The electrical, dielectric and magnetic effect of strontium-substituted spinel ferrites for high-frequency applications

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ABSTRACT
Strontium-substituted spinel ferrites were prepared using the sol–gel method. The sample’s chemical formula was Cu1–xSrxFexO4 (0.00, 0.20, 0.40, 0.60, 0.80 and 1.00). A cubic structure was discovered through X-ray diffraction (XRD) analysis. The lattice, constant, X-ray density and other structural parameters were increased with the substitution of strontium ion due to its larger ionic radius as compared with the ionic radius of manganese. It was discovered that the addition of strontium ions increased both activation energy and dc resistivity, whilst the decrease in resistivity with increasing temperature proved the semiconducting nature of samples. There was an abysmal disparity between the coerciveness and magnetization values. The permittivity was decreased with the addition of strontium ions. The low permittivity and high specific resistance suggested that prepared samples are suitable for high-frequency applications.

1. Introduction

The spinel ferrites have been manufactured a long time because of their variety of applications in technological and industrial fields. Their usage included drug shifting, spintronics, microwave absorption materials and the magnetic inspection of diseases. In some particular reactions, that is, alkylation, they were needed as catalysts [1,2]. The spinel ferrite compounds were improved according to the requirement by changing the following parameters: size and kind of outer element, engineering process, stoichiometric ratios, etc [3]. These spinel ferrite materials owned face-centred cubic (FCC) structure along with eight units in the solitary unit cell. The representative form for spinel ferrite materials can be inscribed as M8Fe16O32. The FCC lattice was formed by the arrangement of anions. The cations may stay in two kinds of inner spaces in the crystal lattice. There were 96 inner spaces in the solitary unit cell. Of which, there were 32 octahedral or B sites and 64 tetrahedral or A sites [4–6]. From the literature review, we found many articles related to spinel ferrite materials, their preparation processes and compositions with various stoichiometric ratios. Different materials were prepared with metal cations doping [7,8]. Following properties of spinel ferrites were found from previous literature: large stability and coercivity, moderate magnetization and hardness. Material chemists tried to substitute many divalent and trivalent ions in spinel ferrites and checked their improved features [8]. The spinel ferrites were used in different switching actions and microwave applications [9]. The chemical and thermal stability have been enhanced by the application of some outer ions in the spinel lattice. The improved catalytic and electronic features of spinel ferrites were noticed, and they were suitable for microwave applications [10–12]. Some divalent- and trivalent-substituted spinel ferrites have applications in the industry. Increased dielectric behaviour, complex magneto plumbite order and enough saturation and coercivity were particular features of spinel ferrites [13,14]. These substances may be used for the making phase shifters, isolators as well as circulators. These apparatuses were further incorporated in the military and commercial applications. In addition, they were used in telecommunication devices, microwave instruments and recording media [15]. The outer ion and microstructure of spinel ferrites would decide their magnetic performances.

The current investigation is about the substitution of strontium in spinel ferrites which is carried out by sol–gel route. The following are the advantages of this route over the other synthesis routes: low cost, reliability, ease to handle, highly fine particle size and homogeneity. The spinel ferrites can be supposed to
be best for high-frequency operating systems owing to their less dielectric losses as well as high dc resistivity.

2. Characterization and synthesis of strontium-substituted spinel ferrites

The sol–gel technique was used for preparation purposes. All the preparation details were displayed in the form of a flow chart, as given in Figure 1. Metallic organic and metallic precursors were used to precede the process. The main purpose of using sol–gel technique was their purest yield, requirement of lower temperature, standard stoichiometry and fine grain size, etc. [16,17]. Many other researchers also used this method for the production of spinel ferrites [18]. Nitrates of various chemicals were chosen. The citric acid was used as a chelating agent. The molarity of the mixture was kept at 0.01 M, and ratios of nitrates were set according to this molarity. One hundred millilitre of DI (deionized) water was taken in the beakers, and the raw chemicals in the nitrate form were poured in the beakers. The solution of citric acid was made separately within the 100 ml of DI water. The separate solution of each chemical was made and then stirred separately on a magnetic stirrer. The temperature of the magnetic stirrer was set at 80°C. The pH of the solution was handled by using NH₄OH solution. After continuous stirring for 3–4 h, the solution was altered into gel form. This gel is placed in the oven for 5 h at 450°C temperature to get brittle flake product with black colour. These flakes were grounded into homogeneous powder after much hard work for one hour by using a pestle and agate mortar. The furnace was used for pre-sintering of powder at 450°C which is increased by 15°C/minute. The product was placed in the furnace for 5 h. The powder is then converted into pellets. For this purpose, polyvinyl alcohol (PVA) was added as a binder. The PVA was mixed with water in a ratio of 1:2. The powder was placed under a hydraulic press. A load of 4 tons was applied for 120 s to get the pellets. The 13 mm diameter pellets were received. The cleaning of pellets was carried out with acetone. Binders were removed from pellets by keeping pellets in an oven at 250°C. Final sintering was carried out at 900°C for nine hours.

