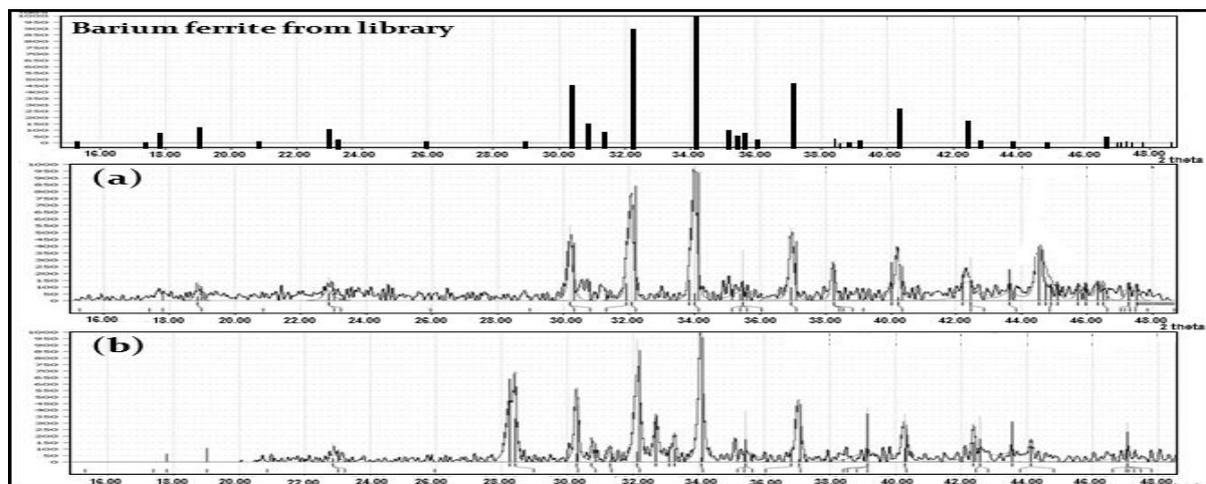


Fig. 3 X-ray Diffraction Patterns for the Prepared Barium Ferrite Samples with Cations to Fuel Ratio (a) 1:2 (b) 1:3 Respectively

The TEM photograph in Fig. 4 of the barium ferrite prepared using cations to fuel ratio (1:2) with calcination temperature 850°C for 4 hr, shows the formation of spherical nano particle with average particle size diameter ranging from 8 to 25 nm with some unidentified amorphous phases.

The effect on the reflection loss of the radar wave in the X and Ku band (8 – 18) GHz due to changing the calcination temperature and calcination time of prepared barium ferrite using cations to fuel ratio (1:2) are shown in Fig. 5 and Fig. 6. The change in the average loss are studied in four regions which are (8 – 10.7) GHz as in Fig.5 (a), (10.8 – 12.4) GHz as in Fig. 5 (b), (12.5 – 16) GHz as in Fig. 6 (a) and (16.1 – 18) GHz as in Fig. 6 (b). The DEAX analysis (Table 1) are used to help in explaining the phenomena of barium ferrite behavior.

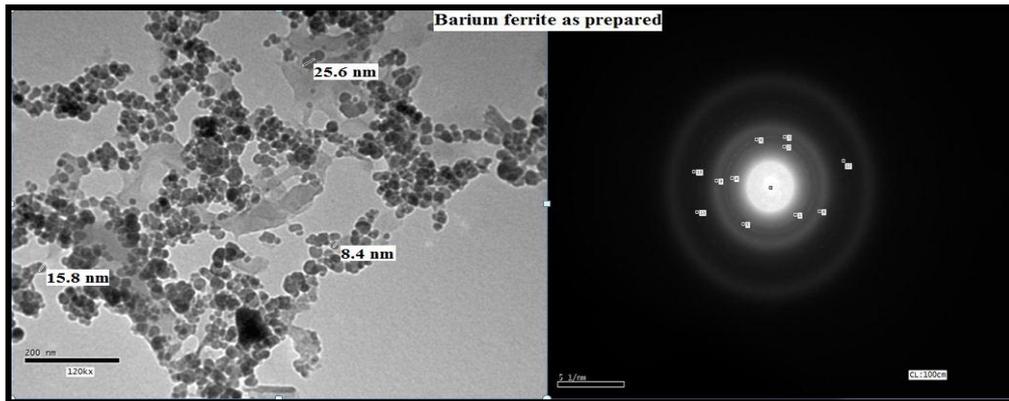


Fig. 4 TEM Photograph of Prepared Barium Ferrite Using Cations to Fuel ratio (1:2)

