1.1 INTRODUCTION:

The magnetic materials such as ferrite are of great interest and importance in magnetism owing to possessing high crystalline anisotropy, high saturation magnetization, good corrosion, and single-phase hexagonal structure. Its composition and degree of chemical order determine the magnetic state of a given magnetic materials. The high anisotropy magnetic materials have attracted much attention due to its vast use in magnetic recording, permanent magnet applications etc.

Ferrite material is usually believed to be fully grown in all fields of science, technology, and application. State of the art and trends in development of ferrite is truly impressive. Ferrite, the magnetic materials is available in numerous classes and types. Ferrite materials are recognized as more important and essential for the further development of electronics than before, and it is believed that the production of ferrites will increase by leaps and bounds as their applications become more diverse. Reviewing past of ferrite, accurately analyzing its present situation, and then thinking of future possibilities will add greatly to further development in the future. A meager but honest, rejoicing effort is thought to be necessary.

Spinel ferrite nanoparticles have been a subject of interest in recent years due to their promising technological applications such as high-density recording devices, ferro-fluids and biomedicine [1–3] and to understand how bulk properties transform to the atomic as the size is decreased. Nanosized ferrite particles exhibit unusual magnetic properties which are not observed in the bulk material, e.g.
single domain behavior, superparamagnetism, and reduced Curie temperature and magnetization [4-6]. The spatial confinement at nanoscale enhances the role of surface atoms with reduced symmetry and the consequent larger number of broken exchange bonds can result in surface anisotropy, frustration and spin disorder [7].

1.2 Nanotechnology:

The first use of the concepts found in ‘Nano-technology’ was in “There’s Plenty of Room at the bottom,” a talk given by the Noble prize winning physicist Richard Feynman at an American Physical Society meeting at Caltech on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, and so on down to the needed scale. The term “nanotechnology” was defined by Tokyo Science University Professor Norio Taniguchi in a 1974 paper as follows: “Nano-technology” mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule”. Nanotechnology and nanoscience got started in the early 1980s with two major developments; the birth of cluster science and the invention of the Scanning Tunnelling Microscope (STM). This development led to the discovery of fullerenes in 1985 and carbon nanotubes a few years later. In another development, the synthesis and properties of semiconductor nanocrystals was studied; this lead to a fast increasing metal & metal oxide nanoparticles and quantum dots. The atomic force microscope (AFM or SFM) was invented six years after the STM was invented. The K. Eric Drexler defined nanotechnology means building machines on the scale of molecules of few nm and smaller than cells like wide motors, robot arms and whole part of computers [8-9].

The prefix “nano” means one billionth. One nanometer (1 nm) is 1/1,000,000,000 of a meter which is close to 1/1,000,000,000 of a yard. To get a sense of the nanoscale, a human hair measures 50,000 nanometers across, a bacterial cell measures a few hundred nanometers across, and the smallest features that are commonly etched on a commercial microchip as of February 2002 are
around 130 nanometers across. The smallest things which are able to see with the unaided human eye are 10,000 nanometers across. Just ten hydrogen atoms in a line make up one nanometer. It’s really very small indeed. To put that scale in another context, the comparative size of a nanometer to a meter is the same as that of a marble to the size of the earth.

Nanotechnology is defined as the “Engineering of functional systems at the molecular scale”. Simply defined, “Nanotechnology is the creation, use or manipulation of matter on the atomic scale”. Nanotechnology is an emerging, interdisciplinary field combining principles of chemistry and physics with the engineering principles of mechanical design, structural analysis, computer science, electrical engineering, and system engineering. Build to atomic specification, the products would exhibit order of magnitude improvements in strength, toughness and efficiency, and be of high quality and low cost. Nanotechnology is the technology of preference to make things small, light and cheap. Nano materials are materials with morphology features smaller than a micron in at least one dimension. The term nanotechnology includes nano particles, nano powders, nano clusters, and nano crystals. Nanotechnology refers to a field of applied science and technology whose theme is construct and fabrication of matter or devices or materials on the atomic and molecular scale in the range of 1-100 nm. The two bottom-up and top-down approaches are used in nanotechnology. In bottom-up approach material and devices are built from molecular atoms which assembled themselves chemically and in top-down approach nano objects are constructed from larger entities without atomic level control. Nanotechnology allows the generation of great variety of matter, devices and products with properties unobtainable by usual invention techniques. Mechanically nano engineering is called molecular technology. Technically nanotechnology means build with intent and design molecule by molecule. Atoms of each element have a tendency to form a fixed number of bonds. To calculate structures of molecules with fair degree of confidence, X-ray crystallography is used.
1.3 APPLICATIONS OF NANOTECHNOLOGY:

