

Immobilization of Metal Ions Using Low-Temperature Calcination Techniques of Spinel-ferrites

Fu Su Yen, Hsiao Chiun Kao, and Wei Chien Chen

Department of Resources Engineering
National Cheng Kung University
1 University Rd.
Tainan, Taiwan 70101, ROC

Formation of stoichiometric lithium-, nickel-, and zinc- ferrites by calcining organo-metallic precursors a temperature below 400°C is examined using DTA/TG, and XRD techniques. It attempts to simulate the immobilization of metal ions in industrial liquid influents (waste) through the synthesis of stoichiometric spinel ferrites (SSF).

Two steps of the SSF formation during thermal treatments are noted. The transformation of magnetite to γ -Fe₂O₃ and subsequent first formation of SSF were observed at temperatures ranging from 200 to 450°C. The formation of cation-containing γ -Fe₂O₃ and subsequent second formation of the ferrite occurred at temperature ranges of < 450°C and 500 to 650°C, depending on the heating rate used. Then the temperature range of 200 to 450°C is critical to the performance of the technique, because a calcination at the range would lead to a complete formation of SSF, avoiding the occurrences of γ -Fe₂O₃ and ion-containing γ -Fe₂O₃. If not, so α -Fe₂O₃ would occur. And annealing at temperature above 650°C must be employed by which solid-state reaction of α -Fe₂O₃ with metal ions (possibly metal oxides) to form SSF can be conducted.

Key words: Spinel-ferrite, iron oxides.

Introduction

The industrial ferrite ($M\text{Fe}_2\text{O}_4$, where the M 's are divalent cations with coordination number, CN=6) is a nonmetallic magnet. It is normally called as ferromagnetic spinel because of having the spinel crystal structure. These spinel structures have a close-packed (fcc) structure of O²⁻ ions with cations selectively positioned in the 6-fold and 4-fold interstitial sites. Theoretically most of the divalent cations can position in the 6-fold interstitial sites (Table I). The ferromagnetic spinel technology has advanced at a rapid rate, due in part to the ease of composition modification to meet specific applications. It has been used as the raw materials for manufacturing soft magnets. For examples, the MnZn-, NiZn- and Li- ferrites are used as antenna rod in communication devices, flyback transformer and power transformer in power converter, deflection yoke in electron beam deflection, and recording head in information recording systems.

Since most of the divalent cations can selectively positioned in the 6-fold and 4-fold interstitial sites of the spinel structure, the structure is able to undertake variable cations released from industrial processes in

the liquid and solid forms, being a scavenger to the metals for industrial wastes. And because of that, the ferromagnetic spinel can be an ultimate disposal mineral for the hazardous element. And comparatively, it can be a medium for collecting usable elements from industrial disposals.

Ferromagnetic spinels are generally synthesized using solid state reactions under higher temperature (>900°C) treatments, being an energy intensive industry. Recent studies reported [2-5] that organo-metallic precursors can be used as the alternative methods to produce ferromagnetic spinels at lower temperatures. However, the lower temperature process encounters the formation of non-stoichiometric ferrites. And in general, two steps of the stoichiometric spinel ferrite (SSF) formation during thermal treatments are noted [6]. The transformation of magnetite to γ -Fe₂O₃ and subsequent first formation of SSF are observed at temperatures ranging from 200 to 450°C. And the non-SSF formation of cation-containing γ -Fe₂O₃ and subsequent second formation of the ferrite occurred at temperature ranges of < 450°C and 500 to 650°C, depending on the heating rate used. The first step results in the formation of α -Fe₂O₃, transformed from γ -Fe₂O₃. The second step induces

the decomposition of the cation-containing γ -Fe₂O₃ into SSF and α -Fe₂O₃. In other words, if ferrites formed are nonstoichiometric, they are thermally metastable. These may initiate two shortcomings: The immobilization of cations can be reduced per unit weight of ferrite, and ultimate disposal stability can be deteriorated.

Since γ -Fe₂O₃ is thermodynamically a metastable mineral of inverse spinel structure with vacancies distributed in its B-sites. The ratio of the vacancy (Δ) to the Fe³⁺ in the B-site is 1 : 5. When the mineral occurs at lower temperature, the ordering of vacancy causes a decrease in the free energy and it is presumably stabilized [6]. However, as the temperature rises, the γ - transforms to the stable α -Fe₂O₃ phase. Studies indicate that the transformation occurs at the temperature range 400 to 450°C. if the γ - is obtained by decomposition of salts.[3,4,8,9]. Studies have also revealed that the presence of cations at the structure can substantially increase the phase transformation (decomposition) temperature. For examples, with 0.2 mole % Na present the temperature can move up to >600°C [10]. Similar studies were reported for ≤ 1 mole % of Co, Ni, Zn, Cu, and Mn (540 - 650°C) [11] and 0.1 mole % of La, Pr, and Nd (~615°C) [12]. Further, the addition of Ba can even stabilize the structure [13].

