Chapter 2

Literature review

2.1 Literature review

Extensive review of literature has been carried out in order to understand the method of synthesis and properties of hexaferrites, CCTO, and rGO. Also, different nanocomposites of rGO with other nanomaterials have been reviewed in details.

N. Adeela et al. (2016) investigated the effect of Mn-substitution on Co_2Y barium hexagonal ferrites with chemical composition $Ba_2Co_{2-x}Mn_xFe_{12}O_{22}$ (x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9) synthesized by hydrothermal method. The prepared sample was sintered at 950 ℃ for 3 hours. The prepared sample was characterised using FT-IR, XRD, EDX, and SEM. The grain size of the sample increases from few nanometres to micrometres with increase in Mn-concentration. The magnetic properties of prepared sample was improved as a result of substitution of Co^{2+} ions by Mn^{2+} ions which is due to the large values of magnetic moment of Mn^{2+} ions in comparison with that of Co^{2+} ions. The enhanced magnetics properties of the sample were found to be suitable candidate for perpendicular magnetic recording and high frequency application [82].

M. Ahmad et al. (2013) synthesized Co-substituted Mn_2Y barium hexagonal ferries with chemical composition $Ba_2Mn_{2-x}Co_xFe_{12}O_{22}$ (x = 0.0, 0.5, 1.0, 1.5, 2.0) by sol-gel auto-combustion method. Sintering of the prepared powdered sample and pellets was done at 1000 ℃ for 5 hours. The prepared sample was characterised using FT-IR, XRD, EDX FESEM, and DTA/TGA. Within the temperature range 30-100℃, DC electrical resistivity increases with increase in Co-substitution while dielectric constant decreases with increase in Co-substitution. The prepared samples shows high electrical resistivity as well as dielectric constant which make the prepared sample a suitable candidate for microwave device application. FESEM images show densification of the sample with increase in Co-substitution, this property is suitable for high frequency application [83].

M. Awawdeh et al. (2014) conducted magnetic and Mossbauer studies of M-type barium hexagonal ferrites with chemical composition $BaFe_{12-x}M_xO_{19}$ where M represents Gallium (Ga), Aluminium (Al) or Chromium (Cr). The sample is prepared via ball milling method, calcination was done at 1100 ℃ and characterisation was done using XRD, EDX, VSM, SEM and Mossbauer spectroscopy. Analysis of the characterisation result shows that coercive field increase whereas saturation magnetisation decreases with variation in the concentration of the dopants (Al, Cr and Ga). The high coercivity of the sample makes it suitable for production of low cost permanent magnet [84].

I. Ali et al. (2013) employ sol-gel method and synthesized La-substituted Co_2Y strontium hexagonal ferrites with chemical composition $Sr_2Co_2La_xFe_{12-x}O_{22}$ (x = 0.00, 0.05, 0.10, 0.15, 0.20) and study the influence of La^{3+} ions substitution on the magnetic and structural properties of the prepared sample. The prepared sample was sintered at 1100 ℃ for 5 hours at the rate of 3 ℃/min. The prepared sample was characterised using FT-IR, XRD, DTA/TGA, FESEM, and VSM. Magnetic properties such as coercivity and retentivity increase whereas saturation magnetization decreases with the variation in the concentration of La^{3+}. Since the coercivity of the prepared sample is a few hundred oersteds (Oe), then it may be useful in applications such as security, sensing, switching, high frequency and microwave devices [85].

T. Kaur et al. (2015) synthesized and studied the influence of calcination temperature on the microstructure, dielectric, magnetic and optical properties of M-type barium hexagonal ferrites with chemical composition $Ba_{0.7}La_{0.3}Fe_{11.7}Co_{0.3}O_{19}$ (T = 700 ℃, 900 ℃, 1100 ℃, 1200 ℃). The sample was synthesized via sol-gel auto combustion method and the techniques employed to characterise the prepared sample include FT-IR, XRD, VSM, TGA, UV–visible NIR spectroscopy FESEM. VSM analysis indicates that the increase in temperature increases properties such as saturation magnetization, remnant magnetisation and squareness ratio. It was observed that the sample calcinated at 900 ℃ have higher coercivity and anisotropy constant as compared to those calcinated at 700 ℃, 1100 ℃ and 1200 ℃. Optical studies show that the band gap of the prepared sample increases with La-Co substitution [86].

