EVOLUTION OF FERRO ELECTRIC AND FERRO MAGNETIC PROPERTIES OF RARE EARTH ALUMINIUM SUBSTITUTED M-TYPE BARIUM HEXA FERRITES AT ROOM TEMPERATURE

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The ferro-electric and ferro-magnetic properties of rare earth aluminium substituted Mtype barium hexa-ferrites with the composition of $BaAl_xFe_{(12-x)}O_{19}$ where (x=0.2, 0.4, 0.6, 0.8, 1.0 and 1.2) have been prepared by oxides as precursors employing powder metallurgy route. The structural properties, functional groups, 3-D visualization, elemental analysis, surface morphology, magnetic, optical properties and ferro electric properties of the prepared samples have been characterized through X-Ray Diffractometer (XRD), Fourier Transform Infrared Spectroscopy (FTIR), diamond visualization software, Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscopy (SEM), Vibrating Sample Magnetometer (VSM), UV-Visible spectroscopy (UV-VIS) and ZT-IA measurement system respectively. The structural measurements depict the confirmation of M-type barium hexa-ferrite structure. EDS spectrum illustrate the elemental composition of the prepared materials for every corresponding 'x' values. The surface morphology shows the existence of platelet like intergranular pores. Magnetic measurements shows that the saturation magnetization (Ms) decreases and coercivity (Hc) increases with increasing aluminium contents. The optical band gap energy increases as the crystallite size decreases. The variation of electric polarization has also been occurred due to the shifting of iron ions in the unit cell structure of oxygen octahedron FeO₆.

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1. Introduction

Ferrites are very important due to its technological applications like permanent magnets, magneto-electric devices and microwave applications [1]. Barium ferrite is permanent magnet having hexagonal structure which is widely used in permanent magnets and magnetic storage devices but recently a third new application was found, known as multi-ferroic. Multi-ferroics are the materials that exhibit significant coupling between magnetic and electrical properties [2, 3]. These type of materials are widely used in spintronics applications. On the other hand hexaferrites magnetic and electrical properties are dependent on microstructural properties and these microstructural properties have been determined by variety of functional factors like material quality, annealing temperature, time factors, composition and many more. These microstructural properties develop during sintering which gives us informations about crystallite size, shape, distribution, porosity, agglomeration states, chemical bonding, phase compositions etc. Similarly the intrinsic magnetic effect of hexaferrites can be easily improved by substitution of different ions such as copper, gallium, niobium, aluminum, titanium, other metals and semiconducting materials. Although the study of Al substitution in BHF materials have been limited but Al substitution provides large magnetic and electrical properties and also improved their microstructural properties which play a vital role in ceramic applications as well as magneto-electric coupling.

There are many methods have been used in manufacturing of BHF materials like sol-gel, auto-combustion, co-precipitation but in the present project solid state ceramic method is used due

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to its simplicity and accuracy, inexpensive precursors are used in this process, and we can easily obtain a single phase structure.

Hexagonal ferrites have complex crystal structure which is the combination of certain spinel and hexagonal blocks [4-6]. The M-type hexagonal ferrites have very complex structure among the others. The Gorter [7] proposed M-type barium hexaferrite structure, implies that magnetically active Fe³⁺ cations for one formula unit are located at five nonequivalent crystallographic sites, which have octahedral, bipyramidal and tetrahedral oxygen surroundings. Below the Curie temperature (740 K), 12 Fe³⁺ cations forming five magnetic sub lattices are ordered antiparallel (1Fe1[↑], 2Fe2[↓], 1Fe3[↑], 2Fe4[↓], 6Fe5[↑]) and at 0 K give the total magnetic moment equal to 20 µB per formula unit [8]. The spontaneous magnetization depends upon the substitution of diamagnetic ions for iron ions. This type of substitution results in the competition of exchange interactions and in the appearance of conic magnetic structures. Furthermore, the small amount of diamagnetic cations substitution can significantly increase the electric resistivity of the hexaferrite [9, 10]. A significant role of the resistivity in the detection of the magneto-electric effect in magnetic materials was mentioned in many works [11].

