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Variation of Various Properties of Spinel Ferrite due to Grain Size, Site Preference of Metal Ion

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The Spinel ferrites are a type of material with the chemical formula MB_2O_4, where M and B are transition metal ions. These materials have a spinel structure, which is made up of a cubic array of oxygen ions, with metal ions inhabiting both A(tetrahedral) and B (octahedral) sites. Spinel ferrites are versatile materials with excellent electrical and magnetic properties. The properties of spinel depend on several factors, including the preparation method, grain size, and the substitution of metal ions. The structural, dielectric, and magnetic properties of these ferrites should be altered by introducing different dopants. The broad range of applications for spinel structures includes electromagnets, where increasing the grain size can decrease residual loss. This paper discusses how changes in the metal ion site preference and the effect of grain size can impact various properties of spinel ferrites.

Keywords: Spinel ferrites, Transition metal ions, Grain size, The structural, dielectric and magnetic properties.

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1. INTRODUCTION

Ferrites are a class of magnetic material that contains iron as the main component. These materials have very vital electric and magnetic properties. These materials have gained significant attention in industry and are utilized in various applications, including electromagnetic shielding, phase shifters, and isolators. They are categorized into two types: hard and soft, based on their material properties. Additionally, based on their structure, they can be classified into four types: Spinel, Garnet, Magneto-Plumbite, and Garnet. These ferrites are in the cubic structure having general formula MFe_2O_4 where M is, a divalent metal ion and also a combination of the metal ion. Spinel ferrite is the category of soft ferrite, and these can be distributed in different types (i) Normal (ii) Mixed (iii) inverse ferrite. Spinel ferrites such as Ni-Zn, Mg-Mn, and $CoFe_2O_4$. Spinel ferrites are taken because these are used in phase shifters, isolators, self-switching modes, drug delivery, biomedical, etc.

2. CHEMICAL ASPECT OF SPINEL FERRITES

2.1 Spinel Ferrite

Spinel structure was determined by Bragg. These ferrites got their name from a naturally occurring mineral (spinel) which has a similar chemical formula ($MgAl_2O_4$). These ferrites crystallize into a face-centered cubic (or cubic close-packed) structure with oxygen ions at corners and face centers whereas the metal ion and ferric ions are placed at different interstitial sites or voids. The unit cell of this structure contains 8 formula units, therefore, having a total of 56 (= 8 × 7) ions per unit. The oxygen ions have large ionic radii (1.32 Å) and hence are closely packed together forming the FCC structure. A and B sites are the two interstitial sites. Each unit cell has 32 octahedral sites whereas 64 tetrahedral sites hence making a total number of 96 interstitial sites per unit cell [1] in Fig (1). Cations distribution in A and B sites can be represented following equation:

$$(M\ 2 + x\ Fe\ 3 + 1 - x)A\ (M\ 2 + 1 - x\ Fe\ 3 + 1 + x)B$$

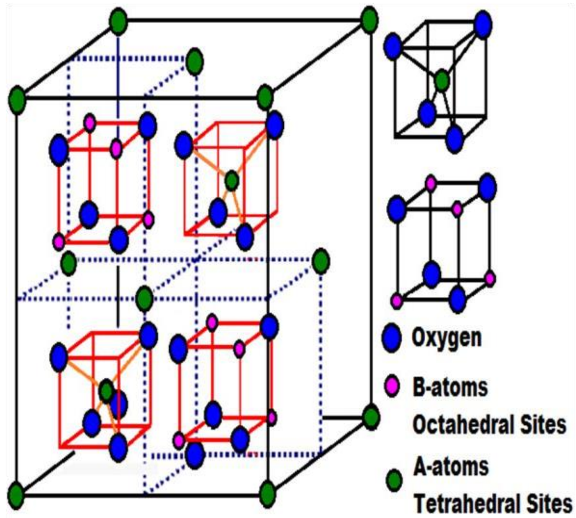

Fig. 1 – Structure of Spinel Ferrites (AB_2O_4/MFe_2O_4)

Experimental: The sample $Mn_{0.5}Mg_{0.5}Ni_{1-x}Fe_{2-x}O_4$ was prepared by combustion technique. Stoichiometric quantities of $Mn(NO_3)_3{\cdot}6H_2O$, Mg $(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, and $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in distilled water. Citric acid is often used as a chelating agent in the synthesis of metal oxides and ferrites. It can help to dissolve metal salts and create a homogenous solution of metal ions, which is important for achieving a uniform distribution of the metal ions in the final product. When the solution is heated to dehydrate the water, the citric acid molecules can also interact with the metal

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ions and help to prevent their precipitation as metal nitrates. This is because citric acid has multiple oxygen atoms that can coordinate with the metal ions and form stable complexes. By preventing the formation of metal nitrates, citric acid can promote the formation of a homogenous single-phase ferrite at relatively low temperatures. Surface morphology and granular microstructure were depicted using a scanning electron microscope (SEM), Hitachi, and a magnetic property of synthesized nano-ferrites was determined using a vibration sample magnetometer (Lakeshore).

