Magnetic Properties of Magnesium Substituted Y-Type Hexaferrite

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Abstract- In the present work, we have synthesized Y-type hexaferrite $\text{Ba}_2\text{Mg}_x\text{Al}_{1/2}\text{Cr}_{x/2}\text{Fe}_{12-x}\text{O}_{22}$ ($x=0.0, 0.5, 1.0$) using solution gel method. The structural and magnetic properties have been investigated using XRD, FTIR and VSM. X-ray study shows that grain size lies in nano range. Presence of two prominent peaks near 550-600 cm$^{-1}$ to 500-600cm$^{-1}$ in FTIR indicates the formation of hexaferrite. From VSM analysis, it is found that with increasing the amount of co-dopants (Al – Cr) the saturation magnetization, retentivity and increases for $x = 0$ and $x = 0.5$ it was observed that coercivity is zero which indicates that material is super-paramagnetic in nature.

1. INTRODUCTION

Development of ferrites materials is one of the major advances in the field of the nanotechnology. The Magnesium substituted hexaferrite has great importance for the modern society because they are component of a variety of electronic devices used in means of medical equipment, communication, distribution and generation of electric energy, automotive and magnetic recording [1]. Y-type hexagonal ferrite is a frontier material for these applications and has attractive for researchers for many years. This type of ferrite is composed of Y-type Magnesium hexagonal, maintaining a hexagonal structure, with the easy direction of magnetization along the c-axis. However, Co$_2$Y, Mg Y (where Co and Mg are present as divalent cations) are known as ferroxplana ferrites because they have an easy plane (basal plane) of magnetization perpendicular to the c-axis [2].

To synthesize Nano-ferrites there are lot of methods like mechanical grinding [3], glass crystallization [4], hydrothermal reaction sintering [5], micro-emulsion technique [6], route etc. In addition, many synthetic techniques such as combustion method [7], spray pyrolysis [8], ammonium nitrate melt [9], co-precipitation [10], Sol-gel [11], oxidation in nitric acid [12] have been exploited extensively. The sol-gel method is one of the most widely used methods for the formation of pure hexagonal ferrites. Using this method, it is possible to obtain to order of submicron particles for attaining useful properties for nano materials.

In the present work, we have investigated the effects of Mg substitution for Ba$_2$ in barium based Y-type hexagonal ferrites ($\text{Ba}_2\text{Mg}_x\text{Al}_{1/2}\text{Cr}_{x/2}\text{Fe}_{12-x}\text{O}_{22}$) synthesized by sol–gel auto combustion method. The structural and magnetic properties have been investigated using X-ray diffraction (XRD) Fourier Transform Infrared Spectroscopy (FTIR) and Vibrating sample magnetometer (VSM).
2. CHARACTERIZATION TECHNIQUES

Y-type hexagonal ferrites \( \text{Ba}_2\text{Mg}_2\text{Al}_{1/2}\text{Cr}_{1/2}\text{Fe}_{12-x}\text{O}_{22} \) powders have been synthesized via sol gel combustion method using AR grade Barium Nitrate (\( \text{Ba(NO}_3\text{)}_2 \)), Chromium Nitrate Nonahydrate (\( \text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \)), Aluminium Nitrate Nonahydrate (\( \text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \)), Magnesium Nitrate Hexahydrate (\( \text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \)), Ferricnitrate Nonahydrate (\( \text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \)) and Monohydrate Citric Acid (\( \text{C}_6\text{H}_4\text{O}_7\cdot\text{H}_2\text{O} \)) citric acid. Aqueous solution of iron and metal salts are prepared separately in stoichiometric proportions by dissolving them in distilled water. Aqueous solution of citric acid is added to the salt solution with cations to citric acid molar ratio of 1:1.5. Ammonium hydroxide solution is further added drop by drop to attain the 7 pH value. Then the solution is heated at 80°C–85°C for 4–6 hours with continuous stirring using magnetic stirrer. After evaporation of water, the liquid gets converted into a homogenous brown colored gel. The viscous solution is dried over hot plate at 280–300°C for 3 hours to form the precursor material. Presintering is done at 500°C for 2 h. Then the precursor material is calcined at 700°C, 900°C, 1100°C and 1200°C for 5 h. Following devices were used to know the properties of synthesized Y-type hexaferrites.

