SYNTHESIS AND ELECTRICAL PROPERTIES OF COBALT SUBSTITUTED Y-TYPE CALCIUM HEXAFERRITES

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Abstract:
The series of samples of cobalt substituted calcium hexaferrite with composition Ca$_{3-x}$Zn$_x$Fe$_{12}$xCo$_{3+}$O$_{22}$ where x varies from 0 to 1 were synthesized by microwave induced sol-gel auto-combustion route. X-ray diffraction patterns of all prepared samples manifest that the synthesized samples has single phase Y-type hexagonal crystal structure. The influence of substitution of Co$^{3+}$ ion for Fe$^{3+}$ ion on the lattice constants, cell volume, X-ray density, bulk density and porosity of samples has been studied. The DC electrical conductivity of the samples were measured as a function of temperature from 300 K to 873 K using two probe techniques. The phenomenon of conduction was explained on the basis of a Verwey hopping model.

Key words: Y-type hexagonal ferrite, Structural property, Electrical property, Sol-gel auto-combustion route.

Introduction:
Hexagonal ferrites has attracted much attention for technological applications in wide range of frequencies. The electrical and magnetic properties make hexaferrites one of the important materials today[1,2]. The hexaferrites have a very good magnetic and dielectric properties that depend on several factors such as processing condition, sintering temperature and time, chemical composition and substitution of different cations[3-5]. The hexaferrites have been classified according to structure into six main classes: M-type, Y-type, W-type, Z-type, X-type and U-type. Y-type ferrite is a very useful in radar satellite, radar absorbing paint, industrial heaters, dryers multiplier chip inductors, LC filters and high power microwave devices[6]. Recently, Y-type ferrite fibres have been reported as a part of development of ceramic fibre[7].

In current research, the samples of Y-type cobalt substituted calcium hexaferrite have been synthesized by microwave induced sol-gel auto-combustion route. The influence of substitution of Co$^{3+}$ ion for Fe$^{3+}$ ion on the lattice constants, cell volume, X-ray density, bulk density and porosity of samples have been investigated.

Experimental:
Sample preparations:
The starting materials to synthesize cobalt substituted calcium hexaferrite samples with generic formula Ca$_{3-x}$Zn$_x$Fe$_{12}$xCo$_{3+}$O$_{22}$ are AR grade calcium nitrate, iron nitrate, cobalt nitrate, zinc nitrate and urea. The appropriate amounts of metal nitrates Ca(NO$_3$)$_{3}$·4H$_2$O, Fe(NO$_3$)$_{3}$·9H$_2$O, Co(NO$_3$)$_{3}$·9H$_2$O were dissolved in minimum amount of deionized water at the temperature of 50 °C placed in a beaker. These metal nitrates were used as oxidants. The fuel urea then added into the prepared aqueous solution. The initial composition of solution containing metal nitrates and urea was based on the total oxidizing and reducing valences of the oxidizer and the fuel using the concept of propellant chemistry [8].

The solutions as prepared in beaker were mixed together to form a homogeneous transparent aqueous solution. The aqueous solution was then heated into the micro-wave oven. After few minutes aqueous solution gets converted into wet gel by evaporating the water. After the wet gel reaches the point of spontaneous combustion, it begins burning and becomes a solid which burns at a temperature above 1000 °C. The combustion is not completed until all the flammable substances are consumed and the resulting material is a loose, highly friable substance exhibiting voids and pores formed by escaping gases during combustion reaction. The ash of cobalt substituted calcium ferrite was obtained after complete combustion. The ash was then ground in agate mortar and then pressed into pellets using PVA as binder. These pellets were finally annealed at 950 °C for 2 hour at a heating rate of 5 °C/min.

Characterization:
The phase identification of samples were carried out by using a Philips X-ray diffractometer (PW-1710) and Cu-Kα radiation with the wavelength λ = 1.54056 Å. The X-ray pattern showed the formation of a single phase of Y-type hexagonal ferrite without any impurity.
The values of lattice parameters $a$ and $c$ and the unit cell volume $V$ were calculated by using following equations.

$$
\frac{1}{d^2} = \frac{4l^2 + ak + k^2}{3a^2} + \frac{l^2}{c^2}
$$

(1)

where, $a$ and $c$ are lattice parameters

$$
V = 0.8666a^2c
$$

(2)

The experimental density (bulk density) $D$ of the samples was calculated using relation:

$$
\text{Density } D = \frac{\text{mass}}{\text{volume}} \ (gm/cm^3) \ (3)
$$

where mass of the sample was determined using digital balance and the volume was calculated by measuring the sample dimensions.

