Electromagnetic Properties of La-Co Substituted Zn$_2$Y Type Hexagonal Ferrite for Microwave Device Applications

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Abstract—In the recent decade, ferrites which possess low losses, good permeability, and permittivity, has been proposed as materials for microwave device applications. In this article, La-Co substituted Ba$_{2-x}$La$_x$Zn$_2$Fe$_{12-x}$Co$_x$O$_{22}$ (Zn$_2$Y-type) hexagonal ferrite was synthesized through conventional solid state reaction route with composition; $x$ equals to 0.0, 0.1, 0.3 and 0.5. The phase formation behavior and changes in crystal structure parameters of the ferrite with substitution were investigated using X-ray diffraction (XRD) analysis. Accurate lattice parameters were evaluated through Rietveld refinement of XRD pattern. The XRD, as well as SEM-EDS analysis, showed that there was the formation of lanthanum iron oxide phase at the grain boundary of the ferrite phase. The densities of the substituted ferrites were lower than the pure ferrite due to the formation of La-ferrite phase. The microstructural analysis showed the decrease in grain growth with an increase in the substitution. Both the permittivity and permeability were decreased with the substitution due to the decreased densification. In substituted ferrite, both the permittivity and permeability were in the range 11 to 18 and they were stable in the frequency range 1 to 500 MHz. The ferrites with $x = 0.1$ and 0.3 composition reveal to be very promising candidates for the design of antennas with good impedance matching to free space and miniaturization factor. A ferrite antenna was designed and antenna parameters were simulated.

1. INTRODUCTION

Due to the large anisotropy field of the hexagonal ferrites, they can be used at much higher frequencies compared to spinel or garnet ferrites. Hexagonal ferrites have high coercivity field ($H_c$), strong remanent ($M_r$) and saturation magnetization ($M_s$). These properties make them attractive for applications in recording media, medical equipment, data storage, electronic device components and microwave devices [1–3]. Depending upon crystal structure and chemical composition, the hexagonal ferrites are classified in to six different types of families such as M, Z, Y, W, X, and U-types [1, 2]. Among these families, the Y type hexagonal ferrite, having the preferred plane of magnetisation perpendicular to the c-axis and excellent soft magnetic properties, has been proposed as a potential material in very high frequency (VHF) and ultrahigh frequency (UHF) applications [4, 5]. The chemical composition of the BaMe$_2$Y ferrites is Ba$_{2x}$Me$_{2-x}$Fe$_{12}$O$_{22}$, where Me is a small divalent cation like Zn or Co or Ni or Mn. Among the different Y type ferrites the highest $M_s$ of 72 emu/g was found in Ba$_2$Zn$_2$Fe$_{12}$O$_{22}$ (Zn$_2$Y) ferrite [2], and $M_s$ decreases in the sequence Zn > Mn > Co > Ni [6]. Also, the hexagonal ferrites containing Zn have proven to be a material suitable for applications in high frequency devices due to its large initial permeability and low magnetic loss [7]. The effect of different substitution on electromagnetic properties of Zn$_2$Y ferrite have been extensively investigated by many researchers, such as Sr$^{2+}$ [8], Co$^{2+}$ [9], Cu$^{2+}$ [10], Cu$^{2+}$-Cd$^{2+}$ [11], Co$^{2+}$-Cu$^{2+}$ [5], Zn$^{2+}$-Cu$^{2+}$ [12], etc.

The microwave device characteristics of ferrite materials depend mainly on its permittivity and permeability. Yang Bai et al. [5] have studied the effect of Co-Cu substitution on the properties of Zn$_2$Y ferrites and reported that the magnetic anisotropy increases, permeability decreases, and the resonance frequency increases with Co substitution. Recently F. Kools et al. [13] reported that the intrinsic magnetic properties of SrFe$_{12}$O$_{19}$M-type ferrite could be improved by substituting La and Co for Sr and Fe respectively. E. H. Nejad et al. [14] reported the effect of La-Zn co-doping in Ni$_2$Y ferrites. It has been observed that the presence of La$^{3+}$ cation enhanced the soft magnetic properties and acted as grain growth inhibitors. However, no reports are available on the effect of La-Co substitution on the properties of Zn$_2$Y ferrite.

