Effect of Sol-gel preparation Technique on the properties of magnetically substituted Y-type hexaferrite

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Abstract - The effect of sol-gel preparation technique on the properties of magnetically substituted Y-type hexaferrite with nominal chemical composition $Sr_2Ni_{2-x}Co_xFe_{12}O_{22}$ (x=0.5) have been examined in order to study the substitution effect of Cobalt-doping on the properties of Strontium Y-type hexaferrite. The structural, morphological and thermal study were characterized by employing X-Ray Diffraction (XRD), Scanning electron microscopy (SEM), Fourier trasnsform infrared spectroscopy (FTIR) and Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA). XRD spectra revealed that the high purity hexagonal $Sr_2Ni_{2-x}Co_xFe_{12}O_{22}$ single phase was formed at synthesis temperature of 950^0 C for 48 hours. The lattice parameter was found to be $a=5.8979A^0$ and $c=44.4527A^0$.The morphological study carried by SEM shows that the prepared ferrite is hexagonal in shape. The infrared absorption study carried by FTIR shows that the vibrational bands are at the standard frequencies which is usually observed in hexagonal structure. The thermal properties of the prepared sample were investigated by Thermogravimetric analysis (TGA) which confirms the thermal stability of strontium hexaferrite. The DTA confirms the completion of Sr-ferrite phase formation by showing exothermic peak at 600^0C.Thermoelectric study will be carried out up to 250^0C for determining the seebeck coefficient (Q).From dielectric study the Curie temperature is found to be 120^0C i.e 393K.

Key Words - Hexaferrite, Sol-gel, XRD, SEM, FTIR, TG-DTA, Thermoelectric study, dielectric constant.

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I. INTRODUCTION

There has been an increasing degree of interest in the hexagonal ferrites, also known as hexaferrites, which is still growing exponentially today from their discovery [1].The hexagonal ferrite are a group of magnetic compounds discovered by Philips between 1952 [2] and 1956 [3]. They all have high resistivity, magnetocrystaline anisotropies and saturation magnetization, low dielectric losses and thermal stability well above their curie temperature [4]. Hexagonal ferrites are classified into six main types depending on chemical formula and crystal structure. These are M (A $Fe_{12}O_{19}$), W (A$Me_2Fe_{16}O_{27}$), X ($A_2Me_2Fe_{28}O_{46}$), Y($A_2Me_2Fe_{12}O_{22}$), Z ($A_3Me_2Fe_{24}O_{41}$), U ($A_4Me_2Fe_{36}O_{60}$), where A represents Sr, Ba, Ca or Pb ions and Me represents a bivalent transition metal ions [5]. Among all these hexaferrites Y-type hexaferrite is an important type of high frequency soft magnetic material. Owing to its planar magnetocrystallineanysotrophy and high permeability, the Y-type hexaferrite is attractive for practical applications such as microwave devices [6]. The metallic cations are distributed among six sublattices as two tetrahedral and four octahedral sublattices [7]. It is constructed from basic units of hexagonal barium M ferrite [8] and cubic spinel ferrites, which retains hexagonal structure, usually with the direction of magnetization parallel to the c-axis. However if the metal me=cobalt II, then Co_2Y is formed, known as ferroxplana ferrite because it Possess an easy plane (basal plane) of magnetization perpendicular to c-axis [9]. The Y-type hexagonal ferrite has a crystalline structure built up as a superposition of S and T blocks. The unit cell is composed of the sequence STSTST including three formula units. There are numerous techniques such as chemical co-precipitation [10], hydrothermal [11]; sol-gel [12] and glass crystallization [13] have been developed to synthesized Y-type hexaferrite. The other method like Conventional solid state method, as a classical ceramic route for preparing hexaferrite, requires high calcinations temperature (1200-1300 ^{0}C) which induces sintering and aggregation of particles. Furthermore the milling process to reduce the particle size from multidomain to single domain, generally yields non-homogeneous mixture on microscopic scale and results in lattice strain in the material [14].To this end the sol-gel approach has recently raised interest since it is one of the most successful and promising techniques for preparation of phase with tailored structure and morphology [15].

