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Synthesis, structure and electromagnetic properties of Mn–Zn ferrite by sol–gel combustion technique

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ABSTRACT

The electromagnetic absorbing behaviors of a thin coating fabricated by mixing Mn–Zn ferrite with epoxy resin (EP) were studied. The spinel ferrites $Mn_{1-x}Zn_xFe_2O_4$ ($x=0.2$, 0.5 and 0.8) were synthesized with citrate acid as complex agent by sol–gel combustion method. The microstructure and surface morphology of Mn–Zn ferrite powders were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The complex permittivity and complex permeability of the fabricated ferrite/EP composites were investigated in terms of their contributions to the absorbing properties in the low frequency (10 MHz to 1 GHz). The microwave absorption of the prepared ferrite/EP composites could be tailored by matching the dielectric loss and magnetic loss and by controlling the doped metal ratio. The composites with the ferrite composition $x=0.2$ are found to show higher reflection loss compared with the composites with other compositions. It is proposed that the prepared composites can potentially be applied in electromagnetic microwave absorbing field.

1. Introduction

As a specific environmental pollution, electromagnetic interference (EMI) has currently attracted great attention due to the extensive utilization of electronic devices in various fields. In order to suppress the electromagnetic interference, development of ferrite composites, which has improved electromagnetic absorption, has been focused on by many researchers [1–4]. Spinel ferrite is becoming one of the most concerns for the following merits including the high magnetic moment, ease of synthesis and stable performance etc. [5,6]. In particular, Mn–Zn ferrite is widely used as microwave electromagnetic absorbing material and its unparalled performances, i.e. the controllable size and structural features, easy synthesis process and tunable electromagnetic properties, are responsible for the advantageousness over others.

The morphology and size of the synthesized ferrite can be tailored by different preparation methods such as ceramic method [7], coprecipitation [8], combustion method [9] and hydrothermal processing [10]. However, the problem is that that performance of ferrite prepared by traditional technique is far from the expectation. And the low purity, heterogeneousness as well as the aggregation limits the application in electromagnetic absorbing field. In addition, the electromagnetic properties of ferrite are dependent on the distribution of metal ions in the structure of crystalline Mn–Zn ferrite. Recently, the wide application of sol–gel combustion technique is connected to homogeneous and fine crystals resulting from its accurately controlled stoichiometric ratio and simple preparation [11–13]. To meet the increasing demand for electromagnetic absorbing films or coatings, ferrite and polymer matrix composites have been developed. Among the matrixes, Epoxy resin is one of the well-known matrixes. Its unique properties are quite attractive in terms of optical property and good mechanical properties and retaining the flexibility of the polymer [14]. It is the cost-effective method and flexible shaping that gives the potential application for ferrite/epoxy resin films or coatings.

In the present paper, Spinel ferrites $Mn_{1-x}Zn_xFe_2O_4$ ($x=0.2$, 0.5 and 0.8) with highly crystalline structure and excellent electromagnetic absorbing properties were synthesized by sol–gel combustion method. In the process of crystallite nucleus formation, aggregation of ferrite could be solved by introduction of citrate acid as complex agent which was conductive to high purity and homogeneous particles. The microstructure and morphology of the synthesized ferrites were characterized and analyzed. The complex permittivity, complex permeability and reflection loss of Mn–Zn ferrite/EP coatings were investigated in the low frequency (10 MHz to1 GHz). The structure and electromagnetic properties of the ferrite prepared were discussed for its potential application in electromagnetic absorbing field.

2. Experimental

$Mn_{1-x}Zn_xFe_2O_4$ powders were synthesized by sol–gel combustion method using citrate acid as complex agent. Fig. 1 shows an illustrated reacted process for the synthesis. High pure manganese

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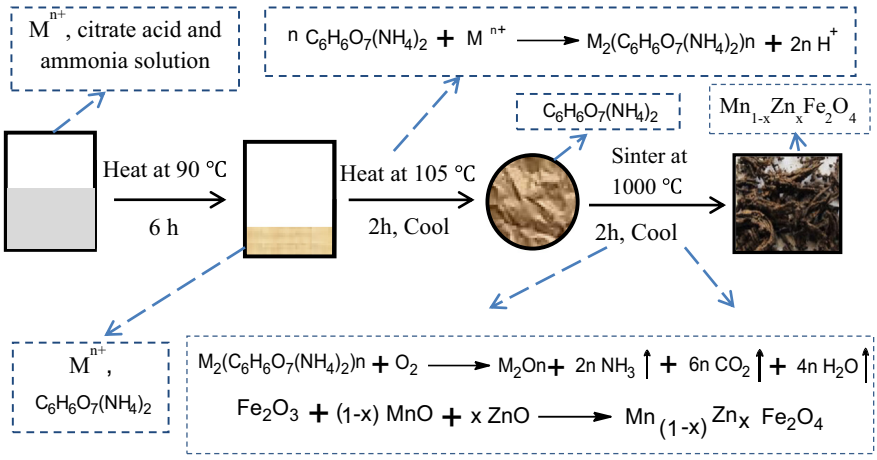

Fig. 1. An illustrated sol–gel combustion method process for the synthesis of $Mn_{1-x}Zn_xFe_2O_4$ (x=0.2, 0.5 and 0.8) ferrite.

chloride, zinc nitrate, and iron nitrate were weighted according to the required stoichiometry proportion of Mn–Zn ferrite by varying x=0.2, 0.5, 0.8, and dissolved in deionized water with continuous stirring. Citrate acid (citrate acid/metal ions=1:1 by molar ratio) was added to the prepared solution. Then, the solution was stirred vigorously with a magnetic needle to form a homogeneous solution at 80 °C. Ammonia solution was added by drop-wise to control the pH to 7. The final solution was heated at 90 °C for 6 h to obtain the wet gel by using a water bath. After that, the wet gel was heated at 105 °C for 2 h in oven, and then cooled down to the room temperature naturally to obtain dry gel. Finally, the fine ferrite powders were obtained by sintering the dry gel at 1000 °C for 2 h in sintering furnace. The structure of crystalline Mn–Zn ferrite was confirmed by XRD using Cu-Kα radiation.

