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Effect of urea and glycine fuels on the combustion reaction synthesis of Mn–Zn ferrites: Evaluation of morphology and magnetic properties

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ABSTRACT

The goal of this study is to evaluate the influence of the urea and glycine fuels on the synthesis of Mn–Zn ferrite by combustion reaction. The morphology and magnetic properties of the resulting powders were investigated. The powders were characterized by X-ray diffraction (XRD), nitrogen adsorption (BET), scanning and transmission electron microscopy (SEM and TEM), and magnetic measurement of $M \times H$ curves. The X-ray diffraction patterns indicated that the samples containing urea resulted in the formation of crystalline powders and the presence of hematite as a secondary phase. The samples containing glycine presented only the formation of crystalline and monophases (Mn,Zn)Fe_2O_4. The average crystallite size was 18 and 35 nm and saturation magnetization was 3.6 and 75 emu/g, respectively, for the samples containing urea and glycine. The samples synthesized with glycine fuel showed better magnetic properties for application as soft magnetic devices.

1. Introduction

Mn–Zn ferrites are ferrimagnetic ceramic materials of high permeability and low hysteresis and parasitic current loss. These ferrites are widely used in electronic applications such as broad band impulse transformers, recording heads and others, due to their excellent properties, particularly their high initial permeability, high saturation magnetization, high resistivity and low power loss. The magnetic properties of Mn–Zn ferrites are affected by their compositions, additives and annealing conditions, as well as the raw materials [1].

Nanosized Mn–Zn ferrites are synthesized by several methods, e.g., sol–gel [2], citrate precursor [3], chemical coprecipitation [4], hydrothermal synthesis [5], and combustion synthesis reaction [6]. The main purpose is to obtain single-phase materials with controlled microstructures and electromagnetic properties, which is achieved by controlling the characteristics of the powders (purity, chemical homogeneity, morphology and particle size). Combustion reaction synthesis has been used successfully to obtain powders with nanosized particles (<100 nm) and high surface areas. This method of synthesis is advantageous due to its simplicity, short reaction time from the preparation of reagents to the end product, elimination of intermediary calcinations stages, and lower consumption of energy during synthesis [7,8]. Therefore, the objective of this study was to investigate the effect of the urea and glycine fuels on the synthesis of Mn–Zn ferrites by combustion reaction, and to evaluate their morphology and magnetic properties.

2. Experimental

Mn–Zn ferrite powders with a nominal composition of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ were prepared by combustion reaction using iron nitrate, manganese nitrate, zinc nitrate, glycine and urea. The precursors were diluted in distilled water to completely homogenize the reagents. Stoichiometric compositions of metallic nitrates and fuels (glycine and urea) were calculated based on the total oxidizing and reducing valences of the components. These valences serve as the numerical coefficients for stoichiometric balance, such that the equivalence ratio (Φc) is unity and the energy released is maximum, according to the concepts of propellant chemistry [9,10]. The reagents were placed with the fuel in a vitreous silica crucible and heated to 480 °C on a hot plate. After water evaporation, gas release, ignition and combustion, the powder was transferred to a furnace preheated to 550 °C, where it was held for 10 min. The resulting powder was characterized by X-ray diffraction (XRD) using a SHIMADZU diffractometer (XRD 6000 model, Cu Kα radiation). The average crystallite size was calculated starting from the enlargement line of X-ray (d_{311}) through deconvolution of the line of secondary diffraction of the silicon polycrystalline calculated by Scherrer's equation [11]. The surface area was determined by the nitrogen/helium adsorption method (BET) [12], using a Micromeritics Gemini 2370 analyzer. The morphology of the particles was examined in a field emission gun scanning electron microscope (Philips XL 30 FEG-SEM). The magnetization measurements were taken with an EG&G PAR model 4500 VSM vibrating sample magnetometer mounted on an electromagnet with a bipolar source (maximum applied field of 20 KOe).

