A CHRONOLOGICAL REVIEW AND APPLICATIONS OF FERRITES

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Abstract--The study of diluted magnetic materials such as ferrites comprising ferrimagnetic and insulating properties have prominent role in the development of electronics industries. The systematic growth in the different ferrites prepared in various form like polycrystalline ferrites, nano ferrites, thin film and ferrite composites is reviewed in this paper. Different figures and statistics are given in this paper to elucidate the progress and applications in the ferrites. An over view of different ferrites with available methods of sample preparation, comparative results and the role of international conference on ferrites (ICF) is provided through this paper which will be useful to the researchers working in the field of ferrites.

Keywords: History and applications of Ferrites, spinel ferrites, Bulk and nano-ferrites, soft-ferrites, circulator.

I. INTRODUCTION

It is well known that ferrites are homogeneous ceramic materials composed of various oxides as iron oxide is their main constituent. Due to a combination of two main characteristics high magnetic permeability and high electrical resistivity it is useful in the electronic industries. In general ferrites crystallize in three different crystal structures like spinel, garnet and magneto-plumbite. The simplest in between ferrites are the spinel type[1]. In 12th century, the Chinese were known to use lodestone (Fe_3O_4) in compass for navigation[1]. Naturally available magnetite (Fe_3O_4) is a weak hard ferrite. Hard ferrites are permanent magnetic material and having high coercive magnetic field. The rest ferrite are called soft ferrites which can be easily magnetize and demagnetize and having low coercive magnetic field.

The formula of spinel ferrite is $M^{2+}OFe_2^{3+}O_3$, where M is divalent metal such as Fe, Mn, Cu, Co, Zn, Ni, Mg etc. The structure derived from the mineral spinel. The interesting electrical and magnetic properties of these compounds are governed considerably by their chemical composition, preparation method and cation distribution in various sites available in crystal structure[1]. When S. Hilpert reported his study on magnetic insulator in the year 1909, many researchers have worked on ferrites in order to find new ferrites with specific electrical and magnetic properties. Main two factors responsible for the electrical and magnetic properties of prepared ferrites are sintering conditions[2] and method of preparation.[3] Among the various types of ferrites, spinel ferrites[4,5] are widely used in electrical and magnetic applications. Spinel structure of ferrites was first determined by Bragg and Nishikawa in 1915.[6,7]

II. FERRITE STUDIES

II.I Ferrite study between 1909 -1950

In the year 1909, S. Hilpert announced that iron oxide is not suitable magnetic material for high frequency applications and published magnetization curves as a function of temperature for Zinc, Copper, Magnesium and Nickel Ferrites. In the year 1930, Dr. Takashi Takei discovered that composite oxides with Zinc and Iron added have special magnetic properties and got patent for his research (Japan PAT-98844) in the year 1932. TDK Corporation was founded in 1935 to commercialize the newly invented ferrite cores prepared with Cu-Zn substitution.

In the year 1937, Dr. J.L. Snoek found that hysteresis losses and magnetic after effects can be reduced if carbon and nitrogen are removed from iron alloys. He prepared an iron-nickel-cobalt alloy with less than 0.001% carbon and less than 0.001% nitrogen. This alloy named fernico was used in communication cables. It was having very low hysteresis losses, less after effects and a high permeability.

Neel explained the magnetic behaviour of oxides in the year 1948 and combined his theory on anti ferromagnetism with Kramer's (1934) idea of exchange between metal ions through oxygen ions to explain behaviour of ferrites. In 1950, Anderson explained this theory on a mathematical basis and called it super exchange.