2.2 The Magnetic and Structural Properties Changed due to Site Preference

The tetrahedral and octahedral sites changed with the site preference of ions at two sites tetrahedral and octahedral sites. The site preference of ions depends on various factors (i) ionic radii and (ii) electrostatic energy. The smaller ionic radii ion occupies in A site and the larger ionic radii ion occupies the B site [2]. The interaction between metal ions i.e. A-A, B-B, and A-B interaction was determined by site reference. Also, we determine the bond angle and interaction between the metal ions. The A-B interaction appears strong due to the shortest distance between these metal ions. Apart from the A-A, B-B interaction is the weakest because of the large distance between these. Neel [3] described that the A-B interaction is the strongest interaction that explained the ferromagnetism behavior of ferrites. Due to the preference for metal ions, the structural properties also change.

Table 1 – Shows the site preference of different metal ions.

Material	A-Site preference	B-Site preference
$MnFe_2O_4$	Fe^{3+}	$Fe^{3+}Mn^{2+}$
$Mn_{0.5}Mg_{0.5}Fe_2O_4$	Fe^{3+} Mg^{2+}	Fe^{3+} Mn^{2+}
Fe_3O_4	Fe^{3+}	Fe^{3+} Fe^{2+}
$NiFe_2O_4$	Fe^{3+}	Fe^{3+} Ni^{2+}

Islam et al. [4] explained the magnetic properties affected by the calcination temperature of the material, and the microstructure of the sample. With the variation of sintering and calcination temperature the material properties changes. Due to the temperature change, the density and porosity of the material are affected. Many researchers have studied magnetic properties [4-6].

The properties of polycrystalline are controlled by density and porosity. These two parameters are inversely proportional to each other. If the density of the material that means the density decreases. It is accepted that porosity is a significant microstructure highlight restricting the development of domain walls. The grain growth pins out due to the pores.

2.3 Influence of Microstructure and Domain on the Magnetic Properties

The size and distribution of these nonmagnetic grain boundaries can significantly affect the magnetic properties of polycrystalline ferrite. In general, the permeability of polycrystalline ferrite is lower than that of the single crystal due to the existence of grain boundaries, and other defects can impede the movement of magnetic domain walls. When grain size decreases, the number of grain boundaries decreases, resulting in a higher magnetic permeability. However, if the grain size becomes too small, the magnetic anisotropy energy may become comparable to the thermal energy, which can lead to a decrease in magnetic permeability. The magnetic properties of polycrystalline material also changed with the existence of nonmagnetic grain boundaries. In general, the more nonmagnetic grain boundaries there are, the lower the magnetic permeability will be, as these boundaries should behave as barriers by the movement of magnetic domain walls. Overall, these properties of polycrystalline ferrite are strongly affected by grain size and the distribution of nonmagnetic grain boundaries, and understanding these relationships is important for optimizing the performance of ferrite-based magnetic materials and devices [7-9]. The crystal anisotropy energy of the multidomain depends on the width of the domain walls [10].

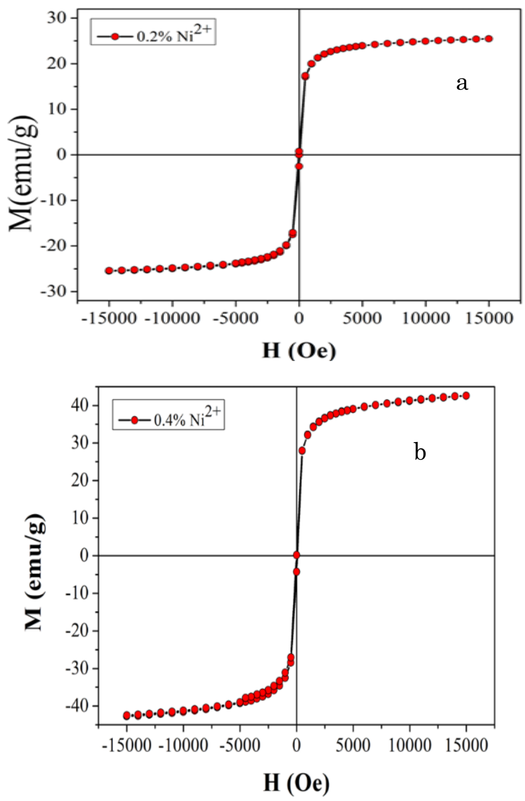
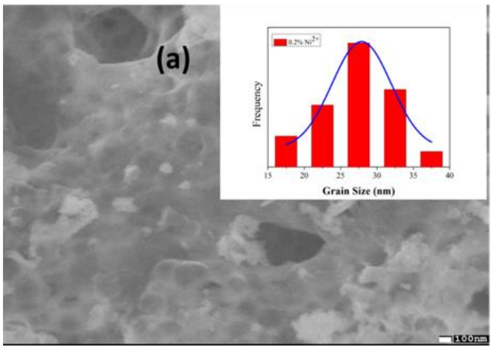


Fig. 2 – MH curve of ($Mn_{0.5}Mg_{0.5}Ni_{1-x}Fe_{2-x}O_4$) ($x$ = 0.2, 0.4)

In magnetic materials, eddy current losses can be caused by the presence of eddy currents that circulate within the material due to the changing magnetic field. These currents can generate heat and dissipate energy, leading to a loss of efficiency in magnetic devices. Eddy's current losses are also strongly influenced by the grain size. In general, smaller grain sizes lead to higher eddy current losses, due to the higher number of grain boundaries and defects that can act as barriers to the flow of eddy currents. This loss is found to increase with increasing grain size. Residual loss is a type of energy loss that happens with the vibration of magnetic domains within a magnetic material. This loss is found to increase significantly at a grain size in Fig 2 This result suggests that as grain size is greater than the size of the monodomain then the smallest magnetic domain can exist in a material [11-13].

2.4 Grain Size Affects the Electrical Properties of Nanocrystalline Ferrite

Because there are fewer defects and impurities present in the material, which can cause energy dissipation. In addition, smaller grains also result in fewer grain boundaries, which can impede the movement of charge carriers and reduce the overall conductivity [16]. The dielectric loss also increases with increasing grain size due



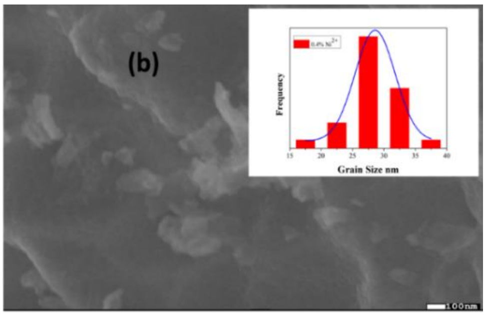


Fig. 3 – SEM micrograph of ($Mn_{0.5}Mg_{0.5}Ni_{1-x}Fe_{2-x}O_4$) ($x$ = 0.2, 0.4)

to the presence of more defects and impurities at the grain boundaries. The electric and dielectric properties of ferrite are strongly influenced by the grain size, and understanding these relationships is important for optimizing the performance of ferrite-based devices and materials [14, 15] as shown in Fig. 3.

3. CONCLUSION

In this present work, we analyze that the various properties depend on various factors viz density, porosity, and site preferences of a metal ion. Structural and magnetic properties change with the preference for the metal ion. From this, we reveal that with the increase or decrease the magnetic properties are effected. A domain wall is a major role in the magnetic properties. With a small grain size, it is like a superparamagnetic, large grain size it is like a multidomain. With the increase of grain size, the magnetic properties also changed that used in the application of electromagnet.

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Зміна властивостей фериту зі структурою шпінелі внаслідок зміни розміру зерна, переваги розташування іонів металу

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Ферити зі структурою шпінелі – це тип матеріалів з хімічною формулою MB_2O_4, де M і B – іони перехідних металів. Такого типу матеріали мають структуру шпінелі, яка складається з кубічного масиву іонів кисню з іонами металів, що населяють A (тетраедричні) і B (октаедричні) місця. Ферити зі структурою шпінелі – це універсальні матеріали з високими електричними та магнітними властивостями, які залежать від кількох факторів, включаючи спосіб отримання, розмір зерна та заміщення іонів металу. Структурні, діелектричні та магнітні властивості таких феритів слід змінювати шляхом введення різних легуючих добавок. Широкий діапазон застосувань шпінельних структур включає електромагніти, де збільшення розміру зерна може зменшити залишкові втрати. У даній статті обговорюється питання впливу типу іонів металу та розміру зерна на властивості феритів зі структурою шпінелі.

Ключові слова: Ферити зі структурою шпінелі, Іони перехідних металів, Розмір зерен, Структурні, діелектричні та магнітні властивості.