Research Article

Synthesis and Characterization of $\text{Ca}_x\text{Sr}_y\text{Ba}_{1-x-y}\text{Fe}_{12-z}\text{La}_z\text{O}_{19}$ by Standard Ceramic Method

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The polycrystalline compounds with chemical formula $\text{Ca}_x\text{Sr}_y\text{Ba}_{1-x-y}\text{Fe}_{12-z}\text{La}_z\text{O}_{19}$ (CSBFLO) were synthesized via standard ceramic method. The chemical phase analysis was carried out by X-ray powder diffraction (XRD) method, which confirmed the formation of the magnetoplumbite phase belonging to ferrite structure. The frequency dependence of AC conductivity and dielectric constant was studied in the frequency range of 10 Hz to 2 MHz. The experimental results revealed that AC conductivity increases with increasing frequency, which is in agreement with Koop’s phenomenological theory. However, variation in dielectric constant required explanation in light of dielectric polarization. Magnetic characterization included studies of parameters such as $M_s$, $M_r$, $H_c$, and $T_c$, and results were explained via magnetic dilution and canting spin structure.

1. Introduction

M-hexaferrite is a hard ferrimagnetic material possessing magnetoplumbite phase of hexagonal structure which is widely used in various industrial applications. Along with M-hexaferrites, various other members like W, Z, Y, X, and U belong to this family and they can be distinguished as per their stoichiometry. However, M-hexaferrites have gained more attention because of their special characteristic of being magnetoplumbite in nature which leads to greater structural stability compared to other members. The general chemical formula by which M-hexaferrites are represented is $\text{MeFe}_{12}\text{O}_{19}$ where Me is the divalent alkaline metal cations and can be replaced by a suitable cation or their combinations. Among various hexaferrites, M-hexaferrite is preferred as permanent magnetic material due to its cost effectiveness, reasonable magnetic performances, and wide availability of raw materials needed for synthesis [1].

It finds numerous applications in diverse fields like high-density magnetic recording, microwave absorption devices, high power transmitters, high permeability ferrite components for digital switching equipment for the telecom requirement, high frequency microwave ferrites for VHF/UHF communication sets, defense radar requirement, and transmitter and receiver application in railway projects and can be used as building blocks for hexaferrite isolators [2–4]. The ferrimagnetic oxides with hexagonal crystal structure were first synthesized at the Philips laboratory in 1950 and were called hexagonal ferrites in order to distinguish them from the ferrimagnetic oxides with Spinel and Garnet structure [5]. The basic crystallographic and magnetic properties of the main hexagonal ferrites have been reviewed by Smit and Wijn [6]. The literature survey shows that a lot of works on various combinations of Sr²⁺, Ca²⁺, Ba²⁺, Pb²⁺, and La³⁺ as alkali earth metals cations have been carried out, which revealed the evolution of the uniaxial anisotropy in M-hexaferrite [7–17]. Furthermore, combination of Sr-La is found to be affecting positively the magnetic properties of the M-hexaferrites in comparison to Ba-La and Ca-La combination [18–21].

In addition to magnetic properties, the exhaustive work on dielectric properties of M-hexaferrites has also been reported by various researchers. Perieria and his group have shown that combined substitution of Sr²⁺ and Ba²⁺ in
M-hexaferrite possesses high value of dielectric constant with low loss in radio frequency range [22, 23]. High values of complex relative permittivity and low loss tangent for pure Ba-M hexaferrites have been reported by Mallick [24]. Deb Nath et al. have studied dielectric properties of Sr, La-M hexaferrite wherein high value of loss tangent is observed at lower frequency side [25].

From the literature review, it is depicted that very meager work is carried out on the simultaneous combinational effect of these cations, namely, Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, and La$^{3+}$, on electric, magnetic, and dielectric properties of the M-hexaferrites. Hence, attempt has been made to study the electric, dielectric, and magnetic properties of M-type hexaferrite with combined substitution of divalent ions Ca, Sr, and Ba (CSB) along with trivalent La with compositional formula $\text{Ca}_x\text{Sr}_z\text{Ba}_{1-x-y}\text{Fe}_{12-z}\text{La}_y\text{O}_{19}$ synthesized using standard ceramic method.

