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Journal of Magnetism and Magnetic Materials

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Fuel additives and heat treatment effects on nanocrystalline zinc ferrite phase composition

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ARTICLE INFO

Article history:

Received 15 January 2010

Received in revised form

11 October 2010

Available online 28 October 2010

Keywords:

Zinc ferrite

Fuel additive

Heat treatment

Phase composition

ABSTRACT

Nanocrystalline ZnFe₂O₄ powder was prepared by the auto-combustion method using citric acid, acetic acid, carbamide and acrylic acid as fuel additives. Pure spinel zinc ferrite with the crystallite size of about 15 nm can be obtained by using acrylic acid as fuel additive. Samples prepared using other fuel additives contain ZnO impurities. In order to eliminate ZnO impurities, the sample prepared with citric acid as fuel additive was annealed at different temperatures up to 1000 °C in air and in argon. Annealed powders have pure ZnFe₂O₄ phase when annealing temperature is higher than 650 °C in air. Sample annealed at 650 °C in air is paramagnetic. However, annealed powders become a mixture of Fe₃O₄ and FeO after annealing at 1000 °C in argon atmosphere due to Zn volatility and the reduction reaction.

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1. Introduction

Zinc ferrite (ZnFe₂O₄) has normal spinel structure; it is a commercially important material and has been widely used in magnetic applications [1,2], gas sensors [3], catalysts [4], photocatalysts [5,6] and absorbent materials [7,8] because of its excellent electrical and magnetic properties.

Recently, nanocrystalline ferrites have been extensively studied because of their superior physical and chemical properties compared with bulk counterparts [9,10]. To prepare high electromagnetic performance zinc ferrites, various synthesizing methods have been reported, including high-energy ball milling [1–2], hydrothermal technique [4], co-precipitation [11,12], ferrocenyl precursor method [13], ultrasonic cavitation [14], thermal plasma [15], etc. However, some of these methods encountered problems such as the requirement of complicated equipment or long processing time caused by multiple steps, thus being economically unfeasible for large-scale production. Lately more attention has been paid to the auto-combustion method, which is an exothermic redox reaction between metal nitrates (oxidizing agents) and appropriate fuel additives (reducing agents) and had been successfully used for synthesizing nanocrystalline ferrites [16]. The advantages of this method are chemically homogeneous composition, processing simplicity, low energy loss, high-production efficiency and high-purity products [17].

The auto-combustion method has been demonstrated for zinc ferrite production [18–22]. However, few studies considered the influence of fuel additives and heat treatment conditions on the phase composition of nanocrystalline zinc ferrite. In the present work, nanocrystalline zinc ferrite was prepared by the auto-combustion method using citric acid, acetic acid, carbamide, and acrylic acid as fuel additives. The effects of different fuel additives on crystallite phase composition and microstructure of zinc ferrite were characterized. Then as-prepared powders were annealed at different temperatures ranging up to 1000 °C for 1 h in air and in argon. Influence of heat treatment conditions on microstructure and magnetic properties of annealed zinc ferrites were investigated.

2. Experiment

Nanocrystalline zinc ferrite (ZnFe₂O₄) was prepared by the auto-combustion method using ferric nitrate Fe(NO₃)₃·9H₂O, zinc nitrate Zn(NO₃)₂·6H₂O as raw materials and citric acid C₆H₈O₇·H₂O, acetic acid CH₃COOH, carbamide CO(NH₂)₂, and acrylic acid C₂H₃COOH as fuel additives for samples labeled S1, S2, S3 and S4, respectively. Appropriate proportion of metal nitrates and fuel additives were dissolved in distilled water, and the solution pH value was adjusted to 7 with ammonia. The solution was heated to 60 °C and continuously stirred using magnetic agitation. After 4 h the solution became a homogeneous viscous gel. Then the gel was oven dried at 120 °C for 24 h to obtain a dried gel. A loose and very fine zinc ferrite powder was produced after the dried gel had spontaneously combusted in air.

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In order to investigate the influence of annealing temperature on structural and magnetic properties, as-prepared auto-combusted S1 powders were annealed between 300 and 1000 °C for 1 h in air and in argon.

X-ray diffraction (XRD) was used to determine the phases and crystallite size. XRD patterns were recorded on a Philips APD-10 diffractometer using Cu radiation. The morphology of particles was observed by scanning electron microscopy (SEM) (LEO 1450). LDJ 9600 (LDJ Electronics, Troy, MI, USA) vibrating sample magnetometer (VSM) was used to investigate the magnetic properties at room temperature.

3. Results and discussion

3.1. Phase analysis of products with different fuel additives

The dried gel for sample S4 combusted rapidly and more intense than S1 during its ignition in air. However, the dried gel for sample S2 and S3 began to smoke after 2–3 min preheating and combusted slowly and mildly. Fig. 1 shows the XRD patterns for samples S1, S2, S3 and S4 with different fuel additives. These measurements show that only S4 has a pure spinel zinc ferrite structure (JCPDS # 22-1012) by gel precursor auto-combustion, and samples S1, S2 and S3 contain XRD reflections coming from impurities due to the ZnO phase (JCPDS # 36-1451).

The synthesis of ZnFe₂O₄ by auto-combustion can be explained as follows. Dried gels first generate metal oxide ZnO and Fe₃O₄ in the beginning of the combustion process. Combustion releases large amounts of heat, and the following combination reaction occurs:



The sample S4 has pure ZnFe₂O₄ phase due to intense combustion and large amount of heat, so reaction (1) for sample S4 fully completes and produces pure ZnFe₂O₄. However, samples S1, S2 and S3 retain some ZnO phase due to their mild combustion and

incomplete reaction (1). Moreover, Fe₃O₄ can form a solid solution with ZnFe₂O₄ for the same spinel structure, but ZnO cannot be dissolved in ZnFe₂O₄ due to its hexagonal crystal structure. Therefore, ZnO remains in samples S1, S2 and S3 as a separate hexagonal phase.

