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Introduction

1.1 MOTIVATION

Microwaves (MW) are electromagnetic (EM) radiation with frequency ranging from 300 MHz to 300 GHz in general. These waves are used in satellite, cellular, radar communication etc. One could not imagine the world's technological advancement without MW radiation. Microwaves are comparatively coherent and polarized than visible light, yet comply with the optical laws (transmission, reflection, and absorption) [Bronwelland Beam, 1947]. Such specific characteristics make MWs useful for strategic applications e.g. detection of strategic military objects through radars at distances up to a few to hundreds of kilometers [Upton and Thurman, 2000], false/ghost images coming out from radar systems due to specular reflection. On the other side, MWs also have adverse effects on human health [Gupta, 1988; Banik *et al.*, 2003] and may also exhibit communicational interference between electronic devices leading to information losses.

The radar signature is mostly related to the Radar Cross Section (RCS) values of an object, which can be viewed as a comparison of the strength of the reflected signal (reflected power density) from a target such as ship and aircraft towards the radar to the signals intercepted (received power density) by the target [Knott *et al.*, 1993]. Thus RCS is an important parameter of any military object, particularly airborne systems, for strategic applications and needs to be reduced as much as possible for avoiding any radar tracking. An aircraft target is very complex, having many reflecting elements and shapes. Stealth, the technology for delay or denial of detection of a target, aims minimize the back reflections to the radar by either diverting away incident microwaves or by the absorption of MW using specially designed radar absorbing materials [Saxena, 2012]. With rapid advancements in antenna technology, today a wide range of radars are operating over a wide range of MW frequencies e.g. tracking radar (8-12.4 GHz & 12.4-18 GHz), surveillance radar (1-3 GHz) and various other types of radars [Locomme *et al.*, 2001] etc. are posing challenges to achieve the required levels of MW signature reduction using conventional radar absorbing materials. Further, with the rapid strides being made in the area of telecommunication technology, the MW radiation emitted by the large number of electronic devices are causing serious concern about the EM radiation pollution of the environment thereby demanding much more serious efforts for better radiation management in form of EMI shielding/suppression.

Microwave (MW) absorbing materials (MAMs) with wide band absorption capabilities have gained interest due to their potential in the development of radar absorbing products for RCS reduction of strategic military objects. These materials have special electromagnetic properties to attenuate/suppress the back reflected EM energy incident on the surface of the absorber layer by dissipating the magnetic/electric field of MW radiation into heat with hardly any noticeable temperature rise, since the energies involved are extremely small. The main desirable characteristics of these materials include strong MW absorption over a wide MW frequency spectrum, light weight, non-corrosive, environmentally stable, easy processing and application on targets etc. [Yanmin *et al.*, 2011]. These functional materials can either be used in the structures of the object or in the form of coatings/sheets, specially designed for reduced or tailored reflectance, emittance or absorbance to achieve the desired stealth properties. The advanced stealth aircraft like F-117A and B-2 bomber from North American Air Force are the excellent examples of very low detection by radars, achieved using the low RCS geometry as well as the potential functionality of materials applied on selected portions of the airframe. Worldwide concurrent efforts are going on to modify/improve the MW absorption capabilities of existing microwave absorption materials and to explore a new class of advanced materials to address the growing threat of advancements in MW/radar technologies [Folgueras and Rezende, 2008]. Being a highly classified domain, the stealth related technology is generally denied/undisclosed by almost all the countries, and there are very few reports and references available in the open literature however without much of details of information. The limitation of commercially available MW absorbing products and their export restriction compels for the indigenous design and development of such strategic materials for stealth applications.