I. Ali et al. (2014) investigated the influence of calcination temperature on the microstructure, dielectric, magnetic and optical properties of M-type barium hexagonal ferrites with chemical composition $BaCr_xGa_xFe_{12-2x}O_{19}$ (T = 700 ℃, 800 ℃, 900 ℃, 1000 ℃). Synthesis of the sample was done using sol-gel auto combustion method and the techniques employed for the characterisation of the prepared sample are XRD, FESEM, EDX, TGA, DSC, and impedance analyser. The formation of single-phase M-type barium hexagonal ferrites was confirmed by XRD analysis in sample heat treated at 1000 ℃. With increase in applied frequency, the dielectric constant and dielectric loss tangent decreases while AC conductivity increases. Hence, the prepared sample can be useful in applications such as radar absorbing waves and reduction of eddy current in high frequency application [87].

Y. Bai et al. (2008) studied the dielectric and magnetic properties of Bi-Zn substituted Y-type hexagonal ferrites with chemical composition $Ba_{2-x}Bi_xZn_{0.8+x}Co_{0.8}Cu_{0.4}Fe_{12-x}O_{22}$ (x = 0.0-0.4). The sample was synthesized by solid-state reaction method and sintered at 900 ℃ for. Characterization of the sample was done using FT-IR, XRD, Impedance analyser, pA meter/dc voltage source and FESEM. Within the temperature range 30-100 ℃, DC electrical resistivity increases with Co-substitution while dielectric constant decreases with Co-substitution. Substitution of small amount of Bi reduces the formation temperature significantly and also enhances resistivity. Permittivity and permeability was observed to be stable in the measured range of frequency. The synthesized material can be used for hyper frequency application [88].

I. Ali et al. (2015) synthesize Sr-Co substituted Y-type strontium hexagonal ferrites with chemical composition $Sr_2Co_{2-x}Mn_xTb_yFe_{12-y}O_{22}$ (x=0.0 to 1.0 and y=0.0 to 0.1) via micro-emulsion method and sintered the prepared sample at 1050 ℃ for 8 hours. The influence of Tb-Mn substitution on the electrical properties of the prepared sample was investigated. The prepared sample was characterized via X-ray diffraction (XRD), impedance analyser and two probe. It was observed that with increase in Tb-Mn substitution, the activation energy and the crystallite size increases. The increase in crystallite size is as a result of grain growth occurring at high temperatures. Resistivity of the prepared sample increases with temperature which indicates semiconductor behaviour of the prepared sample. Initially, there is a sharp decrease in dielectric constant with increase in frequency while it decreases at higher frequency. It was observed that with increase in frequency, dielectric loss and tan δ decreases. The prepared material can be suitable for application in multi-layer chip conductor as a result of small dielectric loss and enhanced resistivity [89].

I. Ali et al. (2015) synthesize and studied the magnetic properties of Y-type hexagonal ferrite with chemical composition $Sr_2Co_{2-x}Ni_xEu_yFe_{12-y}O_{22}$ (x=0.0 to 1.0 and y=0.0 to 0.1) via surfactant assisted co-precipitation technique. Sintering of the sample was done for 8 hours at 1050℃. The prepared sample was characterised using FESEM and VSM. The high coercivity value (2300 Oe) of the prepared sample makes the sample potential candidate for perpendicular recording media (PRM) and high frequency application [90].

