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Ferrite materials: A chronological review

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ABSTRACT

Ferrite is very important technological material having both electrical and magnetic properties. This paper represents some of the important developments in the study of ferrite. A review of ferrite study from 1909 to till date is presented here regarding science and technology of ferrite. The paper highlights the work of some great scientists like S.Hilpert, J.L. Snoek, Neel, Anderson, Goldman, Takashi Takei etc. The role of international conference on ferrites (ICF) is also given in this paper. Various illustrations given in this paper explains the history and applications of the ferrites. It gives an over view of ferrite study from bulk to nano scale preparations of ferrites. It is the need of the present day to prepare samples of ferrite with one composition using many available methods of preparation and compare the results of such studies. This will give useful data for the user and designer interested in ferrites for various applications.

Keywords: History and applications of Ferrites, Bulk and nano-ferrites, soft-ferrites, ferrites as a technological material, electrical and magnetic properties of ferrite.

INTRODUCTION

Ferrite is an important technological material having both electrical and magnetic properties. In 12th century, the Chinese were known to use lodestone (Fe_3O_4) in compass for navigation.[1]

Naturally occurring magnetite (Fe_3O_4) is a weak hard ferrite. Hard ferrites possess a magnetism which is essentially permanent and have high coercive field. Other types of ferrite are called soft ferrites which are easy to magnetize and demagnetize and have low coercive field. Magnetic materials with low coercivity of the order of 12.5 Oersted are termed as soft and those with coercivity above 12.5 Oersted are hard magnetic materials.

The molecular formula of ferrites is $M^{2+}OFe_2^{3+}O_3$, where M stands for the divalent metal such as Fe, Mn, Cu, Co, Zn, Ni, Mg etc. The properties of soft ferrites that are of prime oncern are saturation magnetization, initial permeability, magnetic loss factor, coercive force, remanance, Curie temperature, resistivity, dielectric constant, thermopower etc.

Since 1909, when S. Hilpert reported his study on magnetic insulator, many researchers have worked on ferrites in order to find new ferrites with specific electrical and magnetic properties. The 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]

FERRITE STUDY BETWEEN 1909 AND 1950

In 1909, S. Hilpert announced in Germany that iron oxide is not practical magnetic material for high frequency applications. S. Hilpert published magnetization curves as a function of temperature for Zinc, Copper, Magnesium and Nickel Ferrites. Dr. Takashi Takei discovered in 1930 that composite oxides with Zinc and Iron substituted have special magnetic properties. His research got published by Japanese Electro-Chemical society.

In 1932, Dr. Takashi Takei got patent for his research (Japan PAT- 98844). TDK Corporation was founded in 1935 to commercialize the newly invented ferrite cores prepared with Cu-Zn substitution.

In 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 also 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

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communication cables. It resulted in very low hysteresis losses, no after effects and a high permeability.

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

FERRITE STUDY BETWEEN 1950 AND 2000

Our modern telecommunication system would not be possible without ferrites. The large scale production of television in 1950's was main reason for expansion of ferrite industry. Steward started producing hard ferrites which are used in the automotive industry where as soft ferrites deflection yokes for TV's. In 1952, Philips researchers prepared Ni-Zn and Mn-Zn ferrite for the use in TV tube deflection yokes and high voltage fly back transformers. Later, ferrites with specific resistivity of the order of 10^2 Ω-cm and relative permitivity in the range 5-20 were used. In 1966, R. Gerber, Z. Simsa and M. Vichr reported the result of measuring activation energy, Seebeck coefficient and Curie temperature for manganese ferrite[8]. Chappert and R.B. Frenkel, in 1967 found through Mossbauer 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]. The first commercial soft ferrite product in Korea was radio antenna core in 1970.Goldman (1975) produced Ni-Zn ferrites for microwave application. In 1976, Sam wha electronics Co. Ltd prepared high quality soft ferrite for use in new technology. In the era of 1950 to 1970 approximately 20 years steward become a supremo producer of ferrite in both hard, soft ferrite and also in materials having application in telecommunications, electronics, copiers, military and automotive industries.