The objective of this work is to prepare substituted M-type barium hexaferrites with diamagnetic aluminum content $BaAl_xFe_{12 - x}O_{19}$ (x= 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2). These hexa ferrites having ferro electric properties are the promising candidates as Multiferroic.

2. Experimental Setup

2.1. Sample Preparation

The polycrystalline aluminium doped M-type barium hexa-ferrite powders were prepared from high purity oxides Fe_2O_3 , $BaCo_3$ and Al_2O_3 by powder metallurgy route. The starting materials in stoichiometric proportion were mixed together in an acetone, for homogeneous mixture. After wet mixing the samples were subjected for heat treatment at 1100°C for 2 hours. On sintering, the samples were slowly cooled down to prevent them from quenching. Then the samples are ready for characterization. The flow chart for the preparation of $BaAl_xFe_{(12-x)}O_{19}$ is shown in Fig. 1.



Fig. 1. Flow chart for the preparation of $BaAl_xFe_{(12-x)}O_{19}$ where x=0.2, 0.4, 0.6, 0.8, 1.0 and 1.2.

2.2. Characterization Technique

Different characterization techniques have been carried out for the analysis of aluminium doped M-type barium hexaferrites. Structural analysis of the aluminium doped M-type barium hexa-ferrites have been carried out by using X-ray Diffractometer (D-1 discover, Bruker, Germany, source scincillacion Cuk α detector; eudetube current=40mA, Tube voltage=40KV, scan speed=3deg/min increment=0.05degree). The functional group analysis of Al_xFe_(12-x)O₁₉ having x= (0.2-1.2) have been carried out by using Fourier Transform Infrared spectroscopy (MIDAC 2000 USA, background subtraction, Scan range 400-4500). Diamond software has been used for the 3-D structural view of the prepared samples. Elemental composition of the solid solutions has been analyzed through EDS. Scanning Electron Microscope have been used for the surface morphology

of the prepared samples. Magnetic properties have been carried out by using Vibrating Sample Magnetometer (Lake shore, 3 Tesla). The optical measurements of the hexa ferrites have been carried out using UV Visible spectrometer (UV=2800 model, hitatchi japan, wavelength=300-900 nm, quartz). ZT-IA measurement system has been used for ferro-electric loop.

3. Results and discussion

3.1. Structural analysis

The comparative XRD pattern of $BaAl_xFe_{(12-x)}O_{19}$ is shown in figure 2 (a) having concentration x=0.2, 0.4, 0.6, 0.8, 1.0, 1.2. These XRD patterns exhibit characteristics diffraction peaks corresponding to the aluminium doped M-type barium hexa-ferrite structure. The diffraction peaks of all the samples are exactly matched with standard JCPDS card (00-051-1867), of aluminium doped M-type barium hexa-ferrite, which has standard peaks at 20 values corresponding to (101), (114) and (107) planes respectively. The absence of any other secondary peaks (apart from $BaAl_xFe_{(12-x)}O_{19}$ peaks) in the XRD pattern confirms the purity of the prepared M-type hexagonal ferrites.

The magnified view of the most intense peak (114) is shown in Fig. 2 (b) to see the effect of Al^{+3} doping in M-type barium hexa-ferrites. This shows that the peak slightly shifts towards higher angle with the increase of aluminium concentration. It might be due to the strain induced in the crystal lattice, by Al^{3+} ion substitution with smaller ionic radii (0.567Å) as compared to Fe⁺³ ion (0.76A°) [12].



Fig. 2. (a) Comparative XRD pattern of $BaAl_xFe_{(12-x)}O_{19}$ having x = 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2. Fig. 2. (b) Zoomed view of (114) peak.