### 3. Results and Discussion

#### 3.1. Structural Analysis

The lattice parameters, X-ray density, bulk density, and porosity are calculated for each sample and are presented in Table 1. It is observed that not only the values of lattice parameter $a$ vary from 5.8079 to 5.9208 Å but also the lattice parameter $c$ changes from 22.7442 to 23.2143 Å. The XRD profiles of the standard M-hexaferrite are presented in Figure 1 along with the recorded X-ray diffraction patterns of all the samples. In comparison, the presence of reflection planes (006), (107), (114), (201), (108), (220), and (304) corresponding to pure magnetoplumbite phase of hexaferrite family which belongs to the space group P63/mmc was found (no. 194) [14]. The recorded values of lattice parameters also strengthen the results, as the values lie within the lattice parameter range ($a = 5.8-5.9$ Å and $c = 22-23$ Å) of pure magnetoplumbite phase of hexaferrite. Moreover, due to high sintering temperature, the intensity of the peaks becomes stronger and narrower, indicating a better structural quality of materials.

However, it seems that substitution of La$^{3+}$ for Sr$^{2+}$ ion leads to decreasing lattice parameters “$a$,” since La$^{3+}$ ion (1.13 Å) has ionic radius less than those of Sr$^{2+}$ (1.27 Å) ion. Hence, it was concluded that the lattice expansion is higher for the sample having lowest amount of La$^{3+}$ ion. Whereas overall variations of lattice parameter can be attributed to average ionic radius of substituted cations, as the ratio of $a/c$ has remained fairly constant. Similar behavior was

### Table 1: The structural properties of mixed M-hexaferrite samples.

<table>
<thead>
<tr>
<th>Code</th>
<th>$x$</th>
<th>$y$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$</th>
<th>$D_s$</th>
<th>$D_M$</th>
<th>Mol. Wt.</th>
<th>Porosity</th>
<th>$a/c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.7</td>
<td>5.8569</td>
<td>23.1070</td>
<td>686.45</td>
<td>5.32</td>
<td>4.13</td>
<td>1100.09</td>
<td>22.33</td>
</tr>
<tr>
<td>R2</td>
<td>0.1</td>
<td>0.4</td>
<td>0.5</td>
<td>5.8157</td>
<td>22.7836</td>
<td>667.35</td>
<td>5.42</td>
<td>4.02</td>
<td>1090.14</td>
<td>25.85</td>
</tr>
<tr>
<td>R3</td>
<td>0.1</td>
<td>0.6</td>
<td>0.3</td>
<td>5.8170</td>
<td>22.7823</td>
<td>667.61</td>
<td>5.37</td>
<td>3.99</td>
<td>1080.20</td>
<td>25.66</td>
</tr>
<tr>
<td>R4</td>
<td>0.25</td>
<td>0.2</td>
<td>0.55</td>
<td>5.8278</td>
<td>22.7442</td>
<td>668.97</td>
<td>5.43</td>
<td>3.96</td>
<td>1093.80</td>
<td>27.01</td>
</tr>
<tr>
<td>R5</td>
<td>0.25</td>
<td>0.4</td>
<td>0.35</td>
<td>5.8158</td>
<td>22.7633</td>
<td>666.78</td>
<td>5.39</td>
<td>3.87</td>
<td>1083.85</td>
<td>28.13</td>
</tr>
<tr>
<td>R6</td>
<td>0.25</td>
<td>0.6</td>
<td>0.15</td>
<td>5.8079</td>
<td>22.7410</td>
<td>664.32</td>
<td>5.36</td>
<td>3.83</td>
<td>1073.92</td>
<td>28.57</td>
</tr>
<tr>
<td>R7</td>
<td>0.4</td>
<td>0.2</td>
<td>0.4</td>
<td>5.8959</td>
<td>23.0741</td>
<td>694.63</td>
<td>5.19</td>
<td>3.97</td>
<td>1087.52</td>
<td>23.57</td>
</tr>
<tr>
<td>R8</td>
<td>0.4</td>
<td>0.6</td>
<td>0.0</td>
<td>5.8956</td>
<td>23.1369</td>
<td>695.71</td>
<td>5.14</td>
<td>3.81</td>
<td>1077.58</td>
<td>25.91</td>
</tr>
<tr>
<td>R10</td>
<td>0.4</td>
<td>0.1</td>
<td>0.6</td>
<td>5.9028</td>
<td>23.0910</td>
<td>696.76</td>
<td>5.23</td>
<td>3.89</td>
<td>1097.47</td>
<td>25.63</td>
</tr>
</tbody>
</table>
Figure 1: XRD pattern for the samples belonging to different composition (sample code).
reported in La$^{3+}$ substituted M-type strontium ferrites \[15-17\]. Hence, the behavior confirmed that interaction and solubility between Sr$^{2+}$ ion and La$^{3+}$ ion is higher than other divalent ions with La$^{3+}$ ion in the compounds.

