



# MORPHOLOGICAL, ELECTRICAL AND MAGNETIC BEHAVIOR OF AL SUBSTITUTED BA-Y-TYPE HEXAFERRITES NANO POWDER AT DIFFERENT CALCINATION TEMPERATURES BY CHEMICAL CO-PRECIPIATION METHOD.

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**Abstract:** Barium Y-type hexaferrite  $BaAl_2Fe_{12}O_{22}$  powders have been synthesized by using chemical co-precipitation method calcinated at temperatures  $1000^\circ C$  and  $1100^\circ C$  for 4 hrs and 6 hrs. The samples were characterized by XRD and SEM to analyze its morphology, its electrical behavior and VSM characterization has been done to study the magnetic properties. Experimental result shows that calcination temperatures ranging from  $1000^\circ C$  and  $1100^\circ C$  for 4 hrs and 6 hrs will not affect significantly on change in the phase formation. Slight modifications in the values of lattice parameter, electrical behavior and magnetic properties have been observed. DC conductivity and electrical permittivity has been observed decreasing trend with the decrease in temperature which shows phase reversal of hexaferrites at particular temperature of Ba-Y-type hexaferrite. Curie temperature increases with different calcination temperature for 4 hrs and 6 hrs due to strong superexchange interaction. The change in magnetic parameters results in possible use of substituted ferrite for recording media, permanent magnets etc.

**Keywords:** XRD, SEM, Magnetic Properties, Nano Particles, Porosity, Curie temperature.

## I. INTRODUCTION

The numerous investigations on Y-type hexagonal ferrite have been studied. These hexagonal ferrites have been a topic of interest due to their high resistivity and low eddy current losses [1-2]. Due to their low eddy current losses, there does not exist other materials with such wide ranging values to electronic applications in terms of power generation, conditioning and conversion. A Y-type ferrite with chemical composition  $BaAl_2Fe_{12}O_{22}$  powders have been synthesized by using chemical co-precipitation method calcinated at temperatures  $1000^\circ C$  and  $1100^\circ C$  for 4 hrs and 6 hrs. Y-type hexaferrites are widely used in high density magnetic recording media, overcoat-free, contact or semi-contact recording media and microwave tunable devices working at high frequency, above 70 GHz [3-4]. In Ba Y-type hexaferrites, the  $Fe^{3+}$  ions occupy seven non-equivalent sub-lattices within R-block and S-block, i.e.  $12k$  (R-SS),  $4f_2$  (R),  $6g$  (S-S),  $4f_2$  (SS) (octahedral coordination),  $4e$ (SS),  $4f_1$ (SS) (tetrahedral coordination) and  $2d$ (R) (bipyramidal coordination) [5]. The magnetic properties of the samples have been studied by using Vibrating Sample Magnetometer (VSM). The study of magnetic parameters such as coercivity ( $H_c$ ), remanance ( $M_r$ ),

saturation magnetization ( $M_s$ ), magnetic moment ( $\mu$ ), squareness ratio ( $M_s/M_r$ ) and relative permeability ( $\mu_r$ ) has to be carried out. The synthesized samples belong to single magnetic domain. The studied samples may be useful at high frequency due to high value of resistivity and coercivity [6].

## II. EXPERIMENTAL TECHNIQUE

The barium Y-type hexaferrite powder was obtained by using chemical co-precipitation method containing AR grade nitrates. Stoichiometric amount of barium nitrate, aluminium nitrate, ferric nitrate (99.99%) were dissolved one by one in 100 ml of de-ionized water. Ammonia solution (30%) was added slowly in the mixture to adjust the pH  $\approx$  8. The mixed solution were stirred for two hours and kept at room temperature for 24 hours for aging. The barium hexaferrite precipitates has been separated by centrifuged at 2500 rpm for 20 minutes. The prepared precipitate was washed in 1:1 mixture of methanol and acetone followed by 100% de-ionized water to remove impurities. The precipitate was kept for drying at 100°C for 24 hours. Finally it was calcinated at 1000°C and 1100°C for 4 hrs and 6 hrs. and grinded in agate pestle-mortar for 6 hours to obtain BaY-type hexaferrite [7]. Polyvinyl acetate (PVA, 10 vol.%) used as binder to reduce to brittleness and by applying a pressure of 10 tones psi using hydraulic press tor 15 to 20 min, pellets were prepared using dye punch of 16.3 mm diameter. These pellets are slowly heated in an air atmosphere in the furnace at 300°C for 3 hrs and slowly cooled at a rate of 5°/min to room temperature to remove the binder concentration. The pellets were weighed and densities were measured.