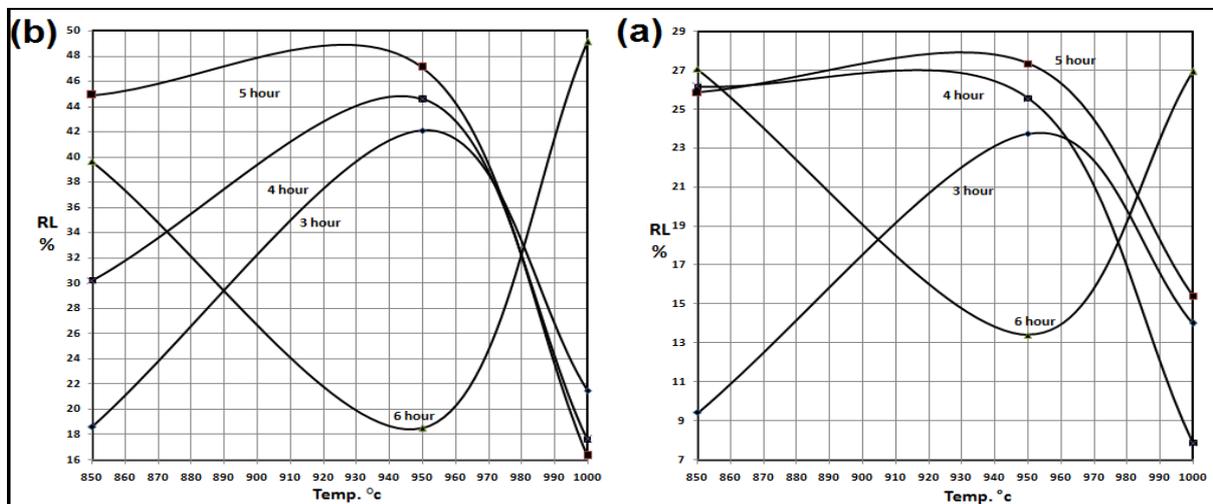


Fig. 5 Effect of Change Calcination Temperature and Time on the Average Reflection Loss in the X Band (a) Average of (8 – 10.7) GHz (b) Average of (10.8 – 12.4) GHz

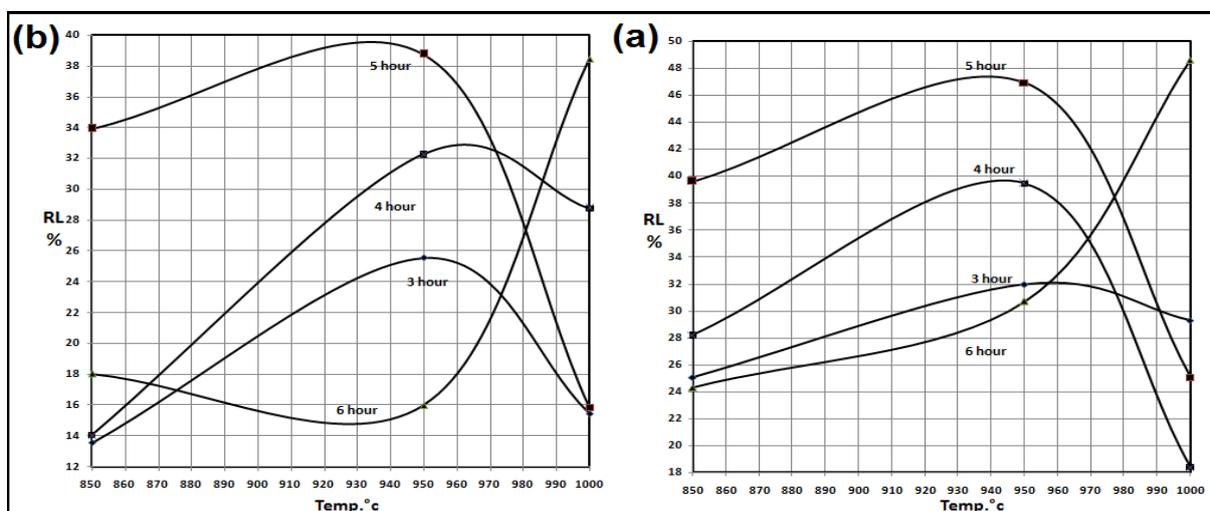


Fig. 6 Effect of Change Calcination Temperature and Time on the Average Reflection Loss in the Ku Band (a) Average of (12.5 – 16) GHz (b) Average of (16.1 – 18) GHz

