



Electrical and dielectric properties of chromium substituted barium hexaferrites”

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ABSTRACT

The nanocrystalline barium hexaferrite having chemical formula $BaFe_{12-x}Cr_xO_{19}$ (where $x=0.00, 0.25, 0.50, 0.75, 1.00$) synthesized by sol-gel auto combustion technique. The DC electrical resistivity was measured by two point probe technique. The DC resistivity of the barium hexaferrite increases with increase in Cr^{3+} substitution of x. The enhanced resistivity of the chromium substituted material has potential applications in microwave devices. The Curie temperature obtained from DC resistivity and Loria technique was in close agreement with each other and were decreases with increase in Cr^{3+} substitution x. The dielectric constant (ϵ') was measured in the (20Hz - 1 MHz) frequency range. The dielectric constant goes on decreasing with increase in Cr^{3+} substitution x.

Keywords: sol-gel auto combustion, barium hexaferrite, dc resistivity, dielectric properties etc.

INTRODUCTION:

Nanomaterials represent a novel class of materials in which a significant fraction of atoms is present on the surface that induces properties distinctly different from those of the normal polycrystalline materials [1, 2]. Very recently, attention has been drawn towards nanocrystalline ferrites because of their wide applications in industry and technology [3].

Hexaferrite are classified into five types depending on chemical formulae and crystal structure. These includes M-type ($BaFe_{12}O_{19}$), W-type ($BaMe_2Fe_{12}O_{22}$), X-type ($Ba_2Me_2Fe_{28}O_{46}$), Y-type ($Ba_2Me_2Fe_{12}O_{22}$) and Z-type ($Ba_3Me_2Fe_{24}O_{46}$). M-type barium hexaferrite $BaFe_{12}O_{19}$ has been intensively studied as a material for permanent magnets, high density magnetic recording media and microwave devices [4-7].

M-type hexaferrite $MFe_{12}O_{19}$ (M= Ba, Sr, Pb) crystallizes in a complex hexagonal structure belonging to magnetoplumbite structure [8], such materials are known to be hard ferrites due to high values of electrical resistivity, saturation magnetization, Coercivity, curie temperature, mechanical hardness and chemical inertness. For this reason they are useful in the fabrication of permanent magnets, plastic ferrites, DC-motors for automotive industry, perpendicular magnetic and magneto optical recording media [9, 10]. However, the electrical and magneto dielectric properties of hexaferrite may effectively vary in wide ranges by doping with cations that define their use in various devices and instruments. These properties are strongly dependent on the electronic configuration, atomic magnetism and site preference of the substituted ions [11].

As communication and electronic systems are moving up to higher working frequencies, soft ferrites seem to fall short on new demands, due to intrinsic restrictions imposed by the occurrence of their natural ferrimagnetic resonance up to 1 GHz.

The barium hexaferrite particles have been prepared by various methods such as sol-gel auto combustion [12, 13], hydrothermal method [14], Glass crystallization method [15], Micro-emulsion [16], Co-precipitation method [17], Citrate precursor [18]. However a number of difficulties in obtaining high purity ultrafine and homogeneous particles of barium hexaferrite with narrow size distribution have been pointed out by several investigators. Excessive demand for M-type hexaferrite, due to their exclusively high electrical resistivity and low eddy current losses, has initiated exhaustive research efforts to synthesize them for use as stable permanent magnets with best performance to cost-ratio [19].

We have used a sol-gel auto combustion method to synthesize chromium substituted barium hexaferrite $BaFe_{12-x}Cr_xO_{19}$ samples with $x= 0.00-1.00$. The DC resistivity (ρ_{dc}), Curie temperature (T_c) (by DC resistivity, Loria technique,) and frequency dependence of dielectric properties are reported in this paper.

2. Experimental:

Nanocrystalline chromium substituted barium hexaferrite samples were prepared by sol-gel auto combustion technique. AR grade barium nitrate $Ba(NO_3)_2$, ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$, chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ were dissolved in minimum amount of deionised water. Citric acid (C_6H_8COOH) was then added into the prepared aqueous solution to chelate Ba^{2+} and Fe^{3+} ions in the solution. The pH of the mixed solution was kept 8 by adding ammonia solution. The mixed solution was evaporated to dryness by heating at $100^\circ C$ on a hot plate with continuous stirring and finally formed a very viscous brown gel. This viscous brown gel was ignited by increasing the temperature up to $150^\circ C$

and the loose powder of the samples was obtained. Finally, the as burnt powder was sintered at 900 °C for 8 h to obtain chromium substituted barium hexaferrite nanoparticles.

