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The influence of different fuel additives at different molar ratios on the crystallite phase formation process, structural characteristics and morphology of dispersed zinc ferrite powders by sol-gel auto combustion

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The dispersed nanocrystallite particles of $ZnFe_2O_4$ have been synthesized by sol-gel auto-combustion with the aid of ultrasonic irradiation methods using different fuel additives of glycine, urea and thiourea. The ratios of fuel- to- nitrates were maintained variously at 1.2 : 1, 2 : 1, and 3 : 1. The results revealed that, the difference in the phase composition formed are mainly attributed to the combustion process. In turn, different fuel additives exert a direct influence in the combustion reaction on the formation of a homogeneous gel, the formation of a good complex with metal cations and release chemical energy; as well as, showed that, the crystallite size of Zn ferrite powders is affected by the compositional ratios of fuel–to-nitrates. High fuel/ oxidant ratios increase the particle size and may enhance dopant segregation. The studies on the composition of phases, crystallite sizes, and morphology of the powder ferrite formed were investigated by X-Ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The results demonstrated that, the average crystal sizes distribution obtained were in the range 11-38 nm for all compositions.

Key words: Auto combustion, Ultrasonic, Nanocrystallite particles, Zn ferrite, Fuel additives.

Introduction

Nanosize particles exhibit unique chemical and physical properties [1]. Nanoparticle science and technology have been generating extensive interest in recent research areas. These research studies reveal rather different physical and chemical properties when compared to those of bulk materials.

Nanocrystallite ferrite materials of the general formula MFe_2O_4 have opened up a new outlook in the frontier area of materials science and technology. Zinc ferrites ($ZnFe_2O_4$) has the normal spinel structure with the space group Fd3m, which are an important material and widely used in magnetic applications, gas sensors, catalysts, photo-catalysts, and as absorbent materials [2]. The properties of these materials mainly depend on their shape, size, and structure, which are strongly determined by the synthetic processes, sintering process, the type and amount of constituent elements or additives [3]. Among the many synthetic methods proposed, the sol–gel auto combustion route is a unique combination of the combustion and the chemical gelation process. In general, this method is the preferred option due to its main advantages, mainly, inexpensive precursors, short preparation time, modest heating and relatively simple manipulation capabilities [4-6]. Additionally, this provides an exothermic redox reaction process between metal nitrates (oxidizing agents) and the appropriate fuel additives (reducing agents) [7].

In the combustion process, fuels serve two objectives: Firstly, they are a source of carbon and hydrogen (the reducing elements), which form CO_2 and H_2O on combustion and release heat; however, the chemical energy released from the exothermic reaction between various fuels is different. Secondly, they form complexes with the metal ions, facilitating homogenous mixing of the cations in solution [8]. The term combustion covers smoldering (heterogeneous) flaming (homogenous phase gas) as well as an explosive reaction [9].

The introduction of an ultrasonic irradiation bath in this method is an innovative and powerful tool for dispersing the particles. It has some advantages, mainly, uniformity of mixing, reduction in crystal growth, morphological control, reduction in agglomeration, and can also break the agglomerates to produce a uniform composition [10].

In the present study, an effort has been made to identify the effect of fuel type at different molar ratios on zinc ferrite syntheses at a pH value of about 7 and their influence on size, microstructure, morphology (crystal shape) and determination of phase composition.

Experimental

Materials

Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), zinc nitrate ($Zn(NO_3)_2 \cdot 4H_2O$), glycine ($C_2H_5NO_2$), urea ($CO(NH_2)_2$),

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thiourea ($CS(NH_2)_2$) and NH_4OH were obtained of analytical grade. All chemicals used were purchased from Merck (Germany) without further purification. De-ionized water was used in all the experiments.

Instruments

$ZnFe_2O_4$ powders were synthesized by a combustion ultrasonic irradiation (HF- 35 kHz/240 W) method. The identification of phases of the burnt powders of $ZnFe_2O_4$ was done using XRD (Philips, XPERT-MPD, which operated at 40 kV/40 mA). The structural morphology was investigated using SEM (Phillips XL30 with a 40 kV operating voltage).