Table 1. The EDAX Analysis of Selected Barium Ferrite Samples Calcinated at Different Temperatures

Time Temperature	Exact	4 hr			5 hr			6 hr		
		850°C	950°C	1000°C	850°C	950°C	1000°C	850°C	950°C	1000°C
O	27.3	21.68	24.97	25.65	24.29	23.52	24.08			
Ba	12.3	14.01	13.87	13.23	13.5	14.52	13.35			
Fe	60.4	64.31	61.16	61.12	62.21	61.95	62.58			

The average loss increase as the calcination temperature increase up to 950°C and then it is decrease. This behavior is clear when the calcination time is constant (3, 4 and 5 h), this increase in the reflection loss could be due to the increase in thermal energy is consumed for the transformation of the other phases of the barium ferrite to hexagonal phase and this are shown when comparing the elements ratio of sample which calcinated at 850°C for 4 hr with other which calcinated at 850°C for 6 hr and also all samples which calcinated for 5 and 6 hr shows approximately the same elements ratios near to the exact elements ratio which mean that single hexagonal phase is reached and any further calcinations temperature or time increase lead to increase in the particle size which lead to increase in the reflection loss until particle size diameter reach a certain value (critical diameter) which give the best magnetic properties lead to make the best microwave absorption, any increase in diameter after this value lead to decrease microwave absorption. When the calcination time increase from 3 to 5 h the average loss increase giving maximum average loss at 950°C for 5 hr, but increase the time further lead to decrease in the average reflection loss. Figure 7 shows the broadband absorption curve of barium ferrite sample which calcinated at 950°C for 5 hr.

The TEM photograph in Fig. 8 of the barium ferrite prepared using cations to fuel ratio (1:2) with calcination temperature 950°C for 5 hr, shows the formation of shaped nano particles with average particle size diameter ranging from 40 to 70 nm with highly crystalline phases (Fig. 7).

The calcination time of 6 h curve behave on opposite way and this could be to that 850°C for 6 h give energy able to form single phase hexagonal barium ferrite with particle size greater than a critical size then any further increase in temperature lead to increase the size and decrease the average reflection loss until 950°C then the energy is higher enough to change the shape of the nano particles from spherical to shaped particles (could be pyramidal shape) which may enhance the absorption [12].