The theoretical density (X-ray density) $D_x$ was calculated from the relation:

$$
D_x = \frac{ZM}{N_AV} \ (gm/cm^3)
$$

(4) where $Z=3$ is the number of molecules for Y-type hexagonal unit cell, $M$ is the molar mass, $N_A = 6.023 \times 10^{23}$ (molecules per mole) is Avogadro’s number and $V$ is the unit cell volume.

The porosity $P$ is calculated using relation:

$$
P = 1 - \frac{D}{D_x} \ (5)
$$

where $D$ and $D_x$ are the experimental and theoretical densities respectively.

As these ferrites have very high resistivity, so the four probe method was employed to study DC electrical resistivity of the said ferrites system in the temperature range 300K to 873 K. The DC electrical resistivity of all the samples decreases with increasing temperature in accordance with Arrhenius equation[6]

$$
\rho = \rho_0 \exp\left(\frac{\Delta E}{k_B T}\right)
$$

(6)

where, ‘$k_B$’ is the Boltzmann constant, ‘$T$’ is temperature and ‘$\Delta E$’ is the activation energy, which is the energy needed to release an electron from the ion for a jump to neighboring ion, giving rise to the electrical conductivity.

The activation energy of the cobalt substituted calcium hexaferrites have been determined from the slope of plots of $\ln(\sigma)$ versus temperature ($1000/T$) above and below the transition temperature ($T_t$).

Results and discussion:

**XRD analysis**

The XRD patterns of the samples are shown in Fig 1. The crystallographic data are tabulated in Table 1. The XRD data are analyzed by using computer software PCPDF Win, PowderX and FullProf Suite. By comparing the patterns with JCPDS, the phases in the different samples are determined. It is being observed that most of the hexagonal grains are of same size. Using $2\theta$, the observed d-values and intensity calculations, d-value is recalculated and (h k l) planes are finalized. The values shown in the Table 2(a) and (b) confirm the formation of single phase Y-type hexagonal ferrites. The lattice parameters $a$ and $c$ are found to be 5.0418 and 44.1876 for the sample $Ca_2Zn_2Fe_{11.5}Co_{0.5}O_{22}$ and 5.0274 and 44.0628 for the sample $Ca_2Zn_2Fe_{11}CoO_{22}$. The space group for the samples is observed to be $R3m$ ( SG No. 166).

![Fig. 1: X-ray diffraction spectra (a) Sample $Ca_2Zn_2Fe_{11.5}Co_{0.5}O_{22}$ (b) Sample $Ca_2Zn_2Fe_{11}CoO_{22}$](image-url)


Table 1: Lattice constants a and c, cell volume V, X-ray density D_x, Bulk density D, and Porosity P of cobalt substituted calcium hexaferrite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>V (Å³)</th>
<th>Dₓ(gm/cm³)</th>
<th>D(b)(gm/cm³)</th>
<th>P(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca₂Zn₂Fe₁₁.5Co₀.5O₂₂</td>
<td>5.0274</td>
<td>44.0628</td>
<td>1232.32</td>
<td>2.1634</td>
<td>4.2583</td>
<td>49.20</td>
</tr>
<tr>
<td>Ca₂Zn₂Fe₁₁.5Co₁O₂₂</td>
<td>5.0418</td>
<td>44.1876</td>
<td>1242.93</td>
<td>2.9268</td>
<td>4.2168</td>
<td>30.60</td>
</tr>
</tbody>
</table>

