1.1 Introduction to Garnets

Material science today assumes various manifestations. The study of the science of different types of material has led to the development of variety of devices that have found application in man’s everyday life. Much of recent progress in science and technology is due to the advances made in physics and chemistry of condensed matter. It not only draws attention to chemical composition, atomic configuration, etc. of the solid, but also correlates the physical and chemical properties of solid and helps in solving variety of problems of practical and technological importance.

Ferrite materials are known for a long time but now have been exploited for a number of communication and defense applications. Of this development in the technology of ferrite material, the scientists still prefer to examine the structure and transport properties of these materials in a systematic manner to evolve correlations between them. The interest now spreads to different material covering chemists, physicists, electrical engineers and materials scientists. The electrochemists have specific interest in ionic conductors; the physicists have further interest in amorphous and crystalline semiconductors, magnetic semiconductors like ferrites, ferroelectric materials, and so on.

Among the magnetic ceramics, magnetic oxides are the most important and the only relevant from the point of view of their applications. Magnetic oxides, which are commonly known as ferrites, are ferromagnetic in magnetic structure. The most common magnetic oxides, which find wide applications as soft, hard or moderate ferrites, are spinels, garnets and hexaferrites.
Ferrite possesses high values of magnetization due to the imbalanced magnitude of magnetic moments. The high value of resistivity, low dielectric loss, as well as moderate saturation magnetization and high Neel temperature have made ferrites the most versatile material for various technological applications in the field like microwave technology, radars, space technologies etc.

Mixed metal oxides with iron (III) oxides as their main component are known as ferrites. Ferrites crystallize in three different crystal types, namely spinel, garnet and orthoferrite or hexaferrites. The interesting electrical and magnetic properties of these compounds are governed critically by their chemical composition. Hence, preparation of ferrite composites with specific properties has gained much importance.

Garnet refer to a group of mineral which have the same type of composition as Mg$_3$Al$_2$(SiO$_4$)$_3$ which is a common metamorphic mineral crystallizing in the cubic system. By replacing Si atoms with Fe, we obtain a group of ferrimagnetic garnet M$_3$Fe$_5$O$_{12}$ where, M is rare earth elements such as Dy, Cu, Gd, ho, Er, Tm, Yb, Lu or Y. All these metal ions are trivalent.

Samarium, Gadolium, Yttrium, and Dysprosium iron garnet have interesting magnetic properties. These materials have been widely used as both transmitter and transducer of acoustic energy, laser host and in memory devices.

Various methods are used for the synthesis of garnets, including usual double sintering ceramic technique [1], hot pressing [2], co-precipitation [3], hot spraying (evaporative decomposition of salts) [4], sol-gel [5], combustion [6] etc. Each technique has its own advantage and disadvantage.
Polycrystalline Yttrium Iron Garnet (YIG) and substituted YIG have been investigated extensively because of their technical importance and the case with which the properties can be modified so as to suit various applications.

Garnet provide superior performance in microwave devices because they have narrow resonance line width, one of the most important parameters from application point of view besides wide range of magnetization and very low dielectric loss. Line widths of good polycrystalline YIG are approximately 50 Oe, whereas single crystals have been made with line widths less than 0.5 Oe.

The most important properties of ferrites include high magnetic permeability and high electrical resistance. High permeability to magnetic field is particularly desirable in devices such as antennas. High resistance to electricity is desirable in the cores of transformers to reduce eddy currents. Ferrites, of a type known as square – loop ferrites, can be magnetized in either in either of two directions by an electric current. This property makes them useful in the memory cores of digital computers, since it enables a tiny ferrite ring to store binary bits of information.

In short, even after sixty years of first preparation of garnet, still it carries lots of potential from both fundamental and applied research point of view.

1.2 Literature Survey

Yttrium Iron Garnet (YIG) is microwave ferrite that in polycrystalline form has specific characteristic. Substituted and mixed garnet has found extensive use
in wide band non-reciprocal microwave devices [7]. Since 1956, when Yttrium Iron Garnet was first prepared, there has been great amount of literature concerning material preparation and properties and the design and performance of components. Though number of papers are available in literature covering various aspects of pure, substituted and mixed garnet systems in polycrystalline, single crystalline and thin film form, we have restricted ourselves to polycrystalline YIG based systems only.