With nanotechnology, a large set of materials and improved products rely on a change in the physical properties when the feature sizes are shrunk. Nanoparticles, for example, take advantage of their dramatically increased surface area to volume ratio. Their optical properties, e.g. fluorescence, become a function of the particle diameter. When brought into a bulk material, nanoparticles can strongly influence the mechanical properties of the material, like stiffness or elasticity. For example, traditional polymers can be reinforced by nanoparticles resulting in novel materials which can be used as lightweight replacements for metals. Therefore, an increasing societal benefit of such nanoparticles can be expected. Such nanotechnologically enhanced materials will enable a weight reduction accompanied by an increase in stability and improved functionality. Practical nanotechnology is essentially the increasing ability to manipulate (with precision) matter on previously impossible scales, presenting possibilities which many could never have imagined - it therefore seems unsurprising that few areas of human technology are exempt from the benefits which nanotechnology could potentially bring [10].

1.4 FERRITE NANOPARTICLES:

Ferrites are magnetic ceramics containing iron oxide as a major constituent in it. It is now some 70 years since ferrites debuted as an important new category of magnetic materials. These are now very well established group of magnetic materials. Today ferrites are employed in a truly wide range of applications, and have contributed materially to the advances in electronics. In the area of new materials, ferrites with permeabilities up to 30,000 and power ferrites for frequencies up to 10 MHz have been made available commercially. Even though, improvements and innovations continue to take place; many new applications, theories and preparation technologies are currently under development in field of ferrites. Ferrite is a kind of having a ferromagnetic metal oxide. The Electrical characteristics, electrical resistivity than metal, alloy material is much larger, but also the high dielectric properties. Ferrite magnetic properties
were also performed at high frequency with high permeability. Thus, ferrite has become high frequency weak areas of extensive use of Non metallic Magnetic materials. As a result of ferrite in unit volume stored magnetic energy is low, saturation magnetization is also low (usually only 1/3 of iron -1/5), thus limiting is its higher energy density in low power and high power applications. Ferrite (ferrites) ferrites are a kind of non metallic Magnetic materials, also called ferrite. It is composed of ferric oxide and one or several metal oxide (for example: nickel oxide, zinc oxide, manganese oxide, magnesium oxide, barium oxide, strontium oxide, preparation of sintering), Its reactive magnetic permeability can be high for thousands, resistivity of metal 1011 times, small eddy current loss, suitable for the production of high-frequency electromagnetic device. Hard, soft magnetic ferrites, magnetic moment, magnetic and magnetic are five classes. Formally they have known as the ferrite magnetic material or a ferrite, its production process and appearance similar to ceramic also known as magnetic ceramics. Ferrite iron and one or more other appropriate metal are composite oxides. Nature belongs to the semiconductor, usually as a magnetic media applications, ferrite magnetic materials and metal or alloy magnetic material between the most important differences is that a conductive. Usually the former resistivity of 102~108 cm is 5, while the latter is only 10-6~10-4 cm is 5.

Ferrites are chemical compounds consisting of ceramic material with iron oxide (Fe₂O₃) as their principal component. Many of them are magnetic materials and they are used to make permanent magnets, ferrite cores for transformers, and in various other applications.

Properties

Ferrites are usually non-conductive ferrimagnetic ceramic compounds derived from iron oxides such as hematite (Fe₂O₃) or magnetic (Fe₃O₄) as well as oxides of other metals. Ferrites are like most other ceramics, hard and brittle. In terms of their magnetic properties, the different ferrites are often classified as “soft” or “hard”, which refers to their low or high magnetic coercivity.
1.4.1 Chemical formulae:

Many ferrites are spinels with the formula $AB_2O_4$, where A and B represent various metal cations, usually including iron Fe. Spinel ferrites usually adopt a crystal motif consisting of cubic close-packed (FCC) oxides ($O^2-$) with A cations occupying one eighth of the tetrahedral holes and B cations occupying half of the octahedral holes. If one eight of the tetrahedral holes are occupied by B cation, hen one fourth of the octahedral sites are occupied by A cation and the other one fourth by B cation and it’s called the inverse spinal structure. It’s also possible to have mixed structure spinel ferrites with formula $[M^{2+}_{1-\delta}Fe^{3+}_\delta][M^{2+}_{1-\delta}Fe^{3+}_{(1-\delta)}]O_4$ where $\delta$ is the degree of inversion.

The magnetic material known as “Zn Fe” has the formula $ZnFe_2O_4$, with $Fe^{3+}$ occupying the octahedral sites and $Zn^{2+}$ occupy the tetrahedral sites, and it’s an example of normal structure spinel ferrite.

1.4.2 Soft ferrites:

Ferrites that are used in transformer or electromagnetic cores contain nickel, zinc, and or manganese compounds. They have a low coercivity and call soft ferrites. The low coercivity means the materials magnetization can easily reserve direction without dissipating much energy (hysteresis losses), while the material’s high resistivity prevents eddy currents in the core, another source of energy loss. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of RF transformers and inductors in applications such as switched-mode power supplies.