The variation in the densities shows general behavior; that is, the X-ray density is higher than the apparent density. The densification of samples depends on oxygen ions which diffuse through the material during sintering process. The variation in porosity attributes to function of lattice parameters; it is reported that variation in porosity is inverse to variation in effective cross sectional area of grain-to-grain contact. This concludes that if densification increases, the volume of unit cell and lattice constant ultimately decreases and vice-versa \[23, 26\]. This showed a good agreement with our results.

3.2. Compositional Variation of Electrical Conductivity and Dielectric Constant. Electrical conductivity and dielectric constant, both are basically electrical properties and it has been recognized that the same mechanism, namely, exchange of electron between Fe$^{2+} \leftrightarrow$ Fe$^{3+}$, is responsible for variation in both properties. Figure 2 represents variation in electrical conductivity and dielectric constant with respect to compositions or sample codes (R-1 to R-10). An increase is observed along with the increasing substitution of Sr$^{2+}$ and La$^{3+}$ ion till compound R-7, which is further followed by a decrease up to R-10. The maximum value is obtained for electrical conductivity and dielectric constant for sample R7 (Table 2) having proportion of Ca$^{2+} = 0.4$, Sr$^{2+} = 0.2$, Ba$^{2+} = 0.4$, and La$^{3+} = 0.3$.

These results can be explained with small polaron hopping mechanism and Maxwell Wagner interfacial polarization. Both of the mechanisms deal with the production of Fe$^{2+}$ ions resulting from the partial substitution of Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ at octahedral site \[4f\] or \[2b\] and volatilization of substituted ions during sintering process. As the structure possessing cations and anions separately in tetrahedral site and octahedral site surrounded by oxygen ions (excluding only trigonal bipyramidal site) can be treated isolated from each other. Thus the localized electron model, namely, hopping mechanism, is more appropriate to discuss the condition mechanism rather than the band model. It is expected that till R7 the interaction and solubility of Sr$^{2+} \leftrightarrow$ La$^{3+}$ ion dominate semiconducting phenomenon, to compensate the charge neutrality at \[4f\] or \[2b\] site and produce electron transfer between Fe$^{2+}$ and Fe$^{3+}$ \[27\]. Moreover, in compound R-7, high value of electrical conductivity reflects transfer of maximum number of Fe$^{2+}$ ions which are involved in the phenomenon of exchange interaction between Fe$^{2+}$ and Fe$^{3+}$, giving rise to maximum conduction process. It may be due to high activation energy \(E_A = 0.31\) eV among the compounds having the high concentration of La$^{3+}$ ion along with Ba$^{2+}$.
and Sr$^{2+}$. As reported, the transition energy between Fe$^{3+}$ and Fe$^{2+}$ is 0.2 eV and if the activation energy of resistivity is greater than 0.28 eV, the energy is mainly utilized in moving the charges, not for the production of further charge carriers [26]. Hence, higher concentration of La$^{3+}$ ion, which resides at the grain boundaries, results in high mobility of charges and the decrease of Fe$^{3+}$ ion concentration, which ultimately enhances conductivity and reflects semiconducting behavior [28, 29]. However, further decrease in conductivity can be attributed to migration of Fe$^{3+}$ ions to 12k site due to higher substitution of Ba$^{2+}$ and Sr$^{2+}$, separately, along with La$^{3+}$ ion in M-hexaferrites, resulting in weakening the hopping mechanism and increasing resistivity [30]. Whereas, the high value of dielectric constant for the series of synthesized compounds is due to high conductivity. As it was already reported that sintered ferrites with high conductivity at low frequencies have a high dielectric constant [30].

3.3. Magnetic Measurements

3.3.1. Compositional Variation of Magnetic Parameters. In general magnetic moment found in the range between 43 and 70 emu/g, retentivity between 19 and 36 emu/g, and the coercivity between 1074 and 2905 G for all the samples confirming the good quality of samples are shown in Figure 3 and Table 2.