The X-ray diffraction was applied to the sample, and the results were obtained within 2θ range of 20°–70°. Different structural parameters were obtained by applying the Bragg’s Law which is written as [19]:

\[ 2d \sin \theta = n\lambda \]  

In this relation, the wavelength, Bragg’s angle and interatomic spacing were represented by \( \lambda \), \( 2\theta \) and \( d \), respectively.

The resistivity of spinel ferrites was examined through two-probe method. The exchange of holes and

![Flow chart of sol–gel method](image-url)
electron’s movements were the main factors that were considered for finding the resistivity [20]. A particular relation was used for determining the activation energy, and the Arrhenius plot was drawn.

\[ \rho = \rho_0 \exp \left( \frac{E_a}{K_B T} \right) \]  

(2)

In the equation of activation energy, ‘\( E_a \)’ indicates activation energy and ‘\( K_B \)’ shows the Boltzmann constant [21].

The magnetic investigations were completed through a magnetometer within the field of +2 to −2 kOe, and the M–H loop was drawn. A particular relation was used to obtain magnetic moments of samples.

\[ n_B(\mu_B) = \frac{M_w \times M_s}{\rho_b \times 5585} \]  

(3)

The molecular weight, saturation magnetization and the bulk density were denoted by \( M_w, M_s \) and \( \rho_b \), respectively. A simple relation was used to get the anisotropy constant \( K_1 \).

\[ K_1 \frac{M_s \times H_s}{0.96} \]  

(4)

3. Results and discussions

3.1. Structural properties

The X-ray diffraction patterns are displayed in Figure 2. The cubic spinel structure was confirmed, and no other phase was noted. The intensity of peaks declined with the addition of more strontium ion concentration. For all the well-defined peaks, the miller indices were 2 2 0, 3 1 1, 4 0 0, 4 2 2, 5 1 1/33 3 3 and 4 4 0. From these miller indices values and the value of \( d \), one can easily find the lattice parameter [22]. The increase of strontium concentration enhanced the value of lattice parameter ‘\( a \)’, as shown in Table 1.

\[ a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \]  

(5)

This increment in the value of ‘\( a \)’ is attributed as the bigger ionic radius of strontium as compared with copper ion. Moreover, the stretching capabilities were produced in the lattice due to the introduction of strontium. Thus, the unit cell becomes enlarged. The value of the lattice constant was also enhanced by the substitution of a bigger ionic radius in different spinel ferrites [21,22]. The crystallite size, bulk and X-ray density and percentage porosity were found through the following equations [23]:

\[ D_x = \frac{8 M}{N_a a^3} \]  

(6)

\[ D_m = \frac{M}{\pi \ell^2} \]  

(7)

Both bulk and X-ray density were enhanced with the addition of strontium content. The molecular weight of the substituted ion is larger than the based ion.

\[ P = 1 - \left( \frac{D_m}{D_x} \right) \]  

(8)

The percentage porosity was determined by using molecular weight value. The porosity value increased initially and then reduced as the strontium content enhanced. The reason for this initial upturn is the aggregated grains growth. It leaves the holes behind. Famous Scherrer’s relation was introduced to find crystallite size [24].

