Synthesis and Characterizations of nano-sized Barium Hexa Ferrites using Sol-Gel Methods

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ABSTRACT

Nanosized Barium Hexaferrites were synthesized using sol gel auto combustion method. Samples of different composition with varying molar ratio of metal nitrates and citric acid i.e. (*MN\CA* = 0.5, 1, 1.5, 2, 3) were prepared. Pellets of powders of each composition were sintered at 1100 ˚C for 1 hr. All samples were structurally characterized by X-ray diffractometer. Lattice parameter, volume of unit cell and particle size was determined. It has been found that size of the particle increases by decrease in the citric acid content. It reconfirmed the particle size calculated by debey Sherrer formula. Resistivities of specimens indicate semiconducting behavior. Measured values of resistivity are well in agreement with standard Barium ferrites.

Keywords: Barium Hexaferrite, Sol gel method, particle size, debey Sherrer, conductivity, XRD,

1. INTRODUCTION

Barium Hexaferrite is hard magnetic material with quite large magnetocrystalline, anisotropy, high curie temperature, large saturation magnetization, good chemical stability and high coercivity, low density and low cost make barium hexaferrite the most commercialized permanent magnet. Because of its incredible magnetic properties barium hexaferrite has potential for being used as high density magnetic and magneto-optic recording media [1-2]. Nanosized barium hexa ferrite are of great importance because of its application as MLIC (multilayer chip inductors [3] which are important components of camcorders, pagers and notebook computer [4].

Preparation methods of barium Hexaferrite are also of great importance because homogeneity, particle size and material's magnetic properties are strongly determined by synthesis method.Hexaferrite can be prepared by classical ceramic method but magnetic particle so obtained are large and results in multi-domains structure, ball milling can reduce size of particles but it results in non homogeneous mixtures and lattice strains also appears [5]. In order to achieve homogeneity various techniques such as hydrothermal copreciptation [6], ion exchange resin method [7], glass crystallization [8], sol gel etc has been adopted .to achieve homogeneity and nano sized particles. In sol gel technique *MN/CA* molar ratio plays a very significant role on formation of Barium Hexaferrite. The objective of this paper is to examine the influence of *MN/CA* molar ratio on the phase formation, particle size and microstructure of Barium Hexaferrite prepared by sol gel combustion method.

2. EXPERIMENTAL PROCEDURE

Sol gel auto combustion method was used to prepare nanosized barium hexa ferrite ($BaFe_{12}O_{19}$) powders. The starting materials were barium nitrate $Ba(NO_3)_2$,iron nitrate $[Fe(NO_3)_2.9H_2O]$, ,citric acid $C_6H_8O_7$ and liquor ammonia$[NH_3OH]$,all of analytic purity. Measured stoichiometric amounts of $[Fe(NO_3)_2.9H_2O]$ and $Ba(NO_3)_2$ in the molar ratio of 1:1, where disslolved in a minimum amount of deionized water to get a clear solution. To chelate ions Ba^{2+} and Fe^{3+} in the solution the citric acid $[C_6H_8O_7]$ was added in to prepared aqueous solution. Then liquid ammonia was slowly added to neutralize solution to PH 7. By heating the neutralized solution at 100 ˚C on a hot plate with continuous stirring it

was evaporated to dryness. While water is evaporated, the solution became thick and finally a very thick brown gel formed. Temperature was increased up to 200 ˚C which lead to explosion of gel. The dried gel burnt in a self propagating combustion manner until all gel were completely burnt out to form a loose powder, during combustion, exothermic redox reaction associated with fuel oxidation and nitrate decomposition took place. Sol gel method used energy produced during this reaction. A large amount of gases such as N_2, H_2o, Co, No and CO_2 were also evolved during formation of particle ashes contain the oxide product after only a few minutes. As a final point this as burnt powders were calcined in air at 850 ˚C for 1 hour with a heating rate of 10 ˚C/ min.

Five samples with different molar ratios of metals nitrates to citric acid (*MN/CA*) of 0.5, 1, 1.5, 2, 3 were prepared and marked as A, B, C, D, E. Powders of each composition was pressed help of die and hydraulic press (model OGAWA-STIKICO) by applying load of 7 ton before sintering. Two pellets of each composition with diameter of 16.131 mm of each pellet were made.