To insure the phase structure, the resulting powders were investigated by X-ray diffraction (XRD) technique at room temperature with a powder diffractometer PW 3071/60, XPERT-PRO system with Cu-K $\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) with scan step of 0.013°/s which was operate at 40 kV and at 30 mA. The Bragg's angles  $2\theta$  were scanned and over a range of 10.01° to 119.98°. The single phase formation of the hexagonal structure is confirmed form the study of powder X-ray diffraction. The output data extracted from Rietveld refinement [8] was used to calculate the average crystalline particle size. The analysis of particle size was determined using the Debye-Sherrer's equation (Eqn.(1)),

$$D = k\lambda/b\cos\theta \quad (1)$$

where, k is the shape coefficient (value between 0.9 to 1.0),  $\lambda$  is the wavelength ( $\lambda = 1.54060 \text{ \AA}$ ), b is the full width at half maximum (FWHM) in radians of each phase and  $\theta$  is the diffraction angle. The lattice constants 'a' and 'c', X-ray density, porosity and possible physical structure determined.

Scanning electron micrograph (SEM) studies have been provided to probe nano-structured features to understand the surface morphology and the absence of impurity phase or the segregation of the second phase of grains. Nano-scale dimensions of the grains with hexagonal structure of the prepared samples have been confirmed by SEM images [9]. To carry out SEM studies, ZEISS ULTRA55 FESEM set up was employed.

In order to study the electrical conduction mechanism in ferrites, the electrical properties like electrical conductivity as a function of composition and temperature have been studied. To carry out the electrical properties, Wayne Ker Impedance Precision Analyzer 6500B up was employed.

Magnetic characterization of the studied samples have been investigated by using vibrating sample magnetometer (VSM) which reveals the parameters such as saturation magnetization ( $M_s$ ), coercivity ( $H_c$ ), remanance ( $M_r$ ) and squareness ratio ( $M_r/M_s$ ) of the samples. To carry out the magnetization measurement, LAKESHORE VSM-7410 set up was employed [10].

## III. RESULT AND DISCUSSION:

### 1. MORPHOLOGICAL PROPERTIES:

The XRD patterns for three compounds of BaAl<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> Y-type hexaferrites are shown in Fig. 1.1(a),(b),(c). The nature of XRD patterns shows the formation of the isolated phase Ba-Y-hexaferrites. All the diffraction peaks were indexed by applying a hexagonal crystal system and space group R-3m. The planes (0 0 12), (1 1 0), (1 0 14), (1 1 6), (1 1 8), (2 0 6), (0 2 10), (0 0 22), (2 1 7), (3 0 0), (2 1 13), (2 1 15) and (2 1 20) have been identified in agreement with the reported haexagonal crystal structure [11]. The

Rietveld refinement confirmed the formation of a hexagonal crystal structure. Lattice parameters 'a' and 'c' of Ba-Y-hexaferrites has been calculated using eqn. (2) as shown below.

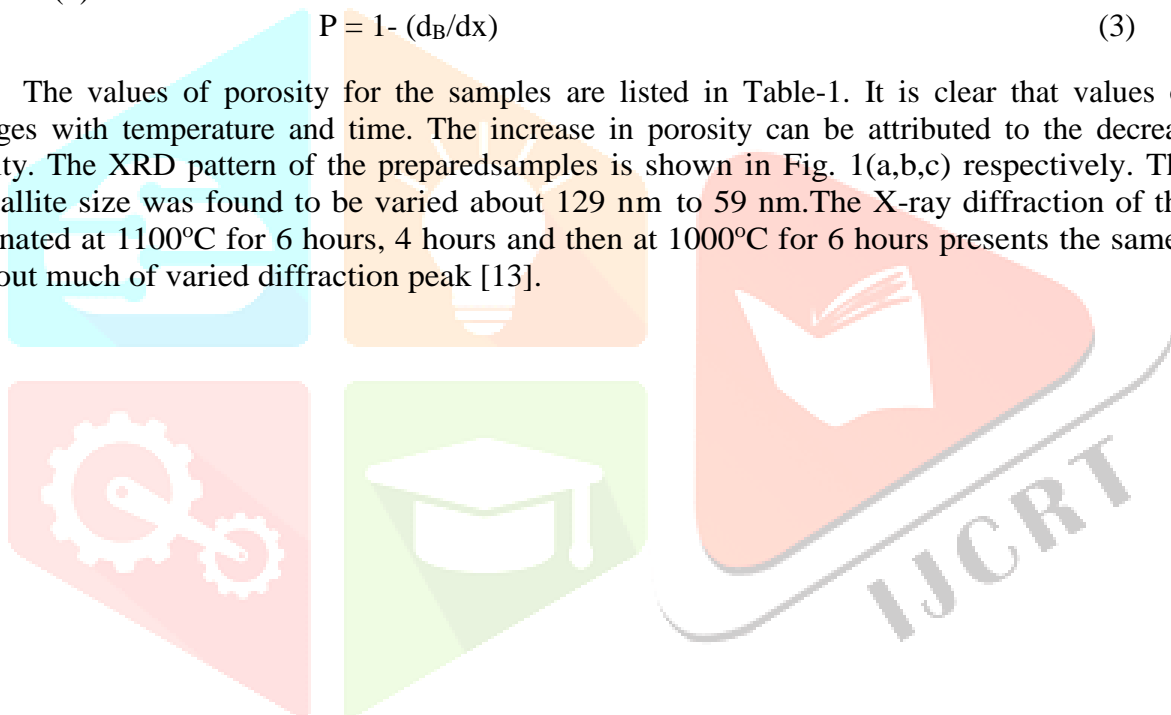
$$\frac{1}{d_{hkl}^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad (2)$$