3. RESULTS AND DISCUSSION

3.1 Structural properties

3.1.1 FTIR Analysis

Fourier Transform Infrared Spectroscopy is a technique that helps to know the chemical, structural and phase changes present in the sample during combustion and sintered process. Nearly 2 mg of ferrite powered is mixed with powdered \( \text{KBr} \) in the ratio 1:100 by weighing to ensure uniform dispersion. The infrared spectra of prepared sample \( \text{Ba}_2\text{Mg}_2\text{Al}_{1/2}\text{Cr}_{1/2}\text{Fe}_{12-x}\text{O}_{22} \) was recorded in the range of 4000 \( \text{cm}^{-1} \) to 400 \( \text{cm}^{-1} \).

For the sample \( \text{Ba}_2\text{Mg}_2\text{Fe}_{12-x}\text{O}_{22} \) spectra is shown in the Fig 1.1. The band is in the range of 4000-400 \( \text{cm}^{-1} \). They have dominant absorption bands at range of 400-600 \( \text{cm}^{-1} \), 1250-1600 \( \text{cm}^{-1} \) and 3600-4000 \( \text{cm}^{-1} \). The bands in the range of 400-600 \( \text{cm}^{-1} \) assigned to be for broadening of metal oxygen bonds which is the characteristics of hexaferrites. Further, the band in the range of 1250-2000 \( \text{cm}^{-1} \) indicates the presence of carboxylic acid (citric acid) and nitrile. The downward peak at 2400 \( \text{cm}^{-1} \) is due to presence of \( \text{OH}^- \). The band from range 3400-4000 \( \text{cm}^{-1} \) exhibit the stretching of hydroxyl group which indicates the presence of free or absorbed moisture in the sample.
Fig 1.1: FT-IR Spectra of $Ba_2Mg_2Fe_{12}O_{22}$ at pH=7

Similarly, Spectra of sample $Ba_2Mg_2Al_{0.25}Cr_{0.25}Fe_{11.5}O_{22}$ is shown in Fig 1.2. The band is in the range of 4000-400 cm$^{-1}$. It have dominant absorption band at range of 400-600 cm$^{-1}$, 1250-1600 cm$^{-1}$, and 3500-3900 cm$^{-1}$. The bands are in the range of 400-600 cm$^{-1}$ is assigned to be for broadening of metal oxygen bonds which is the characteristics of hexaferrites. Further, the band in the range of 1250-1700 cm$^{-1}$ indicates the presence of carboxylic acid (citric acid) and nitrile. The downward peak at 2400 cm$^{-1}$ and 2800 cm$^{-1}$ is due to presence of OH$^-$. The band from range 3400-4000 cm$^{-1}$ exhibit the stretching of hydroxyl group which indicates the presence of free or absorbed moisture in the sample.

Fig 1.2: FT-IR Spectra of $Ba_2Mg_2Al_{0.25}Cr_{0.25}Fe_{11.5}O_{22}$ at pH=7

Similarly, Spectra of sample $Ba_2Mg_2Al_{0.25}Cr_{0.25}Fe_{11.5}O_{22}$ is shown in Fig 1.3. The band is in the range of 4000-400 cm$^{-1}$. It have dominant absorption band at range of 400-600 cm$^{-1}$, 1250-1600 cm$^{-1}$, and 3500-3900 cm$^{-1}$. The bands in the range of 400-600 cm$^{-1}$ is assigned to be for broadening of metal oxygen bonds which is the characteristics of hexaferrites. Further, the band in the range of 1250-1700 cm$^{-1}$ indicates the presence of carboxylic acid (citric acid) and nitrile. The downward peak at 2400 cm$^{-1}$ and 2800 cm$^{-1}$ is due to presence of OH$^-$. The band from range 3400-4000 cm$^{-1}$ exhibit the stretching of hydroxyl group which indicates the presence of free or absorbed moisture in the sample.
$cm^{-1}$ is assigned to be for broadening of metal oxygen bonds which is the characteristics of hexaferrites. Further, the band in the range of 1250-1800 $cm^{-1}$ indicates the presence of carboxylic acid (citric acid) and nitrile. The downward peak at 2400 $cm^{-1}$ and 2900 $cm^{-1}$ is due to presence of OH$^-$. The band from range 3600-4000 $cm^{-1}$ exhibit the stretching of hydroxyl group which indicates the presence of free or absorbed moisture in the sample.

