Integr. Res. Adv. 2014, 1(1), 11-13 Article

Integrated Research Advances

History and applications of important ferrites

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Received Date: 04-June-2014 Accepted and Published on: 07-Nov-2014

ABSTRACT

Ferrites are very important materials having both electrical and magnetic properties. These materials are used in various applications. The present work represents the history and application of some important ferrites called spinel ferrites. It gives overview of the earlier scientific works done by the pioneers in the field of ferrite preparation and characterization technology. All the important historical developments are given in this paper. It also focuses on the applications of spinel ferrites. These materials are important from technological view point and properties like physical structure, resistivity, dielectric constant, dielectric loss factor, Curie temperature, magnetic susceptibility, initial permeability and magnetic loss factor etc. are to be investigated and there are no fixed rules framed which can be used to fabricate novel ferrites with all desired properties. Research field area has spread over hundred years now and will continue in the near future

Keywords : History of Ferrites, Applications of Ferrites, Electrical Properties of Ferrites, Magnetic Properties of Ferrites, Spinel Ferrites.

INTRODUCTION

Magnetic materials which have combined electrical and magnetic properties are known as ferrites. Iron oxide and metal oxides are the main constituents of the ferrites. The value of ferrites material has been known to mankind for their centuries. As early as the 12th century the Chinese were known to use lodestone (Fe_3O_4), in compasses for navigation.[1]

In the early days of electrical industry, iron and its magnetic alloys were used as magnetic materials. However, with the advent of higher frequencies, these materials were not cost effective and process to reduce eddy current loss became complicated. This realization stimulated a renewable interest in “magnetic insulators” as first reported by S.Hilpert in Germany in 1909. Research to develop such a material was being done in various laboratories all over the world, such as by V.Kato, T. Takei, and N. Kawai in the 1930’s in japan and by J. Snoek of the Philips Research Laboratories in the period 1935-1945 in the Netherland. By 1945 Snoek had laid down the basic fundamentals of the physics and technology of practical ferrite materials. In 1948, the Neel theory of ferrimagnetism provided the theoretical understanding of this type of magnetic material.

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Cite as: *Integr. Res. Adv., 2014,1(1), 11-13.*

Ferrites are ceramic, homogeneous materials composed of various oxides with iron oxide as their main constituent. Ferrites can have several distinct crystal structures.

On the basis of their crystal structure they can be grouped in to three categories namely; cubic garnet, spinel ferrite and hexagonal ferrites.

The molecular formula of ferrites is $M^{2+}O.Fe^{3+}{}_2O_3$, where M stands for the divalent metal such as Fe, Mn, Cu, Co, Zn, Ni, Mg, Cd etc. There are 32 oxygen (O^{2-}) ions, 16 Fe^{3+} ions and 8 Fe^{3+} ions per unit cell. Out of them, 8 Fe^{3+} ions and 8 Me^{3+} ions occupy the octahedral sites. Each ion is surrounded by 6 oxygen ions.

During last almost 100 years, scientists and other researchers are working to produce various compositions of ferrite material in order to produce new ferrites with optimum value of their physical, electrical and magnetic parameters. Right from the beginning and till date it is not possible to produce novel ferrites. Research and development of some types of promising materials are under investigation.

Each prepared sample has got its own advantages and disadvantages. Scientists have not yet been able to formulate rigid set of rules of ferrites about any physical, electrical or magnetic property. Scientist will still continue their effort to achieve the optimum parameters of ferrites like, crystalline structure, resistivity, dielectric constant, dielectric loss, Curie temperature, AC susceptibility, initial permeability and magnetic loss factor etc with other electrical and magnetic properties. The optimum conditions depend upon the sintering conditions[2] and method of preparations[3].

Among all the additives used to alter the electrical and magnetic properties of ferrites the most important are namely Mn, Cu, Co and Zn. Combined substitution of these ions can produce new ferrite materials with better electrical and magnetic properties. Among the various types, most important and useful are the spinel ferrites[4,5].

SPINEL FERRITES

They are also called cubic ferrite. Spinel is the most widely used family of ferrite. High values of electrical resistivity and low eddy current losses make them ideal for their use at microwave frequency. The spinel structure of ferrite as possessed by minerals spinel $MgAl_2O_4$ was first determined by Bragg and Nishikawa in 1915[6,7].

The chemical composition of spinel ferrites can be written in general as MFe_2O_4 where M is divalent metal ion such as Fe^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+} , Zn^{2+} or a combination of these ions such. The unit cell of spinel ferrite is FCC with eight formula units per unit cell. The formula can be written as $M_8Fe_{16}O_{32}$. The anions are the greatest and deep form of FCC lattice. Within these lattices two types of interstitial positions occur and these are occupied by the metallic cations. There are 96 interstitial sites in the unit cell, 64 tetrahedral (A) and 32 octahedral (B) sites.

The spinel ferrites have been classified into three categories due to the distribution of cations on tetrahedral (A) and octahedral (B) sites: (1) Normal spinel ferrite (2) Inverse spinel ferrite (3) Intermediate spinel ferrite.

1. Normal spinel ferrite.

If there is only one kind of cation on octahedral (B) sites, the spinel is normal. In these ferrites the divalent cations occupied tetrahedral (A) sites while the trivalent cations are on octahedral (B) sites. Square brackets are used to indicate the ionic distribution of the octahedral (B) sites. Normal spinel have been represented by the formula $(M^{2+})_A[Me^{3+}]_BO_4$. Where M represent divalent ions and Me for trivalent ions. A typical example of normal spinel ferrite is bulk $ZnFe_2O_4$.