where, h, k, l are Miller indices and d is interplaner distance and 'a' and 'c' are lattice parameters. It was found that Y-type hexaferrites has average lattice parameters (a = 5.8835Å and c = 45.103Å) that agrees well with Sr<sub>2</sub>Cu<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> type hexaferrites. It is also found that, almost all the reflection of the reported compounds have been indexed in studied samples. The matching of crystallographic data of the samples to that of reported one confirms the formation of all the compound in a single homogeneous phase with hexagonal structure. The variation in the value of 'a' and 'c' isobvious as ionic radii of Al<sup>3+</sup>(0.535Å) is smaller as compared to Ba<sup>2+</sup>(1.35Å) than Fe<sup>3+</sup>(0.645Å) ions which has replaced Fe<sup>3+</sup> ions i.e. atoms shrinks towards a and c axis [12].

The values of X-ray density are listed in Table-1. It is observed that X-ray density is varied by the change in temperature and time. It can be observe that the values of bulk density were found to be in general less than those of X-ray density dx, which was expected due to the presence of unavoidable pores created during sintering process. Moreover the porosity (P) of all the samples was calculated by using equation (3) as shown below the relation.

$$P = 1 - (d_B/d_x) \quad (3)$$

The values of porosity for the samples are listed in Table-1. It is clear that values of porosity changes with temperature and time. The increase in porosity can be attributed to the decrease in bulk density. The XRD pattern of the prepared samples is shown in Fig. 1(a,b,c) respectively. The average crystallite size was found to be varied about 129 nm to 59 nm. The X-ray diffraction of the samples calcinated at 1100°C for 6 hours, 4 hours and then at 1000°C for 6 hours presents the same behavior, without much of varied diffraction peak [13].



