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Microwave study of CNTs-Fe_3O_4/Fe_2O_3 composites

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ABSTRACT

A comparative study of the microwave absorption and magnetic properties of CNTs-Fe_3O_4/Fe_2O_3 composite has been reported in paper. In that, CNTs-Fe_3O_4/Fe_2O_3 composites were prepared through chemical co-precipitation method, by dispersing the functionalized CNTs in ionic (Fe^{2+}/Fe^{3+}, in 1:2). The X-ray diffraction pattern confirms the composite phase formation without any trace of impurity. The small amount of prepared composite were annealed under argon atmosphere for 2 hours at 700°C and the microwave absorption properties of as such and annealed composites have been investigated at room temperature. The investigation results revealed that the microwave absorption properties and the saturation magnetization (Ms) of the CNTs-Fe_3O_4/Fe_2O_3 composites have been enhanced very much through annealing. The saturation magnetization value increases from 32.49emu/gm to 47.30 emu/gm on annealing of the CNTs-Fe_3O_4 composite.

KEYWORD: Composite materials, Magnetic materials, Chemical vapour deposition

1. INTRODUCTION

In the modern era, researchers have been keenly focused on the EMI shielding and microwave absorption based electronic properties of the materials useful for the civil and defence fields (Makeiff, 2006; Zhan, 2011; Meena, 2010; Meena, 2010; Zhao, 2009; Cui-ling Hou, 2013). The unique microwave absorption properties of carbon based materials lead them for the preparation of electromagnetic shielding and microwave absorbing composites (Kwon, 2002). Since after the discovery of the carbon nanotube by Ijimma in 1991, due to their large surface area and higher aspect ratio, these have been densely utilised in the synthesis of CNTs and iron oxide based composites for shielding purpose (Ma, 2005). The composites have excellent magnetic, electric and chemical properties along with wonderful stability. The various mathods have been used to modify the surface of CNTs and to coat them with magnetic materials. In earlier research, the Co/CNTs material has synthesized by catalytic pyrolysis method and shown good EM wave absorption properties (Zheng, 2008). Beside it, the CNTs/$CoFe_2O_4$ composites (Che, 2006), and MWCNTs/Fe_3O_4 material have also been focused due to their versatile application in the field of high-density magnetic recording media (Chou, 1994), microwave absorption (Zhan, 2011; Lin, 2007; Zhang, 2015; Liangjun Yin, 2015), and biomedicine (Huang, 2009). In various places, CNTs and iron based decomposites were synthesized by treating CNTs with sodium dodecylbenzene sulfonic acid in presence of Fe_3O_4 (Cao, 2006), through decomposition of ferrocene in presence of CNTs at different temperatures (Sun, 2005) and, filling CNTs with ferro fluid (Korneva, 2005). The negatively charged CNTs have also been coated with positively charged Fe_3O_4 particles by dispersing them in solution of Fe^{+2}/Fe^{+3} ions (Stoffelbach, 2005). However, various magnetic particles like $CoFe_2O_4$ (Pham-Huu, 2002), Nickel (Bao, 2002) and iron oxides (Karmakar, 2005) have been used in composites. The CNTs coated of magnetite (Fe_3O_4) and maghemite (Fe_2O_3) particles had promising application in biological technology (Gao, 2006), and targeted drug delivery. In presented research work explored the synthesis of CNTs-Fe_3O_4/Fe_2O_3 composites through the chemical co-precipitation route. For this, the acid treated CNTs were well dispersed in the precursor [Fe^{+2}/Fe^{+3}] ionic solution for the synthesis of Fe_3O_4. After the synthesis, the small amount of composites was annealed in argon atmosphere for 2 hours at 700°C. The microwave absorption properties of as prepared and annealed composites have been investigated in P-band (12.4–18 GHz) at room temperature.