II. II Study of ferrites between 1950 -2000

The ferrites are key materials in our modern telecommunication system. Most of the scientists have started research and study of ferrite because of the large scale production of television in 1950's. That was the main reason for expansion of ferrite industry. Steward has started production of hard ferrites which are used in the automobile industry where as soft ferrites for TV's. In the year 1952, Philips Company prepared Ni-Zn and Mn-Zn ferrite for the use in TV tube deflection yokes and high voltage fly back transformers. Afterwards ferrites with specific resistivity of the order of 10^2 Ω-cm and relative permittivity in the range 5-20 were used. In 1966, R. Gerber, Z. Simsa and M. Vichr showed the result of Seebeck coefficient and Curie temperature for manganese ferrite[8]. Chappert and R.B. Frenkel, in 1967 found through Mössbauer study that magnetic structure of ferrimagnetic $NiFe_2O_4$ is the collinear Neel type. It was found that $NiFe_{0.3}Cr_{1.7}O_4$ has a triangular structure[9]. Radio antenna was the first commercial soft ferrite product in Korea in 1970. Goldman (1975) produced Ni-Zn ferrites for microwave application. In the era of 1950 to 1970 approximately 20 years steward become a well-known producer of ferrite materials having application in the fields of electronics, copiers, military, telecommunications and automotive industries.

In 1980, Kulkarni and Patil[10] studied the Mössbauer spectra of tetragonal copper ferrite from 298K - 613K. The temperature variation shows a sudden change in the region 350 to 425K. That was because of cooperative John-Teller type crystal distortions. New production methods of fine particles of ferrites were used after 1996. Few of them are sol-gel synthesis Freeze drying, Co-precipitation, hydrothermal oxidation, decomposition process, activated sintering, organic precursors etc.

ICF (International Conference on Ferrites) have been a platform for exchange of information of ferrites and related materials. Various ICF's have taken place from 1970 to 2000. These conferences were held in: Tyota, Japan (1970), Bellevue, France (1976), Tyota, Japan (1980), San Francisco, USA (1984), Mumbai, India (1989), Tokyo, Japan (1992), Bordeaux, France (1996) and Tyota, Japan (2000). During this tenure many scientists have showed their results on new ferrites.

In the 1990's ferrites were used as noise filter in all electronic equipments. Li-Mn ferrite was used as magnetic carrier for electro-photography and Cobalt based materials was useful in hard disks in the computers.

Ferrites have been also studied with global environmental protection[11] purpose. Such studies are classified into four categories called waste water treatment process, carbon dioxide decomposition with an excess of ferrite for the utilization of carbon as solar H_2 carriers, hybridization process for mixing solar and fossil energies and solar energy conversion in to hydrogen energy. Biomedical applications like specific X-ray enhancement, drug delivery cell-labelling, peptide synthesis, detoxification, MRI and sono imaging has been demonstrated[12, 13].

II.III Ferrites study after 2000

Martha Pardavi-Horvath[16] (2000) observer the most important microwave device, utilizing the non reciprocity of ferrites, is the circulator, which consists of a circular disk (pucka) of ferrite, with a symmetrical Y-shaped three-port transmission line conductor attached to it in a strip line or micro strip geometry. This device is indeed a resonant cavity, supporting two counter rotating modes typical use of the circulator is in communication (radar, mobile phone) equipment where it enables the radar transmitter to use the same device for transmit and receive signals.

Further research has exploded in the field of nano structured ferrites after 2000 as the properties of nano scale material often differ from their bulk phase material[14] people were concentrated into synthesis and characterization of nanoferrites.

ICFs held between 2004 -2013, the focus of ICFs was in different research field of ferrites are as given below:

1. Emphasized on microwave ferrites, magneto optical properties, applications of ferrite films, nano structural (9th ICF, San Francisco, USA (2004)
2. Manufacturing of processing equipment and characterization equipment (10th ICF, Chengdu, China (2008).
3. Crystal growth, thin films, magnetic fluids, spintronics, soft magnetic material, electro- magnetic compatibility, energy biomedical and environmental applications (11th ICF, Okinawa, Japan (2013).

The focus was also on. Mg-Mn ferrites represent important class of spinel ferrites. These ferrites when substituted with In^{3+}, Al^{3+}, Co^{2+} ions give interesting magnetic properties[15]. The observed values of Curie temperature increase with increase in content of cobalt ions.