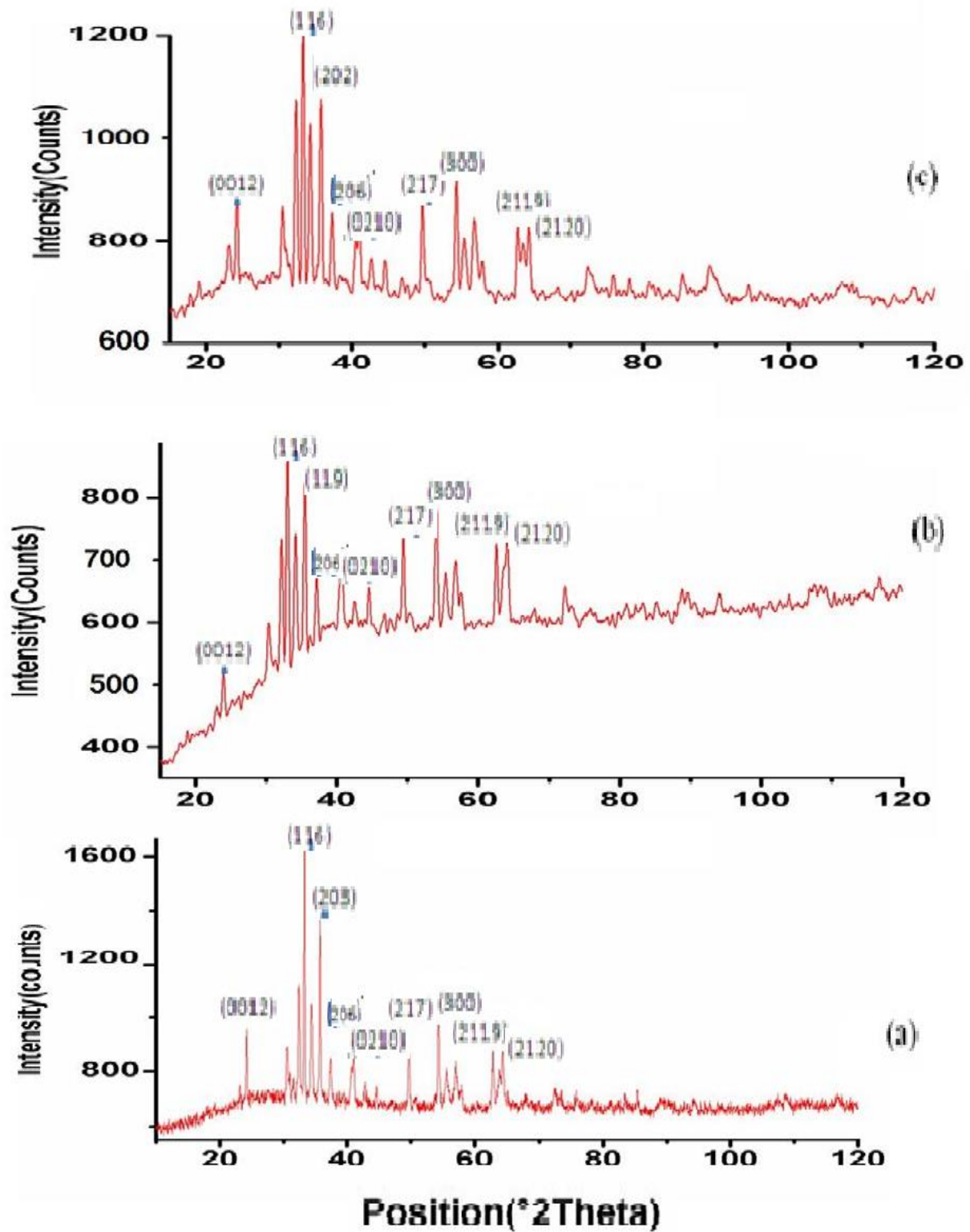


fig. 1.1(a): XRD of  $\text{BaAl}_2\text{Fe}_{12}\text{O}_{22}$  calcinated at  $1100^{\circ}\text{C}$  for 6 Hrs

fig. 1.1(b): XRD of  $\text{BaAl}_2\text{Fe}_{12}\text{O}_{22}$  calcinated at  $1100^{\circ}\text{C}$  for 4 Hrs

fig. 1.1(c): XRD of  $\text{BaAl}_2\text{Fe}_{12}\text{O}_{22}$  calcinated at  $1000^{\circ}\text{C}$  for 6 Hrs

**table-1:** lattice parameter 'a', 'c', cell volume (V), particle size (D), bulk density ( $d_B$ ), X-ray density ( $d_x$ ), porosity of  $BaAl_2Fe_{12}O_{22}$  compounds.

Sample	Calcination Temp ( $^{\circ}C$ )	Time (Hrs)	Lattice Constant			Volume ( $\text{\AA}^3$ )	Particle size (nm)	Bulk density ( $d_B$ ) ( $\text{gm/cm}^3$ )	X-ray Density ( $d_x$ ) ( $\text{gm/cm}^3$ )	Porosity (Fraction)	Molecular wt (gm/mole)	Curie Temp ( $T_c$ ) (K)
			a ( $\text{\AA}$ )	c ( $\text{\AA}$ )	c/a							
$BaAl_2Fe_{12}O_{22}$	1100	6	5.854	44.1	7.5	1309.8	129.7	2.46	4.61	0.465	1213.4	47
$BaAl_2Fe_{12}O_{22}$	1100	4	5.867	44.4	7.5	1325.0	65	2.09	4.46	0.530	1213.4	44
$BaAl_2Fe_{12}O_{22}$	1000	6	5.846	46.1	7.8	1365.2	59.13	2.04	4.42	0.538	1213.4	44

