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Effect of neodymium doping on microwave absorption property of barium hexaferrite in X-band

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\begin{abstract}
M-type barium hexaferrite (BaFe\textsubscript{12}O\textsubscript{19}) particles are synthesized by using sol-gel auto-combustion reaction for microwave absorption study in X-band. Three different materials namely BaNd\textsubscript{0.02}Fe\textsubscript{11.98}O\textsubscript{19} (Nd2), BaNd\textsubscript{0.04}Fe\textsubscript{11.96}O\textsubscript{19} (Nd4) and BaNd\textsubscript{0.06}Fe\textsubscript{11.94}O\textsubscript{19} (Nd6) have been developed by varying doping of neodymium in barium hexaferrite. The synthesis of particles has been confirmed using SEM micrographs and XRD diffraction pattern. The hysteresis study is carried out for saturation magnetization using vibrating sample magnetometer (VSM). As the doping concentration of neodymium increases, the saturation magnetization of the material is decreased from 47.272 emu g\textsuperscript{−1} to 16.479 emu g\textsuperscript{−1}. The vector network analyzer (VNA) is used for complex permittivity and complex permeability measurements of the developed materials. Nd4 material shows highest values of permittivity and permeability losses among other developed materials. From the complex permittivity and complex permeability, the reflection loss results of the developed materials have been calculated. The maximum reflection loss of −33.17 dB was obtained for 2.2 mm pallet of BaNd\textsubscript{0.04}Fe\textsubscript{11.96} and −10 dB bandwidth reaches 2.94 GHz.
\end{abstract}

\section{1. Introduction}

Increase in electronic and telecommunication sector has given rise to environmental problems like electromagnetic pollution and electromagnetic interference (EMI). Therefore, the demand for developing novel microwave absorbing medium has been largely increased (Vinoy and Jha 1995). Electromagnetic wave or microwave absorbers consist of specially engineered materials that by means of impedance matching and energy loss mechanism, reduce radiations or reflections from the surface of scatterer (Saville 2005, Huang et al 2015). Impedance matching of free space and material surface interface ensures maximum power transfer or minimum reflection of the electromagnetic wave. Further, the absorbed electromagnetic energy is attenuated by dielectric and magnetic losses of the material (Huang et al 2015). The microwave absorbers find applications in EMI shielding, anechoic chambers, cavity resonators and prevention of target detection from RADAR (Vinoy and Jha 1995, Dixon 2012). Hexaferrite materials, such as Strontium hexaferrite, Barium hexaferrite etc have been largely studied in literature for microwave absorption properties (Tyagi et al 2010, Trukhanov et al 2017, Tyagi et al 2018). Due to high magnetic anisotropy, hexaferrite materials find applications in high frequency region. However, the performance can be tuned to lower frequencies by doping of metal cations in place of Fe (Sözeri et al 2014). In present work, effect of neodymium (Nd) doping on barium hexaferrite has been studied for microwave absorption application in X-band (8–12 GHz) region. X-band region is used for short range detection and Radar communication. As compared to other frequency bands, X-band has low atmospheric interference and less commercial use which makes it more favorable to be used in military applications.
Barium hexaferrite is a hard ferrite having high magnetic uniaxial anisotropy and high saturation magnetization which makes it suitable for high frequency applications (Pereira \textit{et al} 2009). The molecular formula of barium hexaferrite is BaFe$_{12}$O$_{19}$, having a hexagonal magneto-plumbite structure (Pullar 2012). The methods for barium hexaferrite synthesis include solid-state reaction, hydrothermal reaction, co-precipitation method etc (O’Donoghue 1983, Liu \textit{et al} 1999, Shafi and Gedanken 1999, Huang \textit{et al} 2003, Cullity and Graham 2009). In current work, the barium hexaferrite particles are synthesized by sol-gel auto-combustion method using citrate precursors. Auto-combustion is an exothermic reaction in which the precursor materials are ignited at a low temperature that results in homogenous particles of low density. This method has benefits of high purity, high crystallinity and uniform particle size distribution over other reported method for barium hexaferrite synthesis. Also the processing time and processing cost is less than other reported methods (Sutka and Mezinskis 2012, Tyagi \textit{et al} 2012).

Neodymium is a rare earth metal that has paramagnetic nature at room temperature. Alloys of iron and neodymium exhibits ferromagnetic nature. Neodymium based alloys are widely used for manufacturing of strong permanent magnets for applications in hard drives, microphones, motors and generators etc. Other uses of neodymium include solid-state lasers, glass colorant, light flints and steel manufacturing. These properties make it a suitable candidate to be used as dopant in barium hexaferrite for microwave absorption applications. In present work, neodymium doped barium hexaferrite is synthesized by varying dopant concentration of neodymium in iron. The developed materials were casted in form of pallets and tested for microwave absorption in X-band.