Preparation process

In the sol-gel combustion method, the appropriate amounts of nitrates were dissolved into the minimum amount of de-ionized water. Glycine, urea and thiourea were added separately to the mixed nitrate solution. The fuels molar ratios to metal nitrates were 1.2 : 1, 2 : 1, and 3 : 1. The pH of the solution was controlled by a weak base such as ammonia. The pH was about 7 in all cases. Next, the mixed solution was heated; the resultant water of the solution was slowly evaporated until a high viscosity gel formed in the presence of aN_2 atmosphere. By increasing the temperature, the gel dried and then was heated until the combustion took place spontaneously. Upon the ignition the combustion reaction was completed within a few seconds, forming voluminous, fluffy loose powders with highly porous characteristics [11]. Subsequently, this substance was calcined at 500 °C for 2 hours with a heating rate of 2 °C min^{-1} in order to obtain zinc ferrite nanoparticles. Next, the as-prepared powders of all the samples were placed in an ultrasonic irradiation bath at 25 °C for 15 minutes. The introduction of the ultrasound into the process caused a further increase in the nucleant (crystallization) rate; prevented the crystal growth and aggregation. The samples produced with glycine, urea, and thiourea fuels at different molar ratios 1.2, 2, and 3 will be hereafter called G_1, G_2, G_3, U_1, U_2, U_3, T_1, T_2, and T_3, respectively.

Results and discussion

Phase analysis of dispersed Zn- ferrite powders

Fuel additives have always played an important role in the combustion reaction. The experimental observation showed that, the fuel type has a direct influence on the crystallite size produced; i.e. the crystal size would change with the differing fuel additives. In turn, the crystallite size of Zn ferrite powders is affected significantly by the compositional ratios of the fuel- to-metal nitrates. The average crystal sizes of the as-burnt powders were calculated from X-ray peak broadening of the (2 2 7) peak using Scherer's equation:

$$D_{hkl} = (0.9\ \lambda) / (\beta_{1/2}\ \cos\theta_{hkl}) \quad (1)$$

where λ is the wavelength of the X-ray radiation ($\lambda = 0.154$ nm), $\beta_{1/2}$ is the full width at half maximum (FWHM) of the peak (in radians) corrected for instrumental broadening, θ is the Bragg angle, and D_{hkl} is the crystallite size (Å). The reflection from the (2 2 7) plane was used for the determination of average crystalline sizes. The calculated average crystallite sizes for samples G_1, G_2, G_3, U_1, U_2, U_3, T_1, T_2, and T_3 are 15, 23, 38.74, 25, 30, 37.24, 11, 17and 34 nm, respectively. As a result, high fuel/oxidant ratios increase the particle size and may enhance dopant segregation.

All of the diffraction peaks of samples for G_1, G_2, G_3, U_1, U_2, U_3, T_1, T_2, and T_3 confirmed the formation of the $ZnFe_2O_4$ phase.

It is worth mentioning that, the composition of phases and microstructures are also affected by changing the fuel type in the combustion process.

The XRD patterns of G_1 sample confirmed the formation of $ZnFe_2O_4$, ZnO, and Fe_2O_3 phases as face centred cubic (fcc) spinel, tetragonal, and rhombohedral structured systems, respectively. The phase analysis of diffraction peaks for U_1, U_2, U_3, and G_2 samples showed the formation of $ZnFe_2O_4$, ZnO with fcc spinel and tetragonal structured systems, respectively. The XRD patterns of T_1 and T_2 samples showed the formation of a $ZnFe_2O_4$ single phase composition with the spinel structure. The XRD patterns of G_3 sample confirmed the formation of $ZnFe_2O_4$, ZnO, FeO, and Fe_2O_3 phases. Finally, for theT_3 sample $ZnFe_2O_4$, Fe_2O_3, FeOOH, and $Zn(OH)_2$ phases were shown by XRD patterns. The FeO phase structure hexagonal system. The average crystallite size distribution was obtained in the range 11-38 nm for all compositions, regardless of the fuel type.

The results revealed that, difference in the reducing power agents of the fuel and the compositional ratio of the fuel-to-metal nitrates affected the rate of the combustion [12]. In turn, they exert a direct influence in the combustion reaction and the final characteristics of the resultant powders [13].