2.1 Sintering

These pellets of each composition were sintered at 850 ˚C in digital control furnace for 1 hour. Heat treatment was followed by natural cooling in the furnace. These pellets are again sintered at 1100 ˚C for 1 hour . Phase identification of the sintered pellets at different sintering temperature was performed in a Rigaku Geigerflex D-MAX/A Diffractormeter using Cu-Kα radiation. Scherrer's formula is used to calculate Crystallite sizes

$$D = K\lambda / B\cos\theta \qquad (1)$$

Where D is crystallite size in nm, K is shape factor, B is is full width half maximum of highest peak, is is wave length of X-rays and is Bragg's diffraction angle.

Lattice parameters are calculated by analytical method of indexing. Microstructure features such as crystalline size was examined by S-3400N scanning electron microscope.

3 RESULTS AND DISCUSSION

3.1 XRD analysis

The influence of molar ratio of / on the XRD patterns of synthesis of $BaFe_{12}O_{19}$ can be shown in fig(1-3). The X-ray diffraction patterns of samples with *MN/CA* varying with 0.5, 1, and 1..5, 2, 3 calcined at 850^{o}C for 1 hour. The result of XRD analysis of samples indicates the formation of different crystalline phases with hexagonal type structure.

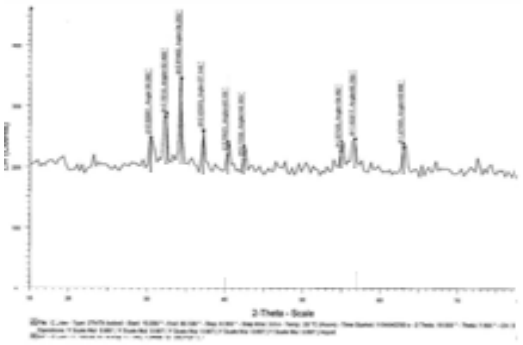


Fig 1: XRD of sample C

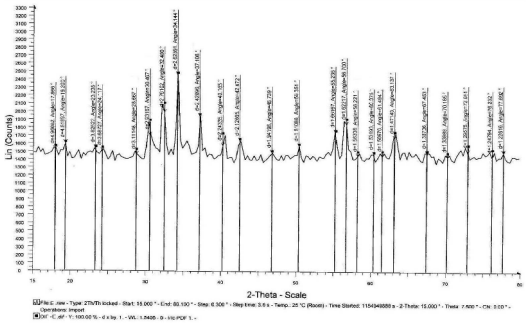


Fig 2: XRD of sample E

Analysis of XRD results of ferrite pellets, calcined at 850^{o}C,with *MN/CA = 0.5, 1, 2, 3* reveals the co-existence of antiferromagnetic phase ($BaFe_2O_4$), hexaferrite ($BaFe_{12}O_{19}$) and other secondary phases i-e. $BaFeO_{3-x}$, $Ba_2Fe_6O_{11}$,

- Fe_2O_3 $Ba_2Fe_6O_{14}$ and $BaFeO_3$. These secondary phases other than BaM indicate that citric acid has not completely chelated iron and barium ions and distribution of ions is inhomogeneous. It is supposed that - Fe_2O_3 is vital phase to form Barium hexaferrite because it is the cubic spinel having chemical formula $Fe[Fe_{5/3}\ _{1/3}]O_4$, stands for cation hole [10]. Its structure is analogous to 'S' block in barium ferrite so it can be easily transformed in $BaFe_{12}O_{19}$.

XRD graph of ferrite pellet with molar ratio (/) = 1.5 shows that all peaks belong to barium hexaferrite and single phase Barium hexaferrite is formed.