3. Results

Fig. 1 shows X-ray diffractograms of Mn–Zn ferrites synthesized with urea and glycine as fuels. Note the formation of a ferrite

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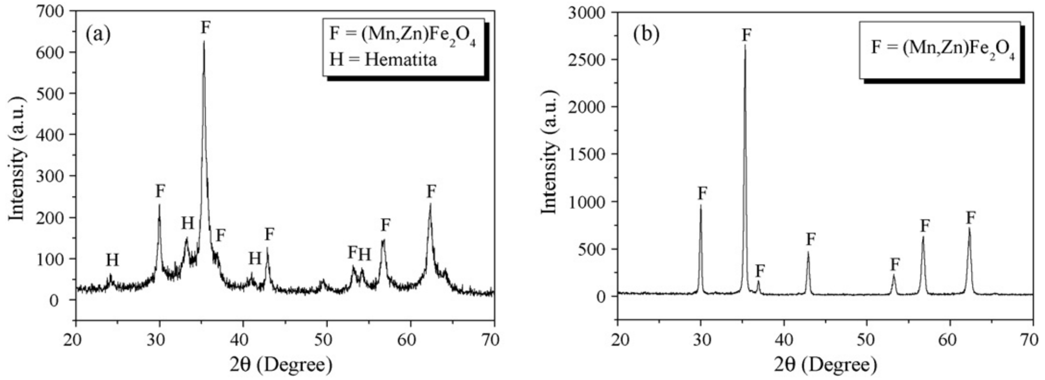

Fig. 1. XRD patterns of the samples obtained by combustion reaction: (a) urea and (b) glycine.

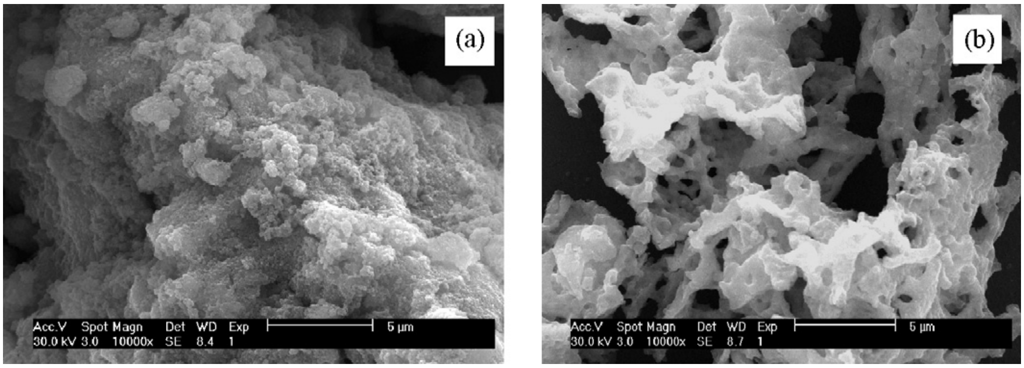

Fig. 2. SEM micrograph showing the morphology of the powder: (a) urea and (b) glycine.