The lattice constants "a" and "c" of the samples have been calculated from the formula [13]:

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

where "d" is the inter-planar distance and h, k and l are the miller indices of each peak.

Pure M-type barium hexa-ferrite having composition $BaFe_{12}O_{19}$ consists of hexagonal structure in the space group P63/mmc, with the standard lattice constants a=5.892 A° and c=23.183 A°. However, Table 1 shows the lattice constants of the prepared ferrites. The lattice constants "a" and "b" decrease with increasing aluminum contents as shown in Fig. 3. The reduction in lattice constants with the increasing aluminum contents can be explained on the basis of the relative sizes of their ionic radii. As the trivalent Al ions are substituted the metal ions in the lattice, the Al⁺³ (0.567 A°) replaces the larger ionic radii of Fe⁺³ ions (0.64 A°) which results in the reduction in lattice constants. It is in good agreement with the previous literature [14].



Fig. 3. Variation of lattice parameter with Al content.

Table 1. Variation in parameters extracted from XRD data for all the composition.

Sample	a (A°)	c (A ⁰)	c/a	V(A ⁰³)	Elastic strain ε (*10 ⁻³)
$BaAl_{(0,2)}Fe_{(11.8)}O_{19}$	5.89	23.33	3.96	699.93	0.049
$BaAl_{(0.4)}Fe_{(11.6)}O_{19}$	5.86	23.31	3.97	693.21	0.050
$BaAl_{(0.6)}Fe_{(11.4)}O_{19}$	5.82	23.28	4.00	683.90	0.052
$BaAl_{(0.8)}Fe_{(11.2)}O_{19}$	5.80	23.24	4.01	677.05	0.055
$BaAl_{(1.0)}Fe_{(11)}O_{19}$	5.77	23.20	4.02	668.91	0.11
BaAl _(1.2) Fe _(10.8) O ₁₉	5.72	23.14	4.05	655.67	0.12

The volume (V) of the unit cell has been calculated using the formula: [15]

V

$$= \cos 30^0 a^2 c$$

(2)

612

The elastic strains of the samples have been calculated using the expression [16, 17].

$$\boldsymbol{\varepsilon} = \frac{\beta}{2cot\theta} \tag{3}$$

Crystallite size have been calculated by using Debye-Scherrer's equation [18]:

$$d_{hkl} = \frac{k\lambda}{\beta cos\theta} \tag{4}$$

where "k" is the shape factor equal to 0.94, λ is the wavelength of CuK α (1.5406 Å), b is the full width at half maximum of the specified diffraction peak and θ is the diffracted angle of the powder samples.

In the present analysis, the peak (110) at $2\theta = 30.3^{\circ}$ has been fitted to find the approximate crystallite size along the basal plane of the hexagonal crystal lattice, while the approximate crystallite size along the *c*-direction perpendicular to the (114) crystallographic planes has been calculated from the most intense peak at $2\theta = 34.1^{\circ}$. The XRD parameters are listed in Table 2, It is observed that the crystallite size along the basal plane is obviously larger than that along the *c*-axis, suggesting that the crystallites grow in platelet-like shapes, which is also evident from SEM images [19].

	D _p (nm)				
Concentration (x)	(110)	(114)			
0.2	419.65	60.26			
0.4	214.96	59.79			
0.6	186.92	55.83			
0.8	162.01	55.76			
1.0	103.08	53.06			
1.2	64.73	51.80			

Table 2. The crystallite size for $BaAl_xFe_{(12-x)}O_{19}$ calculated using different peaks.