Microwave absorbing materials are broadly classified into two categories viz. dielectric and magnetic [Petrov and Gagulin, 2001] based on their wave-matter interaction mechanism [Vinoy and Jha, 1996]. The dielectric materials include carbonaceous materials [Qin and Brosseau, 2012] viz. conducting polymers [Franchitto *et al.*, 2007], carbon black [Jung *et al.*, 2004], Carbon Nano Tubes (CNT's) [Micheli *et al.*, 2011], and non-carbonous materials viz. metal flakes, Barium Titanate [Zhu *et al.*, 2012; Jain *et al.*, 2013; Saini *et al.*, 2016] etc. The magnetic class of materials includes materials viz. carbonyl iron [Qing *et al.*, 2011], ferrites [Zhu *et al.*, 2011], magnetic metal particles etc. Dielectric materials are generally used for microwave absorption over relatively higher frequency range ~ 8-18 GHz due to domain polarization and corresponding relaxation in this range whereas magnetic materials are preferred for MW absorption over lower frequency MW frequency ranges ~ 2-12 GHz at lesser absorber thickness. There are numerous approaches to synthesize these materials. However, most of the reported synthesis methods have limitations of scaling up the process to produce a large quantity of MW absorbing materials, which is necessary for using them for any real applications. Also, the base materials cannot be used directly on target systems for MW absorption applications. Their formulation in the form of products is essential, which can be directly integrated in real target systems. The MW absorbing products can be in the form of coatings, sheets, structural materials, and Frequency Selective Screens (FSS) etc. Among these products, MW absorbing sheets show several advantages over conventional microwave absorbers viz. (i) Flexible, cut and paste type absorber products, which can be custom molded (ii) Their broadband return loss characteristics and (iii) Excellent mechanical strength (tensile and bending). These characteristics make absorber sheets useful for any surface. The elastomeric host matrix, which is used for fabricating these absorber sheets, may also provide entrapment for heavy filler granules in cross-linked rubber structure during mixing and vulcanization process which otherwise is not possible in liquid resin medium. Further, the filler-elastomeric host matrix interactions facilitate multiple scattering of MW radiation via suspended filler granules which may enhance the MW absorption properties in composites [Singh *et al.*, 2012, Saini *et al.*, 2016].

For the practical application of rubber based composites, the critical requirement of these include lesser absorber thickness with optimal MW absorption and flexibility for easy applications. Figure 1.1 shows the possible areas of application of MW absorbing products viz. in stealth technology for military aircrafts, suppression of EM pollution, protection from MW leakage from house hold devices and to provide EM clutter free environment for MW characterization.