## 2. SCANNING ELECTRON MICROGRAPH (SEM) ANALYSIS:

The SEM micrograph of the  $BaAl_2Fe_{12}O_{22}$  samples calcinated at temperatures  $1000^{\circ}C$  and  $1100^{\circ}C$  for 4 hrs and 6 hrs are shown in Fig. 2 (a),(b),(c). It has been observed from this micrographs that the grains are uniformly distributed over the surface of the sample and grain size of the compound is found to be in the range of 129 nm from Fig. 2(a). Fig. 2(b) shows the effect of the time of calcination temperature, the grain size of morphology is varied and found as 65nm. Fig.2(c) shows the effect of temperature of calcination again and the grain size is varied and found as 59 nm. The SEM micrographs shows that the grain size of the samples decreased distinctly and the porosity increased as the calcination temperature and time decreased [14].

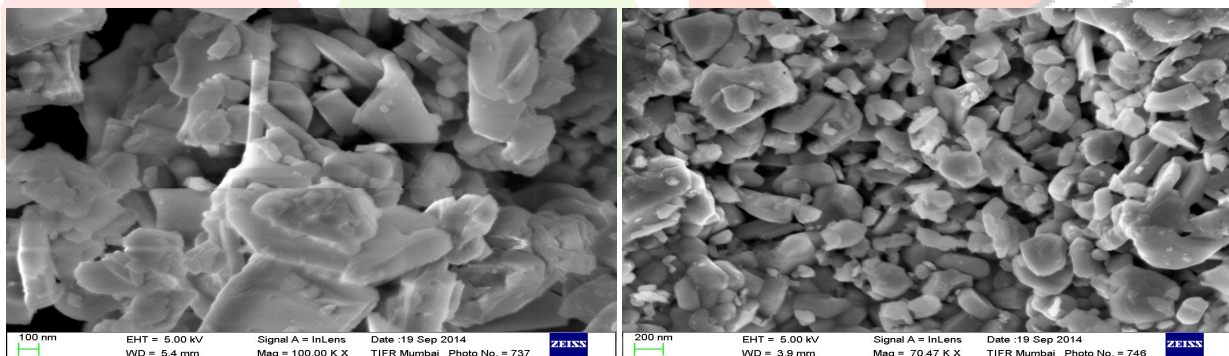


fig.2(a):  $BaAl_2Fe_{12}O_{22}$  calcinated at  $1100^{\circ}C$  for 6 hrs

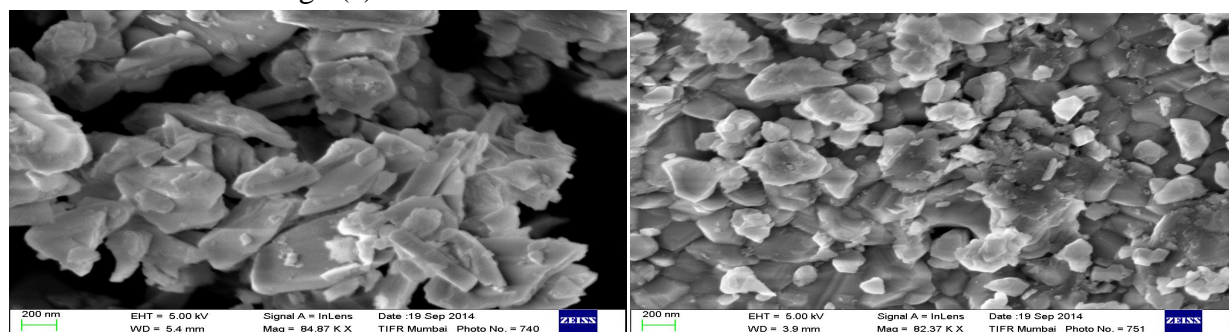


fig.2(b):  $BaAl_2Fe_{12}O_{22}$  calcinated at  $1100^{\circ}C$  for 4 hrs

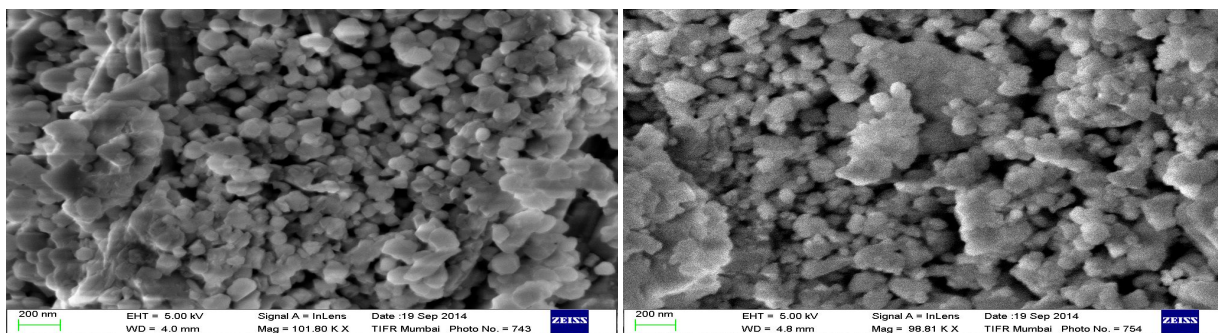


fig.2(c): BaAl<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> calcinated at 1000<sup>0</sup>C for 6 hrs

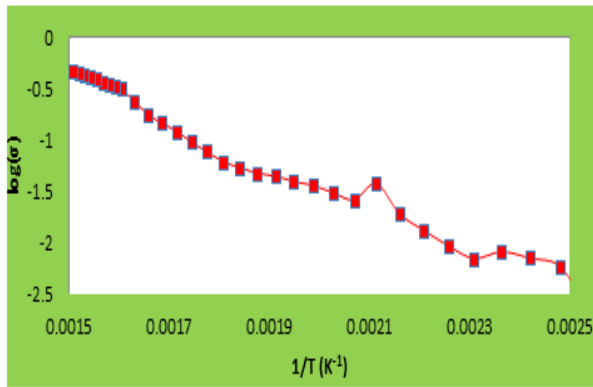
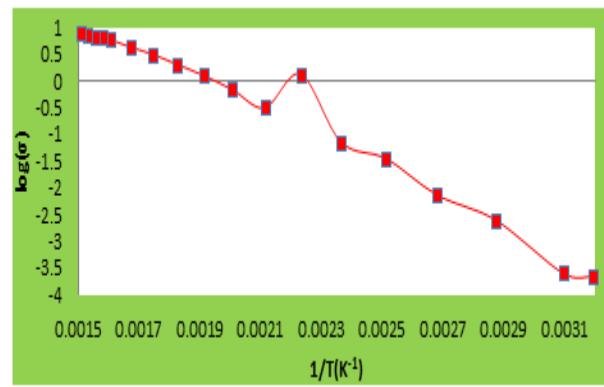
### 3. ELECTRICAL CONDUCTIVITY MEASUREMENT:

The electrical conductivity results obtained at room temperature has been given in Table-2 and logarithmic conductivity ( $\log\sigma$ ) versus inverse of temperature ( $1/T$ ) plots has been shown in Fig.3(a, b, c). The plots are linear indicating any absence of impurity in crystal lattice. An increase of the temperature from room temperature, the resistivity of the sample decreases for each of compound in the BaAl<sub>2</sub>Y series