3.2. FTIR Analysis

The functional group analysis of $BaAl_xFe_{(12-x)}O_{19}$ having x = (0.2-1.2) with the step size of 0.2 have been shown in Fig. 4. The characteristic absorption bands have been recorded in the range of (400-3000) cm⁻¹. The characteristic IR absorption bands of the solids are usually due to the vibration of ions in the crystal structure. The Fig 4 shows the two major absorption bands at 436 cm⁻¹ and 611cm⁻¹ which corresponds to the metal vibrations. The band around 415-600 cm⁻¹ is due to vibration between tetrahedral metal ion and oxygen ion. These two bands confirms the formation of M-Type barium hexaferrite. The band in the range 430-470 cm⁻¹ identify the vibrations of octahedral metal ion and oxygen ion. The v₁-v₃ band positions slightly increases as the aluminium content increases in aluminium doped M-type barium hexa ferrite. Which is due to the fact that the doped Al⁺³ has smaller atomic weight as compared to the host Fe⁺³. The wave number and atomic weight are inversely proportional to each other. The absorption bands located at 1389 cm⁻¹ and 1658 cm⁻¹ corresponds to C=C and C=O bonds respectively. These bands are due to the burning of gases during heat treatment in the furnace.



Fig. 4. FTIR micrograph of $BaAl_xFe_{(12-x)}O_{19}$ where x = 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2.

3.3. Diamond structure

The 3-D structural view of aluminium doped M-Type barium hexa-ferrite having composition $BaAl_{0.2}Fe_{(11.8)}O_{19}$ has been shown in Fig. 5. The crystallographic study of aluminium doped M-Type barium hexa-ferrite shows that all the peak intensities are well indexed with the hexagonal crystal structure having space group P 63/mmc and shows magnetoplumbite structure. In barium hexaferrites crystal structure, there are 24 Fe⁺³ ions in five symmetrical crystallographic sites. There are 3 octahedral site and one in bipyramidal site. Diamond software also shows that aluminum ions are equally substituted in Fe positions at 12k, 2a, 2b, 4f₁ & 4f₂. The x, y, z values and Wyckoff sites of all the elements in $BaAl_{0.2}Fe_{(11.8)}O_{19}$ composition is listed in Table 3.



Fig. 5. 3-D structure of BaAl_{0.2}Fe_(11.8)O₁₉.

	Atoms Wyk-off positi	ons X	Y	Z
Ba	2d	2/3	1/3	1/4
A11	2a	0	0	0
Al2	4e	0	0	0.2522
A13	4f	1/3	2/3	0.0285
Al4	4f	1/3	2/3	0.1895
A15	12k	0.1683	0.3366	-0.1092
Fe1	2a	0	0	0
Fe2	4e	0	0	0.2522
Fe3	4f	1/3	2/3	0.2522
Fe4	4f	1/3	2/3	0.1895
Fe5	12k	0.1683	0.3366	-0.1092
01	4e	0	0	0.1481
O2	4f	1/3	2/3	-0.0556
O3	бh	0.1842	0.3685	1/4
O4	12k	0.1526	0.3053	0.0522
05	12k	0.5050	1.0101	0.1486

Table 3. Atomic coordinates of	f BaAl _{0.2} Fe	$(11.8)O_{19}$
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3.4. Energy dispersive spectroscopy

The EDS spectrum of aluminium doped M-type barium hexa-ferrites having composition $BaAl_xFe_{(12-x)}O_{19}$ where x=0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 are shown in figure 6 (a, b, c, d, e and f) respectively.



Fig. 6. EDS Spectrum of $BaAl_xFe_{12-x}O_{19}(a) = 0.2$ (b) x=0.4 (c) x=0.6 (d) x=0.8 (e) x=1.0 (f) x=1.2

The different peaks in EDS spectra at different energy levels exhibits the presence of respective elements [22-23]. EDS spectrum illustrate the elemental composition of the prepared materials, which confirm the presence of Fe, Ba, O and Al for every corresponding 'x' value.

3.5. Scanning Electron Microscopy

The surface morphology of the samples have been observed by using Scanning Electron Microscope. SEM micrographs of the $BaAl_xFe_{(12-x)}O_{19}$ where 'x=0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 are shown in Fig 7 (a, b, c, d, e and f) respectively. It is observed that the M-type barium hexa-ferrites have typical platelet like morphology, with a small number of intergranular pores. It is also observed that as the concentration of aluminium increases, the grains become thinner and small. This is also evident from XRD, where broader diffraction peaks have been observed as the concentration of aluminium increases.



