Materials Chemistry and Physics 114 (2009) 362–366

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Preparation of Co-substituted MnZn ferrite fibers and their magnetic properties

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ARTICLE INFO

Article history:
Received 27 March 2008
Received in revised form 4 September 2008
Accepted 13 September 2008

Keywords:
Magnetic materials
Chemical synthesis
Magnetomenter
Magnetic properties

ABSTRACT

MnZn ferrite fibers are promising materials for technological applications. The $Mn_{0.4}Zn_{0.6-x}Co_xFe_2O_4$ ($x = 0.0$–0.4) ferrite fibers have been successfully prepared via the organic gel-thermal decomposition process using metal salts and citric acid. The structure, thermal decomposition process and morphologies of the gel precursors and fibers derived from thermal decomposition of these precursors were characterized by Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric and differential scanning calorimetry (TG/DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The saturation magnetization and coercivity of the prepared fibers were measured using vibrating sample magnetometer (VSM). The gel formed at pH 5–6 exhibits a good spinnability. The prepared ferrite fibers having a hollow structure are featured with diameters of 0.5–5 μm and aspect ratios up to 1×10^5. It is found that the $Mn_{0.4}Zn_{0.6}Fe_2O_4$ fibers obtained at low calcination temperature (400 °C) show superparamagnetism due to grain size below the threshold value. With increasing calcination temperature and prolonging holding time, both the saturation magnetization and coercivity of these fibers increase with an increase in crystalline grain sizes and improvement of the crystallization. The substitution of Co for Zn has a remarkable influence on the magnetic properties of the MnZn ferrite fibers. The saturation magnetization and coercivity of the $Mn_{0.4}Zn_{0.6-x}Co_xFe_2O_4$ ferrite fibers increase from 9.57 A m^2 kg^{-1} and 2.74 kA m^{-1} for $x = 0.0$ to 22.31 A m^2 kg^{-1} and 7.17 kA m^{-1} for $x = 0.4$, respectively.

1. Introduction

MnZn ferrites, one kind of functional spinels composed of mixed metallic oxides with a general formula AB_2O_4, are widely used in many electronic and magnetic devices due to their high magnetic permeability and low magnetic losses at high frequencies [1,2]. Many investigations on the preparation and properties of MnZn nanoparticles with different sizes and morphologies have been carried out [3–6]. Recently, microscale and nanoscale fibrous materials have drawn a great interest and stimulated intensive researches because of their potential high-tech applications. Fibrous forms of ceramic materials can be made stronger and often stiffer than the bulk ceramics. The incorporation of a magnetic material in fibrous form and subsequent effects of composite phase geometry on material properties have been reviewed [7] and it has been showed that short fibers with a high aspect ratio can bring a much high magnetic permeability than the same volume of materials in non-fibrous form [8]. There is therefore a great demand for preparative processes for ferrite fibers.

Sol–gel routes provide a mixing of multicomponents at an atomic or a molecular level at low temperatures, resulting in homogenous precursors. Consequently improved sintering rates at lower temperatures can be expected, leading to improved microstructure [9]. The aqueous organic gel route was originally developed by Pechini and Marcilly and coworkers. The process involves the aqueous reaction of single or multiple metal ions with a polyfunctional acid such as citric acid, to prevent precipitation and to produce stable complexes, thus allowing the production of an amorphous gel on drying, which can be subsequently decomposed to the metal oxides on thermal treatment. In comparison with conventional sol–gel processing routes based on alkoxides, the technique requires inexpensive precursors, allows the use of an aqueous based processing system and results in the formation of the oxides on heating. By using the organic gel route, Pullar and Bhattacharya [10] obtained barium M ferrite, $BaFe_{12}O_{19}$ fibers and strontium M ferrite, $SrFe_{12}O_{19}$ fibers with diameter in 3–6 μm. Although organic gel complex processing routes have been previously used to produce various oxide powders with multiple components [11], magnetic metal fibers [12] and refractory ceramic fibers [13], few researches on MnZn ferrite fibers with a hollow structure prepared by this route have been previously reported. The aim of this investigation was therefore to determine the feasibility of utilizing such a process route to produce hollow MnZn

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doi:10.1016/j.matchemphys.2008.09.037

Table 1
Effects of different molar ratio on gel spinnability.