of the hexaferrites, which attributes directly about the tight bonding of ions at room temperature at their interstitial sites, which originates the hopping mechanism in the crystal lattice. The activation energy was found to be increasing with the increasing calcinations temperature. The conduction mechanism may be explained on the basis of Koop's hopping mechanism of the localized d-electron model for Y-type hexaferrites [15]. It is observed that the electrical conductivity increases with the varying temperature for 4 hrs and 6 hrs.

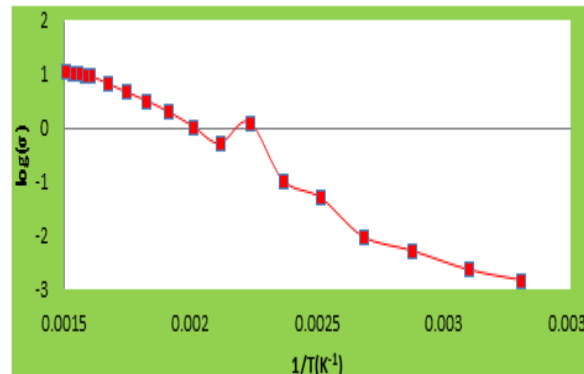
The activation energy of these compounds below and above the Curie temperature ( $T_C$ ) has been calculated as shown in Table-2. It was found that activation energy below  $T_C$  region has been observed to be less than in the above  $T_C$  region. These results are in agreement with the observation made in the case of BaAl<sub>2</sub>-Y hexaferrite. The variation of activation energy in this series of the compound has been explained by considering the mechanism of energy transfer due to migration of hopping of electrons from Fe<sup>2+</sup> to Fe<sup>3+</sup> ions (about 0.6eV) and the formation of energy for Fe<sup>2+</sup> ions on the octahedral site (about 1.21eV). The low activation energy below the Curie temperature ( $T_C$ ) might be due to the energy migration of intrinsic electrons between iron ions on octahedral sites within the spinel blocks. The higher activation energy above  $T_C$  would be attributed to the additional contribution from the excitement of electrons from Fe<sup>2+</sup> ions within the octahedral sites of the spinel blocks [16].

table-2: electrical conductivity ( $\sigma$ ), activation energy of BaAl<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> compounds.