The phase identification of the prepared samples was performed with the help of Philips X-ray diffractometer (Model PW-3710) using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$). The DC electrical resistivity was measured at room temperature by using two probe methods. The frequency dependence of dielectric constant (ϵ') in the range from 20 Hz - 1 MHz was studied using a precision LCR-Q meter bridge (model HP 4284 A).

3. RESULTS AND DISCUSSIONS:

3.1 resistivity measurements:

The DC electrical resistivity was measured using two point probe method [20]. The electrical resistivity increases with increase in chromium content x. The electrical conductivity in ferrite is due to hopping of electrons between ions of the same element present in more than one oxidation state, distributed randomly over crystallographically equivalent lattice sites. Hexaferrite structurally form hexagonal close packed oxygen lattice with the cation at the octahedral, trigonal bipyramidal and the tetrahedral sites. The distance between two ferric ions at octahedral sites is less than the distance between two metal ions at octahedral and tetrahedral site, therefore the hopping between tetrahedral and octahedral has very small probability compared with that for octahedral-octahedral hopping. The hopping between tetrahedral-tetrahedral sites does not exist, due to that there are only Fe³⁺ ions at tetrahedral sites and any Fe²⁺ ions formed during sintering preferentially occupy octahedral sites only. The conduction mechanism in hexaferrite can be explained on the basis of hopping of electrons between Fe³⁺ and Fe²⁺ at octahedral sites and the number and mobility of holes by following reactions



The DC resistivity measured with varying temperature in the range of 373 K to 800 K with varying composition x in BaFe_{12-x}Cr_xO₁₉ (where x = 0.00, 0.25, 0.50, 0.75, 1.00) samples is shown in fig. 1. The variations of logarithm of resistivity (log ρ) with temperature for all the samples are shown in Fig 1. The figure shows increase in the resistivity increase in Cr³⁺ composition x. In Fig.1 a change in slope is observed in the resistivity curve dividing the curve in two regions corresponding to ferromagnetic region and paramagnetic region. The temperature at which slope of the curve change, corresponds to the Curie temperature of the sample.

This resistivity plot obeys the exponential relation given by [21],

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{KT}\right) \tag{3}$$

The observed decrease in the DC electrical resistivity on raising the temperature as shown in Fig. 1 is a typical behavior of semiconductors. According to Rezlescu model [22] the conductivity in ferrites is due to the hopping of electrons between Fe³⁺ and Fe²⁺ at octahedral sites. The resistivity goes on increasing with increase in Cr³⁺ substitution in barium hexaferrite matrix. The energy of activation (ΔE) is calculated from the slope of the linear plots of ln ρ versus reciprocal of temperature in the semiconducting region.

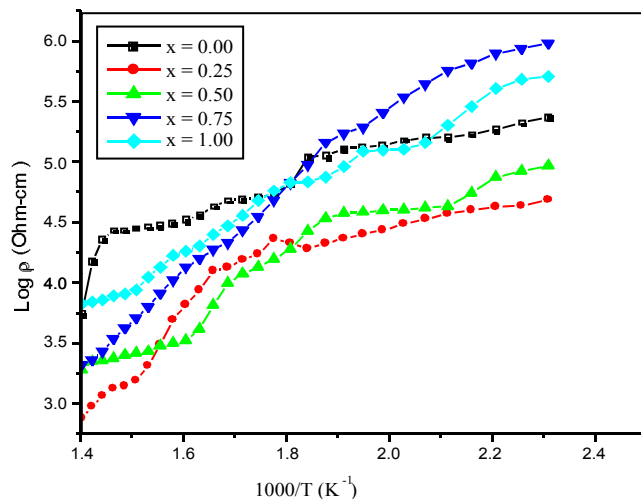


Fig. 1 Variation of DC electrical resistivity (log ρ) with inverse temperature (1000/T) of BaFe_{12-x}Cr_xO₁₉ samples.

The calculated values for both ferri and para activation energy (ΔE) are tabulated in Table 1. The values of ΔE in paramagnetic region are found to be greater than those observed in ferrimagnetic region, this suggests that the process of conduction is affected by the change in magnetic ordering. The values of ΔE as well as the resistivity are found to increase with increase in chromium content x. The magnitude of activation energy for both the compositions with Cr³⁺ contents lies between 0.109 to 0.307 eV which suggests that the conduction process in the present ferrites is due to hopping of polarons.