The composite coatings were fabricated by mixing the Mn–Zn ferrite powders, epoxy resin and curing agent (1:10:1 by weight ratio) with continuous stirring at 60 °C to obtain homogeneousness. After that, the uniform coating was poured into a circular, disk-shaped with 4 holes of 5 mm in diameter. The dimension of the disk is 133 mm in diameter and 2 mm in thickness. Then the coating was heated at 60 °C in vacuum oven for 2 h. Finally, the cured even coatings were obtained after cooling to the room temperature naturally.

Morphological characteristics of Mn–Zn ferrite powders were examined by SEM. Better comparison could be ensured as this examination was conducted at the several locations of the sample. XRD was adopted to investigate the microstructure of the ferrite with Cu Kα radiation. Complex permittivity and permeability of the ferrite/EP composites were measured by an Impedance Analyzer (Agilent E4991A: 10 MHz to 1 GHz). The samples were prepared by mixing the ferrite powders with epoxy resin and curing agent (1:10:1 by weight ratio) and then a circular disk with diameter of 2 cm and thickness of 2 mm was formed. At the same time, a ring with external diameter of 2 cm, internal diameter of 0.5 cm and thickness of 2 mm could be noted. The reflection loss of the composites was measured by a Network Analyzer (Agilent E5062A: 10 MHz to 1 GHz) using a coaxial transmission line method.

3. Results and discussion

The typical XRD pattern of sintered $Mn_{1-x}Zn_xFe_2O_4$ powders (x=0.2, 0.5, 0.8) are compared in Fig. 2. It indicates that the typical XRD pattern of Mn–Zn ferrite is at (210), (220), (311), (113), (511), (440), which is accordance with the JCPDS standard card [15]. Fine crystals and high purity are expected from the strong intense peak and broad peak of $Mn_{0.8}Zn_{0.2}Fe_2O_4$. It also can be seen that the

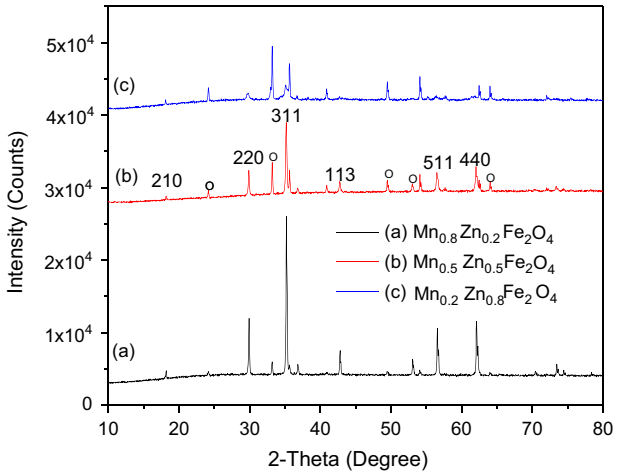

Fig. 2. XRD pattern of synthesized Mn–Zn ferrite (a) $Mn_{0.8}Zn_{0.2}Fe_2O_4$, (b) $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and (c) $Mn_{0.2}Zn_{0.8}Fe_2O_4$.

appearance of secondary phase of γ-Fe_2O_3 accompanying with the ferrite phase. It can be inferred that the natural sol–gel combustion reaction accounts for the formation [16]. Table 1 lists the X-ray peak intensity broadening of the (311) peak for the Mn–Zn ferrite crystalline structure at about 35° and the (119) peak for the γ-Fe_2O_3 at about 33°. It suggests that the content of γ-Fe_2O_3 tends to increase with the increasing content of Zn.

The morphology and microstructure of the synthesized particles are observed by scanning electron microscopy and illustrated in Fig. 3. It is clear that $Mn_{0.8}Zn_{0.2}Fe_2O_4$ particles are homogenous cubic spinel, which is confirmed by the XRD analysis above. In Fig. 3(A), one can note that ferrite particles are estimated to have an average size of 150–350 nm with narrow particle distribution. The SEM image of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ particles (Fig. 3(B)) offers the indication of an anomalous spherical shape and an average size of 200–400 nm. Fig. 3(C) exhibits that the $Mn_{0.2}Zn_{0.8}Fe_2O_4$ particles are clubbed shape and the average size is in the range of 0.5–1 μm. It follows that the size of the synthesized crystalline ferrite appears to increase as Zn substitution increases.

The alteration of complex permittivity ($\varepsilon=\varepsilon'-j\varepsilon''$) over the frequency range of 10 MHz to 1 GHz is given in Fig. 4 (A: real (ε') and B: imaginary (ε'') parts of permittivity). The dielectric properties of the ferrite/EP composite materials are mainly attributed to the interfacial polarization, the intrinsic electric dipole polarization and the space charge polarization [16–18]. As presented in Fig. 4, the real part of the complex permittivity (Fig. 4(A)) is