The divalent substitution Me^{2+} is somewhat interesting because of their occupancies in different blocks at different positions due to differences in site preference [16]. The Ni^{2+}ion occupy 6c position at the boundaries of T-blocks by altering the length and angle of exchange bonds between the ions in the neighboring blocks and give rise to the cycloidal helix in the Y-type hexaferrite structure [17]. The Co^{2+} ion mainly occupy octahedral site with the preference of site 18h contrary to the tetrahedral occupation of cobalt and strongly affects the magnetic properties of Y-type hexaferrite [18]. So it is very inSteresting to study the effect of divalent substitution like Ni^{2+} and Co^{2+} on Y-type hexaferrite.

The present module of research aims to synthesize Y-type hexagonal ferrite by Sol-gel method which facilitates the production of fine hexagonal ferrite particle and to study the effect of two varying divalent substitutions (Me^{2+}) together on their structural, morphological and thermal properties.

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II. EXPERIMENTAL

The cobalt (Co^{2+}) ion substituted Y-type strontium hexaferrite sample were synthesized by Sol-gel method. The chemical used in the present investigation were of analytical grade (AR) with high purity of 99.99% and purchased from Sigma Aldrich, India. Stoichiometric amount of metal nitrate such as $Sr(No_3)_2$, $Ni(No_3)_2.6H_2O$, $Co(No_3)_2.2H_2O$ and $Fe(No_3)_3.9H_2O$ were dissolved in triple filtered deionised water at a temperature of 50^0C in a beaker. During this synthesis, the citric acid was slowly added so as to form homogeneous transparent aqueous solution. Were citric acid treat as a chelating reagent. The solution was then heated to 100^0C with constant stirring. The aqueous ammonium hydroxide was added to the mixture and P^H of the solution was adjusted to 7.The solution of metal nitrate and ammonium hydroxide were put in to digitally controlled oven at 200^0C for 4 to 5 hours so that it converted in to brown gel. The gel gets burnt by self propagating combustion reaction by evolving large volume of gases and finally gets converted in to homogeneous brown powder sample. The brown powder sample was crushed in the agate mortar to have fine hexaferrite powder. The polyvinyl alcohol solution 10% (2-3 drops) has beenmixed before they were pressed in to pellets of about 12mm in dimension above 5-6 mm in thickness using a stainless steel die set under uniaxial pressure for 5 min. The PVA was used as a binder. The pellets of sample were calcined at 950^0C for 48 hours to obtain cobalt doped Strontium Y-type hexaferrite.

III. RESULT AND DISCUSSION

X-Ray Diffraction

In order to confirm the phase formation of $Sr_2Ni_{2-x}Co_xFe_{12}O_{22}$ (x=0.5) hexaferrite , the standard powder X-Ray diffraction technique in the region of $2\theta=(20-80)^0$(x-axis) with the step scan of 0.02^0/min. on the Phillips diffractometer (Model PW-1710) using Cu-Kα radiation ($\lambda=1.5406$ A^O) is carried out at room temperature. The X-Ray diffraction pattern for pure hexaferrite sample is shown in figure (1). All the diffraction peaks are in good agreement with single phase hexagonal ferrite. The phases were in crystalline state and their study revealed pure hexagonal ferrite phases similar to JCPDS file number PDF#511880.
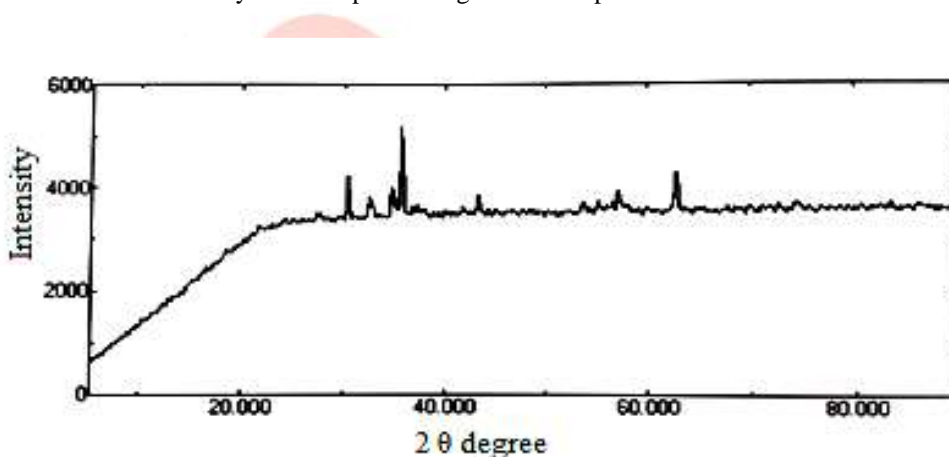