2. Experimental procedure

2.1. Materials

Only AR/GR grade chemicals are used for synthesis without any further purification. Chemicals used for synthesis reaction are barium carbonate (BaCO$_3$, Merck $\geq$99%), iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O, Merck, $\geq$98%), neodymium (III) nitrate (Nd(NO$_3$)$_3$.6H$_2$O, CDH $\geq$ 99.9%), acetic acid (CH$_3$COOH, Merck, 100%), citric acid monohydrate (C$_6$H$_8$O$_7$.H$_2$O, Merck, $\geq$99.5%), ammonia solution (NH$_3$, Merck, 25%) and Mezinskis2012, Tyagi \textit{et al} 2012.

2.2. Synthesis of neodymium doped barium hexaferrite

Neodymium doped barium hexaferrite was synthesized by sol-gel reaction using the following equation:

$$\text{BaCO}_3 + x\text{Nd(NO}_3)_3.6\text{H}_2\text{O} + (12 - x)\text{Fe(NO}_3)_3.9\text{H}_2\text{O} \Rightarrow \text{BaNd}_x\text{Fe}_{12-x}\text{O}_{19}$$

For reaction solution (I) was prepared by completely dissolving barium carbonate (BaCO$_3$) into acetic acid solution. Nitrate solution (solution II) was prepared by adding Fe(NO$_3$)$_3$.9H$_2$O and Nd(NO$_3$)$_3$.6H$_2$O in minimum amount of D.I. water. Both solution (I) and solution (II) were mixed and citric acid was added to the solution in 1:1 ratio of metal ions. The resulting solution (III) was added with ammonia solution to maintain pH value to 7.0 and heated at a temperature of 80 °C until a dry gel is formed. The dry gel then goes through the self ignition reaction that resulted in low density, fine powder of neodymium doped barium hexaferrite. The detailed synthesis process is shown in figure 1. The obtained powder was crushed using P-7 premium line ball mill to obtain the final material.

3. Characterization studies

Ultima IV- Rigaku, powder x-ray powder diffractionometer (XRD) was used for structural analysis and elemental analysis of developed barium hexaferrite particles. Cu-K$_\alpha$ was used for excitation while scan rate and step size was maintained to 0.5s/step and 0.04°/step respectively. From Debye’s Sherrer formula, the crystal size of the barium hexaferrite particle was calculated. Field Emission Scanning Electron Microscope, FESEM (ZEISS GEMINI 300) was used for the morphological study of developed particles. Magnetic studies of the developed material were carried out using vibrating sample magnetometer (32KP Gauss meter, ADE Technologies) in magnetic field ranging from $-5$ to $+5$ kG at room temperature. For the reflection loss study, the developed powder was mixed with epoxy and hardener in 18% and 2% by weight respectively. The composite thus developed was molded into rectangular pallet of X-band size (22.86 mm $\times$ 10.16 mm). The thickness of pallet was maintained to 2.2 mm. The pellet formed is tested to S-parameters in X-band range (8.2–12.4 GHz) using Network Analyzer (Agilent E8364BPN series) and material measurement software 85071. The permittivity and permeability results obtained are used to calculate reflection loss curves, using the formula
Where

\[
RL = 20 \log \left( \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right)
\]  \tag{1}

\[
Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left( j \frac{2\pi f d}{c} \sqrt{\mu_r \varepsilon_r} \right)
\]  \tag{2}

4. Result and discussion

Figure 2 shows the indexed XRD patterns of BaFe_{12}O_{19}, BaNd_{0.02}Fe_{11.98}O_{19}, BaNd_{0.04}Fe_{11.96}O_{19} and BaNd_{0.06}Fe_{11.94}O_{19}. The XRD result concludes that the barium hexaferrite particles are synthesized in ‘as synthesis’ condition (JCPDS No. 01-072-0738) and there is no requirement of post calcination process. The 100% peak of barium hexaferrite is observed at 35.63° which corresponds to (114) plane. From the XRD pattern it can be seen that additional peak emerges at 27.85° when barium hexaferrite is doped with neodymium. This additional peak corresponding to the plane (222) is due to presence of additional Nd_2O_3 phase (JCPDS No. 00-021-0579). The intensity of peak corresponds to (222) phase indicates that the impurity phase is present in very less amount as compared to the desirable barium hexaferrite phase.

The FESEM micrograph (figure 3) shows barium hexaferrite particles of hexagonal plate like structures. This hexagonal plate like structure possesses high surface area which by means of interfacial polarization reduces the...
energy of EM waves. Hexaferrite materials with hexagonal morphologies are reported as potential material for microwave absorbers. The ferrite material being magnetic in nature results in agglomeration of particles. The average particle size is found to be 654.67 nm using ImageJ software.