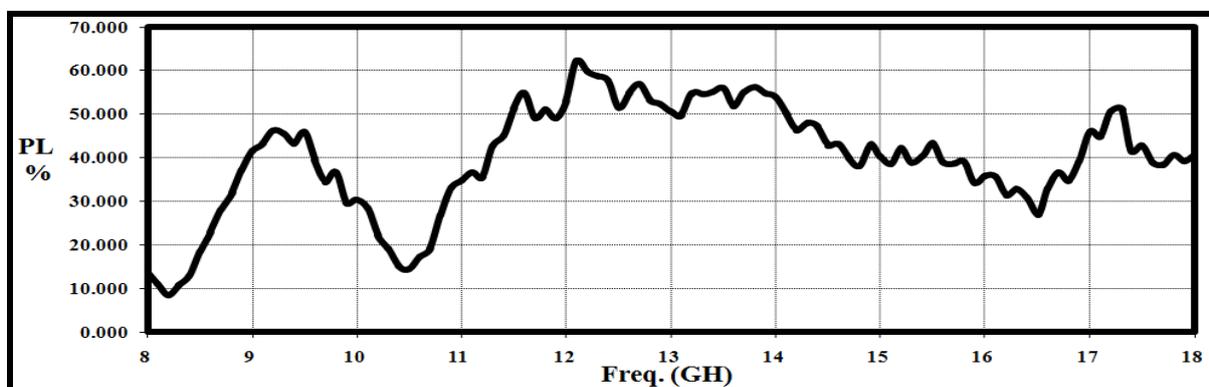


Fig.7. Reflection Loss Curve of Barium Ferrite Calcinated at 950°C for 5 hr

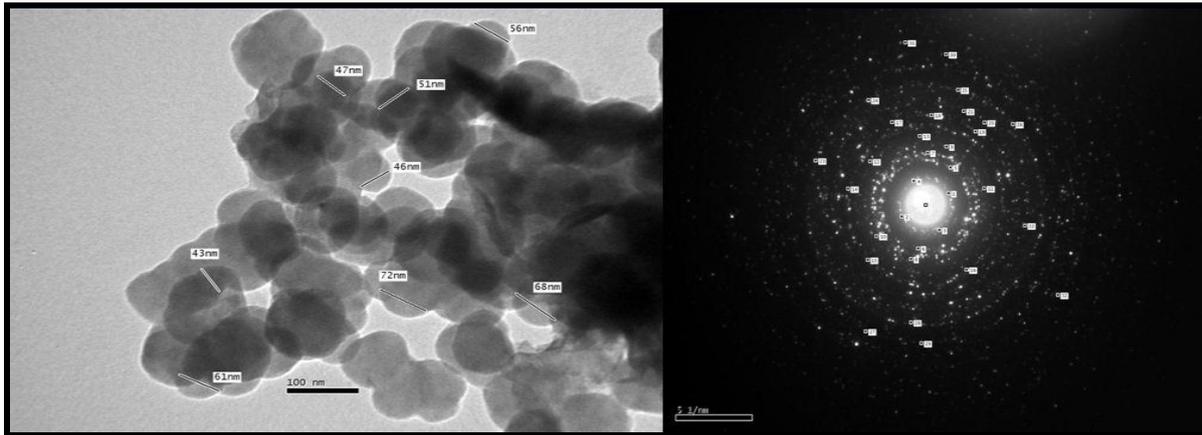


Fig. 8 TEM Photograph of Prepared Barium Ferrite Using Cations to Fuel ratio (1:2)

4. Conclusion

Barium ferrite with hexagonal molecular structure was successfully prepared using citrate sol gel autocombustion method. Cations to fuel ratio of 1:2 is the best ratio to form high content of hexagonal barium ferrite with very fine particle size diameter (8 – 25 nm). The calcination of barium ferrite at 950°C for 5 h provide good magnetic properties and particle size diameter (40 – 70 nm) which give the best average microwave absorption in X and Ku band specially in the range (10.8 – 16) GHz which give about 47 % average reflection loss and maximum absorption of 62.17% at 12.1 GHz.

5. References

- [1] E. F. Knott et al., "Radar Cross Section", 2nd. ed., Boston, USA, 2004, pp. 74, 335.
- [2] K. Cihangir Y., "Radar Absorbing Material Design", MSC, Naval Postgraduate School, 2003, pp. 8.
- [3] P. Saville, "Review of Radar Absorbing Materials", Defence R&D Canada, Atlantic, 2005, pp. 22.
- [4] M. C. Dimri et al., "Electrical and magnetic properties of barium hexaferrite nanoparticles prepared by citrate precursor method," ", *Ceramics International*-30," 2004, pp. 1623-1626.
- [5] P. Xu et al., " Effect of Ni(OH)₂ coating on the electromagnetic properties of hexagonal barium ferrite," ", *Materials Chemistry and Physics*," Vol. 108, 2008, pp. 196–200.
- [6] G. Mu et al., "Preparation and microwave absorption properties of barium ferrite nanorods," ", *Materials Letters*, Vol. 62," 2008, pp. 840–842.
- [7] D. Bahadur et al., "Influence of fuel ratios on auto combustion synthesis of barium ferrite nano particles," ", *J. Chem. Sci.*, Vol. 118, No. 1," 2006, pp. 15–21.
- [8] G. Packiaraj et al., "Synthesis and characterization of Barium Hexaferrite particles by sol–gel auto combustion method," ", *Journal of Biomedical and Bioengineering*, Vol. 1, Issue 1," 2010, pp. 1-2.
- [9] G. Mu et al., "Preparation and microwave absorption properties of barium ferrite nanorods," ", *Materials Letters*, Vol. 62," 2008, pp. 840–842.
- [10] G.Z. Shen et al., "Preparation and microwave absorption of M type ferrite nanoparticle composites," ", *Materials Science-Poland*, Vol. 28, No. 1," 2010, pp. 327-334.
- [11] G. Shen et al., "Double-layer microwave absorber based on ferrite and short carbon fiber composites," ", *Materials Chemistry and Physics*, Vol. 105," 2007, pp. 268–272.
- [12] R. Sharma et al., "Development of radar absorbing nano crystals by microwave irradiation," ", *Materials Letters*, Vol. 62," 2008, pp. 2233–2236.