2. EXPERIMENTAL

Synthesis and treatment of CNTs: CNTs were synthesized by chemical vapour deposition method using toluene as hydrocarbon source and ferrocene as iron catalyst precursor (Mathur, 2008) in inert argon gas at 750°-760°C and amorphous carbon was removed on oxidizing in air at 450°C degree for 45 minutes. As acid treatment of CNTs helped in the attachment of alcoholic and acidic functional group to their ends and surfaces. Thus, CNTs were treated with combined solution of HNO_3:H_2SO_4 and washed and filtered many times with water and dried properly.

Synthesis of CNTs-Fe_3O_4/Fe_2O_3 composites: The composite was prepared by dissolving 0.34g of acid treated CNTs in brown transparent solution having Fe^{+2} and Fe^{+3} ions in deionised water. The oleic acid was added and then co-precipitation done by using NH_4OH (25%) solution under constant stirring at pH 9-10. The several times washing of sample with water has removed the unwanted salt and the composite was obtained by drying samples at 70°C. The small amount of above prepared composite was annealed in argon atmosphere for 2 hours at 700°C. Thus as a set of as such and annealed composites have been prepared for the investigation.

Characterization: The phases present in the composites were analysed by using Rigaku make powder X-ray diffractometer (XRD) equipped with CuKα radiation at 0.02˚/s scanning rate in 2θ range 20-70° at 40 kV, 30 mA with automatic divergence slit. The morphological properties of composites have been investigated by scanning electron microscope (SEM) with Model-LEO 440. The electromagnetic shielding measurements have done by Agilent E8362B Vector Network Analyzer in P-band. The 15.8 x 7.9 x 6mm^3 copper sample holder has been used in measurements of shielding effectiveness. The magnetic measurements of composites were done by search coil method. A polytronic power supply (Model-BCS-1000), electromagnet (Type Hem-100) and flux meter (Model-FM109) were utilized for measurements. The set up was calibrated with Ni probe.

3. RESULTS AND DISCUSSION

XRD: The XRD patterns of composites were shown in Figure.1. The characteristic diffraction peaks at 26˚ (002) and 35˚ (311) confirms the presence of both phases i.e. CNT and Fe_3O_4 phase respectively. It can be seen that the hexagonal Fe_2O_3 phase (JCPDS Card No-080-2377) also present in the sample. The crystallite size corresponds to (311) peaks were calculated using well known Scherrer formula, $D=k\lambda/\beta\cos\theta$ (Manju Arora, 2010; Annveer, 2015). The average crystallite size varied in range of 12-16 nm as given in Table1. The XRD pattern shown that annealed composite was more crystalline than the unannealed composite. It may due to the effect of annealing temperature on grain size.

SEM: The SEM image of annealed composite has shown in Fig.2. It reveals that CNTs were perfectly covered with magnetic particles and thus may providing a strong magnetic interaction between CNTs and magnetic particles.

