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Effect of preparation techniques on the magnetic properties of nano-spinel ferrite

Thesis

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جامعة عين شمس

تأثير طرق التحضير على الخواص المغناطيسية للفيريتات المغزلية النانومترية

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Aim of the Work

The system of $Li_{0.1}$ $(Co_{1-x}$ $Cd_x)_{0.8}$ $Fe_{2.1}$ O_4, $0 \leq x \leq 0.8$ was investigated. It was prepared by two different techniques: sol-gel method and sol-gel auto-combustion method. Then, the effect of Cd-substitution as well as the preparation technique on the micro structure, magnetic and optical properties will be studied. The effect of composition and preparation method on the surface area and catalytic activity will be included.

الملخص العربى

تم تحضير مركب من الفريتات المغزلية النانومترية -تبعا للتركيب الكيميائي:

$[Li_{0.1}(Co_{1-x}Cd_{x})_{0.8}Fe_{2.1}O_{4}]$; x=0, 0.2, 0.4, 0.6 and 0.8- بإستخدام طريقتين مختلفتين و من ثَم أمكن تقسيم العينات إلى مجموعتين:

المجموعة الأولى :تم تحضير العينات بطريقة "sol-gel" و تمت معالجتها حرارياً عند 800 درجة مئوية لمدة ساعتين للحصول على عينات أحادية الطور.

المجموعة الثانية: تم تحضير العينات بطريقة "sol-gel auto-combustion" و تم الحصول مباشرةً على الفريت أحادي الطور دون اللجوء للمعالجة الحرارية.

تم التأكد من التركيب البلوري للفريت بإستخدام تحليل الأشعة السينية و منها تم الحصول على معامل الخلية و حجم الكريستالة ، كما تم أيضاً حساب نسبة الفراغات في العينات و دراسة تأثير أيون الكادميوم (Cd^{2+}) على كل ما سبق.

و بإستخدام الميكروسكوب الإلكتروني النافذ تم حساب متوسط حجم الجسيمات و تجانس توزيعها و قد وُجد أن حجم الجسيمات للمجموعة الأولى أكبر من حجم جسيمات المجموعة الثانية و عزى ذلك إلى الاختلاف في طريقة التحضير المستخدمة. تم التحقق من عدم إختلاف توزيع الأيونات داخل الفريت رغم اختلاف طريقة التحضير بإستخدام تحليل الأشعة تحت الحمراء.

أثبتت القياسات المغناطيسة تأثر جميع الخواص المغناطيسية (قابلية التمغنط M_s و المجال القهري H_c) بتركيز أيون الكادميوم (Cd^{2+})حيث أوضحت الدراسة أن قابلية التمغنط للمجموعة الأولى أعلى من المجموعة الثانية بينما المجال القهري للمجموعة الأولى أقل منه للمجموعة الثانية و تم تفسير ذلك الإختلاف تبعاً لتغير حجم الجسيمات للمجموعتين.

و بدراسة تغير السماحية الابتدائية (initial permeability) مع درجة الحرارة أمكن تعيين درجات حرارة كوري و وٌجد أنها تقل بزيادة أيون الكادميوم في المجموعتين كما تم استنتاج مدى التجانس (homogeneity) في العينات حيث وُجد أن التجانس في المجموعة الأولى أكبر منه في المجموعة الثانية.

و قد تم استنتاج فجوة الطاقة الضوئية من خلال (DRS) حيث وُجد أن فجوة الطاقة الضوئية تقل بزيادة تركيز الكادميوم و أنها تتأثر بحجم الجسيمات كما أنها ناشئة من خلال الانتقال المباشر.

و كتطبيق على استخدام هذا المركب من الفريتات، تم دراسة النشاط الكيميائي "النشاط الحفزي" للعينات و كيفية الاستعانة بها للتخلص من المركبات العضوية مثل الصبغات و بالتالي تنقية المياه و تبعا للنتائج فقد أظهرت تلك العينات أن لهذا المركب نشاطا كيميائياً عالياً.

Chapter 1

Theoretical Background

Ferrite is a type of ceramic compound composed of iron oxide (Fe_2O_3) combined chemically with metal oxide. According to the chemical formula and the ion concentration, different types of ferrites are recognized (Spinel, Garnet and Hexagonal). These types of ferrites will be briefly mentioned. However, intensive discussion of the spinel ferrites will be considered. Therefore, the crystal structure, the distribution of the metal ions and the different interactions between these ions in the spinel ferrites will be discussed. Moreover, molecular field theory and Néel theory will be outlined.

