Solution combustion synthesis of Ca hexaferrite using glycine fuel

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ABSTRACT

$Ca_{1-x}La_xFe_{12}O_{19}$ (x = 0 and 0.4) polycrystalline powders were synthesized by the solution combustion route using glycine as a fuel and nitrates as oxidizers. After the combustion reaction, the prepared powders were calcined at 1100 °C and 1200 °C in a static air atmosphere for 1 h. The thermo gravimetric (TG) study was carried out to understand the ignition temperature. The structural and morphological studies of the prepared hexaferrite powders were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Magnetic properties of these samples were also measured by vibrating sample magnetometer (VSM). The XRD results of the samples which consisted of La as dopant and calcined at 1200 °C for 1 h, indicated the formation of calcium hexaferrite and also α-Fe_2O_3. However, the XRD results showed that $CaFe_4O_7$ and α-Fe_2O_3 phases were formed in the sample with the same condition but without using any dopant. The micrograph of SEM showed that the calcium hexaferrite particles were regular hexagonal platelets with the size range of 1–2 μm. Maximum magnetization (M_{Max}), remanent magnetization (M_r), and coercivity (H_c) were measured from the hysteresis loops. Low values of coercive field (23.52 kA m^{-1}) and maximum magnetization (58.75 Am^2 kg^{-1}) were originated from calcium hexaferrite particle which calcined at the temperature of 1200 °C for 1 h.

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1. Introduction

Hexaferrites have been intensively investigated during the last decades due to their technological interest as a permanent magnet and magnetic recording media. The magnetic properties of this material are largely dependent on the microstructure and its processing routes [1,2].

Hexaferrites with M ($AFe_{12}O_{19}$; A refers to Ba, Sr or Pb) type structure can be easily crystallized in the shape of platelets. However, not many studies have been carried out on the magnetic materials based on Ca-hexaferrites, especially the ones with hexagonal crystal structures [3]. A basic difficulty in the development of this material is that the $CaFe_{12}O_{19}$ does not crystallize in the magnetoplumbite (M) structure in spite of the close chemical affinity of calcium, strontium and barium [4,5]. However, Schiebcr [6] was the first to discover that M phase could be derived by adding La_2O_3 to the CaO-Fe_2O_3 system.

Moreover, Ichinose and Kurihara [7], Lotgering and Huyberts [8] have shown that the M structure in the CaO-Fe_2O_3 system can be stabilized in the presence of ions like La (III) [8,9]. Proceeding along these lines, Abasht et al. [10] have succeeded in synthesizing the mixed $Ca_{1-x}La_xFe_{12}O_{19}$ ferrites with the M-structure.

A wide variety of processes are available for the synthesis of the mixed oxide ceramic powders [11]. Hexaferrite powders have been reported to be synthesized by various routes, such as solid-state reaction [12], co-precipitation [10,13], hydrothermal [14,15], sol–gel [16,17] and the combustion route [18].

Among the above-mentioned processes, the solution combustion process is characterized by fast reaction rate and low cost. In the solution combustion route, a self-sustaining exothermic redox reaction is allowed to take place in the gel that is formed on dehydrating an aqueous solution of a fuel (such as glycine) and an oxidant (metal nitrate) [19–21]. The combustion technique is capable of producing pure, nano-crystalline powders of oxide ceramics at comparatively low external temperatures, in a short time [22,23]. The success of this process is due to an intimate blending among the constituents using suitable fuel (e.g. glycine, *etc.*) in an aqueous medium followed by an exothermic redox reaction between the fuel and an oxidizer (i.e., nitrates) [22]. Rapid evolution of large volume of the gaseous products during the combustion dissipates the heat of combustion and limits the rise of temperature, thus reducing the possibility of premature local partial

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sintering among the primary particles. The gas evolution also helps in limiting the interparticle contact and thus resulting in more easily fireable product [23].

The lack of experimental information about Ca-hexaferrite allows us to start a systematic analysis (structural and magnetic) of this compound. In the present investigation, we report the solution combustion synthesis rout of Ca hexaferrite powders using glycine, for the first time in case of calcium hexaferrite, as a fuel and nitrates as oxidizers. The fuel to oxidant ratio has been taken as the stoichiometric reaction [24]. Also, we here present the recent improvements performed on $Ca_{1-x}La_xFe_{12}O_{19}$. Both structural and magnetic properties of the samples with x = 0.0 and 0.4 are investigated and the influence of the composition is particularly emphasized.