Molar ratio (Me^{2+}:Fe^{3+}:CA)	Spinnability	Gel fiber quality
1:2:2.67	♦♦	gel fibre length <0.1 m
1:2:2.94	♦♦♦	0.1 m < gel fibre length < 0.2 m
1:2:3.20	♦♦♦♦	0.2 m < gel fibre length < 0.4 m
1:2:3.47	♦♦♦	0.1 m < gel fibre length < 0.2 m

ferrite fibers from starting reagents of metal salts and citric acid, and analyze the effects of Co doping on microstructure and magnetic properties on MnZn ferrite fibers.

2. Experimental procedure

2.1. Preparation of Co-doped MnZn fibers

$Mn_{0.4}Zn_{0.6-x}Co_xFe_2O_4$ ($x = 0$, 0.1, 0.2, 0.3 and 0.4) ferrite fibers were prepared by the organic gel-thermal decomposition method and the process was similar to that for $NiFe_2O_4$ ferrite fibers [14]. The starting reagents used were $Zn(NO_3)_2{\cdot}6H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$, $Co(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and citric acid (all are A.R. and from Shanghai Chemical Reagent Corporation). The required metal salts and citric acid were dissolved in deionized water to form aqueous solutions with a continuous magnetic stirring. The pH value of the solution was continually monitored and adjusted to 4–6.5 by adding ammonia solution. The final solution was magnetically stirred for 20–24 h at room temperatures and was transferred to a rotary evaporator and evaporated in a vacuum at 60–80 °C to remove surplus water until a viscous liquid was obtained. The resultant liquid was then poured into an evaporating basin and heated in vacuum at 75 °C until a spinnable gel could be used for drawing gel fibers by handling a glass rod. The spinning performance of the gel was estimated from the capability of fiber formation by immerging a glass rod of about 2 mm in diameter into the gel and then pulling it up by hand. The gel fibers were drawn from the spinnable gels and dried in a vacuum oven at 80 °C for about 10 h. The dried gel fibers were then put in an alumina crucible and subsequently were calcined in the range of 400–600 °C at ambient atmosphere. The MnZn ferrite fibers with a hollow structure were obtained by controlling the chemical composition and heating rate of gel fibers.

2.2. Characterization of the fibers

The structure, composition and morphologies of the gel precursors and the products derived from thermal decomposition of the precursors at different temperatures were examined by Fourier transform infrared spectroscopy (FTIR) using a model of Nexu670 spectrometer, X-ray diffraction (XRD) using a D/max2500PC diffractometer (RIGAKU), and scanning electron microscopy using a JSM-5600LV instrument (JEOL). The decomposition process was investigated by thermo-gravimetric (TG) analysis and differential scanning calorimetry (DSC) using a SDT2960 (TA) system. The magnetic properties were measured at room temperature by using the vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Gel formation and spinning performance

Aqueous organic gel processing routes most commonly utilize citric acid (CA) as the complexing agent. CA is known to form complexes with metal ions in aqueous solution such as Fe^{3+} and Me^{2+} (Mn^{2+}, Zn^{2+} and Co^{2+}). The optimized molar ratio at the pH value range of 5–6 was determined by testing spinning performances of the gel obtained. Table 1 shows the effect of chemical compositions on the gel spinnability. It can be seen that Fe–Mn–Zn citrate gel exhibits a best spinning performance when the molar ratio (Me^{2+}:Fe^{3+}:CA) is 1:2:3.2.