The glycine fuel with the molar ratio of (3 : 1), possess the largest size in comparison to the other fuels. The calculated average crystallite sizes for samples G_3, U_3, and T_3 are 38.74, 37.24, and 34 nm, respectively. Perhaps an explanation would be that, the glycine, due to having more organic bonds, the amount of released heat is also higher during the combustion process; therefore, the enthalpy of the combustion process would increase when compared to the other fuels. This will enhance the crystallite growth, resulting in a full and complete combustion reaction, and will improve the crystallite formation process. On the other hand, the temperature reached in the combustion reaction has an important effect on the crystallite size of the resultant powder. By adjusting the glycine-to-nitrite ratio (G/N), the reaction temperature could be controlled and thereby control the crystallite size of the resultants. The XRD patterns of samples G_3,

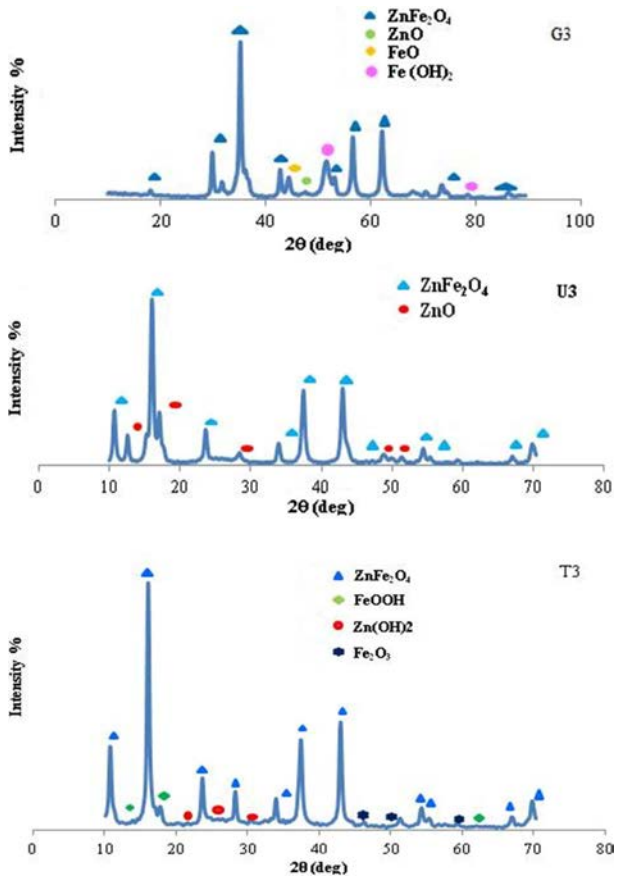

Fig. 1. The XRD patterns of samples G_3, U3 and T_3.

Table 1. The average crystalite sizes, composition of phases, microstructures at 3 : 1 molar ratios (glycine, urea and thiourea) to nitrates.

Fuel ratios to nitrates	G_3	U_3	T_3
Average crystallite size	38.74	37.24	34
composition of phases	$ZnFe_2O_4$ ZnO $Fe(OH)_2$ FeO	$ZnFe_2O_4$ ZnO	$ZnFe_2O_4$ Fe_2O_3 FeOOH $Zn(OH)_2$

U_3, and T_3 are presented in Fig. 1. The average crystallites sizes, composition of phases, and microstructures at 3 : 1 molar ratios are given in table 1.

The zinc ferrite produced using the thiourea fuel additive with the molar ratio of (2 : 1), yield the smallest particle size in comparison to the glycine and urea fuels, at the same molar ratio. The calculated average crystallite sizes for samples G_2, U_2, and T_2 are 23, 30, and 17 nm, respectively. Perhaps, due to the formation of a good and advanced complex, results in homogenous cations and the heat release and therefore, smaller particle sizes. In other words, when thiourea is used at a ratio (fuel/ oxidant, 2 : 1) in comparison with urea and glycine fuels, it easily gives the formation complex with metal cations. A good fuel can act in a combustion process as a complexant for metal cations [14]. In other words,