Table: 1 Measurement of paramagnetic energy (E_p), ferrimagnetic energy (E_f) and activation energy (ΔE) of BaFe_{12-x}Cr_xO₁₉ samples.

Comp. x	E_p (eV)	E_f (eV)	ΔE (eV)
0.00	0.5939	0.4845	0.1094
0.25	0.6536	0.5086	0.1449
0.50	0.8189	0.5810	0.2378
0.75	0.7833	0.5002	0.2831
1.00	0.5715	0.2639	0.3075

The variation in ΔE correspond to the variation in the resistivity, the activation energy ΔE increases with increase in the resistivity of the sample and vice versa.

3.2 Curie temperature

The Variation of Curie temperature T_c (K) of BaFe_{12-x}Cr_xO₁₉ (x=0.00, 0.25, 0.50, 0.75, 1.00) with composition 'x' is as shown in Fig.1. It shows that the value of the Curie temperature T_c (K) decreases with increasing Cr³⁺ content x. This trend can be explained on the basis of the number of magnetic ions present in the two sub-lattices and their mutual contraction. As Fe³⁺ ions are gradually replaced by Cr³⁺ ions, the number of magnetic ions begins to decrease at both sites, thus leading to a decrease of AB exchange interaction of the type Fe³⁺-O²⁻-Fe³⁺. As the Curie temperature T_c (K) is determined by the overall strength of the exchange interactions, the weakening of exchange interactions results in a decrease of the Curie temperature as the concentration of Cr³⁺ ions is increased. The Curie temperature obtained from DC resistivity, Loria technique and AC susceptibility are closely agrees with each other and is in the reported range [23]. The values of Curie temperature as shown in table.2

Table: 2

Curie temperature (T_c) of BaFe_{12-x}Cr_xO₁₉ system from DC resistivity (DCR), Loria Technique

Comp. x	Curie temperature (T_c) (K)	
	DCR	Loria
0.00	737	736
0.25	722	721
0.50	704	699
0.75	639	635
1.00	562	560

Frequency dependence dielectric parameters :

In general dielectric properties depend upon several structural and microstructural factors. The dielectric constant (ϵ') is calculated by the following equation

$$\epsilon' = \frac{C d}{\epsilon_0 A} \quad (4)$$

where, C is the capacitance of the pellet in Farad, d is the thickness of pellet in meter, A is the cross sectional area of the flat surface of the pellet and ϵ_0 is the permittivity constant of the free space.

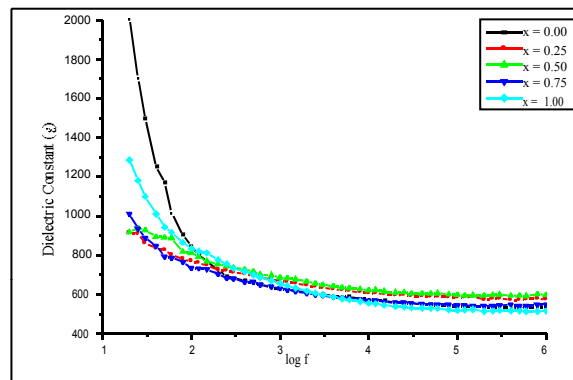


Fig. 2 Variation of dielectric constant (ϵ') with varying frequency ($\log f$) of $\text{BaFe}_{12-x}\text{Cr}_x\text{O}$ samples.

The reduction of the dielectric constant (ϵ') at lower frequencies are due to the predominance of the species such as Fe^{2+} ions, interfacial dislocations, pile-ups, oxygen vacancies, grain boundary defects etc. [24] For our material the Fe^{3+} is the predominant ions, however the electronic exchange between neighbors is still a factor to be taken into account. This behavior is normal ferromagnetic behavior and has also been observed by several investigators [25 -27]. The dielectric constant goes on decreasing with increase in Cr^{3+} Content x .

Conclusions :

The nanocrystalline $\text{BaFe}_{12-x}\text{Cr}_x\text{O}$ (where $x = 0.00 - 1.00$ in step of 0.25) have been successfully prepared by sol-gel auto combustion technique. The DC electrical resistivity increases with increase in chromium content x . The Curie temperature obtained from DC resistivity and IRTA technique are agree with each other and decreases with increase in chromium content x . The dielectric variation with frequency was observed and it has been explained on the basis of electron - hole hopping mechanism, which is responsible for conduction and polarization.

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