Figure (1). X-Ray diffraction pattern of $Sr_2Ni_{2-x}Co_xFe_{12}O_{22}$ (x=0.5)

The lattice parameter a and c are calculated from the XRD data using the following equation.

$$(1/d^2) = 4/3(h^2+hk+k^2)/a^2 + l/c^2$$

here h, k, l are Miller indices and d is the interplaner spacing. The lattice parameter are found to be a=5.8979A^O and c=44.4527A^O.The table depicts the value of miller indices and interplaner spacing for the different angle of 2θ w. r .t peak intensity.

ANGLE(2θ)	PEAK INTENSITY I	dOBS((A0)	dcal (A0)	h	k	L
21.58	3268	4.115	3.9768	1	0	7
30.28	4236	2.949	2.9316	0	1	12
32.4	3819	2.761	2.7699	1	0	13
34.58	3980	2.592	2.5626	0	2	4
35.56	5194	2.523	2.5213	2	0	5
62.9	4281	1.476	1.4658	2	0	24

Scanning Electron Microscopy

Scanning electron micrograph of prepared hexaferrite sample was obtained using a MAKE-LEO / LICA model Steroecan 440 scanning electron microscope. Figure (2) shows SEM micrograph of $Sr_2 Ni_{2-x} Co_x Fe_{12}O_{22}$ (x=0.5) hexagonal powder prepared by using Sol-gel method sintered at 950^0C. The SEM of prepared hexaferrite shows uniformity and homogeneousness in which the porosity arise which results in decrease in density of the compound. From the pictures it is shows that the prepared sample is like hexagonal in their microstructure.
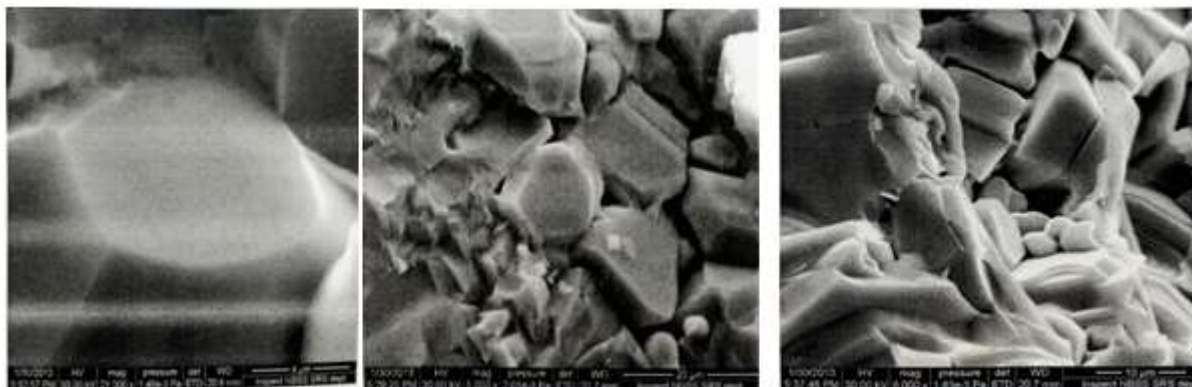

Figure (2). SEM micrographs for $Sr_2Ni_{2-x} Co_x Fe_{12}O_{22}$ (x=0.5)hexaferrites sintered at 950^0C