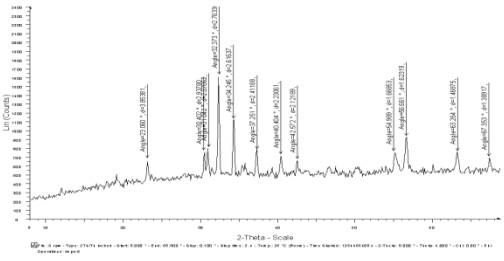


Fig 3: XRD pattern of sample'c' sintered at 1100 C

Fig. 3 shows the XRD patterns of ferrite pellet of sample'c' sintered at 1100 C for 1 hour. From XRD patterns it is clearly evident that single phase barium hexaferrite is formed at this temperature. Actually due to decomposition of carbon chains in citrates adjacent iron and barium ions can come into contact more easily and form a crystal lattice of barium hexa ferrite. Generally it can be said that increasing amount of citric acid results in decrease of intermediate phases. A. Mali A.Ataie has also reported the same fact.

3.2 Analysis of crystallite size and lattice parameter

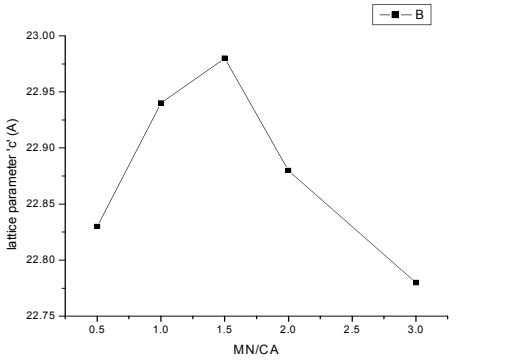
Amount of citric acid is linked with the crystallite size because of nucleation and growth. Therefore molar ratio *MN/CA* took effects on crystallite size. The crystallite size of Barium hexaferrite calcined at 850C is calculated with the help of Scherrer formula and data of XRD.

Also lattice parameters of each sample is calculated by analytical method and it is observed that the lattice parameter varies with varying *MN/CA* ratio. Calculated values of crystallite size and lattice parameter are listed in table 1.

Table 1: XRD parameters of Barium hexaferrite

No.	*MN/CA* Ratio	Crystallite size D (nm)	a A^0	C A^0	Volume V
1	0.5	18.41	5.41	22.83	578.65
2	1.0	36.039	5.32	22.94	562.25
3	1.5	55.274	5.86	22.98	683.38
4	2.0	58.57	5.86	22.88	680.40
5	3.0	73.153	5.74	22.78	649.97

It can be seen that crystallite size decreases with increasing citric acid contents. This fact was also reported in literature [9, 10]. Figure 4 exhibits variation of lattice parameter 'a' and 'c' with varying molar ratios.



(b)

Fig 4: variation of lattice parameter with *MN/CA*

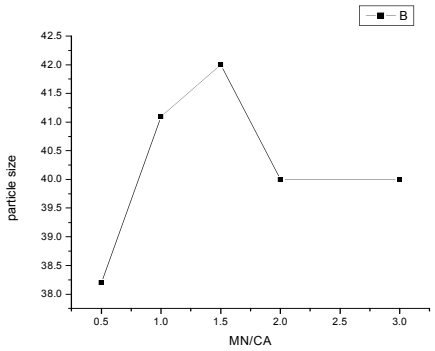
Crystallite size of the sample sintered at 1100 C is also calculated by virtue of Scherrer formula and XRD data. Lattice parameters are calculated by analytical method . Calculated values of crystallite size and lattice parameter are listed in table 2.

Table: 2 parameters of barium hexaferrite at 1100 C

No.	*MN/CA*	Crystallite size D (nm)	a (A)	c (A)
1	0.5	38.2	5.88	23.2
2	1.0	41.1	5.86	23.01
3	1.5	42	5.89	23.4
4	2.0	40	5.87	23.33
5	3.0	40	5.88	23.40

Figue 7 shows various crystallite size with increasing molar ratio of metal nitrate to citric acid.

Figure 7: Plot of *MN/CA* vs partical size



This graph shows increasing citric acid contents results in decrease of crystallite size.

4 CONCLUSION

Nano size barium hexaferrites are obtained after sintering at 1100 C. Crystallite size is greatly influenced by citric acid contents. SEM analysis reveals the presence of rod like and spherical shaped grains with grain size in the range of 200-500 nm. Electric resistivity of all samples is found to be very high. Its variation with applied voltage indicates its semiconducting behaviour.

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