Table 2: XRD data (a) Sample Ca₂Zn₂Fe₁₁.5Co₀.5O₂₂ (b) Sample Ca₂Zn₁₁.5Fe₁₁Co₂O₂₂

<table>
<thead>
<tr>
<th>2θ</th>
<th>dₓₓ</th>
<th>dᵧᵧ</th>
<th>I/I₀</th>
<th>h</th>
<th>k</th>
<th>l</th>
</tr>
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<tbody>
<tr>
<td>17.020</td>
<td>5.2182</td>
<td>5.223</td>
<td>8.5</td>
<td>0</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>18.150</td>
<td>4.8958</td>
<td>4.909</td>
<td>18.1</td>
<td>0</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>24.210</td>
<td>3.6823</td>
<td>3.682</td>
<td>11.5</td>
<td>0</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>28.665</td>
<td>3.1194</td>
<td>3.115</td>
<td>15.2</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>30.035</td>
<td>2.9501</td>
<td>2.956</td>
<td>30.6</td>
<td>1</td>
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<tr>
<td>33.46</td>
<td>2.6821</td>
<td>2.682</td>
<td>70.0</td>
<td>1</td>
<td>0</td>
<td>13</td>
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<tr>
<td>34.725</td>
<td>2.5876</td>
<td>2.599</td>
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<td>0</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td>35.675</td>
<td>2.5209</td>
<td>2.520</td>
<td>49.3</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>40.910</td>
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<td>15.2</td>
<td>0</td>
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<td>20</td>
</tr>
<tr>
<td>42.010</td>
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<td>2.159</td>
<td>14.7</td>
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<td>3</td>
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<tr>
<td>45.630</td>
<td>1.9914</td>
<td>1.994</td>
<td>14.1</td>
<td>2</td>
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<td>9</td>
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<tr>
<td>49.515</td>
<td>1.8439</td>
<td>1.841</td>
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<td>0</td>
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<tr>
<td>53.290</td>
<td>1.7219</td>
<td>1.712</td>
<td>13.6</td>
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<tr>
<td>54.125</td>
<td>1.6973</td>
<td>1.699</td>
<td>27.5</td>
<td>1</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>55.565</td>
<td>1.6567</td>
<td>1.650</td>
<td>15.2</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>59.325</td>
<td>1.5603</td>
<td>1.564</td>
<td>17.5</td>
<td>2</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>62.485</td>
<td>1.4888</td>
<td>1.486</td>
<td>28.3</td>
<td>1</td>
<td>1</td>
<td>24</td>
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<tr>
<td>64.045</td>
<td>1.4563</td>
<td>1.455</td>
<td>18.7</td>
<td>3</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

The lattice parameters a and c increases with increase in the concentration of Co³⁺ ions as shown in Table 1. The variation in lattice parameter with substitution is indicated of desired changes on crystallographic sites. It also implies that easy magnetized c-axis undergoes little more expansion than a-axis with Co³⁺ ions substitution. It is related to larger ionic radii of Co³⁺ (0.68Å) than Fe³⁺ ion (0.64Å)[9].

The X-ray density varies in the range of 4.2168 to 4.2583 gm/cm³ and porosity varies 30.60% to 49.20%. It was observed that experimental values of density D (Bulk density) to be in general less than those of Dₓ (theoretical density), which was expected due to presence of unwanted pores created during synthesis process. It was seen that introduction of Co³⁺ ions in hexagonal ferrites may affect the grain size development during firing process and decrease the porosity[10]. Thus it can be concluded that substitution enhance the firing process and increase the grain size to leading to decrease of porosity.

DC conductivity

Fig. 2 shows the graph of electrical conductivity ln(σ) verses temperature (10³/T) for all ferrites sample.
In the crystal structure, Fe ions hopping is ignored for the reason that small octahedral sites, tetrahedral-tetrahedral distance between metal ions at tetrahedral and metal ions at octahedral sites are smaller than mode of conduction as distance between two octahedral-octahedral hopping is the dominant represented as (TS) and (TS)

type hexagonal ferrites, which is structurally equivalent lattice sites. The widely studied Y-
distributed randomly over crystallographically present in more than one valence state, electrons between ions of the same element in Table 3 and are in the range of 23.8 to 30.8 basis of a Vervey hopping mechanism. The cobalt substituted calcium hexaferrite samples were synthesized by the microwave induced sol-gel auto-combustion route. The XRD data have confirm the formation of single Phase Y-type hexaferrites and the values of a and c of the sample supports this confirmation. The synthesized samples are semiconductors. The dc electrical resistivity as well as activation energy (E) decreases with increasing concentration of Co3 ions. The phenomenon of conduction in the prepared samples was explained on the basis of a Vervey hopping mechanism.