Thus it is noted that when preparing a stoichiometric ferrite it is important to bring about a complete reaction for γ -Fe₂O₃ with the cations at the temperature range of 200 to 450°C, forming stoichiometric ferrite at the temperature range. It is necessary to avoid either leaving residual γ -Fe₂O₃, or forming cation-containing γ -Fe₂O₃.

In this study an attempt is made to investigate the thermal behavior and the relationships between the presence of γ -Fe₂O₃ and cation-containing γ -Fe₂O₃ (hereafter designated as *M*- γ -Fe₂O₃) during the formation of SSF using tartrate gel techniques. To proceed a concise study, three cation, Ni⁺², Zn⁺², and Li⁺ -ferrites were examined. The starting material were organo-metallic gels obtained using tartrate techniques. Studies are focused on the reaction sequence for forming SSF at the temperature range of 200 to 450°C, so that decomposition of the product can be eliminated.

The formation of SSF is believed to perform through a topotactic reaction (TTR) [14] due to the structure similarity between the reactants and products. This is

an energy-saving process of producing ferrite powders at lower temperatures. Moreover, if the process is possible, abundant low quality heat currently generated by various plants can be used as the energy source.

Experiment

Precursor preparation

Reagent-grade acetates of nickel (Ni(CH₃COO)₂ • 2H₂O, Ferak), zinc (Zn(CH₃COO)₂ • 2H₂O, Ferak), and lithium (LiCH₃COO) • 2H₂O, Ferak), ferric nitrate (Fe(NO₃)₃ • 9H₂O, Ferak), and tartaric acid (C₄H₆O₄, Ferak) were dissolved in ethyl alcohol (99.5%, Seoul). Three solutions with Ni : Fe = 1 : 1, Zn : Fe = 1 : 1, and Li : Fe = 1 : 5 were then prepared as to make up the precursors for the three cation-ferrite. Precipitates were then obtained by titrating the as prepared solutions into the stirred tartaric acid solution separately. The quantity of the tartaric acid was 20% in excess over the stoichiometric amount required to meet the charge balance. The precipitate remained in the solution for 30 min with constant stirring to ensure that the reaction was complete. The precipitate was then separated from the solution using a Buchner funnel. Washing and filtration were repeated three times before the precipitate was dried at 75°C for 24 h. The dried gels were ground to -200 mesh (< 74 μ m) and used as the starting material for the investigation. Calcined powders were obtained by calcination of the gel powders at specified temperatures for pre-set times. The heating rates were 2, 5, 10, 15, and 20°C /min. Two sets of calcined samples were examined:

Quenched samples: samples were heated to the pre-set temperatures with heating rates of 2, 5, 10, 15, and 20°C/min then quenched to room temperature.
Annealed samples: Samples were annealed at pre-set temperatures for 2 h with a heating rate of 5°C/min.

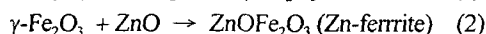
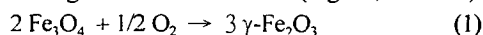
Characterization

Crystalline phases in the gel and the calcined powders were identified by XRD powder methods using Ni-filtered CuK α radiation (Rigaku, Tokyo). Thermal behavior examinations were conducted using DTA/TGA (Setaram TGA92) in air at several heating rate, including 2, 5, 10, 15, and 20°C /min.

Results and discussion

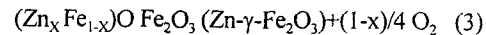
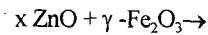
DTA profile