Recently the use of hexagonal ferrites as a substrate for loading of microstrip or patch microwave antennas have attracted the attention of many research groups as they offered variable and adjustable permittivity and permeability with the variation in composition [15–19]. The miniaturization factor ($n$) of an antenna as a function of relative permittivity ($\varepsilon_r$) and permeability ($\mu_r$) of
the ferrite substrate material is given by \( n = (\varepsilon_r \mu_r)^{1/2} \). Hence, the size of an antenna can be reduced significantly using the moderate value of \( \varepsilon_r \) and \( \mu_r \). Also, the characteristic impedance of the substrate material \( Z_i = Z_0(\mu_r/\varepsilon_r)^{1/2} \) should be close to the characteristic impedance of the surrounding medium \( Z_0 \) for proper impedance matching to get better efficiency of an antenna [17, 20]. The present work focuses on the synthesis and characterization of \( \text{La}^{3+} \) and \( \text{Co}^{2+} \) co-substituted \( \text{Zn}_2\text{Y} \) ferrites. The effect co-substitution on phase stability, changes in crystal structure parameters, microstructure, dielectric and magnetic properties of \( \text{Zn}_2\text{Y} \) ferrites were investigated. Based on the magneto-dielectric properties found in \( \text{La-Co} \) substituted \( \text{Zn}_2\text{Y} \) ferrites, an antenna was design and its properties were simulation.

2. MATERIALS AND METHODS

\( \text{Ba}_{2-x}\text{La}_x\text{Zn}_2\text{Fe}_{12-x}\text{Co}_x\text{O}_{22} \) ferrites with \( x = 0, 0.1, 0.3, 0.5 \) compositions were synthesized by solid-state reaction route. The raw materials \( \text{BaCO}_3, \text{Fe}_2\text{O}_3, \text{CoO}, \text{La}_2\text{O}_3, \) and \( \text{ZnO} \) were taken by the molar ratio and ball-milled for 12 h using IPA (propanol) media. Milled powder was dried and calcined at 1050°C for 4 h to get the pure phase ferrite. The calcined powder was further milled for 12 h to get fine particle size. The milled powder was granulated using 5 wt% PVA as binder. The granulated powder was pressed into the form of pellets (diameter 13 mm, and thickness 2 mm) and toroids (inner diameter 3 mm, outer diameter 7 mm and thickness 2 mm) using a uniaxial press at a pressure of 4 Tons. Finally all pressed samples were sintered at 1150°C for 4 h. The crystal structure and phase composition of sintered ferrite specimens was identified by X-ray diffraction (XRD). Microstructure was examined by field emission scanning electron microscopy (FESEM). The chemical composition of the specimen was determined from energy dispersive spectroscopy (EDS). The initial permeability, permittivity, as well as magnetic and dielectric losses, were measured by an LCR meter (Model: Agilent E4982A) in the frequency range of 1 MHz to 1 GHz. Based on the magneto-dielectric properties found in \( \text{La-Co} \) substituted \( \text{Zn}_2\text{Y} \) ferrites, an antenna was design and its properties were simulated using the Ansoft high-frequency structure simulator (HFSS) version 15.0.

3. RESULTS AND DISCUSSION

To investigate the effect of \( \text{La-Co} \) substitution on the change in crystal structure parameter of \( \text{Zn}_2\text{Y} \) ferrite, XRD analysis was carried out. Figure 1 shows the XRD patterns of sintered \( \text{Ba}_{2-x}\text{La}_x\text{Zn}_2\text{Fe}_{12-x}\text{Co}_x\text{O}_{22} \) ferrite. The diffraction peaks of unsubstituted ferrite specimen (Figure 1(a)) were indexed for \( \text{Zn}_2\text{Y} \) ferrite (JCPDS number: 44-0207), and no extra phase peaks were found in the pattern. In case of \( x = 1.5 \) specimens (Figure 1(d)), small amount of \( \text{Fe}_{12}\text{LaO}_{19} \) and \( \text{LaFeO}_3 \) phases were identified. This indicates that \( \text{La} \) is forming a secondary phase at higher substitution level. However, no secondary phase corresponding to \( \text{Co} \) has been found indicating the \( \text{Co} \) is substituting in ferrite lattice. The \( \text{Co} \) substation is feasible because \( \text{BaCo}_2\text{Y} \) ferrite is a well-known member of this group of ferrite.

Accurate lattice parameters of substituted ferrites were evaluated through Rietveld refinement.

Figure 1: XRD pattern of sintered \( \text{Ba}_{2-x}\text{La}_x\text{Zn}_2\text{Fe}_{12-x}\text{Co}_x\text{O}_{22} \) ferrite; (a) pure \( \text{Zn}_2\text{Y}, x = 0.0 \), (b) \( x = 0.1 \), (c) \( x = 0.3 \) and (d) \( x = 0.5 \).
of XRD pattern. Lattice parameters \((a\) and \(c\)), volume of unit cell, X-ray density of ferrite with La-Co content \((x)\) are shown in Table 1. In general, there was very little change in lattice parameters with substitutions due to the similar ionic radius of \(Co^{2+}\) to that of \(Fe^{3+}\).