The most common soft ferrites are:

Manganese-zinc ferrites (MnZn, with the formula $Mn_{a}Zn_{(1-a)}Fe_{2}O_{4}$). MnZn have higher permeability and saturation induction than NiZn. Nickel-zinc ferrite (MnZn, with the formula $Ni_{a}Zn_{(1-a)}Fe_{2}O_{4}$). NiZn ferrites exhibit higher resistivity than MnZn, and are therefore more suitable for frequency above 1 MHz.
1.4.3 **Hard ferrites**

In contrast, permanent ferrite magnets are made of hard ferrites, which have a high remanence after magnetization. These are composed of iron and barium or strontium oxides. The high coercivity means the materials are very resistant to becoming demagnetized, an essential characteristic for a permanent magnet. They also conduct magnetic flux well and have a high magnetic permeability. This enables these so-called ceramic magnets to store stronger magnetic fields than iron itself. They are cheap, and are widely used in household products such as refrigerator magnets. The maximum magnetic field B is about 0.35 tesla and magnetic field strength H is about 30 to 160 kilo ampere turns per meter (400 to 2000 oerasteds). The density of ferrite magnets is about 5g/cm$^3$.

**The most common hard ferrites are:**

- Strontium ferrites, SrFe$_{12}$O$_{19}$(SrO.6Fe$_2$O$_3$), a common material for permanent magnet applications.
- Barium ferrite, BaFe$_{12}$O$_{19}$(BaO:6Fe$_2$O$_3$), a common material for permanent magnet applications. Barium ferrites are robust ceramics that are generally stable to moisture and corrosion-resistant. They are used in e.g. subwoofer magnets and as a medium for magnetic recording, e.g. on magnetic stripe cards.
- Cobalt ferrite, CoFe$_2$O$_4$(CoO.Fe$_2$O$_3$) Used in some media for magnetic recording.

**1.4.4 Uses:**

Ferrite cores are used in electronic inductors, transformers, and electromagnets where the high electrical resistance of the ferrite leads to very low eddy current losses. They are commonly seen as a lump in a computer cable, called a ferrite bead, which helps to prevent high frequency electrical noise (radio frequency interference) from exiting or entering the equipment. Early computer memories stored data in the residual magnetic fields of hard ferrite cores, which were assembled into arrays of core memory. Ferrite powders are used in the coatings of magnetic recording tapes. One such type of material is iron (III) oxide.
Ferrite particles are also used as a component of radar-absorbing materials or coatings used in stealth aircraft and in the absorption tiles lining the rooms used for electromagnetic compatibility measurements.

Most common radio magnets, including those used in loudspeakers, are ferrite magnets. Ferrite magnets have largely displaced Alnico magnets in these applications.

It is a common magnetic material for electromagnetic instrument pickups, because of price and relatively high output. However, such pickups lack certain sonic qualities found in other pickups, such as those that use Alnico alloys or more sophisticated magnets [11]. Ferrite nanoparticles exhibit super paramagnetic properties.

1.5 REVIEW OF LITERATURE:

In recent years, nanotechnology has been the subject of many researchers all over the world because of novel phenomenon and special properties exhibited by nano-particles. The properties of any material in bulk are known to vary drastically and unimaginably as the bulk material approaches to nanoscale and the unusual properties are attributed to the size, shape and distribution of the particles in the material, which in turn depend on the method of synthesis. R. Aquino et. al. have studied magnetization temperature dependence and freezing of surface spins in magnetic fluids based on ferrite nanoparticles [12]. Z.G. Zheng have studied synthesis, structure and magnetic properties of nanocrystalline \( \text{Zn}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4 \) prepared by ball milling [13]. V.T. Zaspalis et. al. have studied the effect of dopants on the incremental permeability of MnZn-ferrites [14]. Alexandre R. Bueno et. al have studied Effect of Mn substitution on the microstructure and magnetic properties of \( \text{Ni}_{0.50-x}\text{Zn}_{0.50-x}\text{Mn}_{2x}\text{Fe}_2\text{O}_4 \) ferrite prepared by the citrate–nitrate precursor method [15]. G. A Petitt et. al. have studied Mossbauer study of cobalt–zinc ferrites [16]. D. Levy et. al. have studied phase transition of zinc ferrite spinel at high pressure, from synchrotron X-ray powder diffraction [17]. M. Veverka have studied magnetic heating by cobalt ferrite nanoparticles [18]. M. A. Ahmed et. al have studied preparation and characterization of nanometric Mn
ferrite via different methods [19]. Qiang-Min Wei et. Al. have studied cation distribution and infrared properties of Ni$_x$Mn$_{1-x}$Fe$_2$O$_4$ ferrites [20]. H.M. Widatallah et. al have studied dynamic magnetic behavior of cluster-glass ZnFe$_2$O$_4$ nanosystem [21].