Figure. 1 illustrates the DTA profiles of Ni-, Zn-, and Li- Fe tartrate gels with a heating rate of 10°C /min. The thermal reaction is comparable to the previous studies[4,5,6] that magnetite appears at X_m and then transforms to γ -Fe₂O₃ at X_γ . Formations of SSF and M - γ -Fe₂O₃ occur at temperature X_{sf} , before the transformation of γ - to α -Fe₂O₃, $X_{\alpha 1}$ takes place. Then the M - γ -Fe₂O₃ transforms to α -Fe₂O₃, and SSF at $X_{\alpha 2}$. Figure 2 demonstrates the typical DTA/TG profile of Zn-Fe tartrate gels measured using heating rates of 2, 5, 10, 15, and 20°C /min. Compared with Fig. 1, it is obvious that the exothermic transformation of γ to α (~400°C) and M - γ to α + Zn-spinel (~600°C) are present as well (Fig. 2, $O_{x\alpha}$ and $O_{x'\alpha}$). The situation is easily observed with a heating rate of 10°C /min. However, as the heating rate varied, the quantity of and the temperature of α -Fe₂O₃ formation changed. Examining the DTA profiles with the phase identification obtained using XRD techniques on the quenched samples (Fig. 3), it is found that samples with higher heating rates, both the α -phase formation at the temperatures ~400 and ~600°C became evident. While the α -formation at both temperatures decreased and even the one occurred at ~600°C disappeared if the heating rate was lowered. The former can be ascribed to the fact that an annealing process conducted at the temperature range of the phase transitions of magnetite to γ -Fe₂O₃ and γ - to α -Fe₂O₃ (~400°C) would presumably result in the overlapping of the thermal reaction temperature range for the following two thermal reactions (Fig. 2b, 2°C/min) :



and depressed the formation of α -Fe₂O₃ through phase transition of γ -Fe₂O₃ to α -Fe₂O₃ (Fig. 2b, IIIx, 2°C /min) and Zn- containing γ -Fe₂O₃ to α and Zn-spinel (~600°C).

This is because the formation of Zn-ferrite eventually expense most of, and perhaps all the γ -Fe₂O₃ transformed from Fe₃O₄ to react with ZnO, forming ZnOFe₂O₃ (Zn-ferrite). Thus the amount of residual γ -Fe₂O₃ will be limited and α -Fe₂O₃ formation can be eliminated. On the other hand, reactions that could not produce Zn-ferrite resulted in the formation of Zn- γ -Fe₂O₃, or



Eventually, the more amount of Zn- γ -Fe₂O₃ formed, the more weight loss will observed. This fact is supported by the TG analysis obtained using 2 and 5°C/min. The former shows weight loss larger than that of the latter at temperature ~425°C. This is also reflected by that the former has a smaller exothermic reaction of γ - to α -Fe₂O₃ phase transition.

Low temperature annealing for Li, Ni, and Zn-containing gels

Application of the low temperature annealing processes can substantially form stoichiometric ferrites and enhance the thermal stability of the compounds. To check whether the formed ferrites are stoichiometric, the DTA technique is employed, because the DTA profile of a stable ferrite will exhibit no exothermic reactions at ~450 and ~600°C. Moreover, the ferrite sample should behave stable, without decomposition, forming α -Fe₂O₃ phase when the sample is annealed at the temperature range of 600 to 700°C. Figure 4 demonstrates the XRD profiles of checking the stoichiometric ferrites of Li, Ni, and Zn cations produced using low temperature annealing processes. The annealing temperature and duration for the three ferrite gels are 250-350°C/2h. The three as prepared ferrite powders are then annealed at 600°C for 2 h. Obviously, the α -Fe₂O₃ is eliminated, indicating that the ferrites formed at 250-350°C for 2 h annealing are stoichiometric.

Reaction mechanism

The thermal treatment conducted for organo-ferrospinel gels with various divalent cations generally produces ferrous iron (Fe²⁺) at the temperature range during the decomposition of starting organic components. As the heating temperature rises, an oxidation reaction proceeds. The ferrous iron becomes Fe³⁺, resulting in the formation of magnetite. The magnetite is subsequently oxidized to form γ -Fe₂O₃ (Fig. 1 and 2). It is very important to find that the γ -Fe₂O₃ is then react with the cations to form ferrospinel, depending on the temperature and duration of annealing processed for the gels.

It is noted that the formation of ferrosipinel takes place at temperatures lower than that for γ - to α - Fe_2O_3 phase transition. A fast heating rate will eventually overlap the steps of γ - Fe_2O_3 and cation-containing γ - Fe_2O_3 formation, and the latter results in, instead of forming stoichiometric ferrosipinel. Thus, on the contrary, the ferrosipinel phase can only be produced at temperatures higher than 650°C (Fig. 2, $20^\circ\text{C}/\text{min}$. Also refer to Table 2). Table 2 demonstraes the thermal reactions occur when three different heating rates are employed.

An annealing at the temperature slightly below that for the starting of γ - to α - Fe_2O_3 phase transition shows the advantage of forming ferrosipinels.