$(Mn,Zn)Fe_2O_4$ phase and traces of secondary hematite in the sample synthesized with urea. The sample synthesized with glycine showed the formation of a highly crystalline monophasic powder (formation of ferrite Mn–Zn phase only). The crystallite and particle sizes, determined by BET, were 18 and 35 nm, respectively, for the powders synthesized with urea, and 18 and 193 nm for those synthesized with glycine. Fig. 2 shows the morphology of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ system analyzed by SEM. The micrograph in Fig. 2a shows the powder synthesized with urea. Note the nanosized particles smaller than 100 nm, which form not very dense agglomerates containing primary particles but no secondary particles (pre-sintering). The powder synthesized with glycine shown in Fig. 2b is porous, sponge-like and has an agglomerate structure. Most of the particles in these agglomerates are secondary and pre-sintered, with an irregular morphology. This morphology is similar to that observed in Mn–Zn ferrite powders prepared by microwave-assisted reflux [13], mechanochemical activation [14], and chemical coprecipitation [4] synthesis. Fig. 3 shows the characteristic hysteresis loop of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ system obtained with an alternative gradient magnetometer (AGM). As can be seen, both samples presented a narrow $\sigma \times H$ cycle and the characteristic behavior of soft magnetic materials using both urea and glycine to synthesize the powders. An analysis of the curves reveals a significant difference in the parameters of the powders synthesized with urea ($Ms = 3.59$, $Hc = 96.61$ and $Mr = 0.54$ *emu/g*) and with glycine ($Ms = 75$, $Hc = 130.72$ and $Mr = 12.63$ *emu/g*). The main reason for this difference is due to the 18 nm particle size of the powders synthesized with urea versus the size of 193 nm of the powders synthesized with glycine. It is well known that nanosized particles have small domain areas whose boundaries or domain walls prevent their rotation and/or spin, contributing to reduce their magnetization. Thus, in this work, the powder particles synthesized

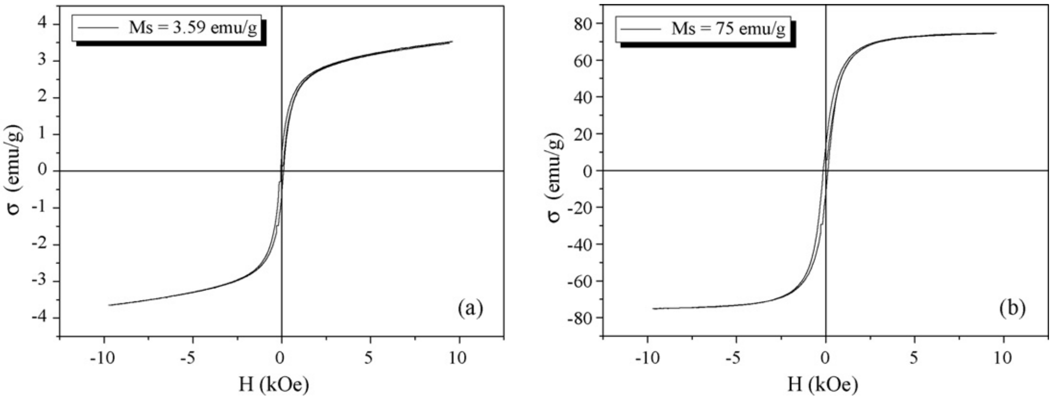

Fig. 3. Magnetic hysteresis loop of the samples: (a) urea and (b) glycine.

with glycine were approximately 82% larger than those synthesized with urea, contributing directly to increase magnetization due to their larger domain area. The powders synthesized with glycine presented a single phase, while those prepared with urea showed traces of hematite phase – a conductor phase, which contributed effectively to reduce magnetization. Therefore, the larger particle size of the Mn–Zn ferrite powders synthesized with glycine showed saturation magnetization values of 75 emu/g. This value was higher than the saturation magnetization values of ferrite prepared, respectively, by the methods of microwave-assisted reflux (45–56 emu/g) [13] and chemical coprecipitation (34–48 emu/g) [4] synthesis.

4. Conclusions

Combustion reaction synthesis using glycine as fuel led to the formation of monophasic crystalline $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrites. On the other hand, using urea as fuel led to the formation of minor secondary hematite phase and Mn–Zn ferrite as the major product. The average crystallite size of the powders synthesized with urea and glycine was 18 and 193 nm, respectively. The micrograph in Fig. 2 shows the formation of nanosized particles of less than 100 nm bound by weak van der Waals forces in the samples synthesized with urea. In contrast, samples synthesized with glycine show the formation of sponge-like agglomerates with pre-sintered secondary particles of irregular morphology. The samples synthesized with glycine presented superior magnetic characteristics.

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