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Dielectric and magnetic properties of $CoFe_2O_4$ prepared by sol-gel auto-combustion method

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ABSTRACT

Cobalt ferrite powders were successfully synthesized by sol-gel auto-combustion method. Influence of sintering temperature on structural, magnetic and dielectric properties was studied. All the obtained samples are spinel ferrite with a cubic symmetry. As the sintering temperature increased from 900 °C to 1300 °C, the average grain size increased from 0.26 μm to 0.83 μm. The dielectric constant and loss tangent measurement showed strong temperature dependence at all frequencies. The maximum magnetization increased while the coercivity and remanent magnetization decreased with the increasing sintering temperature. The non-saturation at high fields may be related to the surface effects in $CoFe_2O_4$ samples. When sintered at 1300 °C, the sample showed a maximum magnetization value of ~87.32 emu/g at room temperature. The highest value of coercivity of all the samples was 1368.33 Oe for the sample sintered at 900 °C.

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1. Introduction

Ferrite magnetic materials have attracted considerable attention in many fields owing to their high electrical resistivity, mechanical hardness, relatively low cost, excellent dielectric and magnetic properties [1,2]. Cobalt spinel ferrite ($CoFe_2O_4$, CFO), a well-known hard ferrite [3], has caused wide attention due to its high coercivity, strong crystalline anisotropy, moderate magnetization (80 emu/g) and high Curie temperature (520 °C) [4]. These properties, along with their great chemical and physical stability [2], make CFO suitable for lithium ion battery [4,5], high-density data storage [4], magnetic recording [6], magnetic fluids [4], magnetic drug delivery [7], catalysis [8], biosensors [9] and hyperthermia [10,11]. In other words, CFO has much potential values for magnetic and electric applications.

CFO has an inverse spinel structure in which Co^{2+} ions occupy octahedral sites (B sites) and Fe^{3+} ions distribute equally between tetrahedral (A sites) and octahedral sites (B sites) [6]. Its remarkable electrical and magnetic properties depend on the nature of the ions, charges and their distribution among A and B sites. In addition, the dielectric properties of CFO depend on sintering temperature/duration, heating rate, cooling rate and so on [12,13]. The dielectric investigation can provide important information on the behavior of localized electric charge carriers, giving rise to a better understanding of the mechanism of dielectric polarization [4]. And the unique magnetic properties of CFO depend on the shape, size and purity which are very sensitive to the synthesis method [4]. Until now, many different techniques are employed such as the ceramic method [14,15], co-precipitation [16–19], the hydrometallurgical processes [20,21], the sol-gel process [22,23], complexometric method [24], microwave [25] and so on. For the co-precipitation method, a main challenge is that desired control of particle size is insignificant during synthesize processes [26]. The ceramic method is easy to execute in the industry, but it has high energy consumption. And the hydrometallurgical processes are quite expensive or inefficient in the industry. Among various preparation methods, the sol-gel method is found to be a suitable method with their simplicity, better control ratio, a higher purity and more homogeneous composition [4,9].

However, there existed some defects for CFO. Such as the stored-up magnetic energy per unit volume is relatively low and the maximum magnetization is not enough high which limited its applications. In terms of magnetic properties, El-Okr et al. found that CFO prepared by co-precipitation showed the maximum magnetization (M_m) of 66.80 emu/g and coercivity (H_c) of 395 Oe at 900 °C [16]. Lu et al. found that the one-dimensional CFO microtubes prepared by the sol-gel method showed the H_c was

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731 Oe and the M_m was 76.6 emu/g at 900 °C [27]. In addition, some reports indicated the sintering conditions would impact the magnetic properties [1,6,27]. For example, Yang et al. found that the H_c and M_m vary with the sintering temperature from 600 °C to 900 °C and sintering time from 4 h to 6 h respectively [1].

In this work, CFO powders were prepared by a sol-gel auto-combustion method. The crystallinity and morphology of CFO samples were characterized by XRD and SEM. The magnetic and dielectric properties of CFO samples prepared at different sintering temperatures were then discussed. Finally, a high M_m value of 87.32 emu/g and a high H_c value of 1368.33 Oe were achieved for CFO sample sintered at 1300 °C and 900 °C for 2 h, respectively. The high M_m and H_c obtained in CFO samples suggested its potential using as one type of permanent magnet or magnetic recording media.

2. Experimental

CFO powders were prepared by a sol-gel auto-combustion method. Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, 98.5%), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$, 99%) and citric acid ($C_6H_8O_7$, 99.5%), all from aladdin, were used as the starting materials while deionized water was used as solvent. Stoichiometric amounts of cobalt and Iron nitrate were completely dissolved in deionized water separately. Citric acid and the cobalt nitrate solution were successively joined to Iron nitrate solution (The molar ratio of metal cation (Fe + Co) and citric acid was kept at 1:1.2). The sol was obtained by stirring the mixed nitrate solution until it became a brown and transparent liquid. Ammonia solution was then added dropwise to make the pH value of mixture to be between 7 and 8. The dry gel was obtained by stirring the sol at 80 °C for about 3 h and dried for 24 h at 100 °C. The precursor powders were obtained by the auto-combustion method. And then, the powders were sintered at 650 °C for 2 h to remove organic matter. After sintering, the resulting powders were fully ground and pressed into pellets with 12 mm in diameter and 1–2 mm in thickness under a pressure of 300 MPa. Finally, the pellets were sintered at 900 °C, 1100 °C, 1200 °C and 1300 °C for 2 h to get the CFO samples.