Fig. 7. SEM micrographs of $BaAl_xFe_{(12-x)}O_{19}$ where (a) x = 0.2, (b) x=0.4, (c) x=0.6, (d) x=0.8, (e) x=1.0 and (f) x=1.2.

3.6. Vibrating Sample Magnetometer

Magnetic properties of aluminium doped M-type barium hexa-ferrites have been carried out by using Vibrating Sample Magnetometer. The M-H loop of $BaAl_xFe_{(12-x)}O_{19}$ (x=0.2, 0.4, 0.6, 0.8, 1.0 and 1.2) is shown in Fig. 8. The broad MH loop has been observed for all the samples, which is the confirmation of the M-type barium hexa-ferrite. It is also observed that the saturation magnetization (M_s) decreases and coercivity (H_c) increases with increasing Al contents.



Fig. 8. Comparative M-H loop of $BaAl_xFe_{(12-x)}O_{19}$ where x = 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2.

In M-type barium hexa-ferrites, the magnetic moment is due to the distribution of iron on five nonequivalent sub lattices of which three are octahedral (2a, 12k 4f2), one tetrahedral (4f1) and one trigonal bipyramidal (2b) [24-27]. The uncompensated upward spins are responsible for total magnetic moment (i.e., 20 μ B). In this case Al³⁺ ions having zero magnetic moment are substituted in Fe³⁺ ions having magnetic moment of 5 μ B. Owing to the magnetic moment of Al³⁺ (0 μ B) ion it is not able to cancel out with spin down moments of Fe³⁺ ions (5 μ B), hence saturation magnetization and remenance decreases. The magnetic parameters extracted from MH loops are listed in table 4. The replacement of Fe³⁺ with diamagnetic Al³⁺ also reduces the super-exchange interaction between Fe³⁺ - O - Fe³⁺ [28-32]. 1, 7, 12 which leads to decrease in exchange interaction and towards non-collinear spin arrangement [33]. The coercivity of aluminium doped M-type barium hexa-ferrites decreases with the increase of aluminium concentration which is due to lattice shrinkage, these lattice shrinkage have also been revealed from the XRD results.

Concentration (x)	Saturation	Coercivity
	Magnetization	(Oe)
	(emu/g)	
0.2	72.55	2032
0.4	68.75	2055
0.6	67.93	2100
0.8	50.22	2150
1.0	42.24	2275
1.2	33.25	2375

Table 4	Magnetic n	roperties o	f RaAL Fear	O_{10} where $x=$	02.04	1060	8 10 and 1	2
<i>1 ubic 7</i> .	mugnence p	<i>iopenies</i> 0	$\int Du u_{1} e_{1} e_{1}$	$r_{1}O_{1}O_{1}O_{1}O_{1}O_{1}O_{1}O_{1}O$	0.2, 0	r, 0.0, 0.	.0, 1.0 unu 1.	, <i>L</i> ,

3.7. UV-Visible analysis

The comparative UV-Visible micrographs of aluminium doped M-type barium hexaferrites is shown in figure 9. The optical band gap of the M-type barium hexa-ferrites have been calculated using the Tauc relationship [34].

$$(\alpha h v)^{n} = \alpha (h v - E_{g})$$
⁽⁵⁾

where ' α ' is the absorption coefficient, 'Eg' is the optical band gap energy of the incident photon and n is theoretically equal to 2(1/2) and 3 (3/2) for allowed indirect and forbidden indirect electronic transition respectively.



Fig. 9. Comparative UV-Visible micrograph of $BaAl_xFe_{(12-x)}O_{19}$ where x=0.2, 0.4, 0.6, 0.8, 1.0 and 1.2.