Table 1 shows the crystallite sizes and phases of all samples in our experiments. The crystallite sizes were determined using Debye–Scherrer's formula [23]. The crystallite size of pure ZnFe₂O₄ sample S4 is about 15 nm. Owing to the intense and rapid combustion using acrylic acid as fuel additive, the crystallite does not have enough time to grow, so the crystallite size of S4 is quite small. However, acrylic acid also causes imperfect crystallization and lower crystallinity for sample S4 (Fig. 1). Therefore, it is very important to select the appropriate fuel additives for phase formation by the auto-combustion method.

3.2. Heat treatment in air

In order to eliminate ZnO impurities and obtain pure ZnFe₂O₄ from samples S1, S2, S3, we chose S1 as a representative sample and subsequently annealed it at different temperatures ranging from 400 to 1000 °C for 1 h in air. The XRD patterns of annealed products are shown in Fig. 2. Below 650 °C annealing temperature, powder has ZnO phase. However, powders have pure spinel ZnFe₂O₄ structure when the annealing temperature is higher than 650 °C. Moreover, with higher annealing temperature, powders have stable structure and fine crystallization. The crystallite sizes of annealed powder increase from 27.7 to 52.5 nm with the annealing temperature increase from 400 to 1000 °C (Table 1).

Nanocrystalline ferrites produced by the auto-combustion method have large specific surface area and good reactivity [17]. Annealed powders are pure ZnFe₂O₄ and ZnO disappeared when the annealing temperature was higher than 650 °C due to the combination reaction (1) at 650 °C. However, annealed powders also have ZnO impurity phase below 650 °C (400 and 600 °C annealing temperatures), possibly due to very slow diffusion rate at lower temperatures.

3.3. Heat treatment in argon

The structure of ferrite depends on the environment and the heat treatment temperature [16]. Sample S1 was annealed at different temperatures ranging from 300 to 1000 °C for 1 h in argon atmosphere and the resulting XRD patterns are shown in Fig. 3. The products contain a mixture of ZnFe₂O₄ and ZnO phases when sample S1 was annealed below 1000 °C in argon. However, annealed powders become a mixture of Fe₃O₄ (JCPDS # 19-0629)

Table 1
Crystallite size and phases for all samples.

Samples	Crystallite size (nm)	Phase
S1	23.4	ZnFe ₂ O ₄ and ZnO
S2	29.2	ZnFe ₂ O ₄ and ZnO
S3	20.3	ZnFe ₂ O ₄ and ZnO
S4	15.1	ZnFe ₂ O ₄
S1 annealed at 400 °C in air	27.7	ZnFe ₂ O ₄ and ZnO
S1 annealed at 600 °C in air	35.1	ZnFe ₂ O ₄ and ZnO
S1 annealed at 650 °C in air	35.9	ZnFe ₂ O ₄
S1 annealed at 700 °C in air	39.6	ZnFe ₂ O ₄
S1 annealed at 800 °C in air	44.1	ZnFe ₂ O ₄
S1 annealed at 1000 °C in air	52.5	ZnFe ₂ O ₄
S1 annealed at 300 °C in Ar	25.6	ZnFe ₂ O ₄ and ZnO
S1 annealed at 500 °C in Ar	35.9	ZnFe ₂ O ₄ and ZnO
S1 annealed at 650 °C in Ar	39.2	ZnFe ₂ O ₄ and ZnO
S1 annealed at 800 °C in Ar	55.8	ZnFe ₂ O ₄ and ZnO
S1 annealed at 1000 °C in Ar	39.7	Fe ₃ O ₄ and FeO

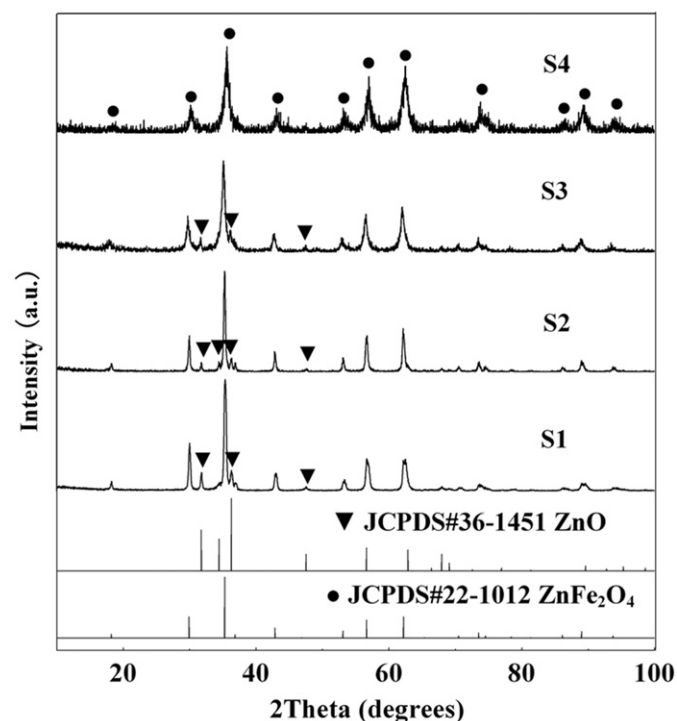


Fig. 1. XRD patterns for samples S1, S2, S3 and S4.

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