Sample	Calcination Temp(°C)	Time (Hrs)	Roomtemp. Resistivity( $\rho$ ) ( $\Omega$ .cm)	Room temp. Condu ctivity( $\sigma$ ) ( $\Omega$ .cm) <sup>-1</sup>	ActivationEnergy $\Delta E$	
					Ferri (eV)	Para (eV)
BaAl <sub>2</sub> Fe <sub>12</sub> O <sub>22</sub>	1100	6	20.03x10 <sup>5</sup>	0.499x10 <sup>-6</sup>	0.374	0.404
BaAl <sub>2</sub> Fe <sub>12</sub> O <sub>22</sub>	1100	4	4.6x10 <sup>5</sup>	2.17x10 <sup>-6</sup>	0.497	0.524
BaAl <sub>2</sub> Fe <sub>12</sub> O <sub>22</sub>	1000	6	0.657x10 <sup>5</sup>	15.22x10 <sup>-6</sup>	0.593	0.667

fig.3(a): BaAl<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> calcinated at 1100<sup>0</sup>C for 6 hrsfig.3(b): BaAl<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> calcinated at 1100<sup>0</sup>C

for 4 hrs

fig.3(c): BaAl<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> calcinated at 1000<sup>0</sup>C for 6 hrs

#### 4. MAGNETIC MEASUREMENT:

Magnetic characterizations of the studied samples have been investigated by using vibrating sample magnetometer (VSM). The hysteresis loops have been traced at varying external applied magnetic field of 15000 Gauss, volume of the sample taken was about 31 to 35 mg. The shape and size of hysteresis loop obtained for these two compounds have been shown in Fig.4(a) and 4(b). If we compare the size and shape of compounds, it is observed that BaAl<sub>2</sub>Y hexaferrites calcinated at 1100<sup>0</sup>C for 6 hours is more magnetic in nature than BaAl<sub>2</sub>Y hexaferrites calcinated at 1000<sup>0</sup>C for 6 hours. The above observation is corroborated with the evidence showing larger value of coercivity, remanance, and saturation magnetization for BaAl<sub>2</sub>Y hexaferrites calcinated at 1100<sup>0</sup>C for 6 hours. From the result, it has been observed that for BaAl<sub>2</sub>Y hexaferrites saturation magnetization ( $M_s$ ) increase but remanance ( $M_r$ ) decreases, as calcinations temperature decreases from 1100 °C to 1000<sup>0</sup>C as shown in Table-3. Same trends observed in other hexaferrites, calcinated at different higher temperatures as reported in Xu Fang *et al* [17] for Ba<sub>2</sub>Zn<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub>. The some modifications in the values are observed due to Fe-O-Fe exchange interaction and reduced in lattice dimension site which directly effects on site distribution, Curie constant and saturation magnetization. The temperature dependence of magnetization can be explained in light of cationic distribution and lattice dislocation among the available tetrahedral and octahedral sites in spinel and garnet site [18].

Table-3: Saturation magnetization ( $M_s$ ), coercivity ( $H_c$ ), remanence ( $M_r$ ), squareness ratio ( $M_r/M_s$ ) and magnetic moment ( $\mu_0$ ) of  $BaAl_2Fe_{12}O_{22}$  compounds at  $1100^\circ\text{C}$  and  $1000^\circ\text{C}$  for 6hrs.