In 1980, Kulkarni and Patil[10] observed the Mossbauer spectra of tetragonal copper ferrite between 298K and 613K. The temperature variation of isomer shifts and quadrupole interactions show a sudden change in the region 350 to 425K. The identified transition was reported to be due to cooperative John-Teller type crystal distortions.

In year 1995, composites based on nano sized magnetic materials were reported for high density information storage, Ferro-fluids and medical diagnosis. After 1996 new methods to prepare fine particles of ferrites were used. Prominent among them are Co-precipitation, sol-gel synthesis, Freeze drying, hydrothermal oxidation, activated sintering, organic precursors and decomposition process.

ICF (International Conference on Ferrites) have been providing a forum for exchanging information on the science and technology 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 period many scientists have reported different results of the new ferrites having permeability 20,000 to 30,000. Mn-Zn ferrites were reported to be used in the range of 3MHz to 10MHz.

After 1990, hard disks in the computer have Cobalt based metallic thin films. In the 1990's ferrites were used as noise filter in power lines on the input to all types of electronic equipments. Li-Mn ferrite was investigated to be used as magnetic carrier for electro-photography.

Ferrites have been investigated from the viewpoint of global environmental protection[11]. Such studies are categorized in to four categories namely 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. During this period potential biomedical uses of magnetic nano ferrites have been investigated. Biomedical applications such as specific cell labeling, drug delivery, peptide synthesis, detoxification, X-ray enhancement, MRI and sono imaging has already been demonstrated[12,13] .

FERRITES STUDY AFTER 2000

After 2000, research into the synthesis and characterization of nano structured systems has exploded. The Properties of nano scale material often differ considerably from their bulk phase material[14]. The ICF held between 2004-2013 made focus on latest science, technology and application of ferrites. Few important points about these ICF's are given below:

9th ICF, San Francisco, USA (2004): The focus was on microwave ferrites, magneto optical properties, applications of ferrite films, nano structural ferrites and multilayer chips inductors.

10th ICF, Chengdu, China (2008): The scientists, researchers, engineers and technologists participated in this conference working in ferrite technology. There was lot of discussion on manufacturing of processing equipment and characterization equipment.

11th ICF, Okinawa, Japan (2013): The research papers on academic, technical and industrial research were presented in this conference related to crystal growth, thin films, magnetic fluids, spintronics, soft magnetic material, magneto-optics, electro-magnetic compatibility. The focus was also on energy biomedical and environmental applications.

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. The results have been explained on the basis of strength of various magnetic exchange interactions. The saturation magnetization increases with increased substitution of indium and cobalt ions and decreases with increased substitution of aluminium. The initial permeability increases with increased substitution of indium and decreases continuously with increased substitution of aluminium and cobalt. The magnetic loss observed is lower as compared to those for samples prepared by conventional ceramic method due to perfect crystallization. These all

results are explained with the help of established theories and models.

With the expanding use of radio, TV, video tape recorders and the internet technology, markets have changed. Hence requirements of ferrites have also changed.

It is interesting that various compositions of nano particles have been prepared for Co-Zn and Mn-Cu ferrites recently. If same compositions are prepared by old ceramic conventional technique and a few other methods of preparations then comparison of physical, electrical and magnetic properties of such ferrites can give useful data for the users and designers involved in ferrite industries. The samples of same compositions prepared with various methods of preparation, need to be investigated for the properties namely lattice parameters, temperature dependent electrical resistivity, activation energy, thermopower, dielectric constant, dielectric loss, saturation magnetization, initial permeability, magnetic loss and Curie temperature.

CONCLUSION

Dr. J.L. Snoek idea of ferrite was used by scientists in Japan to produce first industrial product using ferrite in 1935.Millions of people all around the world are using ferrites for various applications. A number of researchers have studied the effect of substitution of impurity ions and methods of preparations for different ferrite compositions. Till date no ideal ferrite sample exists that meets all the required electrical and magnetic properties. It is established that some ions improve electrical and some ions improve magnetic properties. Simultaneously substitution of such ions can produce new ferrites with better properties. Hence scientists will continue their efforts to achieve optimum parameters for ferrites. During past few decades study has shifted from bulk ferrites to nano ferrites. 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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