Taking these results into account, we can conclude that sample code R3 (having composition Ca = 0.1, Sr = 0.6, Ba = 0.3, and La = 0.1) has shown the maximum value for magnetic saturation ($M_s$), retentivity ($M_r$), and coercivity ($H_c$). The observed increase in saturation magnetic moment, retentivity, and coercivity showed high solubility and interaction between La$^{3+}$ and Sr$^{2+}$ as compared to Ba$^{2+}$ among the substitution. The increase in value of magnetization reflects the substitution of ions at spin down—sublattice at octahedral site [31, 32]. Whereas increase in coercivity can be explained by the loss of magnetocrystalline anisotropy and growth of large shape anisotropy in the magnetic particles [33]. However, substitution of nonmagnetic ion La$^{3+}$ increases for further samples having Sr$^{2+}$ contents constant, reflecting the decrease in magnetic parameters. This variation concerned with phenomenon known as canting spin structure plays its role, when there is the substitution of divalent ion by trivalent ion associates with a valency change of one Fe$^{3+}$ to Fe$^{2+}$ which reduces the strength of interaction. This results into the shift from collinear to non-collinear of magnetically hard axis, for example, c-axis in spin structure. This showed a relevant support to our results and also led to strengthening the assumption that exchange of Fe$^{3+}$ to Fe$^{2+}$ referred to octahedral sites and Fe$^{3+}$ anisotropy on the octahedral site could be dominant in all M-hexaferrites.

3.3.2. Curie Temperature. The variation of the Curie temperature $T_c$ (K) with composition for all the samples is shown in Table 2. It is observed that the Curie temperature $T_c$ (K) was higher in sample having lower amount of La$^{3+}$ ion. This trend may be attributed to the exchange interactions between different magnetic ions, concentration of these ions, and their magnetic moments. It is therefore expected that a greater amount of energy will be required to offset the effects of exchange interactions in the material having a larger number of magnetic ions. As the magnetic moment of La$^{3+}$ ion is 2.78 μB compared to the magnetic moment of 10 μB for the two Fe$^{3+}$ ions [34], this concludes that the replacement of Fe$^{3+}$ ions by lower amount of La$^{3+}$ ion and Sr$^{2+}$ is likely to increase hard magnetic properties and the Curie temperature. However, lower values for other samples can be explained on the basis of the number of magnetic ions present in the two sublattices and their mutual interaction. As Fe$^{3+}$ ions are gradually replaced by rare earth La$^{3+}$ ions, the number of magnetic ions begins to decrease at both sites, thus leading to a decrease of exchange interaction of the type Fe$^{3+}$ – O$^{-}$ – Fe$^{3+}$ [35]. 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 in the Curie temperature [29], which is in good agreement with our result.

4. Conclusions

The structural study of samples reveals that Ca$^{2+}$ does not replace Ba$^{2+}$ in proper quantity as compared to Sr$^{2+}$ and Fe ions. The substitution of La$^{3+}$ for Ba$^{2+}$ and Sr$^{2+}$ in M-type hexaferrite is associated with a valance change of Fe$^{3+}$ ↔ Fe$^{2+}$ at octahedral 2a or 4f$_2$ site. Among the samples having higher concentration of Sr$^{2+}$ with suitable concentration of La$^{3+}$ in M-hexaferrite shows largest variation in AC. Conductivity and dielectric polarization along with conduction enable us to conclude excess formation of Fe$^{2+}$ ion and dually supported by negative value of thermoelectric power. Due to such a high value of dielectric parameters, it can be very useful for application discussed like RAMs. Furthermore, in the magnetic studies we observed high values of magnetic parameters for La-substituted Ca, Sr, Ba, and M-hexaferrite.
(R3) are concerned with high interaction between La\(^{3+}\) and Sr\(^{2+}\) ions and also support the formation of single domain particles as the magnetization process takes place by spin rotation instead of domain wall displacement. These samples can be selected for the production of permanent magnets.

**References**


[17] Y. K. Hong, 1901 5th Avenue East, Unit 1322, Tuscaloosa, Ala, USA, 35401, US.


[34] O. Kubo, T. Ido, H. Yokoyama, and Y. Koike, “Particle size effects on magnetic properties of BaFe_{12−2x}Ti_xCo_xO_{19} fine particles,” *Journal of Applied Physics*, vol. 57, no. 8, Article ID 4280, 1985.