Types of ferrites:

Spinel ferrites:

Spinel is the most widely used family of ferrite. The chemical composition of a spinel ferrite can be written in general as MFe_2O_4 $\{MO+Fe_2O_3 \rightarrow MOFe_2O_3\}$ where M is a divalent metal ion such as Co^{2+}, $Zn^{2+,}$ Ni^{2+}, Cd^{2+}, Cu^{2+} or a combination of these ions.

In the next sections of this chapter the crystal structure and the different properties of spinel ferrites will be discussed in details.

Garnet Ferrites:

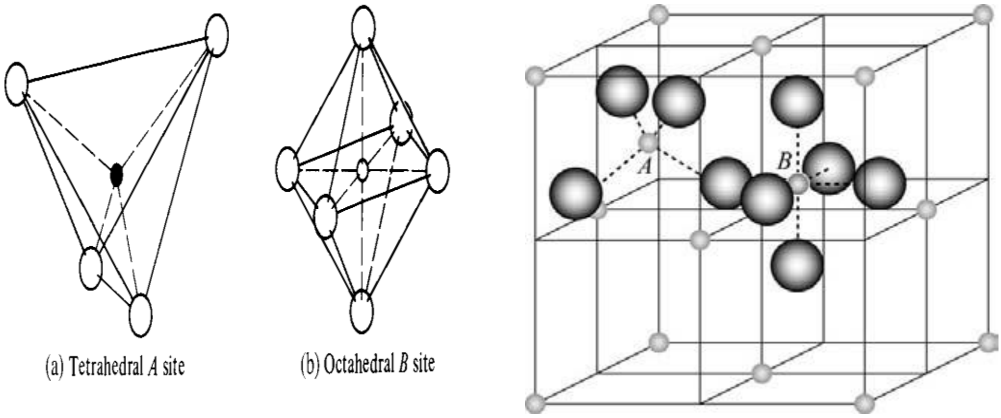
The general formula for garnets is $Me_3Fe_5O_{12}$, where Me is a rare earth metal ions such as Y, La, Nd, Pr, Sm and Gd. The cubic unit cell contains 8 formula units or 160 atoms, which can be described as a spatial arrangement of 96 O_2- with interstitial cations. Yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG) is a well-known garnet. The coordination of the cations is considerably more complex than spinels, with 24 Y^{3+} in dodecahedral sites, 24 Fe^{3+} ions in tetrahedral sites and 16 remaining Fe^{3+} in octahedral sites. Similar to spinels, a wide range of rare earth ions or transition metal cations can substitute Y^{3+} or Fe^{3+}; ions on dodecahedral and octahedral sites. Each type of lattice site will accept other metal ions at dodoctahedral sites, octahedral sites and at tetrahedral sites. Thus pentavalent ions such as V^{5+} and As^{5+} can occupy tetrahedral sites, while Ca^{2+} substitute ions on dodecahedral sites.

Hexagonal ferrites:

Hexagonal ferrites are widely used as permanent magnets and are characterized by possessing a high coercivity .Their general formula is $MeO \cdot 6Fe_2O_3$ where Me can be Ba, Sr, or Pb. The hexagonal ferrite lattice is similar to the spinel structure, with the oxygen ions closely packed, but some layers include metal ions, which have practically the same ionic radii as the oxygen ions. This lattice has three different sites occupied by metals: tetrahedral, octahedral, and trigonal bi pyramid (surrounded by five oxygen ions).

Crystal Structure of Spinel Ferrites:

The unit cell of spinel structure (named after the mineral spinel, $MgO \cdot Al_2O_3$) consists of eight formula units ($8MFe_2O_4$), where M is the divalent metal ion as shown in Fig. (1-1).The oxygen anions are packed in a face-centered cubic arrangement such that there are two kinds of spaces between the anions – tetrahedrally coordinated (*A*) sites as shown in Fig. (1-1a), and octahedrally coordinated (*B*) sites as shown in Fig. (1-1b).The unit cell contains 64 tetrahedral sites and 32 octahedral sites.



(a) Tetrahedral *A* site

(b) Octahedral *B* site

(c)The unit cell of spinel ferrite

Fig. (1-1): Schematic of the spinel structure. The oxygen anions form close-packed with tetrahedral and octahedral interstitial sites occupied by *A* and *B* cations.