I. Ali et al. (2014) investigated the effect of Tb-Mn doping on the magnetic properties of Y-type hexagonal ferrites. The prepared sample having chemical composition $Sr_2Co_{2-x}Mn_xTb_yFe_{12-y}O_{22}$ (x=0.0 to 1.0 and y= 0.0 to 0.1) was synthesize via micro-emulsion technique and sintered at 1050℃ for 8 hours. The sample was characterised using VSM, EDX and FESEM. EDXS investigation indicate that the presence of Tb^{3+} and Mn^{2+} ensures the creation of more space in the T-block so as to incorporate Sr^{2+} ions and FESEM images show that the grain exhibit plate-like shape which is required for microwave absorbance application. It was observed from VSM analysis that both saturation magnetisation (M_s) and remanent magnetisation (M_r) decrease whereas coercivity (H_c) increases. The high value of the coercivity 3170Oe and 3195Oe for in-plane and out-plane respectively makes the prepared sample a suitable candidate for perpendicular recording media (PRM) [91].

I. Odeh et al. (2016) use sol-gel auto combustion method and prepared Zn-doped Y-type hexagonal ferrite. The prepared material with chemical composition $Ba_2Co_{2-x}Zn_xFe_{12}O_{22}$ (x=0, 1, 2) was heated-treated at 1100℃ for 4 hours. The sample was characterised using XRD, impedance analyser, FESEM and VSM. At room temperature, a decrease in the imaginary part of the impedance (Z') was observed at higher frequency whereas at lower frequency, an increase was observed with increase in zinc content. An increase in relative dielectric permittivity (ε' and ε") with increase in frequency was observed and high dielectric constant was observed at lower frequency. Cole-Cole plot obtained at different temperatures show a transition from behaviour of semiconductor for samples having x=0 and x=1 to behaviour of insulator for sample having x=2 [92].

Y. Bai et al. (2009) studied the role of Mn substitution on the properties of Y-type hexagonal ferrite. The sample with chemical composition $Ba_2Zn_{0.8}Co_{0.8}Cu_{0.4}Fe_{12-x}Mn_xO_{22}$ was synthesized via solid-state reaction method and sintered at 1050℃. XRD results show that varying the content of manganese does not destroy the formation of Y-type hexagonal ferrite and FESEM micrographs indicate that the samples have dense microstructure and plate-like grains with homogenous size. Also, varying the amount of manganese does not change the permeability of the sample. From VSM analysis, it was observed that varying the amount of manganese does not change the coercivity and saturation magnetisation. However, the prepared samples show good frequency stability with no dielectric resonance in the frequency test range. The sample with manganese doping of x=0.4 can be used for multi-layer chip inductor (MLCI) [93].

I. Sadiq et al. (2014) employ sol-gel technique and synthesized nano-sized Ce-Zn doped X-type and investigated its microwave absorbance characteristics in X-band. The prepared sample was sintered at 1250℃ for 6 hours. XRD and FTIR analysis of all the samples indicate single phase hexagonal ferrites structure. FESEM micrographs show that the prepared samples exhibit hexagonal plate-like grains. The grains orient in such a way that high permeability is observed and consequently results in improved microwave absorbance characteristics. An increase in saturation magnetisation with increase in amount of doping was observed in VSM analysis. This is as a result of replacement of Sr^{2+} by Ce^{3+} which improves magnetic interaction by producing internal stress. Electrical resistivity analysis indicates that the resistivity of Ce-Zn substituted sample is greater than that of the pure sample, as high as $\approx 10^9 \Omega cm$ value of resistivity was observed. The prepared sample can be used in multi-layer chip inductor (MLCI) and microwave absorbance application, and also in reducing eddy current losses [94].

Z. Yang et al. (2013) synthesized calcium copper titanate using sol-gel method. The prepared sample was characterized using XRD, FESEM, and impedance analyser. The role of sintering in air and in oxygen atmosphere on the dielectric and electrical properties of calcium copper titanate was investigated. Enhancement of activation energy for in grain electrical conduction results in reduced leakage, grain conductivity and the dielectric constant at low frequency for the sample sintered in oxygen atmosphere. The observed improvement of leakage under the influence of higher fields shows that the energy barrier for electrical transport is compensated by the strong electrical field [95].

