PREPARATION AND CHARACTERIZATION OF U-TYPE HEXAFERRITES FOR MICROWAVE ABSORPTION

RAM SWAROOP MEENA

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

RAM SWAROOP MEENA

Department of Physics

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Dedicated to the sweet memory of my father

(Late) Shri Gainda Ram Meena

CERTIFICATE

This is to certify that the thesis entitled "**Preparation and Characterization of U-type Hexaferrite for Microwave Absorption**" being submitted by **Mr. R. S. Meena,** has been prepared under my supervision in conformity with rules and regulations of the **Indian Institute of Technology Delhi**. I further certify that the thesis has attained a standard required for the award of a degree of **Doctor of Philosophy** of the institute. This work, or any part thereof, has not been submitted elsewhere for the award of any other degree or diploma.

Prof. Ratnamala Chatterjee

Physics Department

Indian Institute of Technology Delhi

New Delhi 110016, India

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ABSTRACT

The present thesis explores the formation and characterization of U-type hexaferrite microwave absorbing materials (MAM) in X-band (8.2-12.4 GHz) frequency range. Microwave (MW) is a part of the electromagnetic (EM) spectrum, is the frequency range from 0.30 to 300 GHz or one meter to one millimeter wavelength. MW have been standardized in many frequency bands such as L, S, C, X, K, Ku and Ka known as radar frequency bands. Due to the wideband characteristic of MW, it can be used to process or transfer enormous information at a time; hence the use of MW bands has increased enormously for the growing traffic/crowding in lower VHF/UHF bands. Today we cannot think of life without mobile/cellular phones which work in MW bands. The rapid growth in use of cellular phones and other wireless devices have further added to problem of electromagnetic interference (EMI). EMI is a cause of disturbances on electronically controlled systems for medical, industrial, commercial and military applications. Also MW radiations leave harmful effects on our body organs, if exposed for considerable period of time. These effects include increase in heartbeats, weakening of immune systems, rearrangement of proteins including DNA, increasing possibility of leukemia, sterility, cataract, cancer and many more. Due to these undesirable effects of MW and also for use in radar cross section (RCS) reduction, research in the field of MAM that absorb the incident MW energy and convert it into heat has been of interest since World War II. In recent times too, MAM are gaining immense importance due to their potential of use in controlling the EMI and harmful MW pollution. The X-band is known as most ideal band for communication due to minimum atmospheric attenuation (0.08 dB/ Km) at these frequencies, so the highest potential for use the MAM in this band is obvious.

MAM can be prepared from a number of magnetic, dielectric and composite magnetic- dielectric materials. Depending on the applications, the MAM are used in form of sheets, foams, paints, blocks or powder. The dielectric absorbers have been used effectively below 300 MHz frequencies whereas magnetic absorbers are most suitable in the GHz range absorption. The magnetic materials like ferrite, hexaferrite, garnet and orthoferrites can be tailored very easily over a wide range by doping different transition and rare earth metals in the parent phase. The ferrites/ orthoferrites, having isotropic property can be used only up to 3 GHz and are already studied extensively. The hexaferrites with their anisotropic properties can be used in higher MW frequencies. These anisotropic materials with higher gyromagnetic resonance frequency of precession around the magnetic field can work as wide band absorber. Therefore hexaferrites are the first choice among various magnetic materials for absorber in X-band (8-12 GHz) frequencies.

The various stable phases of hexaferrites are M, Y, X, Z, W and U-type. **Out of these the U-type hexaferrites are least studied and very few work till date (before the present thesis & related publications) has been reported about its MW absorption in X-band frequencies.** The U-type hexaferrite with general formula $Ba_4 Me_2 Fe_{36} O_{60}$, where Me is a divalent transition metal ion is a combination of M & Y-type hexaferrites with crystal structure described by stacking sequence $RSR^*S^*TS^*$. This thesis is focused on studies made on preparation of U-type hexaferrite magnetic material by choosing different combinations of metallic and base ions for obtain best MW absorbing properties in X-band frequencies. For this we synthesized and characterized different U-type hexaferrite series: ($Ba_4M1_{2-x}M2_x Fe_{36}O_{60}$, where M1, M2 were chosen from iron group.

Polycrystalline bulk samples of U-type phase were prepared by solid state reaction route. Experimental techniques employed to investigate/identify the structure & microstructures of the samples are X-ray diffraction (XRD, Philips X-pert PRO machine, using $CuK\alpha$ radiation) and scanning electron micrographs (SEM, ZEISS EVO-50). Complete X-ray analysis was done using XPowder software for calculating the lattice parameters. Theoretical and experimentally measured (by Archimedes principle) densities were compared to determine the porosity of samples. Complex permittivity and permeability were measured using Vector network analyzer (VNA, *Agilent model PNA-L N5230A*). These parameters were used for calculate the reflection loss (R_L) for determine the MW absorption.