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  

(9)

In this relation, full width at half maximum, Bragg’s angle and wavelength were denoted by \( \beta \), \( \theta \) and \( \lambda \), respectively. The value of ‘\( D \)’ varies in-between 70 and 42 nm. The grain growth becomes restricted with the involvement of strontium. The finest particle size was achieved through sol–gel method. A set of Stanley’s equations were used to find the value of B–O and A–O (bond lengths of both sites), \( r_A \) and \( r_B \) (ionic radii of both sites), and the \( L_B \) and \( L_A \) (hopping lengths of both sites) [22].

\[ r_A = \left( \mu - \frac{1}{4} \right) a \sqrt{3} - r \]  

(10)

\[ r_B = \left( \frac{5}{8} - \mu \right) a - r \]  

(11)

\[ L_A = a_0 \frac{\sqrt{3}}{4} \]  

(12)

\[ L_B = a_0 \frac{\sqrt{2}}{4} \]  

(13)

\[ A - O = \left( \mu - \frac{1}{4} \right) a \sqrt{3} \]  

(14)

\[ B-0 = \left( \frac{5}{8} - \mu \right) a \]  

(15)

In these equations, the value of the standard oxygen ion factor is \( \mu = 3/8 \) and ‘\( a \)’ shows lattice constant [25]. All the found parameters were listed in Table 1. All these parameters show an increment in their values with the increase of strontium contents in the spinel ferrite materials.

3.2. Electrical properties

Resistivity is the property of a particular material that shows the opposition given to the moving electrons. The relation between resistivity and resistance is given by the following relation:

\[ \rho = \frac{R}{A} \]  

(16)

In this relation, ‘\( R \)’ is the resistance, ‘\( A \)’ denotes material’s thickness and ‘\( A \)’ signifies the effective area of examined samples. The defect reactions and the composition...
Figure 2. XRD pattern of all the samples.

Table 1. Structural properties of spinel ferrites.

| Composition | 0.0  | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 |
|-------------|------|------|------|------|------|------|
| a [Å]       | 8.35 | 8.37 | 8.40 | 8.43 | 8.44 | 8.45 |
| D_x [gm/cm³] | 5.39 | 5.43 | 5.47 | 5.53 | 5.59 | 5.62 |
| D_y [gm/cm³] | 4.23 | 4.26 | 4.29 | 4.31 | 4.35 | 4.39 |
| % Porosity  | 20.41| 20.62| 20.91| 21.20| 21.65| 21.95|
| Radius of A – site [Å] | 0.4541| 0.4630| 0.4657| 0.4749| 0.4776| 0.4812|
| Radius of B – site [Å] | 0.7315| 0.7421| 0.7487| 0.7560| 0.7585| 0.7632|
| Bond length of A-site [Å] | 1.8161| 1.8130| 1.8187| 1.8239| 1.8276| 1.8302|
| Bond length of B-site [Å] | 2.083 | 2.088| 2.098| 2.115| 2.139| 2.152|
| J_a [Å]     | 3.6141| 3.6251| 3.6374| 3.6489| 3.6513| 3.6595|
| J_b [Å]     | 2.9403| 2.9514| 2.9606| 2.9669| 2.9729| 2.9951|
| Crystallite size [nm] | 70 | 66 | 61 | 56 | 49 | 42 |

The resistivity values of strontium-substituted spinel ferrites are tabulated in Table 2. These values were obtained at room temperature condition. The strontium ions were added into spinel ferrites step by step, and the DC resistivity was found. A similar fashion of obtaining resistivity was applied by different researchers [17–19]. The behaviour of a material at various temperatures was found by using a two-probe method. It was observed that the resistivity upsurges with the involvement of strontium ions in lattice. This trend is shown in Figure 3. The divalent ions have a tendency to move towards tetrahedral sites, and strontium ions will try to move to octahedral sites [27].

Figure 4 consists of Arrhenius Plot. The complete electrical behaviour was understood by considering the Vervey’s Hopping phenomenon [28]. According to this phenomenon, the electrical conduction in ferrites is mainly because of electron movements between ferrous and ferric ions on octahedral sites. The hopping mechanism was linked with inter-ionic spacing and the activation energy. Inter-ionic distance at distinct sites is much larger than the inter-ionic distance of the same site. Hence, the conduction owing to ions present at the same site is more active than the conduction of ions at distinct sites. Therefore, it is suggested that the major conduction took place at octahedral or B site due to the existence of both Fe³⁺ and Fe²⁺ ions at B site. The slope
Figure 3. Room temperature resistivity as a function of strontium concentration.

of graph in Figure 4 gives the value of activation energy ($E_a$). The $E_a$ in spinel ferrites was mainly because of the movement of charges. Its value varied with the addition of strontium content in the lattice. The changing trends of both activation energy and the hopping phenomenon were observed to be similar. Furthermore, the $E_a$ and DC resistivity was behaved in a similar way to the addition of strontium.