J. Liu et al. (2007) used combustion and pyrolysis method to synthesize CCTO. The prepared samples were heat-treated at 600 °C, 700 °C, 750 °C and 800 °C for 1 hour and afterwards calcinated at 1030 °C and 1040 °C for 4 hours. The samples heat-treated at 600 °C, 700 °C and 750 °C show traces of TiO_2 (rutile), CuO and $CaTiO_3$. For the combustion method, the sample heat treated at 800 °C exhibit pure phase. FESEM images of the sample calcinated at 1030 °C shows grain sizes in the range 0.4 μm to 1.0 μm whereas the sample calcinated at 1040 °C show SEM images with large grain size (20 μm). For the pyrolysis method, the sample heat-treated at 800 °C exhibit some impurities which become absent after heat-treating the sample for another 1 hour. FESEM images of the sample calcinated at 1030 °C shows grain sizes in the range 0.5 μm to 1.5 μm whereas the sample calcinated at 1040 °C shows FESEM image with grain size of 3 μm. The dielectric constant of the sample prepared using combustion method was found to be 159330 while that of the sample prepared by pyrolysis was found to be 39008. The difference in dielectric constant for the two different methods does not indicate that one method is better than the other because the dielectric constant of calcium copper titanate depends on the microstructure of prepared sample [96].

M. Wang et al. (2014) synthesized CCTO using non-hydrolytic sol-gel method. The method was developed to overcome the limitation of the traditional sol-gel method such as uncontrolled amount of water used during hydrolysis and dependence of quality of the prepared sample on pH. The sample was heat treated at 400 °C, 600 °C and 800 °C for 2 hours, the sample calcinated at 800 °C exhibit pure phase with no impurity. The synthesized sample was characterised using FT-IR, XRD, TGA/DSC, FESEM and LCR meter. No weight loss was observed after 350 °C in TG graph. FESEM micrograph shows particle size in the between 350 nm t0 450 nm. The maximum value of dielectric constant at 1 kHz is 1.40×10^5 whereas the maximum value of dielectric constant at 10 kHz is 1.39×10^5. The maximum value of dielectric loss is 0.1 for 1 kHz and 0.092. The temperature range considered is 30 °C to 110 °C [97].

A. K. Rai et al. (2012) study the effect of substitution of tantalum on the microstructures and dielectric properties of $CaCu_3Ti_4O_{12}$. The sample was sintered at 900 °C for 6 hours. XRD patterns confirmed the formation of CCTO with little traces of TiO_2 and CuO. FESEM micrograph shows morphology with faceted grain-packed, the grain size vary from 150 nm to 1 µm. EDX spectrum confirm the substitution of tantalum. Capacitance, resistance and dielectric constant increases with tantalum substitution [98].

A. K. Rai et al. (2011) doped calcium copper titanate with iron and studied its dielectric properties. The sample was prepared using semi-wet method. The sample was calcinated at 800 °C and afterwards sintered at 900 °C. XRD patterns of the sample calcinated at 800 °C show traces of CuO whereas that sintered at 900 °C exhibit pure phase. SEM images show dense non-homogenous microstructure comprising of many small grains having size in the range 1 µm to 5 µm and little large grains separated by fine grains. The doping of Fe^{3+} at Cu site significantly reduces the dielectric constant [99].

L. Liu et al. (2008) prepared CCTO ceramics using sol-gel method. The samples were cold pressed into pellets and sintered at relatively low temperature and short sintering time as compared to solid state reaction method. The samples were first calcinated at 900 °C and then sintered at 1040 °C for 3 hours and 30 hours. Three samples were studied, they are (1) sample A: calcinated at 900 °C only, (2) sample B: calcinated at 900 °C and sintered at 1040 °C for 3 hours and (3) sample C: calcinated at 900 °C and sintered at 1040 °C for 30 hours. XRD patterns show pure phase of CCTO in sample B and C whereas sample A shows TiO_2, CuO and $CaTiO_3$ phases. FESEM micrograph of sample B shows duplex microstructure with grain size of 30 μm and isolated regions of fine grains with size less than 3 μm while that of sample C show uniform microstructure grain size approximately 22 μm and some bigger grains of 40 μm. Both sample B and C show similar dielectric properties. The permittivity of sample B is approximately 30,000 whereas that of sample C is approximately 60,000. This improvement in permittivity is attributed to the difference in microstructure and lattice parameters of the samples [100].