The bulk density of sintered specimens was measured by Archimedes principle and values are shown in Table 2. The bulk density decreases with the substitution. That may be due to the formation of La-ferrite phase. Figure 2 shows SEM micrograph of \(Ba_{2-x}La_xZn_2Fe_{12-x}Co_xO_{22}\) ferrites. Two type grains are found. Hexagonal plates of \(Zn_2Y\) ferrite grains are bigger in size and there are small grains found in the grain boundary. Number of those small grains increases with increasing La-Co concentration \(x\). In order to identify the grain boundary phases, SEM EDS analysis was carried out. Figure 3 shows two respective EDS pattern of grain and grain boundary region. The EDS spectra of grain confirmed that the hexagonal plates are \(Zn_2Y\) ferrite phase. The EDS pattern of grain boundary material shows only La, Fe and O elements. This suggests that La is not able to substitute inside the crystal structure of \(Zn_2Y\) ferrite. The XRD phase identification also revealed the formation of \(Fe_{12}LaO_{19}\) and \(LaFeO_3\) compounds. In general, the grain size decreased with increasing La-Co substitution. It is known that La substitution act as a grain growth inhibitor in different ceramics. As La stays at the grain boundary by forming La-ferrite phase, the ferrite grain boundary migration or growth is impeded at the La ferrite phase boundary.

Figure 4 shows the frequency dependency of permittivity \(\varepsilon\), dielectric loss tangent \((\tan \delta_\varepsilon)\) in frequency range 1 MHz to 1 GHz. Permittivity is stable up to about 400 to 500 MHz (Figure 4(a)). Above 500 MHz there is an increase and followed by decrease in permittivity due to the ferroelectric resonance/relaxation processes, where the change in frequency is not being responded by the material. Figure 4 also shows that permittivity decreases with La-Co substitution in \(Zn_2Y\) ferrite. This is due to the decrease in bulk density with increase in substitution.

Table 1: Lattice parameters \((a\) and \(c\)), the volume of the unit cell, X-ray density, with La-Co content, \(x\) in \(Ba_{2-x}La_xZn_2Fe_{12-x}Co_xO_{22}\) ferrite.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(a) ((\AA))</th>
<th>(c) ((\AA))</th>
<th>Volume ((\AA^3))</th>
<th>(D_{X-ray})</th>
</tr>
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<tr>
<td>0</td>
<td>5.908</td>
<td>43.795</td>
<td>1323</td>
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<td>5.905</td>
<td>43.779</td>
<td>1322</td>
<td>5.39</td>
</tr>
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</table>

Table 2: Bulk density, permittivity, dielectric loss, initial permeability, magnetic loss, normalized impedance and miniaturization factor of \(Ba_{2-x}La_xZn_2Fe_{12-x}Co_xO_{22}\) ferrite at 100 MHz.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(d) (g/cc)</th>
<th>Permittivity (\varepsilon)</th>
<th>dielectric loss ((\tan \delta_\varepsilon))</th>
<th>Initial permeability ((\mu))</th>
<th>magnetic loss ((\tan \delta_\mu))</th>
<th>normalized impedance ((\mu\varepsilon^{1/2}))</th>
<th>miniaturization factor ((\mu\varepsilon^{1/2}))</th>
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<tbody>
<tr>
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<td>40.1</td>
<td>0.84</td>
<td>18.3</td>
<td>0.14</td>
<td>0.74</td>
<td>24</td>
</tr>
<tr>
<td>0.1</td>
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<td>11.7</td>
<td>0.18</td>
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<td>0.99</td>
<td>12</td>
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<td>0.05</td>
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<tr>
<td>0.5</td>
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<td>18.2</td>
<td>0.48</td>
<td>14.3</td>
<td>0.12</td>
<td>0.87</td>
<td>16</td>
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Figure 2: SEM micrographs of \(Ba_{2-x}La_xZn_2Fe_{12-x}Co_xO_{22}\) ferrite, (a) \(x = 0.0\), (b) \(x = 0.1\), (c) \(x = 0.3\) and (d) \(x = 0.5\).
Figure 3: EDS spectra of Ba$_{1.5}$La$_{0.5}$Zn$_2$Fe$_{11.5}$Co$_{0.5}$O$_{22}$ ferrite, (a) grain and (b) grain boundary regions.

Figure 4: (A) Permittivity and (B) dielectric loss factor variation as a function of frequency for Ba$_{2-x}$La$_x$Zn$_2$Fe$_{12-x}$Co$_x$O$_{22}$ ferrite, (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.3$ and (d) $x = 0.5$.

The dielectric loss decreases with La-Co substitution (Figure 4(b)) due to the decrease in permittivity. As it is known that the higher is the permittivity, the higher will be the dielectric loss. Figure 5 shows the frequency dependency of magnetic permeability ($\mu$) and magnetic loss tangent ($\tan\delta_\mu$) in the frequency range 1 MHz to 1 GHz. Here again, the permeability is stable up to about 300 to 400 MHz and the same decreases with increase in La-Co substitution. The decrease in permeability is due to the decrease in bulk density and lower magnetic moment of Co$^{2+}$ than Fe$^{3+}$. Table 2 summarizes the permittivity, dielectric loss, permeability, magnetic loss of Zn$_2$Y ferrite at a frequency 100 MHz.