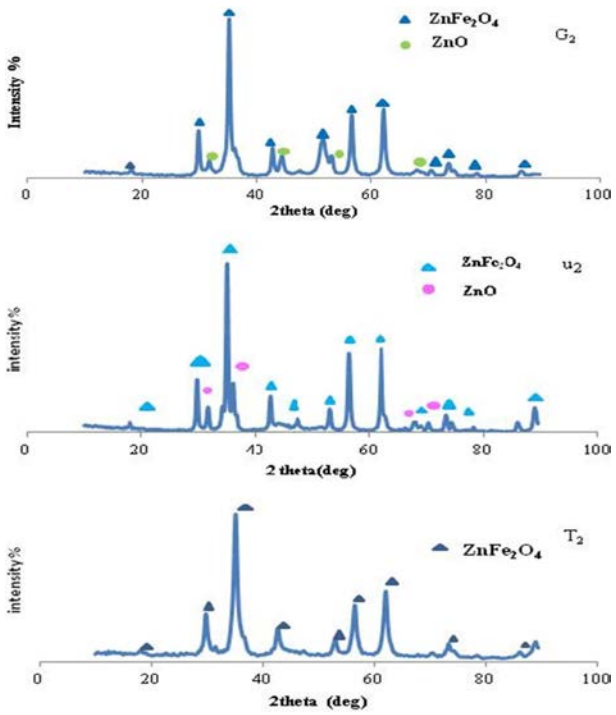

Fig. 2. The XRD patterns of samples G_2, U_2 and T_2.

Table 2. The average crystalite sizes, composition of phases, microstructures at 2 : 1 molar ratios (glycine, urea and thiourea) to nitrates.

Fuel ratios to nitrates	G_2	U_2	T_2
Average crystallite size	23	30	17
composition of phases	$ZnFe_2O_4$ ZnO	$ZnFe_2O_4$ ZnO	$ZnFe_2O_4$
Microstructure	Cubic Tetragonal	Cubic Tetragonal	Cubic

thiourea exhibited good complexing ability in low temperature ignition and may undergo controlled combustion reaction with nitrates. This complex increases the solubility of metal cations (Zn^{2+} and Fe^{3+}) thereby preventing preferential crystallization as the water in the precursor solution evaporates. The XRD results for G_2, U_2, and T_2 are shown in Fig. 2. The average crystallites sizes, composition of phases, and microstructures at 2 : 1 molar ratios (glycine, urea and thiourea) to nitrates are presented in table 2.

The thiourea fuel with a molar ratio of (1.2 : 1) gives the smallest in size. The calculated average crystallite sizes for samples G_1, U_1, and T_1 are 15, 25, 11 nm, respectively. It can be concluded that, the lower auto ignition temperature of thiourea and the early formation of a homogeneous gel, gives a product temperature that decreases; hence the smaller crystallite size when compared to the other fuel additives. The XRD results of G_1, U_1, and T_1 are shown in Fig. 3. Average crystallite sizes, composition of phases, and microstructures at 1.2 : 1 molar ratios (glycine, urea and thiourea) to nitrates are presented in table 3.

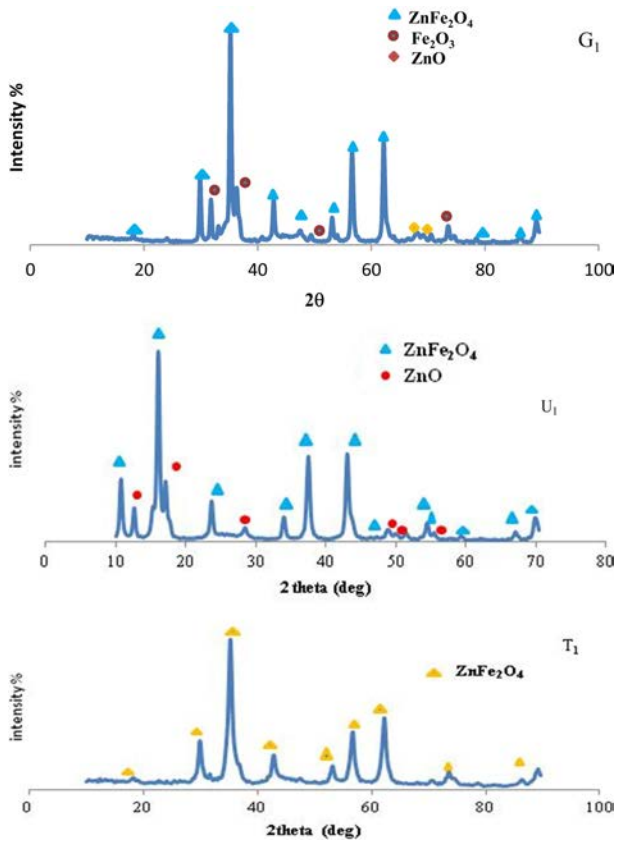

Fig. 3. The XRD patterns of samples G_1, U_1 and T_1.