Nano-crystalline ferrites have been widely studied and has become a field of interest of many researchers because of their unique and improved properties over the bulk crystalline materials. Work on ferrites of some researchers will be discussed here, such as A. D. Sheikh et. al. have studied anomalous electrical properties of nanocrystalline Ni–Zn ferrite [22]. B. P. Ladgaonkar et. al. have studied magnetization and initial permeability studies of Nd$^{3+}$ substituted Zn-Mg ferrite system [23]. Ram Kripal Sharma et. al. have studied variation of structural and hyperfine parameters in nanoparticles of Cr-substituted Co-Zn ferrites [24]. Amarendra K. Singh et. al. have studied magnetic properties of Mn-substituted Ni–Zn ferrites [25]. Shalendra Kumar et. al. have studied electronic structure studies of Mg$_{0.95}$Mn$_{0.05}$Fe$_{2-2x}$Ti$_{2x}$O$_4$ [26]. A. Mahesh Kumar et. al. have studied development of Ni–Zn nanoferrite core material with improved saturation magnetization and DC resistivity [27]. P.K. Roy et. al. have studied enhancement of the magnetic properties of Ni–Cu–Zn ferrites with the substitution of a small fraction of lanthanum for iron [28]. G. Vaidyanathan et. al. have studied synthesis and magnetic properties of Co–Zn magnetic fluid [10]. D. R. Mane et. al. have studied structural and magnetic properties of aluminum and chromium co-substituted cobalt ferrite [29]. A. Lakshman et. al. have studied magnetic properties of In$^{3+}$ and Cr$^{3+}$ substituted Mg-Mn ferrites [30].
1.6 AIM OF THE PRESENT WORK:

Zn ferrites (ZnFe$_2$O$_4$) with the spinel crystal structure have been used in many applications and therefore were subjected to extensive studies [31-36]. The Applications of Mn-Zn ferrites in powder electronics are constantly increasing [37]. Particularly, the growth of the commercial market for switch mode power supplies places demands of the ferrite industry to produce high performance ferrite cores capable of operating increasingly higher frequencies. Recently many efforts have been made to develop low power loss MnZn ferrites for applications at higher frequencies [38, 39], in order to miniaturize electrical devices.

Magnesium ferrites are a commercially important material and have been widely used as magnetic materials [40, 41]. Mg–Mn ferrites were considered as the most versatile ferrites due to their high resistivity and low eddy currents for high frequency application. Microstructure and magnetic properties of Mg–Mn ferrites are highly sensitive to composition, sintering conditions, grain size, type, and amount of additives, impurities and the preparation methodology [42-44]. The Mg– Mn ferrites prepared by the conventional ceramic techniques have been studied by several workers [45, 46]. These ferrites have got a characteristic rectangular hysteresis loop, making these ferrites highly suitable for memory and switching circuits in digital computers and phase shifters. Mg-Cr ferrite is also studied by various workers for their structural and magnetic properties [47]. Though there are no study available in the literature regarding Mn substituted Mg-Cr ferrite with a chemical composition Mg$_{1-x}$Mn$_x$CrFeO$_4$ and Mn substituted Zn-Al ferrite with a chemical composition Zn$_{1-x}$Mn$_x$FeAlO$_4$. The study of these compositions could be very interesting from the fundamental understanding as well from the point of view of application.

Further, the magnetic properties of nanoparticles are depend strongly on the shape and size of the particles, interaction between the particles, superparamagnetic relaxation, finite-size effect, etc. [48]. The magnetic behavior of the nanoparticles surface differs from that corresponding to the core, because of the distinct atomic coordination, concentration and nature of the defects present in both regions, leading to a somewhat disordered spin structure in the surface.
Keeping in view the above facts, it is decided to investigate the magnetic, electrical and dielectric properties of fine particle ferrites prepared by auto-combustion method. In the present investigation studies on the structural, electrical and magnetic properties of two substituted spinel ferrite systems were studied by varying composition. The structural, chemical, electrical and magnetic properties will be investigated by means of TG/DTA, X-ray diffraction, SEM, TEM, Infrared spectroscopy, magnetization, V.S.M., d.c. / a.c. electrical resistivity and dielectric study. Two series of the substituted spinel ferrites prepared by sol-gel auto combustion method are;

1) \( \text{Mg}_{1-x}\text{Mn}_x\text{CrFeO}_4 \) (\( x = 0.0 \) to 1.0 in the step of 0.1)

2) \( \text{Zn}_{1-x}\text{Mn}_x\text{FeAlO}_4 \) (\( x = 0.0 \) to 0.5 in the step of 0.1)