In Chapter 1 brief introduction of MW and various types of MW absorbing materials are given. The suitability of using hexaferrite for MW absorption in GHz frequency range is discussed. Detailed literature survey on U-type hexaferrites has been made in this chapter. Finally, the objectives and plan of the present work are given.

Chapter 2 outlines the details of experimental processes employed for synthesizing the bulk samples. All steps followed in the standard solid state reaction route of sample formation are given in chart form. Full description of S-parameter measurement technique using Vector Network Analyzer (VNA) for measuring complex permittivity and permeability is given. The details of XRD and SEM characterization techniques are also discussed in brief.

In Chapter 3 the detailed results of complex permittivity, permeability and MW absorption properties of the U-type hexaferrite series: $Ba_4Co_{2-x}Mn_xFe_{36}O_{60}$, where $0 \leq x \leq 2.0$ in steps of 0.5, are presented. The variations of these properties with frequency and composition are discussed over X-band frequencies. Co^{2+} ions are well known for introduce positive magnetic crystalline anisotropy and for bring down the ferromagnetic resonance frequency below 50 GHz; whereas manganese ions (Mn^{2+}) have been used for lowering the magnetic anisotropy that will result the ferromagnetic resonances with large amplitude. In this series the $x = 1$ sample $Ba_4CoMnFe_{36}O_{60}$ was observed to show maximum absorption of 99.84% at 8.45 GHz; and the absorption over the entire X-band was > 97% with sample thickness ~1.7 mm.

Chapter 4 discusses the variations in EM as well as MW absorbing properties of U-type hexaferrite with Zn addition in a series: $Ba_4Mn_{(2-x)}Zn_xFe_{36}O_{60}$ (for $0 \leq x \leq 2$ in step of 0.5). The role of non magnetic Zn^{2+} ion has been studied for control the magnetic properties. The Zn^{2+} ion occupies preferably the tetrahedral site and its inclusion in small amount increases the magnetic moment. Zn is also volatile and it vaporizes during calcinations and sintering. When Zn escape it will increase the crystalline defects that can be expected for increase the electrical loss. As discussed in chapter 3 that, manganese ion (Mn^{2+}) lower the magnetic anisotropy that increase the amplitude of ferromagnetic resonance. So the combination of Mn^{2+} and Zn^{2+} as metallic ion in a U-type hexaferrite was expected to show wide variation in EM properties and increased dielectric and magnetic loss in X-band frequencies; which in turn give large wide band MW absorption. The samples show multiple EM resonances and their amplitude is very large in compositions $x = 0$, 1.5 and 2.0. The maximum value of MW absorption is more than 99

% (-32 dB) in sample $x = 1$ and the absorption is > 97.76 % ($R_L \leq$ - 16.5 dB) through out the X-band, when thickness is $t_m = 1.8$ mm.

In Chapter 5 the EM as well as MW absorbing properties of the U-type hexaferrite series: $Ba_4(Co_{1-5x}P_{2x})_2Fe_{36}O_{60}$, where x varies from 0 to 0.20 in step of 0.05 have been discussed. Co^{2+} ions have been substituted with P^{5+} ion to increase the MW loss due to formation of glassy/liquid phase at grain boundaries. The results show that the MW absorption maxima is > 99.99% in sample $x = 0.05$. In this series the EM property of a tunable MW absorber was investigated.

Chapter 6 describes the absorbing properties of the U-type hexaferrite series $(Ba_{1-3x}La_{2x})_4Co_2Fe_{36}O_{60}$, wherein x varies from 0.10 to 0.20 in step of 0.05. the occupation of La^{3+} ion at Ba^{2+} ion site results into partial conversion of Fe^{3+} ion into Fe^{2+} ion that leads to hopping conduction resulting from hopping of electrons between Fe^{2+} & Fe^{3+} in these lattice sites. This electron hopping results into increment of both dielectric polarization and dielectric loss. The maximum absorption of 99.8 % was obtained for a sample with $x = 0.10$ when thickness $t_m = 1.8$ mm. All samples showed a wide band absorption ≥ 96 % over the X-band frequencies. The absorptive property obtained in these samples is also tunable over entire X-band frequency range on thickness variation.

Chapter 7 summarizes the important findings of the entire work and presented in form of a Table. Recommendations for future work are also given in this chapter.

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