Conclusion

Stoichiometric ferrosipinels that can be thermally stable are prepared using lower temperature annealing techniques at a temperature range of 250 to 350°C with duration of 2 hours. During the annealing process the cations can react with γ - Fe_2O_3 through topotactic reaction. Annealed appropriately at the temperature with annealing time can be crucial to the preparation of the stoichiometric ferrosipinel. Otherwise the as- received spinels will be thermally metastable. As the temperature rises either the phase transition for γ - to α - Fe_2O_3 (at $\sim 400^\circ\text{C}$) or decomposition of the cation-containing γ - Fe_2O_3 into α - Fe_2O_3 and ferrosipinel (600°C) occur.

References

- [1]Oh, J. 1991. *Removal of Heavy Metals form Waste Water by Ferrite Processes*, Natl Cheng Uni., Taiwan.
- [2]Peshev, P. and Pecheva, M. 1978. *Mater. Res. Bull.* 13: 419-426.
- [3]Ritter, J. J. 1995, *J. Mater. Synthesis and Processing*, 3, 331.
- [4]Yang, J.M., Tsuo, W. J., and Yen, F.S.1999, *J. Solid State Chem.* 145, 50.
- [5]Tsumura, T. 1993, *J. Mater. Chem.* 3, 995.
- [6]Yang, J.M., Tsuo, W. J., and Yen, F. .S. 2001. *J. Solid State Chem.*, 147.2001
- [7]Andres-Verges, M., de Julian, C., Gonzalez, J. M., and Serna, C. J. 1993. *J. Mater. Scie.* 28: 2962.
- [8]Hirano, S. 1985. *Advances in Ceramics*, 15, 65.
- [9]Nikumbh, A. K. 1992. *J. Magn. Mater.* 114, 27..
- [10]Yamanobe, Y.1991. *Jpn. J. Appl. Phys.* 30, 478..
- [11]Sidhu, P. S. 1988. *Clays and Clay Minerals* 36, 31.
- [12]Nakatami, Y. 1983. *Jpn. J. Appl. Phys.* 22, 233.
- [13]Nallet, M. 1988. *IEEE Trans. Magn.* 24, 1829.

[14]Weat, A. R. 1986. *Solid State Chemistry and It's Applications*. John Wiley & Sons, New York.

Table I. Coordination number with Oxygen for common cation

C.N.= 4			
Be ²⁺			
Al ³⁺			
C.N.= 6			
Cr ³⁺	Ti ⁴⁺	Fe ²⁺	Li ⁺
Fe ³⁺	V ³⁺	Mn ²⁺	Na ⁺
Mg ²⁺		Ni ²⁺	
Ca ²⁺		Zn ²⁺	

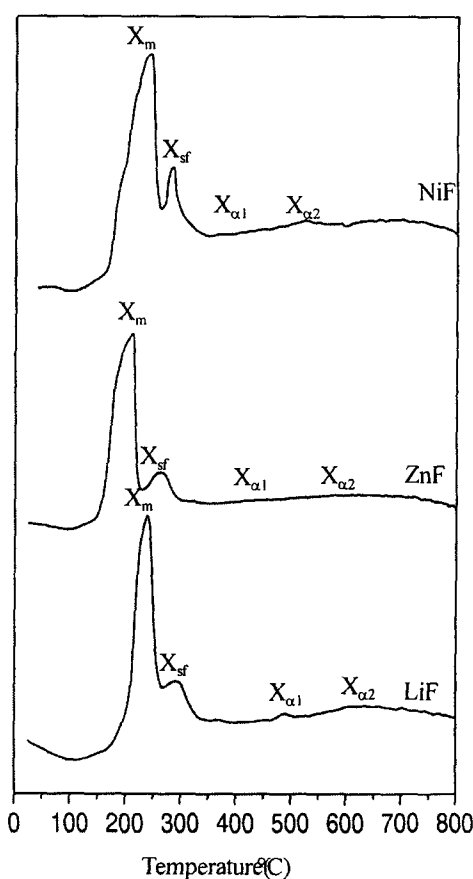


Figure1. DTA profiles of Ni, Zn, and Li-Fe tartrate gels. Heating rate: $10^\circ\text{C}/\text{min}$.