The prepared CFO samples were determined by X-ray diffraction (XRD) with Cu K_α radiation on a MSAL-XD2 diffractometer while the scanning rate is 6° min^{-1} and the step size is 0.05°. The fractured cross-sectional microstructures were investigated with a HITACHI S-520 scanning electronic microscope (SEM). The magnetic properties were measured by a BKT-4600 vibrating sample magnetometer (VSM, with a 2T electromagnet). The dielectric properties were measured by an LCR meter Agilent E4980A with an oscillation voltage of 0.5 V over the frequency range from 20 Hz to 2 MHz. Both surfaces of the CFO samples for dielectric measurements were deposited with Ag.

3. Results and discussion

Fig. 1 shows XRD patterns of CFO sintered at different temperatures. All the observed peaks were indexed to inverted spinel cubic structure with Fd3m (227) space group according to the standard pattern reported in JCPDF card for CFO (No. 22-1086), and there is no evidence of any impurity phases. The lattice parameter, relative density and porosity of all the CFO samples are listed in Table 1. The lattice parameter was found to be 8.38 Å, 8.38 Å, 8.39 Å and 8.38 Å for the CFO samples sintered at 900 °C, 1100 °C, 1200 °C and 1300 °C, respectively. The relative density values indicate an increase with increasing sintering temperatures. The porosity is calculated by using the relation as:

$$P = \frac{\rho_x - \rho}{\rho_x} \quad (1)$$

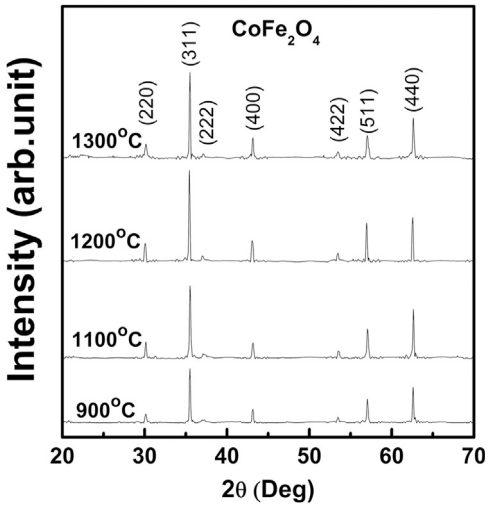

Fig. 1. The x-ray diffraction patterns of $CoFe_2O_4$ samples sintered at 900 °C, 1100 °C, 1200 °C and 1300 °C.

Where, P = porosity, ρ = measured density and ρ_x = X-ray density. The theoretical density of standard CFO is 5.304 g/cm^3. And the porosity decreased significantly with the increasing sintering temperature.

The fractured surfaces of CFO samples sintered at different temperatures were shown in Fig. 2. It is worth to note that the grain size is strongly affected by the sintering temperature. The grain size of the sample sintered at 900 °C is very small and the porosity is very high (Fig. 2(a)). This phenomenon indicates that the degree of densification and microstructural homogenization are limited by the mild sintering conditions (low temperature). The grain sizes beyond nm degree cannot be measured by XRD, therefore, the grain sizes of several um should be observed by SEM. As shown in Table 1, the average grain size (estimated by a line-intercept technique) increases and porosity decreases with increasing sintering temperatures. The sample sintered at 1300 °C became uniform and dense. In a word, the sintering temperature had a sufficient impact on the microstructure of CFO.

Fig. 3(a) and (b) presents the frequency dependence of dielectric constant (ε′) and dielectric loss (tan δ) for different CFO samples sintered from 900 °C to 1300 °C for 2 h in the frequency range from 20 Hz to 2 MHz at room temperature. The ε′ decreases with increasing frequency and the decreasing trend becomes slow in higher frequency region, showing frequency dispersion at low frequency range. This behavior is normal for the polar dielectric materials [28]. The decrease in ε′ can be explained by Maxwell-Wagner type and it is consistent with Koop's theory of dielectrics [4,28,29]. According to the Koop's theory of dielectrics, the dielectric structure is composed of conducting grains and insulating grain boundaries [28]. The grain boundaries are formed due to the oxidation of crystallines or superficial reduction during sintering process in porous ferrite materials. When the dielectric material is placed over the alternating field, owing to the hopping of electrons inside ferrites, electrons arrive at the grain boundaries, accumulating at the grain boundaries due to high grain boundary resistance. This process is called as space charge polarization [30]. At lower frequencies, the effect of grain boundaries dominates over grains and the space charge polarization occupies major status. Thus, the ε′ is high. However, at higher frequencies, owing to the weakly space charge polarization and electrons cannot follow the changes of the applied field, the ε′ decreases and then becomes a constant value beyond a certain frequency limit. Fig. 3(b) shows that there is a relaxation in tan δ for all the CFO samples at low frequency region. According to Rezlescu model, the relaxation peak

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