**Conclusion:**

The activation energies in case of CaZn2Fe12-xCo1xO22 ferrite have been constructed from the slopes of plots of electrical conductivity versus temperature above and below the transition temperature (Tt) and are given in Table 3. By increasing substitution about of Co3 ions, the activation energy decreases from 0.32 to 0.31 eV in paramagnetic region and from 0.23 to 0.21 eV in ferrimagnetic region. It can also be seen than the activation energy in the paramagnetic region is higher than that of ferrimagnetic region. There are several factors for such a variation in activation energy such as change in resistivity including the formation of other secondary phases and change in pososity of the samples. The decrease in porosity causes slight lose packing between the grains. The loose packing could have less retarding force on charge carriers which may lead to help in conduction of free electrons from grain to grain.

**Acknowledgement:**

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\[ E = k T \ln(t) \]

For the sample with a constant value of MΩ-cm. The substituted Co3 ions occupy Fe3 ions position preferable in octahedral sites [13]. As the content of Co3 ions increases there is a decrease in the Fe3 ions in octahedral sites. The number of Fe2 ions formed also decreases as this depends on the content of Fe3 ions. This reduces the hopping electrons between Fe3 and Fe2 ions, resulting in increase of resistance, but in the present series, it is seen that resistance decreases with substitution of dopent, it may due to the face that addition of Co3 ions may be converted to Co2 and vice-versa[14].

The linearity of conductivity in the graph breaks near the Curie temperature, indicative of two conductivity mechanism with different activation energy are present the ferrite compounds. This break from the linearity at transition temperature (Tt) may be assignment to the magnetic order phase transition from ferri to paramagnetic region. The electrical conduction in ferrite can be explained by Verway hopping mechanisms of electrical conductivity accordingly, electronic conduction in ferrites occurs due to hopping of electrons between ions of the same element present in more than one valence state, distributed randomly over crystallographically equivalent lattice sites. The widely studied Y-type hexagonal ferrites, which is structurally represented as (TS) and (TS)', (TS)”, where S is two oxygen layered block having chemical composition Fe3t2O2t2, while T is four layered block having chemical composition Co2t1Fe3t2O2t2. The symbol * indicates rotation of corresponding block through 120°, about the c-axis. In the crystal structure, Fe3t ions prefer six crystallographic site 6c6t, 6c6t, 6c6t, 6c6t, 18h6t and 3a6t, out of these six position, 6c6t and 6c6t are tetrahedral, while 6c6t, 3a6t, 18h6t and 3a6t are octahedral. Oxygen ions occupy 6c and 18h sites[11] Co ions prefix 3a6t, 18h6t and 3b6t sites[12]. The octahedral-octahedral hopping is the dominant mode of conduction as distance between two metal ions at octahedral sites are smaller than distance between metal ions at tetrahedral and octahedral sites, tetrahedral-tetrahedral hopping is ignored for the reason that small amount of Fe2 ions formed during materials synthesis which occupy only octahedral sites. Hence conduction may be taken to be the electronic hopping between Fe3 ions and Fe2 ions at octahedral sites.

The room temperature resistivity of the ferrites compounds at room temperature for all the samples of the series is enumerated in Table 3 and are in the range of 23.8 to 30.8
Table 3: Electrical resistivity and activation energy in Para and Ferri magnetic regions of cobalt substituted calcium ferrite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Room Temperature Resistivity $\rho$(M$\Omega$-cm)</th>
<th>Activation Energy $\Delta E$ (eV)</th>
<th>Trans. temp. $T_1$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$<em>2$Zn$<em>2$Fe$</em>{11.5}$Co$</em>{0.5}$O$_{22}$</td>
<td>30.3</td>
<td>0.23</td>
<td>0.32</td>
</tr>
<tr>
<td>Ca$<em>2$Zn$<em>2$Fe$</em>{11}$CoO$</em>{22}$</td>
<td>23.8</td>
<td>0.21</td>
<td>0.31</td>
</tr>
</tbody>
</table>

References: