UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF Ni-Zn AND Ni-Zn-Cu FERRITE VIA SOL-GEL ROUTE AND SOLID STATE REACTION

SOUILAH ZAHI

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SOUILAH ZAHI

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SOUILAH ZAHI

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Chairman: **Associate Professor Mansor Hashim, Ph.D.**

Faculty: **Institute of Advanced Technology**

A ferrite is an important class of magnetic materials. At present the major material types for application of spinel soft ferrite are nickel-zinc and manganese-zinc ferrites. A majority of these ferrites are synthesised by the classical method which is the conventional ceramic process known as solid state reaction (SSR). Most nonconventional processes for powder preparation are wet methods. Some of these processes are co-precipitation; organic precursors; co-spray roasting; freeze drying; sol-gel route (SGR).

In this research, the compounds $Ni_{0.30}Zn_{0.70}Fe_2O_4$ and $Ni_{0.30}Zn_{0.60}Cu_{0.1}Fe_2O_4$ are prepared by two different processes: the first is solid state reaction and the other is sol-gel route. Different starting materials are used and the process of sol-gel technique is well known. The synthesis of these compounds via sol-gel technique is carried out. Scanning electron microscope, Infrared spectroscopy and X-ray analyses of various gel samples with different thermal history helped in identifying the reaction process and the stages where amorphous-gel-to-crystalline phase transition occurred.

The utilization of sol-gel technique is successful. Comparison of the results for samples demonstrates that the microstructural, magnetic and electrical properties of soft ferrites are improved, and some interesting advantages are realized such as low temperature of preparation, better homogeneity and well-defined polycrystalline microstructure. In addition, a new important advantage has been found in this research, which is short processing time of gel preparation.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

SINTESIS BAGI FERIT Ni-Zn dan FERIT Ni-Zn-Cu DENGAN KEADAH SOL-GEL DAN TINDAKBALAS KEADAAN PEPEJAL

Oleh

SOUILAH ZAHI

Oktober 2000

Pengerusi: **Profesor Madya Mansor Hashim, Ph.D.**

Fakulti: **Institut Teknologi Maju**

Ferit adalah suatu kelas penting bahan magnet. Pada masa ini jenis-jenis bahan utama untuk aplikasi ferit lembut spinel adalah ferit nikel-zink dan ferit mangan-zink. Kebanyakan ferit ini disintesis dengan kaedah klasiks iaitu proses seramik lazim yang juga diketahui sebagai Tindakbalas Keadaan Pepejal. Kebanyakan proses tak lazim bagi penyediaan serbuk menggunakan kaedah basah. Diantaranya ialah ko-penendakan; pendahulu organik; salai ko-sembur; pengeringan beku; laluan sol-gel.

Delam penyelidikan ini, sebatian $Ni_{0.30}Zn_{0.70}Fe_2O_4$ dan $Ni_{0.30}Zn_{0.60}Cu_{0.10}Fe_2O_4$ disediakan melalui dua proses yang berbeza; Yang pertama adalah tindakbalas keadaan pepejal dan yang kedua adalah laluan sol-gel. Bahan awal yang berbeza digunakan dan proses teknik sol-gel telah difahami dengan agak baik. Sintesis sebatian-sebatian ini melalui teknik sol-gel dilaporkan di sini. Mikroskopi inbasan elektron, spektroskopi infra-merah dan analisis sinar-X bagi pelbagai sampel gel dengan sejarah terma yang berbeza membantu pengenalpastian proses tindakbalas dan peringkat-peringkat berlalunya peralihan fasa amorfus gel ke fasa berhablur.

Penggunaan teknik sol-gel ini telah berjaya. Perbandingan keputusan bagi sampel menunjukkan sifat-sifat mikrostruktur, magnet, dan elektrik ferit lembut bertambah baik dan beberapa kelebihan terhasil seperti penyediaan pada suhu rendah, kehomogenan yang lebih baik dan mikrostruktur polihablur yang jelas. Tambahan lagi, suatu kelebihan penting terbaru yang ditemui dalam penyelidikan ialah masa pemerosesan yang pendek bagi penyediaan gel.

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INTRODUCTION

1.1 What are Ferrites?

A ferrite is a member of a whole family of magnetic ceramic materials, including spinels, garnets, magnetoplumbites, ortho-ferrites, or variation of these, such as γ-Fe_2O_3. It is also a member of the class of magnetic metallic oxides, as ferrites are solid solutions of metals containing ferric Fe^{3+} as the main element; furthermore, the name " Ferrite" deduces that iron oxide Fe_2O_3 is generally the common oxide to all ferrites.

Ferrites are dark grey or black in appearance and fairly hard and brittle. Pressing a mixture of powders containing the constituent raw materials to obtain the required shape and then converting it into a ceramic by sintering makes a ferrite core component.

Ferrites are permanent or soft magnetic oxide ceramics. The best soft ferrite (having low coercivity) can be reached by a spinel ferrite, consisting of $Fe_2^{3+}O_4^{-2}$ with a suitable bivalent metallic ion (e.g. Ni, Cu, Zn, Fe, Mg, Mn, Co, and Cd) attached and determining the crystal structure or class. A number of combinations and compositions can be generated such as nickel-zinc ferrites and nickel-zinc-copper ferrites varieties.

Magnetic ceramics or ferrites are classified as ferrimagnetic or a special case of ferromagnetic materials and the magnetic properties compete strongly with metallic magnetic materials. The magnetic properties arise from interactions between metallic ions occupying particular positions relative to the oxygen ions in the crystal structure of the oxide.

1.2 Spinel Structure

The term "spinel structure" is derived from the nonmagnetic mineral spinel $MgAl_2O_4$ (or $MgO.Al_2O_3$), where in the magnetic spinels the divalent ions can replace Mg and the trivalent ions can replace Al. There are exceptions to a few ferrites which contain Mn, Cr and other elements as the main oxide and behaving as magnetic ions. Magnetic spinel has the general formula MFe_2O_4 or $MO.Fe_2O_3$, having a close packed cubic crystal structure of the mineral spinel.

The spinel structure consists of eight formula units or 8 (MFe_2O_4) which form a unit cell of the spinel lattice, which is the smallest repeating unit in the crystal network. Metal ions are surrounded by either four or six neighbouring oxygen ions; thus, they permit two different kinds of lattice site to appear.

Tetrahedral sites have four oxygen ions situated at the corners of a tetrahedron A site and octahedral sites have six oxygen ions situated at the corners of an octahedron B site (Fig 1.1). In the unit cell of 32 oxygen ions of spinel lattice there are 64 tetrahedral sites and 32 octahedral sites. Eight tetrahedral and sixteen octahedral sites are occupied by metal ions, or one tetrahedral and two octahedral sites for each formula unit (64 = total positive charge will be $8\times(+2) + 16\times(+3)$), which is needed to balance the $32\times(-2)$ for the oxygen ions).

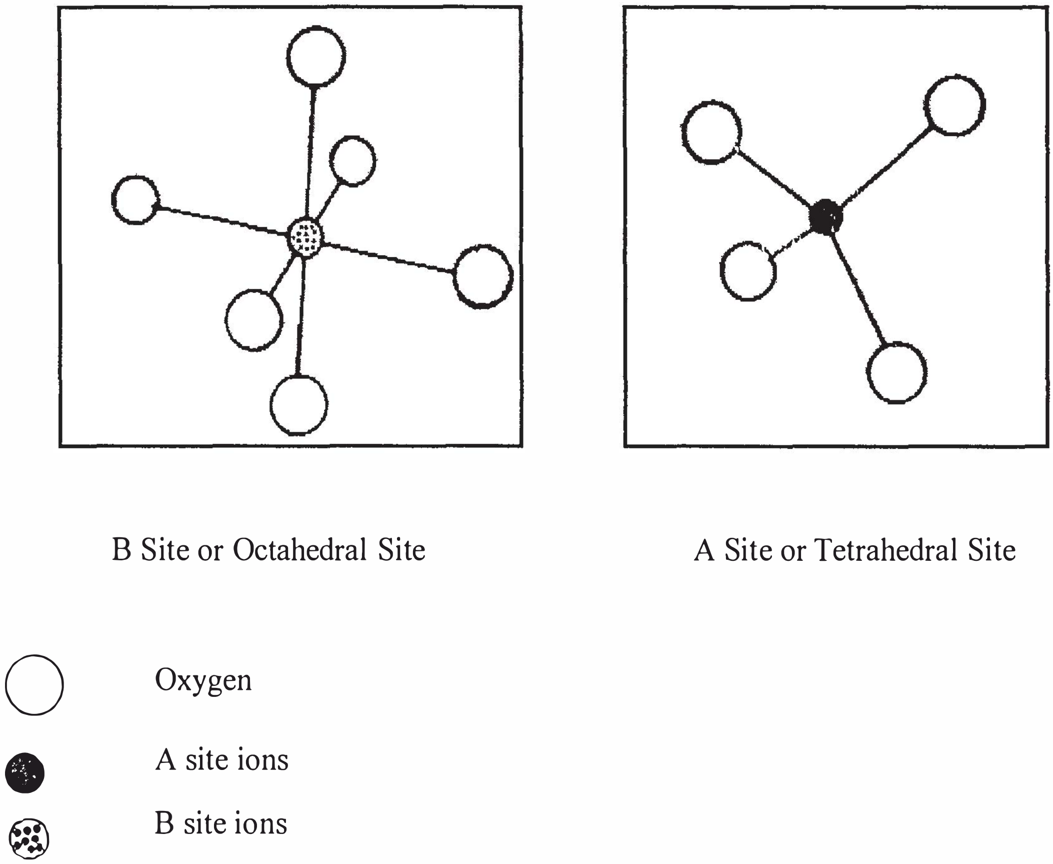

Figure 1.1: Sites of Unit Cell of the Spinel Lattice

The ion distribution for the two lattice sites can be determined by the ionic radii of the ions, the electronic configuration, temperature, the orbital preference for specific coordination, and the size of the lattice site. In general, the divalent are larger than the trivalent ions and the octahedral are larger than the tetrahedral sites. Therefore, the trivalent ions such as Fe^{3+} should go into the tetrahedral sites and the divalent ions should go into the octahedral sites. Exceptions are found in Zn^{2+} and Cd^{2+} which prefer the tetrahedral sites owing to the electronic configuration; further, the trivalent ion Fe^{3+} favours the two site occupancies.

In "normal spinel" M occupies the tetrahedral site ($[M]Fe_2O_3$) and in "inverse spinel" M occupies the octahedral site ($Fe[MFe]O_4$).

Examples of compounds as in the case of $Ni_{0.5}Zn_{0.5}Fe_2O_4$, there are eight formula units of nickel-zinc ferrite which form a unit cell of the spinel structure. The four Zn^{2+} ions fill half the tetrahedral sites, the remaining being filled by Fe^{3+} ions, and the others which are sixteen ions (four Ni^{2+} and twelve Fe^{3+} ions) sit on the octahedral sites.

1.3 Solid State Reaction (SSR) and Sol-Gel Route (SGR)

Before defining the solid state reaction and the sol-gel technique, solid state physics is first defined; it is defined as study of crystals and electron in crystals. The study of solid state physics as a prolongation of atomic physics commenced early in the years of the last century followed by the discovery of X-ray diffraction and prediction of crystalline properties.

Solid state reaction is the classical method of powder preparation to form a compound or solid solution. The preparation starts with a mixture of raw materials and then calcining, pulverizing, granulating, pressing, and sintering. For ferrite synthesis the sintering is carried out at high temperature, usually between 1,200 and $1{,}400^0$ C, depending on the ferrite type.

Sol-gel synthesis is a very new technique in which small colloidal particles are first formed in solution usually by hydrolysis of organic compounds. They then link to form a gel or are formed into ceramic particles by calcination. In the last few years, the sol-gel processing has been receiving a great deal of scientific attention among ceramic and glass scientists; this sol-gel processing offers new approaches to the preparation of ceramics and glasses. It is currently used commercially for production of ceramic fibers and abrasive powders and for thin films and coatings in electrical applications.

1.4 History and Application of Ferrites

Ferrous ferrites, or magnetite (Fe_3O_4 or $FeOFe_2O_3$) is a model of the naturally occurring ferrite which has been known for a very long time and its weak permanent magnetism applied to make compasses by the early navigators. In 1909, Hilpert published the first methodical study of the relation between the chemical and magnetic properties of a number of binary ion oxides. Around 1928 Forestier in France and Hilpert and Wille in Germany conducted examinations and quantitative investigations into the relation between the chemical composition, the saturation magnetization and the Curie temperature. The discovery of modern ferrites is ascribed to Kato and Takei; who examined some cobalt ferrites in the 1930s. Magnetic oxides were also studied in Japan between 1932 and 1935. Snoek (1936) was studying magnetic oxides in the Netherlands and Takei in Japan by in 1937 and 1939. Snoek and his co-workers at the Philips research laboratories in the Netherlands studied one of the most important properties which is the loss tangent divided by the permeability called the loss factor, which led Snoek to the development of the first soft ferrites for commercial application. Neel (1948) published the first explanatory theories on the origin of magnetism in ferrites.

Guillaud and his co-workers made further examination on the technology of ferrites. Since that time there was rapid development of many types of ferrites. The first edition of soft ferrites was in 1969. By that time, ferrites had become established as an important class of magnetic materials.

