Structural, Dielectric and Mössbauer Properties of Mg$_{0.2}$Mn$_{0.5}$Ni$_{0.3}$Al$_{y}$Fe$_{2}$O$_{4}$ Nanoferries Prepared by Citrate Precursor Method

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Abstract

Polycrystalline Mg$_{0.2}$Mn$_{0.5}$Ni$_{0.3}$Al$_{y}$Fe$_{2}$O$_{4}$ ($y=0.0-0.10$) nanoferrites were prepared by citrate precursor method. Particle size decreases from 102.25 nm to 41.65 nm with increasing Al$^{3+}$ ions concentration. The unit cell parameter ‘a’ is found to decrease linearly with Al$^{3+}$ ions due to its smaller ionic radius. Theoretical lattice parameter ‘$a_{th}$’, volume ‘$V$’ of the unit cell, oxygen positional parameter ‘$u$’, ionic radii of A-site and B-site were determined. $^{57}$Fe Mössbauer measurements performed at room temperature shows a six line pattern for sample with larger particle size and a doublet pattern for sample with smaller particle size, owing to weakening of magnetic exchange interaction, which is indicative of their superparamagnetic nature. Dielectric constant and dielectric loss were determined in the frequency range 0.075 MHz – 30 MHz. Dielectric behaviours have been attributed to the Maxwell-Wagner type interfacial polarization.

1. Introduction

The iron oxide and substituted iron oxide nanomaterials known as spinel ferrites are used for magnetic memory and magnetooptical devices, as contrasting agents in magnetic resonance imaging, for refrigeration and as sensors. Spinel ferrites are still one of the basic materials of modern electronics and computers technology. When Fe$^{3+}$ ions are replaced by Al$^{3+}$ ions, the crystal structure becomes a cubic spinel structure. The addition of Al$^{3+}$ ions gives interesting Mössbauer spectra and drastically changes magnetic hyperfine fields and other Mössbauer and X-ray parameters. The aim of present work is to study effect of Al$^{3+}$ ions substitution on physical, electric and Mössbauer properties of Mg$_{0.2}$Mn$_{0.5}$Ni$_{0.3}$Al$_{y}$Fe$_{2}$O$_{4}$ nanoferrites.

2. Results and Discussion

XRD pattern of Mg$_{0.2}$Mn$_{0.5}$Ni$_{0.3}$Fe$_{2}$O$_{4}$ ferrite. Figure 1 indicate that material has a well-defined cubic single phase. Crystalline size was estimated using Scherrer’s formula and it decreases from 102.25 nm to 41.65 nm with increasing Al$^{3+}$ ions concentration.

![FIGURE 1. XRD pattern of Mg$_{0.2}$Mn$_{0.5}$Ni$_{0.3}$Fe$_{2}$O$_{4}$ ferrite.](image-url)

The radii of tetrahedral and octahedral sites were calculated, Table 1, using lattice parameter ‘a’ and equations given by Smit and Wijn [1]:

\[ R_{tetra} = \sqrt{3} (u - \tfrac{1}{4}) a - R_0 \]  
\[ R_{octa} = \frac{5}{8} - u \]  
\[ a_{th} = \frac{8}{3} \sqrt{3} \left[ (R_{tetra} + R_0) + \sqrt{3} (R_{octa} + R_0) \right] \]

Here $R_0 = 1.32$ Å is the radius of oxygen atom. Tetrahedral and octahedral site radii decrease continuously with increasing Al$^{3+}$ ions concentration. The oxygen positional parameter and theoretical value of lattice parameter were calculated using relations [2]:

\[ u = (R_{tetra} + R_0)/a/\sqrt{3} + 0.25 \]  
\[ a_{th} = \frac{8}{3} \sqrt{3} \left[ (R_{tetra} + R_0) + \sqrt{3} (R_{octa} + R_0) \right] \]

Figure 2 shows Mössbauer spectra of $y=0.0$ and 0.10 at room temperature. For $y=0.0$, Mössbauer spectrum exhibits a superposition of two Zeeman sextets, one sextet correspond to higher magnetic field attributed to Fe$^{3+}$ ions on B-site, and other sextet correspond to lower magnetic field attributed to Fe$^{3+}$ ions on A-site. Mössbauer spectra of $y=0.10$ is characterized by simultaneous presence of central paramagnetic doublet.