It is recent time various compositions of nano particles have been prepared for Co-Zn and Mn-Cu ferrites. If we prepare same compositions by old ceramic conventional technique and other methods of preparations then comparison of physical, electrical and magnetic properties of such ferrites can give useful data for the researchers and designers involved in ferrite industries. The properties like lattice parameters, temperature dependent electrical resistivity, activation energy, thermo power, dielectric constant, dielectric loss, saturation magnetization, initial permeability, magnetic loss and Curie temperature can be studied if we prepare a sample of ferrite by different methods of preparations.

With the developments in radio, TV, video tape recorders and the internet technology, markets have changed. So requirements of ferrites have also changed.

III. FERRITES APPLICATIONS IN VARIOUS FIELDS

III.I Inductors:

Ferrites are used as inductive components in a large variety of electronic circuits like low noise amplifiers, filters, voltage-controlled oscillators, impedance matching networks. The multilayer technology has become a key technology for mass production of integrated devices. soft ferrite and a metallic coil are the basic components to produce the inductance. To provide a high permeability, the ferrite film should be prepared by a process compatible with the integrated circuit manufacturing process. Sputtering provides films with high density, but accuracy is not maintained in the composition. Pulsed laser deposition methods can produce high-quality films; however a combination of sol-gel and spin-coating is easier and lower cost [17]. Layered samples of ferrites with piezoelectric oxides can be useful to make a new generation of magnetic field sensors.

III.II High Frequency:

Now a day there is huge demand of magnetic materials for high-frequency applications like telecommunications and radar systems. The microwave technology requires higher frequencies and bandwidths up to 100 GHz. Ferrites are non conducting oxides and therefore allow total penetration of electromagnetic fields, while in metals the skin effect highly limits the penetration of high-frequency fields[18]. At such frequencies, domain walls are unable to follow the fields, and absorption of microwave power takes place by spin dynamics. The usual geometry is to align spins first with a DC magnetic field H and apply the microwave field perpendicular to H. The spins precess around their equilibrium orientation at the frequency of the microwave field. The classical description of this dynamics is the Landau-Lifshitz equation[19] of motion, which can be written in its undamped form:

$$dM / dt = \gamma M \times Hi, \quad (1)$$

Where M is the magnetization, γ is the gyromagnetic ratio (ratio of mechanical to magnetic moment, $\gamma = ge/2mc = 2.8MHz/G$), and Hi is the total internal field acting upon the spin. The magnetization and the field terms can be separated in the static and time-dependent parts as

$$H = Hi + hei\omega t \ , \quad M = Ms + mei\omega t \quad (2)$$

These equations show a singularity at

$$\omega = \omega 0 = \gamma H0 \quad (3)$$

H0 is the total field on the spins (external and internal); (3) expresses the ferromagnetic resonance (FMR) conditions and is known as the Larmor equation. FMR is associated with the uniform (in phase) precession of spins. The upper limit of applications of ferrites is FMR, since the interaction with the microwave field becomes negligible as $\omega > \omega 0$. Spinels are therefore applied at frequencies up to 30 GHz, while this limit is about 10 GHz for garnets and can attain 100 GHz for hexaferrites. The absorption of microwaves by ferrites involves losses; a damping or relaxation term is normally added to (3). Some of ferrite applications rely on the fact that the spin rotation depends on the orientation of the external field, which allows the control of the interaction with the microwave field. For one direction of the field, the ferrite transmits the microwave field; for the opposite, it strongly absorbs it. This is the basis of nonreciprocal devices. Typical devices are circulators, isolators, phase shifters, and antennas. Circulators were developed for radar systems and are now used in mobile phones. They allow the use of the same device for transmission and reception of the response signal. Recently, a non resonant absorption of microwave power at very low magnetic fields has become popular. This absorption, known as LFA (for low-field microwave Absorption), has shown to be clearly dominated by the anisotropy field, of the ferro- or ferromagnetic material [20].