### 3.3. Dielectric properties

The permittivity of samples was explained in Figures 5 and 6. Both real (Re) and imaginary (Img) parts of permittivity were discussed. The value of dielectric constant and dielectric loss was found to inversely relate with the applied frequency. In lesser frequency sections, the dielectric loss and dielectric constant rapidly decreased. However, with increasing value of frequency, this behaviour may change. It became independent upon frequency. Such type of trend can be easily explained with Koop's model [29]. In the Koop's model, the spinel ferrite materials were supposed to be composed of well-conducting grains. These conducting grains were detached by highly resistive borders [30]. As in a lesser frequency section, the grain boundaries were more effective [22]. Therefore, the dielectric constant has a maximum value in a less frequency section. Since the grains were more efficient than the grain boundaries in high-frequency region, dielectric constant possessed lesser values. Owing to the application of external electric field, the scattered electrons reside on resistive grain boundaries. The electrons collectively produce space charge polarization. Consequently, the dielectric constant achieved its highest value in lower frequency sections, and it suddenly reduced with the rise of frequency.

### 3.4. Magnetic properties

The varying applied field versus magnetization was displayed in Figure 7. The numerical value of applied field was in $+2kOe$ to $−2kOe$ range. The hysteresis loop was examined to calculate remanence and saturation magnetization, as well as the coercivity value. All these parameters were inscribed in Table 3. The magnetization values were declined with the addition of strontium. At tetrahedral site, the strontium ions were in abundance with its addition in spinel ferrites. The coercivity value increased with increase of Sr ions in base. The increased value of coercivity obeys the Brown's Relation [23]. The vibrational trend of coercivity and magnetization was opposite to each other. The saturation values were used to find $M_r$ to $M_s$ ratio or squareness ratio. The squareness ration remains below 0.5 showing the soft magnetic nature of samples. Anisotropy constant $k_1$ was found by using this formulation 4. Differences in the applied field and zero-field magnetization measurements are caused by magnetic anisotropy. The anisotropy constant is being increased in the present study. It exhibited the same characteristics as that of coercivity [27]. The magnetic moments of samples were determined through relation 3. The variation of magnetic moment was just similar to magnetization values. The reason behind this variation is the strong dependency of magnetic moment upon magnetization.
Figure 4. Temperature-dependent resistivity as a function of strontium concentration.

Figure 5. Dielectric constant as a function of frequency.
Figure 6. Complex dielectric constant as a function of frequency.

Figure 7. M–H loops of all the samples.
4. Conclusion

The spinel ferrites were successfully synthesized by sol–gel route. Every prepared sample has a cubic phase symmetry. The addition of strontium ion increased the lattice constant from 8.35 to 8.45. The resistivity value for all samples uplifted with the addition of strontium content in the order of $10^9$ $\Omega$ cm$^{-1}$. Activation energy varied in the same way such as resistivity. However, the resistivity reduced with the upsurge of temperature, suggesting the semiconducting behaviour of samples. The dielectric and magnetic parameters declined with the addition of strontium ions. The saturation magnetization decreased from 85 to 28 emu/g. Features such as less dielectric loss and greater resistivity value suggested their capabilities for the system that needs high frequencies for their operation.

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Data availability statement

Data sharing is not applicable to this article as no data sets were generated during the present study.

Disclosure statement

No potential conflict of interest was reported by the author.

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Table 3. Magnetic parameters of spinel ferrites.

| $x$ | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_C$ (Oe) | $M_r/M_s$ | $K_1$ (erg/g) | Magnetic moment ($\mu_B$) |
|---|---|---|---|---|---|---|
| 0.00 | 85.11 | 27.1 | 166 | 0.305 | 12854.32 | 2.39 |
| 0.20 | 75.88 | 23.2 | 191 | 0.3223 | 13676.16 | 2.31 |
| 0.40 | 59.32 | 20.8 | 244 | 0.3621 | 14381.32 | 2.22 |
| 0.60 | 50.33 | 18.5 | 292 | 0.3831 | 15771.11 | 2.14 |
| 0.80 | 37.26 | 16.7 | 328 | 0.4346 | 16455.19 | 1.97 |
| 1.00 | 28.27 | 14.1 | 368 | 0.4564 | 17974.57 | 1.78 |
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