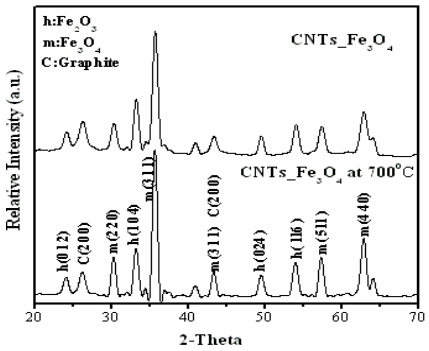

Figure.1.X-ray diffraction pattern of CNTs-Fe_3O_4/Fe_2O_3 composites

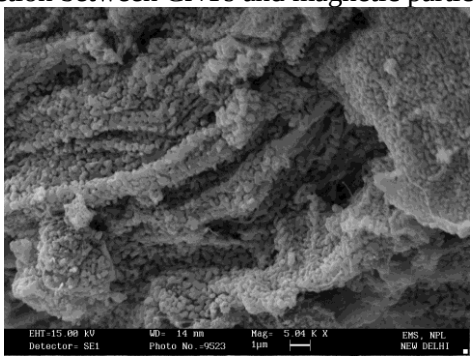

Figure.2.Scanning electron micrograph of annealed

Shielding effectiveness studies in P-band (12.4–18 GHz): The shielding effectiveness of the composites have been calculated (Annveer, 2015), and shown in Figure.3. At 15.0 GHz, the values of SE_A and SE_R for as prepared composites were 30.94 dB and 29.07dB, while for annealed composite 0.007dB and 0.0014dB respectively. The higher absorption and lower reflection property of the composites explored their utility as good microwave absorbing materials. The magnetic loss variation (μ_r''/μ_r') of composite has shown in Fig.4. The annealing caused the variation in magnetic loss from 0.22 to 0.36 at 15GHz and hence improved the microwave absorption properties of composite.

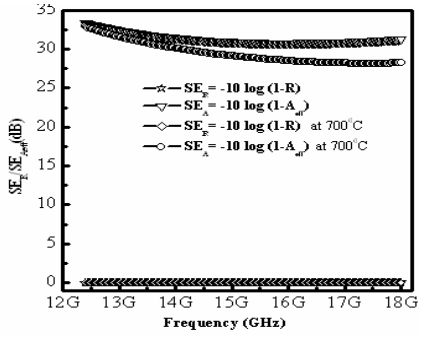

Figure.3.Shielding effectiveness of composites due to absorption (SEA) and reflectance (SER)

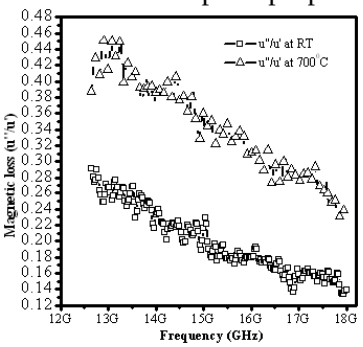

Figure.4.Magnetic losses of composites.

Magnetization measurements: The magnetization measurements were performed using search coil method at room temperature. The hysteresis loops of annealed and unannealed were shown in Fig.5. The coercivity (Hc), saturation magnetization (Ms) and remanence (Mr) of the composites were listed in Table 1. Thus saturation magnetization, coercivity and remanence of composites were increased on annealing. The saturation magnetization value increases from 32.49emu/gm to 47.30 emu/gm on annealing of the CNTs-Fe_3O_4 composite.

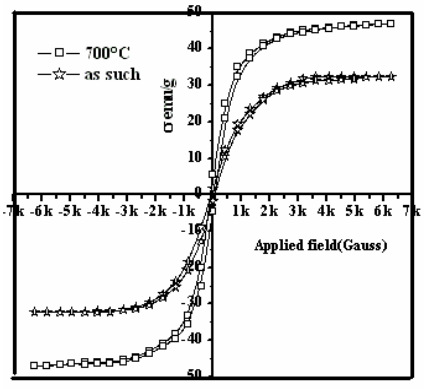

Figure.5.Magnetic measurement of composites.

Table.1.The structural and magnetic parameters of CNTs-Fe3O4 composite

Samples	Crystallite size (nm)	σ_s (emu/g)	Coercivity $H_c = (H_{c1}+H_{c2})/2$	Retentivity (emu/g)
CNTs-Fe_3O_4	12.79	32.49	62.73	1.68
CNTs-Fe_3O_4 (700°C)	15.22	47.30	78.88	4.41

4. CONCLUSION

CNT based magnetic composite has been prepared by chemical route. XRD confirms the presence of both the phase i.e. CNT and Fe_3O_4 in the material. The significant changes in conducting and magnetic properties of the composites have been observed due to annealing them. The enhancement in microwave absorption properties of composite may be due to the increase in crystallite size. These composites may be used as good microwave absorbing materials and also in absorbing paints made of insulating polymers.

5. ACKNOWLEDGEMENT

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