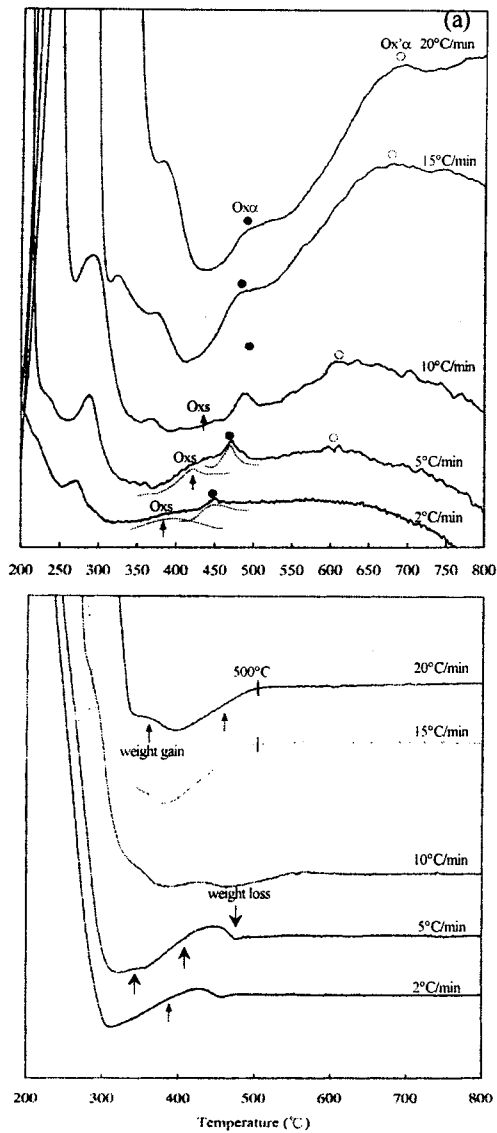


Figure 2. Typical DTA (a) and TG (b) profiles of Zn-Fe tartrate gels measured at various heating rates.

Table II. Lower heating rate favors the formation of stoichiometric ferrosphenel

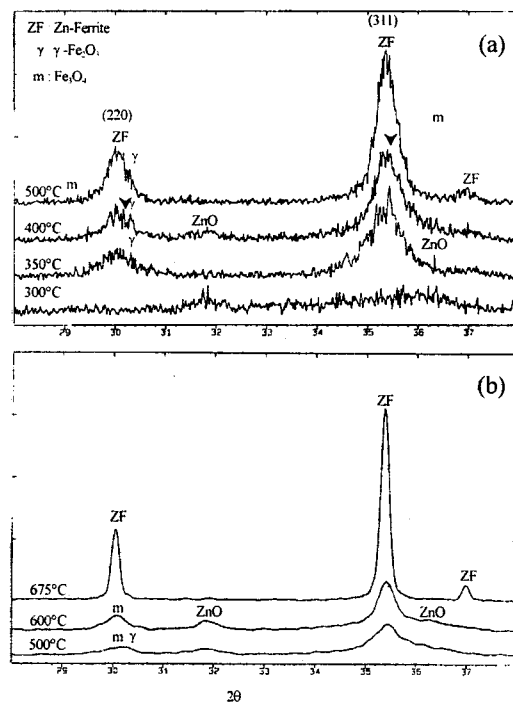
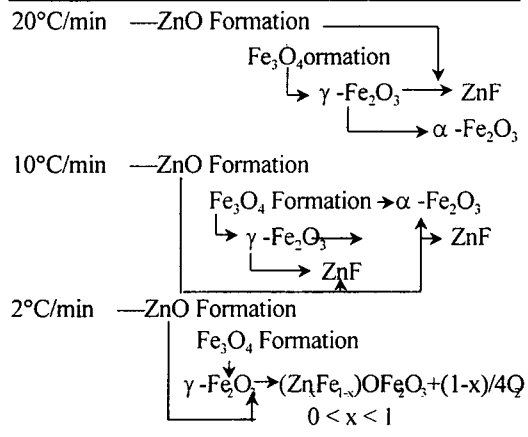


Figure 3. XRD patterns for thermally treated Zn-Fe tartrate gels as shown in Figure 2, using quenching techniques.

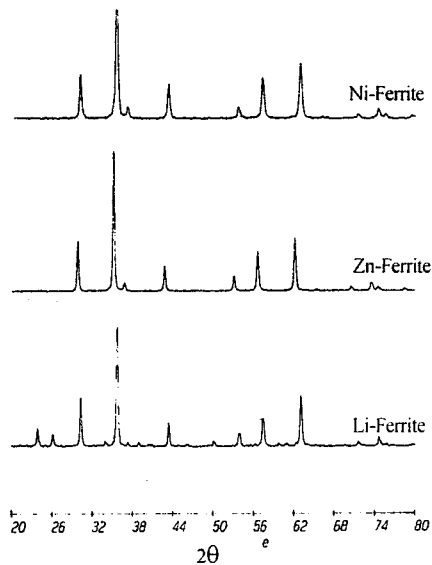


Figure 4. XRD patterns of 600°C/2 hours calcined Li, Ni, and Zn ferrites (LiFe₅O₈, NiFe₂O₄, and ZnFe₂O₄) obtained by calcination of tartrate gels at 350°C (Ni and Zn) and 250°C (Li) for 2 hours.