Compared with the pure Zn$_2$Y ferrite, both magnetic and dielectric losses ($\sim 0.02$–$0.05$) of La-Co substituted ferrites were found to be decreased. In addition, almost equal values of permittivity ($\varepsilon \sim 12$) and permeability ($\mu \sim 12$) were obtained in the specimens with $x = 0.1$ and 0.3 compositions. The dielectric and magnetic properties of both $x = 0.1$ and 0.3 ferrite specimens have great potential as a antenna material due to its stable $\mu$, $\varepsilon$ and lower magneto-dielectric losses in a wide frequency range.

Figure 6 shows the frequency dependency of normalized impedance ($Z_i = (\mu\varepsilon^{1/2})$, miniaturization factor ($n = (\mu\varepsilon^{1/2})$, return loss ($S_{11}$) and gain for La-Co substituted Zn$_2$Y ferrite substrate. From the Figure 6(a), it is observed that $Z_i$ value for the both $x = 0.1$ and 0.3 specimen is almost 1 up to 800 MHz. This indicates that the characteristic impedance is almost equal to the impedance of free space in the wide frequency range which is a basic requirement for an antenna. Also, it
Figure 5: (A) Initial permeability and (B) magnetic loss factor as a function of frequency for Ba$_{2-x}$La$_x$Zn$_2$Fe$_{12-x}$Co$_x$O$_{22}$ ferrite, (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.3$ and (d) $x = 0.5$.

Figure 6: (A) Normalized impedance ($Z_i$) and miniaturization factor ($n$) for composition, (a) $x = 0.1$, (b) $x = 0.3$, (c) $x = 0.5$ and (B) return loss ($S_{11}$), gain versus frequency curve for proposed Zn$_2$Y ferrite substrate antenna; (a) $x = 0.1$, (b) $x = 0.3$ composition. Inset of (B) shows the designed structure of ferrite antenna.

was found that the value of $n$ is about 12 and 14 for the $x = 0.1$ and 0.3 composition respectively. These properties showed desirable characteristics required for the use as magneto-dielectric antenna substrate material in high frequency range.

The measured magneto-dielectric properties of the $x = 0.1$ and 0.3 specimens were used for the simulation of the antenna performance. The inset of Figure 6(b) shows the designed structure of ferrite antenna having ferrite substrate (5 mm × 18 mm × 2 mm) with the copper radiator of the line width of 1 mm patterned on it. The FR4 board (60 mm × 40 mm) with the copper ground size of 60 mm × 20 mm was used as baseboard, and a 50 Ω wave port was used as antenna feeding.

Figure 6(B) shows the simulated return loss ($S_{11}$) behaviour, and gain of designed antenna as a function of frequency for Zn$_2$Y ferrite substrate with $x = 0.1$ and $x = 0.3$ compositions. The antenna with $x = 0.1$ composition substrate shows the maximum return loss ($S_{11}$) of −12.6 dB at a resonant frequency ($f_r$) of 1.5 GHz and gain of 2.32 dB, bandwidth (−5 dB) of 170 MHz. However, $S_{11}$, $f_r$, gain and band width of antenna with $x = 0.3$ decreases to −8 dB, 1.49 GHz, 1.01 dB, and 80 MHz respectively. The better antenna performance of $x = 0.1$ composition is attributed to the low magneto-dielectric loss and equal $\mu$ and $\varepsilon$ compared to $x = 0.3$ composition. These simulated antenna parameter reveals that the $x = 0.1$ ferrite composition is a very promising candidate for the design of antennas with good impedance matching to free space and miniaturization factor.

4. CONCLUSION
La-Co co-substituted BaZn$_2$Y type hexagonal ferrites were synthesised through solid state route. XRD and SEM EDS analysis showed that there was the formation of lanthanum iron oxide phase at the grain boundary of the ferrite phase. The bulk densities of the ferrites decreased with the substitution due to the formation of grain boundary La-ferrite phases. The microstructure analysis
showed the decrease in grain growth with substitution due to the presence of La-ferrite phase at grain boundary. Both the permittivity and permeability decreased with substitution due to mainly lower densification and lower magnetic moment of Co$^{2+}$ than Fe$^{3+}$. Both permittivity and permeability were in the range 11 to 18 in substituted ferrite and the parameters were frequency stable from 1 to 500 MHz. From the magneto-dielectric properties observed, it can be concluded that the ferrite with $x = 0.1$ and $x = 0.3$ compositions are very promising candidates for the design of antennas with good impedance matching to free space and miniaturization factor. The simulated antenna parameter showed that the substituted ferrite material would be applicable for microwave antenna applications.

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