From VSM results (figure 4), the high saturation magnetization of 47.272 emu g⁻¹ is observed for barium hexaferrite particles, which ensures the formation of barium hexaferrite in as-synthesis conditions. As expected, with increase in doping concentration of neodymium, the saturation magnetization of the barium hexaferrite particles follows decreasing trend. The lowest value of 16.479 emu g⁻¹ is observed for saturation magnetization of BaNd₀.₀₆Fe₁₁.₉₄O₁₉ particles.

Vector network analyzer (VNA) is used to obtain the permittivity and permeability results. The real part of complex permittivity and complex permeability represents storage whereas imaginary part represents losses. The complex permittivity and complex permeability graphs, as a function of frequency, are shown in figures 5 and 6 respectively. The maximum average value of real permittivity is obtained for Nd₄(13.41) composite followed by barium hexaferrite(5.57) and Nd₆(5.49). The minimum value is obtained for Nd₂(5.201). Similar trend was observed for imaginary part of complex permittivity where Nd₄ attains the maximum value of 6.157 followed by Barium hexaferrite(0.674), Nd₆(0.65) and Nd₂(0.614). The real permeability graphs shows maximum value for barium hexaferrite(1.046) followed by Nd₂(1.032), Nd₆(1.027) and Nd₄(0.967). The imaginary part of complex permeability however shows similar trend as complex permittivity with Nd₄(0.156) showing maximum average value followed by Barium hexaferrite(0.079), Nd₆(0.075) and Nd₂(0.070).

The average values of complex permittivity, complex permeability are shown in table 1.
For maximum power transfer or minimum reflection, the impedance matching of material with free space is calculated. The impedance is estimated from equation (2) and results are plotted (figure 7). The results depict that the impedance of Nd4 sample lies close to the impedance of free space (377 Ω). Therefore, it can be concluded that the Nd4 sample is best suited for minimum reflection.

Figure 8 shows the reflection loss results of the neodymium doped barium hexaferrite particles. The pure barium hexaferrite exhibits very low value of reflection loss i.e. −3.095 dB. On doping barium hexaferrite to Nd2, the reflection loss is further reduced to −2.58. On again increasing doping to Nd4, the reflection loss achieves the maximum value of −33.17 dB and the −10 dB bandwidth reaches 2.94 GHz. On further increasing doping concentration, the reflection loss is reduced to 2.942 dB. The increase in reflection loss property of Nd4 might be due to substitution of Nd3+ in place of Fe3+. This substitution induces change in the direction of magneto-crystalline anisotropy due to spin-orbit coupling (Jamalian et al 2015). With further addition of

| Property       | Barium Hexaferrite | Nd2     | Nd4     | Nd6     |
|----------------|--------------------|---------|---------|---------|
| $\varepsilon'$ (average) | 5.574 749         | 5.201 108 | 13.4199 | 5.499 935 |
| $\varepsilon''$ (average) | 0.674 949         | 0.614 047 | 6.157 263 | 0.658 92 |
| $\mu'$ (average)  | 1.046              | 1.032 118 | 0.967 825 | 1.027 325 |
| $\mu''$ (average) | 0.079 186          | 0.070 404 | 0.156 367 | 0.075 963 |
neodymium after ND4, the secondary phase of Nd$_2$O$_3$ becomes dominant in the material confirmed by increased intensity peak correspond to Nd$_2$O$_3$ phase (figure 2). The secondary phase causes the magnetic resonance of the material to decrease (Ghasemi et al 2008). As a result, the reflection loss decreases from Nd4 to Nd6. The reflection loss results are shown in table 2.

\begin{table}
\centering
\begin{tabular}{lccc}
\hline
Sample & Reflection Loss (dB) & Bandwidth (−10 dB) \\
\hline
BaFe$_{12}$O$_{19}$ & −3.095 & — \\
Nd2 & −2.58 & — \\
Nd4 & −33.17 & 2.94 \\
Nd6 & −2.942 & — \\
\hline
\end{tabular}
\caption{Reflection loss results of developed materials.}
\end{table}
5. Conclusion

Neodymium doped barium hexaferrite particles are synthesized successfully through sol-gel auto-combustion method. With increasing doping concentration, the saturation magnetization of the barium hexaferrite is reduced. Nd4 sample shows high value of magnetic and dielectric loss tangent. Also, the impedance matching is maximum for Nd4 sample. As a result, the Nd4 sample attains maximum reflection loss of 33.17 dB (99% absorption) and –10 dB (90% absorption) bandwidth covers 70% of the X-band from 8.2 GHz to 11.14 GHz.

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