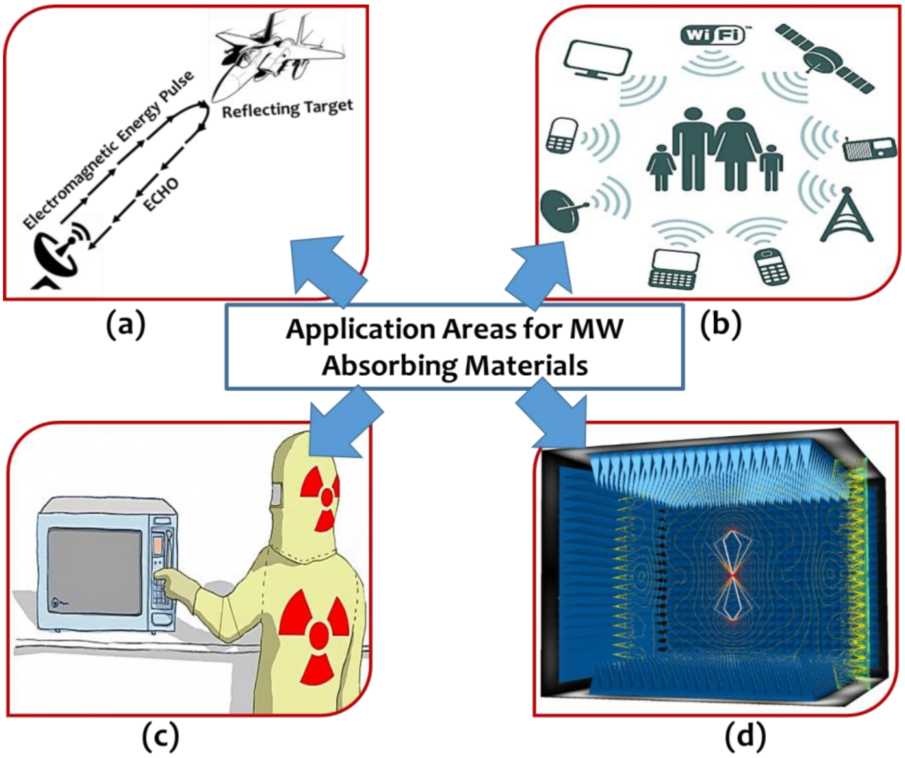

Figure 1.1 : Areas of application for MW absorbing materials (a) Stealth materials for RCS reduction of airborne objects (Source: Vinoy and Jha, 1996) (b) Attenuation of EM pollution (c) MW radiation shielding in house hold devices (d) Suppression of EM radiation during MW measurements (Source: Comsol)

1.2 OBJECTIVE OF THE THESIS

The thesis work is driven by the requirements for development of rubber based composites using conventional multifunctional materials for enhanced MW absorption capabilities over desired frequency bands, by tuning their structural properties. Simultaneously work has focused on exploring the new multifunctional materials for their microwave absorbing properties, interlinked with physical parameters for wide frequency bands. The objectives of these studies are to understand the basic MW loss mechanism in the pristine materials itself and also the effect of dispersion on the behaviour of functional filler materials, including dielectric, magnetic and magneto-dielectric multifunctional systems, in elastomeric matrix in the form of composite rubber sheet . The synthesis of these functional materials has been attempted for phase pure stoichiometric pristine systems and also structurally modified for MW absorption over discrete MW frequency bands e.g. 2-12.4 GHz (S, C & X-band), 12.4-18 GHz (Ku-band), 8-18 GHz (X & Ku-Band). The objective of the present study also includes the investigation of structure dependent physical properties, tuning of MW loss in different frequency bands, fabrication of rubber components by optimizing the filler loading concentration in the host matrix. The computation of reflection loss values has also been attempted to investigate the MW absorption properties vis-a-via matched absorber thickness in MW region of interest.

1.3 BRIEF RESULTS, SCOPE AND FUTURE PROSPECTS OF THE WORK

The extensive review of the literature has been carried out towards understanding the requirements of MW absorbing properties of materials, current status of research, and the commercially available products across the world. This also includes the current research on synthesis of a new class of materials including different synthetic approaches being followed for the preparation of filler materials, limitations of the currently available products for MW absorption etc. The research work performed during the present study has led to following major findings.

The $Ni_{1-x}Zn_xFe_2O_4$ (x=0, 0.25, 0.5 and 0.75) spinel ferrite powders were prepared by gel to carbonate precipitation route followed by annealing at 650°C, 950°C, and 1250°C, respectively for three hours each. The changes in structural and morphological properties of these ferrites were investigated with the varying substitution of Zn^{2+} ions in $Ni_{1-x}Zn_xFe_2O_4$. The magnetic properties and consequently MW absorption properties were observed to have optimal values at x=0.5 Zn^{2+} ion concentration and found to reduce further beyond Zn^{2+} ion concentration. The Acrylo-Nitrile Butadiene Rubber (NBR) based composites with impregnation of identified $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite powder with different loading fractions in the range 50-80 weight percentage (wt%) have been prepared. The effect of loading fraction and thickness of the composite on MW reflection loss characteristics over 2-12.4 GHz (S, C and X-bands) has also been studied. From the computational reflection loss studies it has been found that the 80wt% ferrite powder loaded rubber composite shows two matching frequencies corresponding to thickness values of ~3.25 mm and 4.6 mm at frequencies ~10 GHz and ~5 GHz, respectively. The onset of first matching frequency (fm_1) ~5 GHz is due to the relaxation of spin resonance and that of second matching frequency (fm_2) ~10 GHz is attributed to quarter wavelength thickness of the rubber based composite. Therefore, the developed absorbers can be used for dual MW absorption application in different frequency bands at different thicknesses.