During the decade of late fifties to sixties (1957-1970), majority of fundamental work was carried out by some workers [8-13] and the main contribution in this field was made by Gilleo and Geller [8]. The information regarding unit cell edge, space group, crystal structure including interionic distance and angles in YIG are important one. The study of magnetic interactions and theoretical model for Neel’s temperature determination were their contribution [9-10]. The work of Pauthenet [11] on structural and bulk magnetic properties of most of rare earth iron garnet carried its own importance. Besides this, Sirvetz and Znejmer [12] carried out considerable work on such properties. A mathematical formulation of random localized canting was made by Patton and Liu for YIG with Ge, Si, Zr and Sc substitution.

There are only few studies [14-21] regarding electrical transport behavior of rare earth iron garnets. The only compound which is well studied [14-18] in this respect is YIG (yttrium iron garnet with a chemical formula $Y_3Fe_5O_{12}$). Electrical transport on heavy rare earth iron garnet with a general chemical formula $RE_3Fe_5O_{12}$ ($RE = Y, Gd, Dy, Ho, Er$ and $Yb$) was studied by Yadav et al [20] by means of electrical conductivity and thermo electric power
measurement in the temperature range 450 – 1250 K. It has been concluded that electrical conduction in these solids up to a temperature of 1250 K is extrinsic in which holes localized on Fe\(^{3+}\) sites (Fe\(^{4+}\) centers created by native defects) conduct via a thermally activated hopping mechanism.

Some electrical and magnetic properties of substituted garnets of the forms \(Y_3Fe_{5-x}R_xO_{12}\) and \(Y_{3-x}R_xFe_5O_{12}\) (where \(R = Dy, Er\) and \(Ho\)) have been investigated by means of X-ray diffraction, magnetization, d.c. conductivity, permittivity and permeability measurements by Anderson et al [22]. It was found that Ga-substitution increased the conductivity but decreased the other quantities measured. Rare earth substitution had significant effects on the magnetic moments but produced only slight changes in the other quantities. Furthermore, it is also concluded that low frequency dielectric losses in YIG are probably due to loss of oxygen during preparation, and Ga–additions resulted in a linear decrease of the dielectric constant.

Very fundamental and basic work on mechanism of electrical conduction in garnets was carried out by Dixon and Elwell [20]. The measurement on the conductivity and thermo electrical power of hafnium – doped YIG and a calcium vanadium bismuth iron garnet indicate that the mobility is activated, and hence, that conduction should be described by localized rather than a band model.

Electrical transport in Dysprosium (Dy) and Gadolinium (Gd) iron garnet was studied by Lal et al [23,24]. They got similar results. They concluded that the charge carriers in the solid are extrinsic and conduct via thermally activated hopping holes from Fe\(^{4+}\) to Fe\(^{3+}\) sites between 575 –
1200 K and below 560 K it is due to the band conduction of holes in the valance ($O^{2-} - 2p$) band.

Sintering studies have been carried out both in ball-milled co-precipitated powders of polycrystalline Yttrium aluminium iron garnet with varying Al substitution ($0 < x < 0.9$) by Patni et al [14]. They observed that higher sintering temperature is needed with increasing Al substitution in YIG to obtain density greater than 98% of the theoretical density and grain growth can be controlled in the hot pressing technique. The linear dependence of activation energy on Al content ($x$) reflects that the bond between oxygen and aluminium is stronger than that between oxygen and iron.

The magnetic and electrical properties of Ti-substituted YIG with general formula $\text{Y}_{3-x}\text{Ca}_x\text{Fe}_{5-x}\text{Ti}_x\text{O}_{12}$ ($x = 0.2, 0.5$ and $0.7$) and $\text{Y}_{3-x}\text{Fe}_{5-2x}\text{Ti}_x\text{Ni}_x\text{O}_{12}$ ($x = 0.5, 1.0$ and $1.5$) were investigated by means of X-ray diffraction, magnetization and thermoelectric power measurements by Bahadur and Prakash [25]. On the basis of X-ray data they show that the formation of single phase up to $x = 0.7$ in the Ca – containing system while the garnet phase could not be prepared in the Ni – containing system. In the Ca – containing system canting of spins take place on the tetrahedral sites while curie temperature decreased with increase in $x$. Change in the activation energy has been observed near curie temperature. Seeback coefficients were positive and essentially independent of temperature. They further suggested that electron hopping in the octahedral sites may occur by jumping indirectly through tetrahedral site.