2. Inverse Spinel ferrite.

In this structure half of the trivalent ions occupy tetrahedral (A) sites and half octahedral (B) sites, the remaining cations being randomly distributed among the octahedral (B) sites. These ferrites are representated by the formula $(Me^{3+})_A[M^{2+}Me^{3+}]_BO_4$. A typical example of inverse spinel ferrite is Fe_3O_4 in which divalent cations of Fe occupy the octahedral (B) sites[8].

3.Random Spinel

Spinel with ionic distribution, intermediate between normal and inverse are known as mixed spinel e.g. $(M^{2+}{}_{\delta}M^{2+}{}_{1-\delta})_A[M^{2+}{}_{1-\delta}Me^{3+}{}_{1+\delta}]_BO_4$, where δ is inversion parameter. Quantity δ depends on the method of preparation and nature of the constituents of ferrites. For complete normal spinel ferrite δ=1, for complete inverse spinel ferrite δ =0, for mixed spinel ferrite, δ ranges between these two extreme values. For completely mixed ferrite δ=1/3. If there is unequal number of each kind of cations on octahedral sites, the spinel is called mixed. Typical example of mixed spinel ferrites are $MgFe_2O_4$ and $MnFe_2O_4$.

Neel suggested that magnetic moments in ferrites are sum of magnetic moment of individual sub-lattices. In spinel structure, exchange interaction between electrons of ions in A and B- sites have different values. Usually interaction between magnetic ions of A and B sites (AB-sites interaction) is the strongest. The interaction between AA- sites is almost ten times weaker than that of AB-site interaction whereas BB- sites interaction the weakest. The dominant AB- sites interaction results in to complete or partial (non- compensated) antiferromagnetism known as ferrimagnetisms[9]. The dominant AB- sites interaction having greatest exchange energy produce anti-parallel arrangement of cations between the magnetic moments in the two types of sublattices and also parallel arrangement of the cations within each sublattice, despite of AA- sites or BB- sites anti ferromagnetic interaction[10].

SITE PREFERENCE OF CATIONS FOR TETRAHEDRAL (A) AND OCTAHEDRAL (B) SITES:

The cation distribution in the spinel $Me^{2+}Me^{3+}O^4$ can be as following[3,11];

Normal

The Me^{2+} cations are in tetrahedral positions, while the two Me^{3+} cations are in octahedral sites. The square brackets are generally used to represent the octahedral sites, i.e. $Me^{2+}[Me^{3+}]O_4$.

Inverse

In this case the Me^{2+} cation and one of the Me^{3+} cations are in octahedral positions while the second Me^{3+} cation occupies a tetrahedral site. The arrangement is as $Me^{3+}[Me^{2+}Me^{3+}]O_4$.

Intermediate

The arrangement of the form like $Me^{3+}{}_{1-\delta}Me^{2+}{}_{\delta}[Me^{3+}{}_{1-\delta}Me^{2+}{}_{1+\delta}]O_4$ is often referred as intermediate, where δ is called the inversion parameter. δ =0.0 for completely normal and δ =1.0 for completely inverse spinels and 0< δ <1 for intermediate spinels.

The factors affecting the cation distribution over A and B-sites are as reported earlier by many researcher[6,12]. The cations distribution depends upon size of the cation, electronic configuration, saturation magnetization and electronic energy. The other factors responsible for site preference of substituted ions are sintering temperature, ionic radius and size of interspecies. According to Veryway-Heilman scheme[13,14], the expected site preferences are as given below:

A-site preference: In^{3+}, Zn^{2+}, Ga^{2+}etc.

B-site preference: Sn^{4+}, Cr^{3+}, Ni^{2+}etc.

Mixed preference: Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Al^{3+},Mg^{2+} etc.

Applications of Ferrites

Ferrites are important class of magnetic materials having high permeability, moderate to high saturation magnetism, low magnetic loss factor and also possess a high specific resistance. In the high frequency applications of ferrites eddy currents are negligibly small, whereas at such frequencies eddy currents are main drawback of metals even in laminated form. These intrinsic properties make the ferrite indispensible material in electronic and telecommunication industry. Technological importance of these ferrites is that with the help of such ferrites we can deal easily with the frequencies in the range of 10^3 Hz to 10^{11} Hz. Scientists are working to produce new ferrites for protecting the natural environment[15].Such ferrite can be used for water disposal method for factory drains, heat decomposition of NOx gas using spinel ferrites, transformation of solar energy to hydrogen energy using ferrites as catalysts, heat decomposition of CO_2. Mg-based ferrites are used as humidity sensors, carrier for intensifying X-rays in the human system and spinel ferrites are used as rechargable Lithium batteries[16]. Soft ferrites such as Mn-Zn ferrites have been used for deflection yokes, ferrites with square B-H loop are being used in computer memories and switching cores e.g.Mg-Mn based ferrites, soft ferrites are used as wave absorber equipment. The multilayer soft ferrite chip inductors are used in cordless telephones, video equipment, headphone stereos, T.V receiver, automobile parts, hard disk drive system and personal computers[17]etc. The ferrites are also used in microwave communications e.g Mg-Mn, Ni-Zn and Lithium ferrites etc.

ACKNOWLEDGMENTS

Authors acknowledge the support from RKMV Shimla.

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