先驅物法在製備高品質錳鋅鐵氧磁石的探討
Study on Using a Precursor Technique to Prepare High Quality (Mn,Zn) Ferrites

中文摘要 (關鍵詞：先驅物法、鐵氧磁石、軟性磁石)

　　本研究利用檸檬酸先驅物法來製備高品質之 $MnFe_2O_4$ 和$(Mn,Zn)Fe_2O_4$ 粉體。藉由加入檸檬酸於含有所需鐵、錳或鋅離子之硝酸鹽水溶液中來鰲合溶液中金屬離子，並藉 NH_4OH 來調節溶液之酸鹼度。然後，溶液與乙二醇混合以進行聚酯反應。如此所得之酯類先驅物再經乾燥與熱處理來產製錳鋅鐵氧磁石。研究過程中，溶液酸鹼度與熱處理溫度對最終鐵氧磁石粉體性質之影響作了探討。

Abstract (Keywords: Precursor method, Ferrites, Soft magnets)

　　A citric acid precursor method was used to prepare $MnFe_2O_4$ and $(Mn,Zn)Fe_2O_4$ powder. Citric acid was added into an aqueous solution, which contained nitrates of iron, manganese, or zinc in stoichiometric ratios to form the required ferrites, to chelate the metallic ions. The pH values of stating aqueous solutions were adjusted using NH_4OH. After adding glycol into the solution and raising the solution temperature to 353 K, esterification caused the formation of the required solid precursors. The dried solid precursors so obtained were then pyrolyzed to form the corresponding oxides. The characteristics of solid powder were studied using XRD and SEM. Crystalline $MnFe_2O_4$ powder was obtained at 623 K for all pH of the starting solutions used. In air, Mn^{2+} in $MnFe_2O_4$ powder was oxidized to form Mn^{3+} at temperatures about 873 K, resulting in phase segregation. Zn^{2+} or Mg^{2+} was added into the compositions and succeeded, in some extent, preventing the oxidation of Mn^{2+}. Crystalline $(Mn,Zn)Fe_2O_4$ powder was obtained at 1273 K for all pH range of starting solutions used.

INTRODUCTION

　　Ferrites are iron containing complex oxides with technically interesting magnetic properties. Ferrites, based on the corresponding molecular structure, can be divided into three families: spinel, hexagonal and garnet ferrites. They are used for fabricating high-speed digital tapes, disk recorders, or cores of the high-frequency transformer. These applications require materials with high magnetic permeability, low magnetic losses and proper mechanical properties[1,2]. To have superior magnetic characteristics, there is a strong tendency toward the application of chemical methods in ceramic powder preparation for electronic ceramics. Several chemical methods are used or under development to prepare high quality electronic ceramics, such as coprecipitation, spray drying, frozen-drying, sol-gel, hydrothermal[3,4], and precursor processes. In this study, a citric acid precursor method was used to prepare fine powder of manganese ferrites and manganese zinc ferrites.

　　$MnFe_2O_4$ and $(Mn,Zn)Fe_2O_4$ are soft magnetic ferrites with inverse spinel structure and are important in the electronic and electrical industries. The citric acid precursor method involves five major steps: (1) preparing an aqueous solution that contains the required cations; (2) chelating the cations in the solution by adding citric acid; (3) adjusting the pH of the solution using proper acids or bases; (4) triggering poly-esterification by adding ethylene glycol into the solution, and increasing the solution temperature; (5) thermally treating the obtained solid precursor to form the corresponding oxides. Blank et al.[5] used this method to prepare $Y_1Ba_2Cu_3O_{7-x}$ powder with particle sizes in a range of 50 to 100 nm. Kjekshus and Karen's experimental results[6] showed that $Y_1Ba_2Cu_3O_{7-x}$ prepared using the citric acid precursor method can be sintered at lower temperatures. Lee and Fang[7] showed that high purity barium ferrite can be obtained using a citric

acid precursor method at 973 K and also pointed out that the ratio between the constituent cations and citric acid was important processing parameter.

Mn^{2+} is unstable in air and is ready to oxidize to Mn^{3+}. In air, Mn^{3+} will be reduced to Mn^{2+} above temperatures of 1173 K. Consequently, the formation of crystalline $MnFe_2O_4$ was, in general, carried out at temperatures above 1173 K. Without the existence of O_2 in atmosphere, Mn^{2+} will not be oxidized and $MnFe_2O_4$ was formed at temperatures as low as 923 K[8]. Boy and Wirtz[9] reported that by adding SiO_2 and $CaCO_3$ (0.2~1.0 wt%) into the composition, Mn ferrite can be produced at 873 K in air.