Fig. 1 shows the FTIR spectra for the gel precursor. The two bands at 1407 and 1593 cm^{-1} resulted from the C=O symmetrical and asymmetrical stretching vibration, which are the characteristic absorption peaks for the citrate. This is indicative of the complex formation. The bands appearing at 577, 547 and 466 cm^{-1} can be assigned to the characteristic vibration peaks of Fe–O, Mn–O and Zn–O bonds, respectively. The carbonyl peak at 1721 cm^{-1} can be attributed to surplus citric acid or dissociated carbonyls contained in the gel precursors.

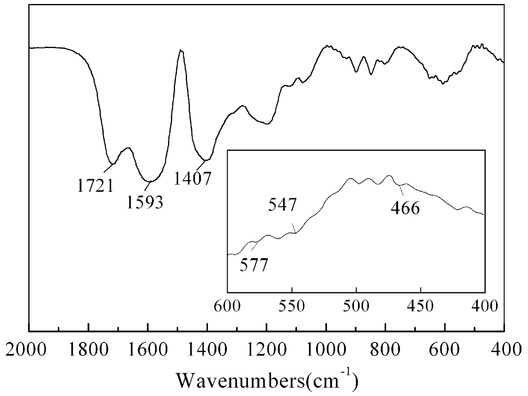

Fig. 1. FTIR spectra of the gel precursor for $Mn_{0.4}Zn_{0.6}Fe_2O_4$ fiber.

The gel spinnability depends on its structure, which is related to the complex structure formed during the complexing process. The complex structure is largely influenced by the liganding type among the carbonyl group and metal ions in aqueous solutions. According to ref. [15], there are three possible liganding types between carboxylate and metal ions. The value $\Delta\nu$ ($\Delta\nu = \nu_a - \nu_s$, ν_a and ν_s are the asymmetry and symmetry stretching vibration peak values of $RCOO^-$, respectively) can be used to classify the liganding type: the single-dentate corresponds to a higher value $\Delta\nu$, the double-dentate corresponds to a lower value $\Delta\nu$ and the bridge corresponds to an roughly equal value $\Delta\nu$ of the C=O in the complex compared to the free carboxylate. So, according to data from the gel FTIR spectra, the $\Delta\nu$ value is 186 cm^{-1}, which is lower than that for citrate–Na (196 cm^{-1}). This indicates that a double-dentate liganding type among the metal ions and citric acid may be dominative and a possible linear molecular structure can be formed during the complexation reaction. The gel consisting of these linear-type structural molecules shows a good spinnability.

3.2. Structural characterization of $Mn_{0.4}Zn_{0.6-x}Co_xFe_2O_4$ fibers

Fig. 2 shows XRD patterns of the gel precursor and $Mn_{0.4}Zn_{0.6}Fe_2O_4$ fibers obtained at different calcination temperatures for 2 h. It can be seen that the gel precursor is amorphous without containing crystalline inorganic salts. After annealing at 400 °C for 2 h, as shown in Fig. 2(b), a pure spinel phase is basically formed, and all of the main peaks are consistent with the characteristic peaks of cubic MnZn ferrite. The XRD lines are

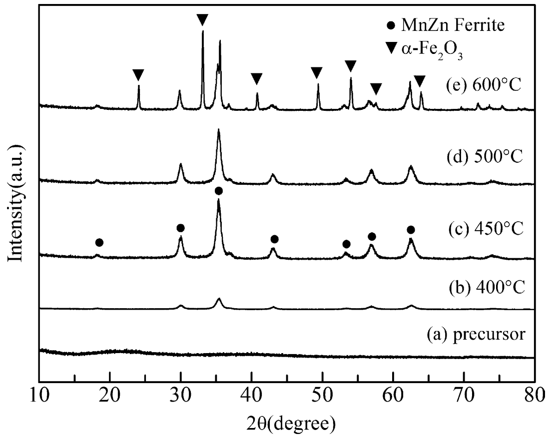

Fig. 2. XRD patterns of gel precursor and products derived from calcination of this gel precursor at different temperatures.