L. Liu et al. (2007) studied the heterogeneity of electrical properties of undoped calcium copper titanate prepared by sol-gel method. The sample was pre-sintered at 900 °C for 2 hours. Sintering of the sample was done at 1060 °C for 48 hours. XRD pattern of the sample sintered at 1060 °C for 48 hours exhibit pure phase of CCTO ceramics. FESEM micrograph of the sample sintered at 1060 °C for 48 hours indicate that grain growth with duplex microstructure comprising of large grains of size 100 μm. The isolated regions show fine grains of size less than 10 μm. Dielectric measurement show that the dielectric constant is greater than 28.000 over the frequency range 100 Hz to 100 kHz. This giant dielectric constant is attributed to the presence of thin re-oxidized grain boundaries on the outer surface of large semiconducting grains of the sample or possibly to a secondary phase at the grain boundary region [101].

S. Chang et al. (2012) substituted cerium in M-type hexagonal ferrites and studied its microwave absorption properties. Two samples ($BaFe_{12}O_{19}$ and $BaCe_{0.05}Fe_{11.95}O_{19}$) were prepared by sol-gel method. The samples were calcinated at 800 °C and characterised using XRD and VNA. XRD patterns show the formation of pure M-type hexagonal ferrites with proper substitution of the dopant. The lattice constant of $BaCe_{0.05}Fe_{11.95}O_{19}$ was found to be $a = 5.8947$ Å and $c = 23.2943$ Å which is a little bit larger than that of $BaFe_{12}O_{19}$. The variation was attributed to the difference in ionic radius of Ce^{3+} and Fe^{3+} which is 1.034 Å and 0.645 Å respectively. Microwave absorption studies were carried out in the frequency range 8 to 13 GHz. The real part of permittivity (ε') of $BaCe_{0.05}Fe_{11.95}O_{19}$ was found to increase with increase in frequency whereas a broad peak of value 1.73 at 12 GHz was observed in the curve of ε′′. The values of μ′ of $BaCe_{0.05}Fe_{11.95}O_{19}$ shows an increase behaviour with frequency whereas the values of μ′′ increases up to 0.969 at 9.9 GHz and then decreases. A minimum reflection loss of -37.4 dB at a frequency of 12.8 GHz and matching thickness of 3.5 mm was observed. This shows that $BaCe_{0.05}Fe_{11.95}O_{19}$ is a good microwave absorber material [102].

N. Zhang et al. (2016) employ facile temperature-free solvothermal approach coupled with thermal treatment procedure and synthesized nanocomposite consisting of hollow microspheres of $ZnFe_2O_4$, SiO_2 and reduced graphene oxide. The microwave absorption studies were carried out in the frequency range 2-18 GHz. Four different sample of the composite was prepared; they are $ZnFe_2O_4$, $ZnFe_2O_4/SiO_2$, RGO/$ZnFe_2O_4$, and RGO/$ZnFe_2O_4/SiO_2$. All the components of the composite were observed in the XRD patterns. SEM images show the hollow structure of the $ZnFe_2O_4$ with an irregular size of about 1μm. EDX spectra indicate the growth of SiO_2 on the surface of the hollow microspheres of $ZnFe_2O_4$ and the presence of Zn, Fe, C, Si and O in the prepared sample. Raman spectra show the two characteristics peaks at 1340 cm^{-1} (D-band) and 1590 cm^{-1} (G-band). RGO/$ZnFe_2O_4/SiO_2$ composites exhibit the highest reflection loss of -45.8 dB at a frequency of 7.6 GHz and absorber thickness of 3.7 mm. Below -10 dB, the reflection loss of RGO/$ZnFe_2O_4/SiO_2$ composites covers the frequency range 3.5-18 GHz. Hence, the material can be used from S to K_u band. It was also observed that the dielectric losses are dominant at high frequency whereas the magnetic losses are dominant at low frequency [5].