EXPERIMENTAL TECHNIQUES

$(Mn,Zn)Fe_2O_4$ ferrite powders were prepared by a citric acid precursor method. Starting solutions containing Fe^{3+}, Mn^{2+}, Zn^{3+} or Mg^{2+} ions were prepared by dissolving the predetermined amount of $Fe(NO_3)_3 \cdot 9H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3) \cdot 6H_2O$ into deionized water. The concentration of the starting solution was 0.15 mol/L in all experiments. Citric acid was added into the aqueous solution to chelate the metallic ions. The pH of the solution was adjusted using NH_4OH, ranging from 3 to 9. Ethylene glycol was then added into the solution with continuous stirring. Raising the solution temperature to 353 K caused the solution to undergo poly-esterification. The obtained solid precursor was dried at 393 K, followed by heat treatment at 623 K for 1hr and/or then 873 K for another hour. The powder so obtained was characterized using x-ray diffraction (XRD) and scanning electron microscopy (SEM). The resulting results are discussed.

RESULTS AND DISCUSSION
Mn-Fe Oxides System

Figure 1 shows the XRD patterns for the particles obtained by heating the solid ester-precursors, without addition Zn^{2+} or Mg^{2+} additives, at 623 K and 873 K, respectively. At 623 K, the particles were composed of crystalline $MnFe_2O_4$ only, regardless of the pH of starting solutions used. Although the sizes of $MnFe_2O_4$ crystallites at pH = 3 and 7 were bigger than those at other pH conditions, the $MnFe_2O_4$ crystallites were small for all the pH of starting solutions used. Raising the heating temperature to 873 K, the

particles obtained at all pH conditions contained Fe_2O_3 and Mn_2O_3 (fig. 1(b)). It is known that Mn^{2+} is unstable in air. Heating $MnFe_2O_4$ in air at 873 K caused Mn^{2+} in $MnFe_2O_4$ to oxidize to Mn^{3+}, resulting in the decomposition of $MnFe_2O_4$ and the formation of Fe_2O_3 and Mn_2O_3. To retard the oxidation of Mn^{2+} in air, small amounts of Zn^{2+} or Mg^{2+} were added into the starting solution and the effects of the additives on the phase stability were investigated.

Figure 2 shows the XRD patterns for the particles obtained by heating the solid ester-precursors, with pH = 7 and various amounts of Zn^{2+} additions, at 623 K and 873 K, respectively. At 623 K, the particles with three different Zn^{2+} additions, like those without any additives, were all composed of tiny $MnFe_2O_4$ crystallites. At 873 K, the particles with 0.5% Zn^{2+} additions contained bigger $MnFe_2O_4$ crystallites and did not appear any distinguishable phase segregation. It is evident that adding 0.5% Zn^{2+} additions into the starting solution and controlling the starting solution at pH = 7 can retard the oxidation of Mn^{2+} in $MnFe_2O_4$ and increase the thermal stability of $MnFe_2O_4$ in air. The effects of pH of the solution on the phase stability can be examined from the fig. 3. Figure 3 shows the XRD patterns of the particles, with two different amounts of Zn^{2+} additions (0.5% and 5%) and three different pH of the starting solutions (1.17, 7, and 9), obtained at 873 K. For 0.5% Zn^{2+} additions, the thermal stability of Mn^{2+} in $MnFe_2O_4$ was increased when the pH of the starting solution was controlled at 1.17 or 7; however, the phase segregation was observed for the particles prepared at pH = 9. On the other hand, 5% Zn^{2+} additions could not effectively prevent the oxidation of Mn^{2+} at 873 K for three different pH conditions used in this study.