FTIR Analysis

The study of infrared absorption spectra is an important tool to get the information about the position of ions in the crystal [19]. Fig. shows the FTIR spectra of $Sr_2Ni_{2-x} Co_x Fe_{12}O_{22}$(x=0.5) samples in a wave number ranging from 3500 to 500 cm^{-1}.They are recorded at room temperature by using SHIMADZU. FTIR spectrum using KBr pellet method. From the FTIR studies w. r. t. spectrum transmittance (%) against wave number (cm^{-1}) is used for interpretation of the results. The dominant absorption bands are observed at 3862.93 cm^{-1}, 3737.71 cm^{-1}, 3421.74 cm^{-1}, 1644.94 cm^{-1}, 1450.84 cm^{-1}, 668.05 cm^{-1} and 593.08cm^{-1}. The bands below 650 cm-1 are due to the iron-oxygen bonds which are characteristics of hematite (γ-Fe2O3) [20]. The adsorption bands at 3862.93 cm^{-1} and 3737.71 cm^{-1} exhibit the stretching vibration of hydroxyl group (O-H) [21]. The two absorption bands around 593.08 and 668.05 cm-1, which are due to metal oxygen stretching vibrations confirming the formation of hexaferrite [22]. The other bands are at 3421.74 cm^{-1}, 1644.94 cm^{-1}, 1450.84 cm^{-1} , corresponding to the stretching and bending vibrations of C=O, H-C-H, C-H and C-C respectively[23].
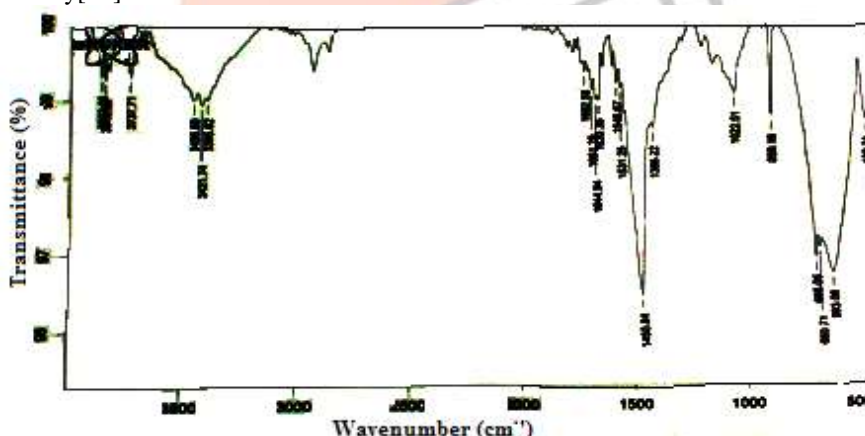

Figure (3):- FTIR-Spectra of $Sr_2Ni_{2-x} Co_x Fe_{12}O_{22}$(x=0.5)

TG-DTA Analysis

The thermal behavior of the prepared sample was investigated by TGA. The TGA has been found to be one of the most useful technique for evaluating the one set of thermal decomposition temperature and thermal stability. The TGA curve is shown in figure (4a). Significantly no loss was noted in the TGA curve for the dried nitrate gel at 117.31^0C with decomposition steps between the analyzed temperatures of $100-500^0C$.From TGA curve it has been observed that there is no loss of water molecule. From DTA curve as shown in figure (4b) the exothermic peak at about 600°C belongs to the crystallization of Sr-ferrite phase. After 600°C no reaction could be detected from the curves, which means the completion of the Sr-ferrite formation.
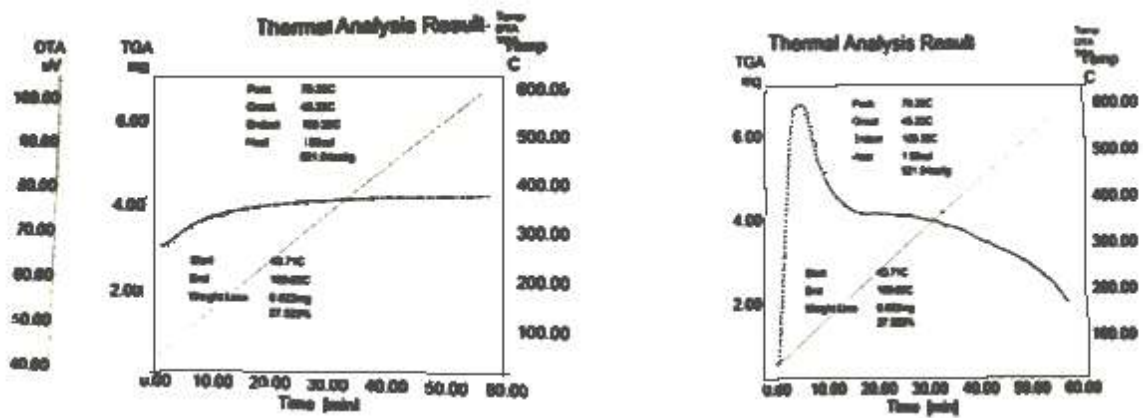
Figure 4:- (4a) TGA & (4b) DTA of Sr$_2$Ni$_{2-x}$ Co$_x$ Fe$_{12}$O$_{22}$ (x=0.5)