The difference between the paramagnetic and the ferromagnetic behaviour can be explained by super paramagnetic relaxation time ‘$\tau$’. Using equation:

\[ \tau = \tau_0 \exp \left( \frac{KV}{k_B T} \right) \]

Magnetic sextets corresponds to ferromagnetic particles of larger size and for these particles ($\tau > \tau_{obs}$). When $\tau$ is less than Larmor precession time $\tau_{obs}$ i.e. ($\tau < \tau_{obs}$) a super paramagnetic doublet is observed in Mössbauer
Presence of doublet alone in the Mössbauer spectra can be attributed to super paramagnetic relaxation due to extremely small size of crystallites [3].

There is no significant change in the values of isomer shift corresponding to Fe$^{3+}$ ions at A- and B-sites with an increase in Al$^{3+}$ ions concentration. This indicates that there is negligible influence on the ‘s’ electron charge density around Fe$^{3+}$ nuclei at both the sites. Quadrupole interaction has values close to zero for A-site and B-site. The hyperfine magnetic field at A-site and B-site shows a gradual decrease with increasing Al$^{3+}$ ions concentration. This can be explained on the basis of super transferred hyperfine field at central cation which originates from magnetic moments of nearest-neighbour cations. The introduction of Al$^{3+}$ ions, which replaces Fe$^{3+}$ ions from the B-site decreases intra-sub lattice contributions, which in turn decreases hyperfine magnetic field. Net magnetic field is due to dominant Fe$^{3+}$-$\text{A-O}^-$-$\text{Fe}^{3+}_B$ linkage, because A-B interaction is stronger than A-A and B-B interactions. The distribution of Fe$^{3+}$ ions amongst the A- and B-sublattices can be understood from the relation between the area ratio of B- to A-sites subspectra and (molar ratio) y, Table 2. The decrease of this ratio against y indicate that the substitution process often reduces the Fe$^{3+}$ ions number in the lattice at the expense of the number of Fe$^{3+}$ ions at the B sublattice.

Figure 3 shows the variation of dielectric constant and dielectric loss with frequency at different temperature of y=0.0. There is initial decrease in dielectric constant and dielectric loss with frequency followed by appearance of the resonance which may be due to matching of frequency of charge transfer between Fe$^{3+}$ - Fe$^{3+}$ ions and that of applied electric field. Dielectric constant of any material in general is due to dipolar, electronic, ionic and interfacial polarizations.

### TABLE 1. Structural parameters of ferrite samples.

<table>
<thead>
<tr>
<th>y</th>
<th>a(Å)</th>
<th>a0(Å)</th>
<th>(Å)$^3$</th>
<th>R$_{om}$</th>
<th>R$_{ov}$</th>
<th>u (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.399</td>
<td>8.397</td>
<td>592.53</td>
<td>0.5849</td>
<td>0.7294</td>
<td>0.3808</td>
</tr>
<tr>
<td>0.05</td>
<td>8.394</td>
<td>8.393</td>
<td>591.58</td>
<td>0.5860</td>
<td>0.7305</td>
<td>0.3807</td>
</tr>
<tr>
<td>0.10</td>
<td>8.390</td>
<td>8.388</td>
<td>590.71</td>
<td>0.5914</td>
<td>0.7364</td>
<td>0.3809</td>
</tr>
</tbody>
</table>

### FIGURE 3. Variation of (a) dielectric constant (b) dielectric loss (inset) with frequency at different temperature of y=0.0.

### TABLE 2. Mössbauer and dielectric parameters.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Area ratio (B/A)</th>
<th>1 MHz</th>
<th>1 MHz</th>
<th>Tan δ</th>
<th>Q-Factor (x10$^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>y = 0.0</td>
<td>0.710</td>
<td>214</td>
<td>3.9</td>
<td>0.0917</td>
<td>1.090</td>
</tr>
<tr>
<td>y = 0.05</td>
<td>0.556</td>
<td>207</td>
<td>1.9</td>
<td>0.643</td>
<td>1.555</td>
</tr>
<tr>
<td>y = 0.10</td>
<td>0.492</td>
<td>202</td>
<td>1.3</td>
<td>0.643</td>
<td>1.555</td>
</tr>
</tbody>
</table>

At low frequencies, dipolar and interfacial polarizations are known to play most important role. Both these polarizations are strongly temperature dependent. At high frequencies, electronic and ionic polarizations are main contributors and their temperature dependence is insignificant. Figure 3 [Inset], shows that dielectric loss decreases initially with increasing frequency which can be explained on the basis of Koops' phenomenological model [2,4], followed by appearance of a resonance with peak occurring at frequencies higher than 30 MHz.

**Conclusions**

Mössbauer spectra exhibit broad doublet with increasing Al$^{3+}$ ions concentration which suggest super paramagnetic nature and collapse of long range ferromagnetic ordering due to smaller particle size. Very low dielectric losses even at high frequencies make these materials suitable for microwave applications.

**References**