Figure 4 shows the XRD patterns for the particles obtained by heating the solid ester-precursors, with pH = 7 and three different amounts of Mg^{2+} additions, at 623 K and 873 K, respectively. The present of small amounts of Mg^{2+} in the composition seemed to decrease the mobility of constituent ions in the samples, resulting in the formation of non-crystalline particles at 623 K. It is suggested that Mg^{2+} be dissolved into Mn-Fe oxides to form a solid solution and retards the rearrangement of Mn^{2+} and Fe^{3+} to form crystalline $MnFe_2O_4$ at 623 K. At 873 K, the constituent ions received sufficient

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energy to arrange themselves to form crystalline $MnFe_2O_4$ (fig. 4(b)). Fig. 4(b) also indicates that at pH = 7, addition of small amounts of Mg^{2+} in the composition could effectively increase the thermal stability of $MnFe_2O_4$. Figure 5 gives the SEM photomicrograph of the particles, at pH = 7 and with 5% Mg^{2+} additions, obtained at 873 K. It is clear that the derived $MnFe_2O_4$ powder was composed of submicron primary particles and agglomeration of the particles was observed.

Mn-Zn-Fe Oxides System

Figure 6 shows the XRD patterns for the particles obtained by heating the solid ester-precursors in air at 873 K, with four different pH of the starting solutions (0.1, 3, 7, and 9). When the pH of the starting solution was controlled at 0.1 or 10 the particles were composed of crystalline $(Mn,Zn)Fe_2O_4$ only; however, the phase segregation was observed for the particles obtained at pH=3 and 7. The particles obtained at pH=3 and 7 contained Fe_2O_3 and $(Mn,Zn)Fe_2O_4$. Raising the heating temperature to 1273 K for 12hr, the particles were composed of well-crystallized $(Mn,Zn)Fe_2O_4$, regardless of the pH of starting solutions used (fig. 7).

CONCLUSIONS

Without adding any additives, crystalline $MnFe_2O_4$ powder was obtained at 623 K for all the pH of starting solutions used. Heating this $MnFe_2O_4$ in air at 873 K caused Mn^{2+} in $MnFe_2O_4$ to oxidize to Mn^{3+}, resulting in phase segregation. To retard the oxidation of Mn^{2+} in air, small amounts of Zn^{2+} and Mg^{2+} were added into the starting solutions. Addition of small amounts of Zn^{2+} or Mg^{2+} in the composition the thermal stability of Mn^{2+} in $MnFe_2O_4$ did increase. For Zn^{2+} addition, the best composition to obtain crystalline $MnFe_2O_4$ is to add 0.5% Zn^{2+} into the starting solution at pH=1.17 and heat the specimen at 873 K. For Mg^{2+} addition, the best compositions in preparing $MnFe_2O_4$ is to introduce 2%, 3% or 5% Mg^{2+} in the starting solution at pH=7 and heat the powder at 873 K. In Mn-Zn-Fe Oxides System, crystalline $(Mn,Zn)Fe_2O_4$ powder was appeared at temperatures as low as 873 K.

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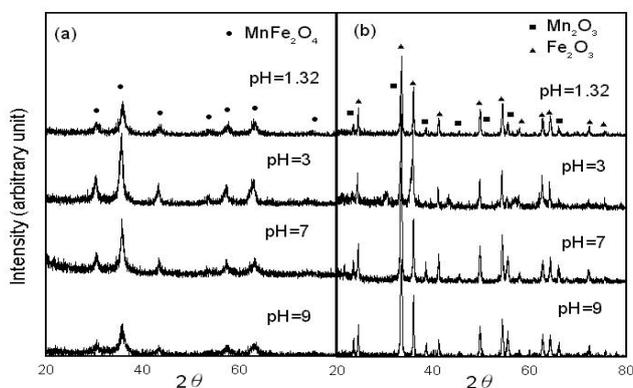
Figure 1. XRD patterns for the particles obtained by heating the solid ester-precursor in air at (a) 623K and (b) 873K, for 1 hr.
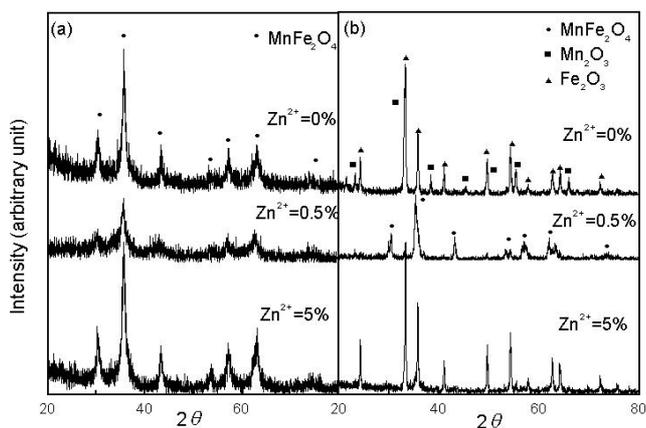
Figure 2. XRD patterns for the particles obtained by heating the
solid ester-precursor in air at (a) 623K and (b) 873K, with pH=7.