Thermoelectric study

In the present investigation, we used a ferrite specimen having dimension of approximately 1.77096cm^2 and 0.6932cm in thickness to determine the type of conduction in a given semiconducting material. The graph is plotted in between themo-emf and temperature difference. It is concluded that as the temperature difference increases thermo-emf also increases. The observed emf shows positive value which predicts that the prepared material is P-type semiconducting material. The seebeck coefficient (Q) is found to be 0.2656mv/k.
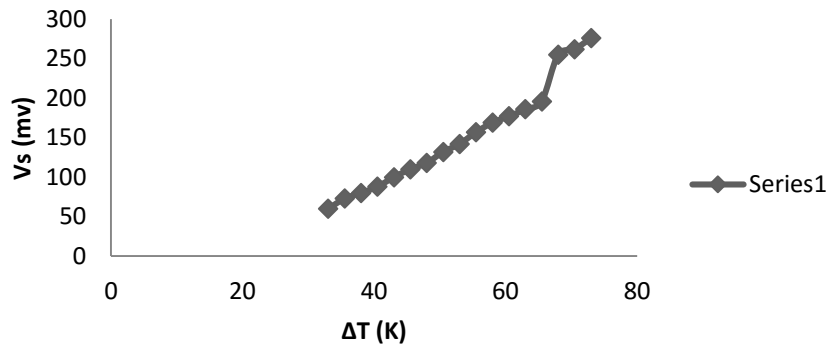

Figure (5):-Thermo-emf Vs Temperature difference

Dielectric Constant

The plot of dielectric constant at 1 KHz versus temperature is shown in figure (6).From the graph it is observed that there is decrease in dielectric constant initially from 50^{0}C to 57^{0}C. The sharpnees of fall is characterized by temperature coefficient of dielectric constant. At higher temperature the dielectric constant exhibits the hysteresis associated with the transition temperature 60^{0}C-90^{0}C, after which it is to be decrease up to 110^{0}C. This transition is likely due to the magnetic Curie temperature which is found to be 120^{0}C (i.e 393K) for prepared Sr-hexaferrite.
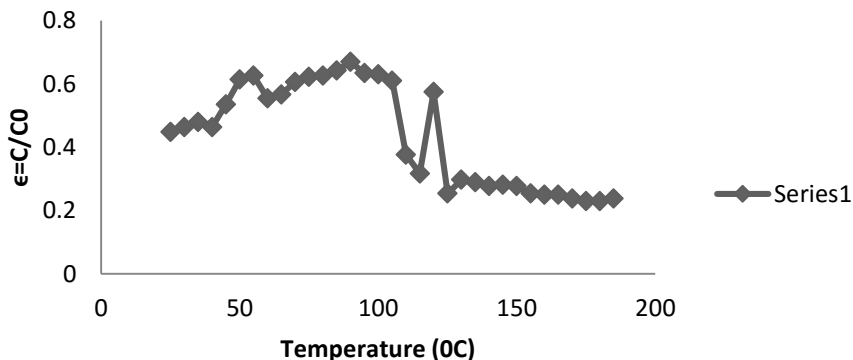

Figure (6): - Dielectric constant Vs Temperature.

IV. CONCLUSION

The cobalt ion substituted strontium Y-type hexaferrite was synthesized by sol-gel method. The XRD data have confirm the formation of Y-type hexaferrite and a and c values support this confirmation. Even low sintering temperature of about 950^0c is sufficient for this substitution in strontium Y-type hexaferrite. The surface morphology of the sample studied by SEM confirms that the sample exhibit microstructured hexagonal shape. The FTIR study reveals the good correlation with a crystalline phase observed in the XRD. The study of dielectric constant is very important in view of application of hexaferrites in RF component and circuits.

V. REFERENCES

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