The spinel soft ferrites, manganese-zinc and nickel-zinc ferrites were the major application of spinel ferrites where high permeability and low loss have been the principal requirements. The first application started in a branch of telecommunication in the field of telephony transmission where the combination of good magnetic properties and high resistivity made these ferrites very appropriate in this application. In family television receivers, manganese-zinc ferrites and other ferrite compositions such as Li-Zn, Ni-Zn or Mg-Zn ferrites were used as magnetic core materials in field-shaping transformers and yoke rings for the deflection coils for picture tubes, in domestic radio receivers, and used as antenna rods. Other applications are found in recording heads for audio, digital information, duplicating magnetic tapes and video recording where both manganese-zinc and nickel-zinc spinel ferrites are used as magnetic elements. Other uses of ferrites are linear applications, such as cores for transformers in switched mode power supplies, and magnetic core memories for computer applications.

However, hexagonal ferrites (or permanent ferrites) are used in a wide variety of permanent magnets, the main applications are Direct Current (DC) motors particularly for the automobile industry and loudspeaker magnets. They are also used in travelling wave tubes, seals and latches in refrigerator doors and toys, telephone rings and receivers, and bubble memories.

Table 1.1: Survey of Some Ferrite Grades

Class	Initial permeability	Approx-freq range (MHz)	Main applications
		Manganese-zinc ferrites	
I	800 – 4000	< 0.2	Inductors for resonant circuits
II	500 – 1000	0.1 – 2	Inductors for resonant circuits, ferrite antennas for medium and long wave broadcast bands
III	3000 – 20000	low.f.– 200	High permeability application; low-power wide–band and low–power pulse transformers
IV	2000 – 5000	0.01 – 1	Applications requiring high saturation flux density and low loss at high flux densities, in transformers and chokes for switched mode power supplies and line scanning transformers in television receivers
		Nickel-zinc ferrites	
V	> 1000	1 – 300	Wide-band and pulse (for short duration pulses) transformers
VI	500 – 1000	5 – 300	Wide-band and pulse transformers, ferrite antennas and cores for electromagnetic interference suppression
VII	150 – 500	0.5 – 5	Ferrite antennas for medium and long wave broadcast bands, power transformers and cores for electromagnetic interference suppression.
VIII	70 – 150	2 – 20	Inductors for resonant circuits, ferrite antennas for short wave broadcast bands, power transformers and cores for electromagnetic interference suppression.
IX	35 –70	10 – 40	Inductors for resonant circuits and cores for electromagnetic interference suppression
X	12 – 35	20 – 60	Inductors for resonant circuits and cores for electromagnetic interference suppression
XI	< 12	> 30	Inductors for resonant circuits and cores for electromagnetic interference suppression
		Manganese-zinc or nickel-zinc ferrite	
XII	-	-	Ferrites dedicated to electromagnetic interference suppression or special applications not listed in other classifications

Finally, a survey and classification have been made from catalogues and commercial literature concerning with manganese-zinc and nickel-zinc ferrites, and the application classification is given in the Table 1.1.

1.5 Magnetoplumbite Structure

Magnetoplumbites are a class of magnetic oxides which have hard (permanent) magnetic properties and a hexagonal crystal structure. The Magnetoplumbites have a general chemical formula of $MFe_{12}O_{19}$, or $MO.6Fe_2O_3$, where M represents barium (Ba), strontium (Sr) or lead (Pb). The Fe_2O_3 can be partially replaced with Al, Cr, Ga or Mn. They are characterized by having very large coercivities. A strong magnetization remains after a magnetizing field has been removed, and residual magnetization is stable even if certain strength of demagnetization field is applied.

Compared with soft magnetic ferrite, hard magnetic ferrite is weak in structural sensitivity, and is relatively little influenced by impurities and by firing conditions. To obtain high coercive force with high density, however, it is essential for sintering to proceed at low temperature, controlling grain growth. At times, additives such as silicon oxide or bismuth oxide must be used (Somiya, 1989).

Basically, however, the production method is not very different from that used for soft magnetic ferrite. Some specialized strategies are used, however, such as pressing in magnetic field in advance for anisotropic magnets. At present the wet method (wet pressing in a magnetic field) has become the main force in improving the characteristics of anisotropic magnets.

1.6 The Objective of Work

This study is focused on comparison of nickel-zinc and nickel-zinc-copper ferrite synthesised by conventional solid state reaction and sol-gel technique. The choice of composition of a soft ferrite is made to achieve one or more of the properties of ferrite. The objectives of work can be described as follows:

1. To improve the properties of ferrite by reaching the following:

1.1 Maximum permeability

1.2 Minimum losses

1.3 Adequate saturation magnetization and low coercivity

1.4 Required frequency band

1.5 High electrical resistivity

1.6 Mechanical hardness for wear stability

1.7 High Curie temperature

1.8 Low porosity

1.9 High density

1.10 Finally but by no means the least important, minimum cost

2. To realize an easy manufacturing process

3. Shorter time of preparation

4. To find or create new raw materials with reasonable cost