The unit cell of edge “a” can be divided into eight octants, each of edge a/2, as shown in Fig. (1-2).The four shaded octants have identical contents, and so do the four unshaded octants. One tetrahedral site occurs at the center of the right octant and other tetrahedral sites are the same. One octahedral site is connected by dashed lines to six oxygen ions, two of which, shown dotted, are in adjacent octants behind and below. The oxygen ions are arranged in the same way for each octant.

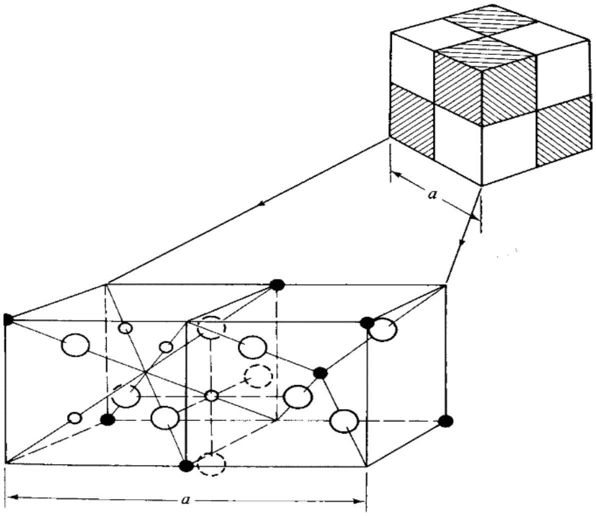


Fig.(1-2): Eight octants of a unit cell of spinel ferrites. The locations of metal ions in four shaded and unshaded octants are identical.

Distribution of the Metal Ions over Octahedral and Tetrahedral Sites in Spinel Ferrites:

The distribution of metallic ions between A and B sites, in spinel ferrites, are divided into three types:

(i) Normal spinel: In this type, the divalent metal ions (M^{2+}) are in tetrahedral sites (A) while trivalent metal ions are in octahedral site (B). Examples for normal spinels are cadmium and zinc ferrites. Their chemical formula can be written as:

(Cd^{2+}) [Fe_2] O_4 and (Zn^{2+}) [Fe_2] O_4. The brackets ( ) and [ ] refer to A and B sites respectively.

(ii) Inverse spinel: In this type, the divalent metal ions (M^{2+}) and half of Fe^{3+} ions are in octahedral sites B. The other half of Fe^{3+} ions occupy the tetrahedral sites A. Nickel ferrite, (Fe^{3+})

[Ni^{2+} Fe^{3+}] O_4, and cobalt ferrite, (Fe^{3+}) [Co^{2+} Fe^{3+}] O_4, are examples of the inverse spinels.

(iii) Intermediate spinel: In this type, both divalent and trivalent metal ions are distributed in tetrahedral and octahedral positions. For example the Manganese ferrite in which the two metal ions are divided between the two sites and can be written as $\left(Mn_x^{2+}\,Fe_{1-x}^{3+}\right)\left[Mn_{1-x}^{2+}\,Fe_{1+x}^{3+}\right]O_4$.

Therefore, the general cation distribution can be represented as

$$\left(M_\delta^{2+}\,Fe_{1-\delta}^{3+}\right)\left[M_{1-\delta}^{2+}\,Fe_{1+\delta}^{3+}\right]O_4^{2-}$$

, where δ is the degree of inversion, i.e. it denotes the fraction of divalent cations in tetrahedral sites,

$\delta = 1$ for normal spinel

$\delta = 0$ for inverse spinel

The value of δ depends upon the method of preparation and some other factors that will be discussed in the next section.

Factors affect the Cation Distribution in Spinel Ferrites:

The cation distribution of metal ions between tetrahedral and octahedral sites is affected by different factors such as ionic radius, valence. The site preference of the various ions as a result of their electronic configurations plays also an important role in the cation distribution.

(i) The Ionic Radius:

According to the atomic radii we have to expect that the smaller ions will tend to occupy (A-site) because the tetrahedral sites are smaller than the octahedral (B-sites) and vice versa.

The values of the radii r_A and r_B are given by:

$$r_A = (u - 1/4)\, a \sqrt{3} - r(O^{2-}) \qquad (1\text{-}1)$$

$$r_B = (5/8 - u)\, a - r(O^{2-}) \qquad (1\text{-}2)$$

where u is the oxygen parameter; u=3/8 and $r(O^{2-})$ is the ionic radius of oxygen ion.