Sample	Calcination Temp ( $^\circ\text{C}$ )	Time (Hrs)	Coercivity ( $H_c$ ) (Gauss)	Remanence ( $M_r$ ) (emu/gm)	Saturation Magnetization ( $M_s$ ) (emu/gm)	Squareness Ratio $M_r/M_s$	Magnetic Moment ( $\mu_B$ )
$BaAl_2Fe_{12}O_{22}$ <sub>2</sub>	1100	6	1877.8	0.1444	0.22431	0.6439	0.0487
$BaAl_2Fe_{12}O_{22}$ <sub>2</sub>	1000	6	1149	0.119	0.22742	0.5233	0.0494

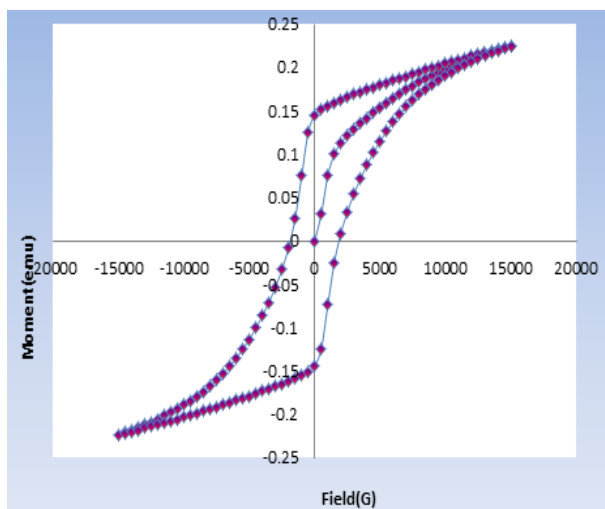


fig.4(a): VSM of  $BaAl_2Fe_{12}O_{22}$  calcinated at  $1100^\circ\text{C}$  for 6 hrs

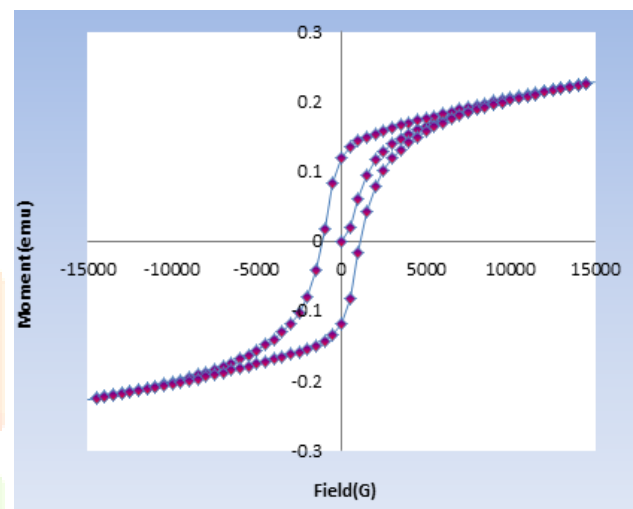


fig.4(b): VSM of  $BaAl_2Fe_{12}O_{22}$  calcinated at  $1000^\circ\text{C}$  for 6 hrs

## 5. CONCLUSION:

The Ba-Y-type hexaferrite  $BaAl_2Fe_{12}O_{22}$  powders have been synthesized by using chemical coprecipitation method calcinated at temperatures  $1000^\circ\text{C}$  and  $1100^\circ\text{C}$  for 4 hrs and 6 hrs. The analysis of X-ray diffraction (XRD) of the studied samples using Rietveld refinement method confirmed the formation of single phase compound with a parameter 'a' and 'c' of hexagonal crystal structure. The surface morphology of the samples studied by SEM, gives the grain size and from XRD particle size have been calculated in the order of 129 nm to 59 nm. It is observe that the grains are uniformly and densely distributed over the surface of the compound. The grain size of the samples decreased distinctly and the porosity increased.

The electrical conductivity results obtained at room temperature has been given in Table-2 and logarithmic conductivity ( $\log\sigma$ ) versus inverse of temperature ( $1/T$ ) plots has been shown in Fig.3(a, b, c). It is observed that the electrical conductivity increases with the varying temperature for 4 hrs and 6 hrs. The activation energy was found to be increasing with the increasing calcinations temperature. In ferromagnetic region activation energy is less than that of the paramagnetic region.

The shape and size of hysteresis loop obtained for these two compounds have been shown in Fig.4(a) and 4(b). The above observation is corroborated with the evidence showing larger value of coercivity, remanence, saturation magnetization for  $BaAl_2Y$  hexaferrites calcinated at  $1100^\circ\text{C}$  for 6 hours. From the result, it has been observed that for  $BaAl_2Y$  hexaferrites saturation magnetization ( $M_s$ ) increase but remanence ( $M_r$ ) decreases, as calcinations temperature decreases from  $1100^\circ\text{C}$  to  $1000^\circ\text{C}$  as shown in Table-3.



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