The value of indirect optical band gap (E_g) have been calculated by extrapolating the linear portion taking their intercept at x-axis. The Table 5 shows the indirect optical band gap (E_g) values

of M-type barium hexa-ferrites. The increase in aluminium concentration leads to the variation in optical band gap energies. The optical band gap strongly depends on the density of localized states. XRD is a useful technique to find the detail of the localized states. If the full width at half maximum increases with increasing AI^{+3} concentration, than it results in the reduction of localized states and also decreases in the crystallite size [35]. The relation between the optical band gap energy and crystallite size is shown in Fig. 10.



Fig. 10. Relation between the crystallite size and band gap of $BaAl_xFe_{(12-x)}O_{19}$ where x=0.2, 0.4, 0.6, 0.8, 1.0 and 1.2.

Table 5. The Full width at half maximum and band gap of $BaAl_xFe_{(12-x)}O_{19}$.

Concentration (x)	FWHM (nm)*10 ⁻³	D _p (nm)	Band gap (eV)
0.2	2.51	60.26	3.44
0.4	2.53	59.79	3.59
0.6	2.71	55.83	3.64
0.8	2.72	55.76	3.92
1.0	2.89	53.06	4.13
1.2	2.95	51.80	4.22

It has been observed that the optical band gap increases with the decrease of the crystallite size. As the grain size decreases or gets finer, it reaches to the Nano scale where every particle made up of only finite number of atoms. The electron hole pairs becomes very close together that the columbic force is no longer neglected and gives to overall higher kinetic energy. Hence the larger band gap means larger energy is required to excite an electron from valence to conduction band. Band gap energy may also be increased because as the grain size decreases the number of atoms becomes finite, the energy levels or overlapping orbitals decreases and the width of the band starts to broaden. This broadening of the band gap results in the increase in band gap energy.

3.8. Ferro-electric properties

Ferroelectric properties has been characterized through pulse polarization measurements. The polarization cycle of aluminium doped M-type barium hexa-ferrite having x=0.2 to 1.2 with the step size of 0.2 is shown in Fig. 11.



Fig. 11. Polarization-electric field (P-E) loop for $BaAl_xFe_{(12-x)}O_{19}$ at room temperature.

The polarization cycle exhibits the clear ferro-electric hysteresis loops under the applied electric filed at room temperature. The oxygen octahedron FeO6 in the unit cell of magnetic materials are responsible for the mechanism of electric polarization. In M-type barium hexa ferrite, the oxygen octahedron in unit cell has been located at three different crystallographic sites. By the application of external electric filed, the iron ions in the octahedron shifts in the unit cell. This shifting actually responsible for induction of electric polarization.

Fig. 11 shows that as the concentration of aluminium oxide increases, the value of saturation polarization increases. This might be due to the smaller ionic radii of aluminium as compared to iron ions. The aluminium ions creates disturbance in the bond length between Al^{+3} and Fe^{+3} ions. Fig. 11, also shows that with the further increase of the aluminium content, saturation polarization decreases. The decrease in saturation polarization for x > 0.8 sample might be due to the formation of long range order ferro-electric domain by the further substitution of Al^{+3} by Fe^{+3} ions. The value of maximum remanent polarization (P_r) and the coercive electric field (E_c) obtained from F-E hysteresis loop are 22.5 μ C/cm² and 14.9 KV/m respectively.

4. Conclusion

A series of M-type barium hexa-ferrites doped with aluminium having x=0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 have been synthesized by powder metallurgy route. The structural measurements revealed the confirmation of M-type hexagonal phase. SEM shows the platelet like particles. EDS confirms the elemental composition of the prepared material. Magnetic properties exhibits the decrease in M_s and increase in H_c with aluminium content. Band gap energy increases with the increase of aluminium concentration. Ferro-electric loop exhibits the induction of electric polarization in these magnetic materials at room temperature. These type of multi-phase magnetic materials could be well suited as multi ferroics at room temperature.

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