**Fig 1.3:** FT-IR Spectra of $Ba_2Mg_2Al_{1/2}Cr_{0.5}Fe_{11}O_{22}$ at pH=7

### 3.1.2 XRD Analysis

Fig 1.4 shows the X-ray diffraction pattern of samples $Ba_2Mg_2Al_{1/2}Cr_{x/2}Fe_{12-x}O_{22}$ ($x=0.0, 0.5, 1.0$) nanoparticles. Pure hexaferrites phase was the formation at a temperature of 1000$^o$C for 6 hrs. The average crystallite size of the Nano-crystalline hexaferrite synthesized at different molar ratios of substitution for the peaks was calculated from the XRD data using the Scherrer formula.

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where $D$ is the crystallite size. The shape factor of $K$ can be 0.62–2.08 and is usually taken as about 0.89 for hexagonal systems. $\lambda$ is the X-ray wavelength (1.54Å). It was observed and calculated and was found out to be 44.9434nm for $x=0$, 57.9684nm for $x=0.5$ and 38.379nm for $x=1$. 
Fig 1.4: XRD Patterns of hexaferrite $Ba_xMg_{2-2x}Al_{1/2}Cr_{1/2}Fe_{12-x}O_{22}$ at different composition

The lattice parameter ($a$ and $c$) and cell volume ($V$) was also calculated using formula given below.

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

$$V = 0.8666a^2c$$

With usual parameter. The lattice parameters of all the samples synthesized at different concentrations were calculated and is shown in the Table1.1. It was observed that lattice parameter ‘$c$’ decreases and lattice parameter ‘$a$’ increases with increase in dopants.

Table 1.1: Value of different parameter calculated for hexaferrite

| S.No. | Sample  | Lattice constant $a$ (Å) | Lattice constant $c$ (Å) | Cell Volume (Å) |
|-------|---------|-------------------------|-------------------------|-----------------|
| 1     | $x = 0$ | 4.40                    | 47.86                   | 802.956         |
| 2     | $x = 0.5$ | 5.85                   | 44.432                  | 1317.12         |
| 3     | $x = 1$  | 5.87                    | 39.76                   | 1187.24         |
3.1.3 VSM Analysis

Figure 1.5 to 1.7 shows the room temperature hysteresis loop plots for all of the Nano size samples with the chemical formula of $Ba_xMg_{2x/3}Al_{x/2}Cr_{x/2}Fe_{12-x}O_{32}$ sintered at 1000°C for 6hrs. The values of saturation magnetization ($M_s$) and coercivity ($H_c$) for all samples were accomplished from the loops, and variation of these parameters as a function of aluminum and chromium contents. According to Figure it is clear that by an increase in substitution content, the saturation magnetization was gradually increased. For $x = 0$ and $x = 0.5$ the value of coercivity is zero, which says nanomaterial is super-paramagnetic in nature whereas for $x = 1$ it is 838.7025. The retentivity also gets increasing with increase in substitution contents. The value of Retentivity, Coercivity and Saturation Magnetization is shown in Table1.2 for each sample.

Table 1.2: The value of Retentivity, Coercivity, and saturation magnetization for ($x = 0, 0.5,$ and $1$)

| S. No | Samples ($x$) | Retentivity ($M_r$) (emu/g) | Coercivity ($H_c$) (Oe) | Saturation Magnetization ($M_s$) (emu/g) |
|-------|---------------|-----------------------------|------------------------|-----------------------------------|
| 1     | $x = 0$       | 4609.39                     | 0                      | 19441.4095                        |
| 2     | $x = 0.5$     | 5183.01011                  | 0                      | 19796.5037                        |
| 3     | $x = 1$       | 9628.5168                   | 838.7025               | 21510.5163                        |

![Figure 1.5: Magnetic-Hysteresis loop for $x=0$](image-url)
5. CONCLUSIONS

The Y-type Nano-hexaferrites have been synthesized using sol-gel technique and was characterized using FT-IR, XRD and VSM. X-ray study shows that grain size lies in Nano range. Presence of two prominent peaks near 550-600 cm$^{-1}$ to 400-600 cm$^{-1}$ in FTIR indicates the formation of hexaferrite. From VSM analysis, It is found that with increasing the amount of co-dopants (Al - Cr) the saturation magnetization, retentivity and increases for and it was observed that coercivity is 0 for $x = 0$ and $x = 0.5$ which indicates that material is super-paramagnetic in nature.

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