The magnetic and electrical properties of aluminium and chromium co-substituted Yttrium iron garnet was studied by Kulkarni et al [1] for $0 < x < 1.0$
by means of X-ray diffraction, magnetization, a. c. susceptibility and electrical resistivity measurement. They suggested that co-substitution of Al and Cr in YIG result in low loss in $4\pi M_s$ value. They further suggested that magnetic data can be explained assuming collinear spin ordering model and activation energy remains nearly independent of $x$ for $x > 0.2$. On the same line, X-ray diffraction, electrical resistivity and a. c. susceptibility measurements on Ga and Cr co-substituted YIG were carried out by Murumkar et al [26]. They observed picking effect for $x > 0.6$ in thermal variation of resistivity plots and have explained on the basis of metal to insulator type of transition. The result of a. c. susceptibility exhibit normal ferrimagnetic behavior which decreases with increase in $x$, in consistent with decrease in $T_c$ and magnetization values.

To our knowledge very few reports are available on structural, magnetic and electrical properties of substituted YIG particularly on c-cite, by the cations other than rare earths. Fe$^{3+}$ and In$^{3+}$ substituted YIG systems have been investigated by means of X-ray diffractometry at room temperature for typical composition $x = 0.0, 0.18$ and $0.33$ by Lee et al [27]. They found that for entire composition range garnet structure been maintained and Fe$^{3+}$ as well as In$^{3+}$ occupy c-site. They noticed that c-sites substitution also could characteristically modify magnetic properties of the garnet and lattice constant values calculated theoretically are in agreement to those found experimentally.

Earlier, Shah et al [28] in her work has studied structural, bulk magnetic and electrical properties of $Y_{3-x}Fe_{5+x}O_{12}$ system by means of X-ray diffraction, EDAX, magnetization, a.c. susceptibility and d.c. resistivity. It was concluded that substituted Fe$^{3+}$ ions occupy c-sites and increase in lattice
constant for $x > 0.3$ is due to the presence of small amount of larger Fe$^{2+}$ ions (0.64 Å) determined through EDAX measurement on smaller octahedral sites. The magnetic data can be explained assuming collinear spin ordering model and the Neel temperature values deduced experimentally from a.c. susceptibility and d.c. resistivity measurement are in agreement to those calculated theoretically using modified molecular field theory.

1.3 Aims and outline of the present work

The present work aims:

1. To synthesize magnetic Cr$^{3+}$ ions (3 $\mu_B$) substitution for highly magnetic Fe$^{3+}$ ions (5 $\mu_B$) in yttrium iron garnet (YIG) with general chemical formula: $Y_3Fe_{5-x}Cr_xO_{12}$, with variable compositions, $x = 0.0, 0.2, 0.4,$ and $0.6$ by high temperature solid state reaction route.

2. To study structural and micro structural properties by means of energy dispersive analysis of X-rays (EDAX) at 300 K, X-ray powder diffractometry at 300 K, scanning electron microscopy (SEM) and infrared spectroscopy measurements.

3. To study the magnetic properties of the synthesized samples by means of high field magnetization (300 K and 80 K), compositional and thermal variation of low field a.c. susceptibility and compositional, temperature and frequency dependent permeability measurements.

4. To study the electrical properties by two probe d.c. resistivity and thermo electric power measurements.
5. To study the compositional, frequency and temperature dependent dielectric performance by means of dielectric parameters measurements.

The stoichiometry of the prepared compositions has been confirmed by EDAX analysis. The phase formation and structural parameters like lattice constant, X-ray density, site radius, have been calculated by means of X-ray powder diffraction patterns analysis. The grain morphology (shape, size and distribution) has been studied by SEM analysis, while study on vibration modes has been carried out by infrared spectral analysis.

The saturation magnetization, magneton number and spin structure in the garnet compositions have been studied with the help of high field magnetization measurements. On the other hand, type of magnetic ordering and Neel temperature have been determined from thermal variation of a.c. susceptibility measurement. The probable conduction mechanism, type of charge carriers responsible for conduction, activation energies and verification of ferri to para magnetic transition temperature have been performed by dc resistivity and thermo electric power measurements.

A comprehensive study on dielectric properties helps to understand relaxation phenomenon in the materials.
References

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