Graphite encapsulated Ni nanoparticles were synthesized using the pyrolytic decomposition of nickel hydroxide nanocomposite at elevated temperatures of 550°C, 700°C, and 850°C under inert ambient. The core-shell structure, having Ni nanoparticles as a magnetic core and graphitic dielectric shell, has been confirmed by X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) studies. This hybrid structure facilitates the attenuation of MW radiation due to interfacial polarization between core and shell boundaries. MW characterization was carried out for real and imaginary permittivity, loss tangent and dispersion behaviour. The 850°C annealed sample was dispersed in NBR at different loading fractions, in the range of 40-75 wt%. The computed reflection loss for 70wt% loaded rubber composite show >10 dB over Ku-band (12.4-18 GHz) at absorber thickness in the range of 1.0-1.5 mm. Loading of functional filler powder beyond 70wt% in rubber composite, reduces the reflection loss values due to the impedance mismatch at absorber surface. This material system provides significant MW absorption at quite low absorber thicknesses over 12.4-18 GHz (Ku-band).

Ferroelectric materials exhibit spontaneous polarization effects because of electric dipoles, which may be harnessed for MW absorption due to the dipolar relaxation at these frequencies. However, in this context there very few reports available in the literature for this class of materials. In the present study, pure tetragonal phase barium titanate ($BaTiO_3$) powders were prepared by solid state reaction of oxide precursors followed by annealing of the samples in a temperature range of 700-1100°C. The tetragonal phase of $BaTiO_3$ was confirmed by XRD and Raman spectroscopic studies. The $BaTiO_3$ powder annealed at 1100°C was identified as the filler material for making rubber sheets due to its higher loss tangent values as compared to other annealed samples. It was observed that the increase in filler loading fraction (50-80wt%) showed not only the increase in reflection but also resulted into the reduced MW absorber thickness corresponding to optimal reflection loss. Further, all the $BaTiO_3$ loaded samples showed dual band MW absorption at particular thicknesses, over the frequency range 8-18 GHz. The 80wt% loaded $BaTiO_3$ sample showed MW absorption at ~9.5 GHz and ~16.5 GHz with reflection loss values ~ -9 dB and ~ -18 dB, respectively. Therefore, this type of absorber can be useful in MW absorption application in both X-band and Ku-band, simultaneously. $BiFeO_3$ multiferroic powder having ferroelectric as well as weak ferromagnetic behavior, was prepared by sol-gel process followed by sequential annealing at 350°C and 600°C for 1h each. Confirmation of $BiFeO_3$ pure phase materials was done with the help of XRD and FTIR studies. Further, different $BiFeO_3$ filler loaded rubber composites (50-80wt%) show onset of dual band MW absorption starting from the filler loading of 70wt%, due to sufficient ferroelectric interaction in the materials system.

Z-type cobalt substituted strontium hexaferrite ($Sr_3Co_2Fe_{24}O_{41}$) was synthesized by gel to carbonate precipitate route. The complex geometrical structure of Z-type Sr hexaferrite and simultaneous co-existence of different crystallographic phases posed challenges for the synthesis of a crystallographically phase pure material. In addition, the stochiometric control of chemical composition is another challenge for such materials. An innovative sequential heat treatment process including controlled annealing at 650°C, 950°C, and 1250°C, has been established to get the phase pure ferrite materials in desired crystallographic phase. The pure Z-phase ferrite material showed improved saturation magnetization (M_s) and MW loss tangent values as compared to the M and W-phases ferrite materials. It has been observed that the thickness of rubber composite corresponding to optimum MW absorption has reduced significantly as compared to $BaTiO_3$-NBR system over the frequency range 8-18 GHz, with filler loading concentration in the range 50-80wt%.

The developed materials and their rubber based composites are highly useful in strategic stealth applications for defence sector as well as for other MW absorption applications in civil sectors, as discussed earlier. Further, the synthetic methods used for bulk materials preparation and process adopted for fabrication of rubber based MW absorbers, are reproducible and scalable for mass production. The carried out thesis work may be useful to realize the real time application for different MW frequency bands. Further, the present thesis work may also provide insight to researchers and developers, for further exploration of other structure dependent MW absorption properties of reported material systems.

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