SEM images

The SEM images for ferrites prepared with fuels (glycine, urea and thiourea) at three different molar ratios are shown in Fig. 4. The morphology of the oxides is mostly spherical with some agglomeration.

Table 3. The average crystallite sizes, composition of phases, microstructures at 1.2 : 1 molar ratios (glycine, urea and thiourea) to nitrates.

Fuel ratios to nitrates	G_1	U_1	T_1
Average crystallite size	15	25	11
composition of phases	$ZnFe_2O_4$ ZnO Fe_2O_3	$ZnFe_2O_4$ ZnO	$ZnFe_2O_4$
Microstructure	Cubic Tetragonal Rhombohedra	Cubic Tetragonal	Cubic

The results demonstrated that, type fuel, along with fuel additive-oxidant ratio and auto ignition temperature were important factors to reduce the degree of agglomeration and control crystallite size in the synthesized powders. Agglomeration is commonly divided into soft agglomeration and hard agglomeration according to the strength of the attractive force between particles [15].

Conclusions

Nanocrystallite particles of $ZnFe_2O_4$ have been synthesized by sol-gel auto-combustion with an assisted ultrasonic irradiation technique. With the addition of the fuel to the initial precursor, the pH of the solution remains fixed, therefore the difference in the type of Zn species are mainly attributed to the combustion process. The results demonstrated that, fuel additives always played an important role in the combustion. In turn, the crystallite size, structural and morphology of the resultant powders are affected by the mole ratios of fuels-to-nitrates. High fuel/oxidant ratios increase particle size and may enhance dopant segregation. It is worth

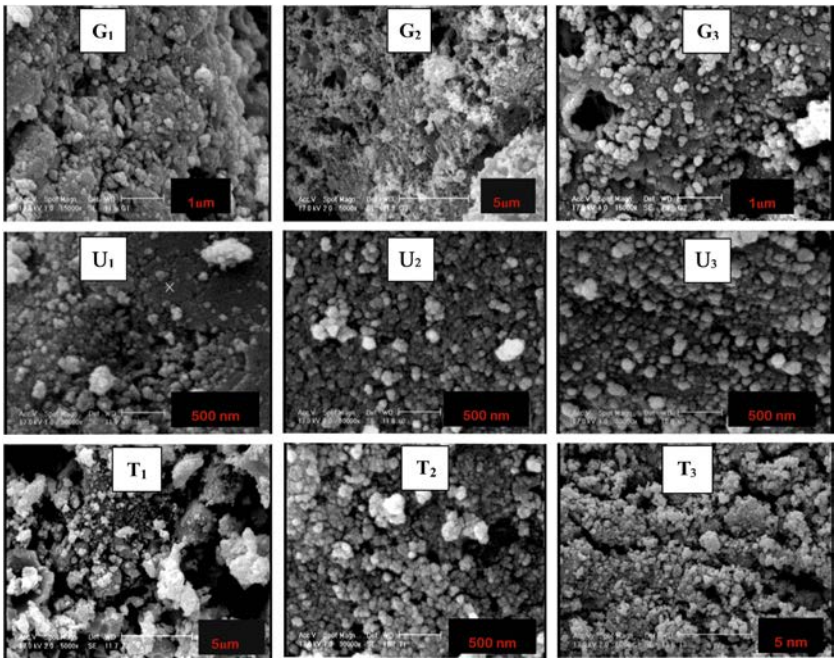

Fig. 4. SEM images of $ZnFe_2O_4$ nanopowders at different fuels of glycine, urea, and thiourea fuels at three different molar ratios 1.2, 2.0 and 3.0.

mentioning that, a non-suitable ratio of fuel-to-nitrate resulted in some unwanted impurity phases such as such ZnO, FeO, and $Fe(OH)_2$ in sample G_3; FeOOH, $Zn(OH)_2$, and Fe_2O_3 in sample T_3; ZnO in samples U_3, G_2, U_2 and U_1; Fe_2O_3 in sample G_1, as illustrated in Fig. 1, Fig. 2, Fig. 3, respectively.

The pure spinel zinc ferrite samples were obtained from the thiourea fuel additive at 1 : 1.2 (in sample T_1) and 1 : 2 (in sample T_2) molar ratios (metal nitrates to fuel thiourea), as illustrated in Fig. 3 and Fig. 2, respectively. The results demonstrated that, the average crystal sizes distribution obtained were in the range 11-38 nm for all compositions.

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