III.II Power:

Few applications of ferrites are the power supplies of computers, TV and video systems, and all types of small and medium instruments. The main application is in the systems known as switched-mode power supplies (SMPSs). In this application, the mains power signal is first rectified it is then switched as regular pulses (typically rectangular) at a high frequency to feed into a ferrite transformer, and finally it is rectified again to provide the required power to the instrument. A recent approach to increase efficiency of the ferrite cores is based on the decrease of eddy currents, by increasing resistivity. Beside the use of non-conducting additives that locate preferentially on grain boundaries and limit the intergrain conductivity, MnZn and NiZn are combined as $MnxNi_{0.5-x}Zn_{0.5}Fe_2O_4$ and obtained through a citrate precursor method[21]. An additional difficulty appears in the case of power applications at high temperature, as is the case of some automotive power devices. Due to the closeness to the car engine, the working temperature increases from the usual 80–100°C for standard applications, to 140°C. A proposed solution involves the modification of the MnZn ferrites (used previously for these applications) in order to produce a higher fraction of Fe^{2+} [22], such as $(Mn_{0.76}Zn_{0.1}7Fe^{2+}_{0.07})$ Fe_2O_4. This ferrous concentration presents a minimum in the magneto crystalline anisotropy close to 140°C, and therefore, a minimum in losses appears at this temperature.

III.IV Electromagnetic Interference (EMI) Suppression:

The increase in the amount of electronic equipment such as high-speed digital interfaces in notebooks and computers, digital cameras, scanners in small areas, has seriously enhanced the possibility of disturbing each other by electromagnetic interference (EMI). The fast development of wireless communications has led to interference induced by electric and magnetic fields. Electromagnetic interference can be defined as the degradation in performance of an electronic system caused by an electromagnetic disturbance [23]. The noise from electric devices is usually produced at frequencies higher than circuit signals. To avoid or reduce EMI suppressors should work as low-pass filters that is, circuits that block signals with frequencies higher than a given frequency value. There are many approaches to build EMI suppressors: soft ferrites[24], ferromagnetic metals[25], ferromagnetic metal/hexaferrite composites [26], encapsulated magnetic particles [27], and carbon nanotube composites [28]. In the recent years ferrite multilayer components have been developed as a response to form essentially by a highly conductive layer embedded in a ferrite monolithic structure, produced by ceramic co processing technologies. Mostly, Ni-Zn ferrites are used for the 20–200MHz frequency range. Multilayer suppressors behave like a frequency-dependent resistor; at low frequencies, losses in the ferrite are negligible. As frequency increases, losses increase also, and, as ferromagnetic resonance is approached, the inductor behaves as a frequency independent resistor and no longer as an inductor. Hexaferrites represent an interesting alternative to cubic ferrites as EMI suppressor components; they possess higher resonance frequencies, relatively high permeability sand high electrical resistivity. Metallic ferromagnets, in contrast, show a larger saturation magnetization, but, as frequency increases, they exhibit a strong decrease in permeability due to eddy currents However, in combination with hexaferrites, they have shown a strong potential for EMI suppressor devices[26]. Co_2Z and Zn_2Y hexaferrite particles (10–30 μm), mixed with metallic Ni particles (2-3 μm), and prepared with a polymer (polyvinylidene fluoride) by hot pressing at low temperature led to high shield effectiveness.

IV. CONCLUSION

Ferrites have been studied and applied for more than 50 years and are considered as well-known materials with "mature" technologies ranging from hard magnets to magnetic recording and to microwave devices . Millions of people all around the world are using ferrites for various applications. During past few decades study has shifted from bulk ferrites to nano ferrites. However, the advances in applications and fabrication technologies in the last 10 years have been impressive. Bulk ferrites remain a key group of magnetic materials, while nanostructured ferrites show a dramatic promise for applications in even significantly wider fields. It will be interesting to compare result of bulk and nano ferrite of particular compositions prepared by different techniques. From the present review it is concluded that ferrites are very important technological materials.

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