Figure 5. SEM photomicrograph of the particles obtained by heating the
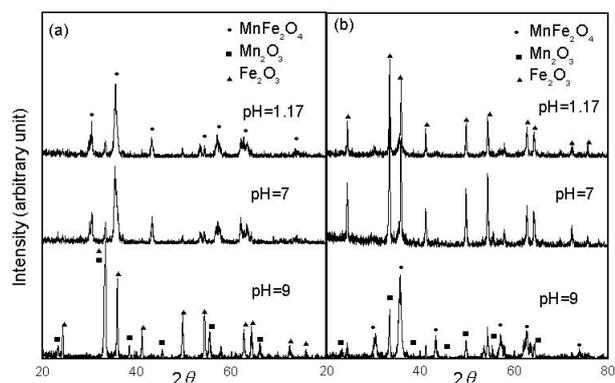solid ester-precursor in air at 873 K, with pH=7.

Figure 3. XRD patterns for the particles obtained by heating the solid
ester-precursor in air at 873K, with (a) 0.5% and (b) 5% Zn^{2+} additions.
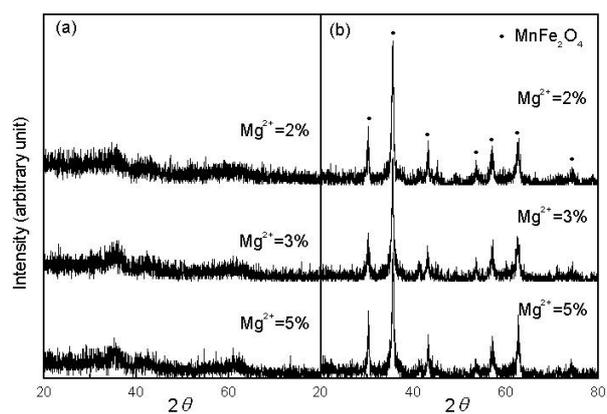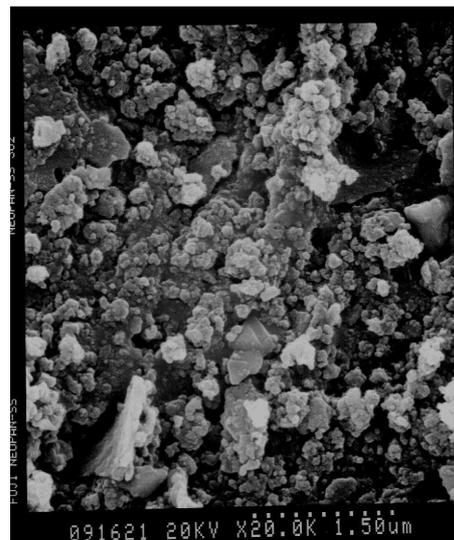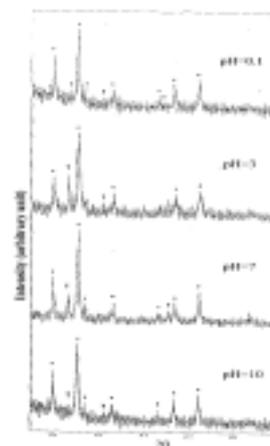

Figure 6. XRD patterns for the particles obtained by heating
solid ester-precursor in air at 623 K, with pH=0.1, 3, 7 and 10.

Figure 4. XRD patterns for the particles obtained by heating the
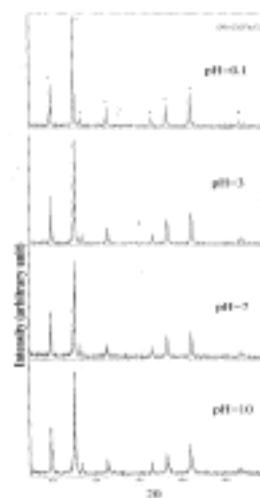solid ester-precursor in air at (a) 623K and (b) 873K, with pH=7.

Figure 7. XRD patterns for the particles obtained by heating
solid ester-precursor in air at 873 K, with pH=0.1, 3, 7 and 10.