2. Experimental

2.1. Materials synthesis

The solution combustion method was used for the synthesis of $Ca_{1-x}La_xFe_{12}O_{19}$ (x = 0.0 and 0.4) powders. Chemical grade ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) and lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$) were used in the required ratio and dissolved in de-ionized water to obtain transparent aqueous solutions. Glycine as a fuel was added separately to the mixed nitrate solution and thoroughly mixed by a magnetic stirrer with the speed of 650 rpm for 1 h until the reactants were dissolved completely to get a homogenous solution. These solutions after the thermal dehydration (at $\approx 80\ °C$) resulted in the highly viscous liquids, hereafter, termed as precursors. The precursors were swelled and auto-ignited at about 200 °C with a rapid evolution of large volume of gases to produce voluminous powders. Then calcination of the powder was carried out at 1100 °C and 1200 °C for 1 h to remove any traces of fuel and to obtain a pure phase powder.

2.2. Instrumental details

Prior to sample synthesis, the thermal decomposition of dried powders were investigated by thermo-gravimetric analysis (TGA) using a 409 PC-Netzsch instrument with a heating rate of 5 °C/min in the air atmosphere. The X-ray diffraction analysis was carried on the combustion-synthesized powders for phase identification, using Co-K$_\alpha$ ($\lambda = 0.179$ nm) radiation on a Philips X-ray diffractometer, model PRO 3040/60. Microstructural studies were carried out by (SEM) (VEGA\\TESCAN). The magnetic properties of the samples were measured by using a vibrating sample magnetometer (VSM)-(MDK), in the applied field up to 1.4 T at room temperature.

3. Results and discussion

3.1. Combustion reactions: theoretical analysis

One of the cheapest amino acids, glycine (NH_2CH_2COOH) is known to act as a complexing agent for a number of metal ions since it owns a carboxylic acid group at one end and an amino group at the other end [25]. Such types of zwiter-ionic character of glycine molecule can effectively complex metal ions of varying ionic sizes, which help in preventing their selective precipitation to maintain the compositional homogeneity among the constituents. On the other hand, glycine can also serve as a fuel in the combustion reactions, being oxidized by nitrate ions [23].

As per the propellant chemistry, the ratio of fuel and oxidant in combustion reaction is fixed in such a way that the net reducing valency of the fuel equals to the net oxidizing valency of the oxidant
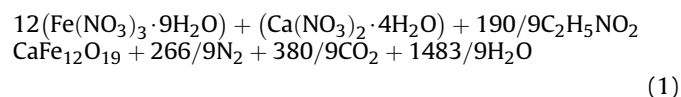
[24]. The oxidizing valences of the oxidants and the reducing valences of glycine fuel are given in Table 1.

Chick et al. [25] showed that in the case of glycine-nitrate combustion, primarily N_2, CO_2, and H_2O are evolved as the gaseous products. Therefore, carbon and hydrogen are considered as reducing elements with the corresponding valencies 4 + and 1+, whereas oxygen is considered as an oxidizing element with the valency of 2-, and nitrogen is assumed to have a valency of zero [23].
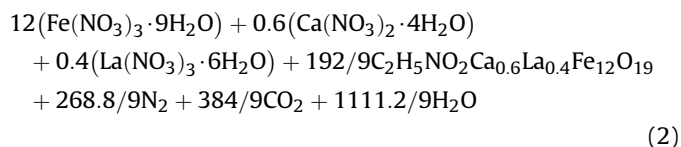
The molar ratio of fuel to metal nitrate has been determined based on the above concept [25]. According to reaction (1), the net oxidizing and reducing valency of nitrates and glycine are: −190 and + 9, respectively. Thus, for the complete combustion of 1 mol of nitrates, 190/9 mol of glycine are required. As well, according to the reaction (2), the net oxidizing and reducing valency of nitrates and glycine are: −192 and + 9, respectively. Thus, for the complete combustion of 1 mol of nitrates, 192/9 mol of glycine are required.

For evaluating the relative exothermicity of combustion reactions involving fuel, a simplified theoretical approach has been taken. This approach is similar to that reported by Purohit et al. [23]. The following combustion reactions that are balanced to give calcium ferrite (without and with La) have been considered:

Without La ($CaFe_{12}O_{19}$):

$$12(Fe(NO_3)_3 \cdot 9H_2O) + (Ca(NO_3)_2 \cdot 4H_2O) + 190/9 C_2H_5NO_2$$
$$CaFe_{12}O_{19} + 266/9 N_2 + 380/9 CO_2 + 1483/9 H_2O$$

$$(1)$$

With La ($Ca_{0.6}La_{0.4}Fe_{12}O_{19}$):

$$12(Fe(NO_3)_3 \cdot 9H_2O) + 0.6(Ca(NO_3)_2 \cdot 4H_2O)$$
$$+ 0.4(La(NO_3)_3 \cdot 6H_2O) + 192/9 C_2H_5NO_2 Ca_{0.6}La_{0.4}Fe_{12}O_{19}$$
$$+ 268.8/9 N_2 + 384/9 CO_2 + 1111.2/9 H_2O$$

$$(2)$$

Available thermodynamic data in the literature [26,27] for various reactants and products are presented in Table 2. It is well known that the heat of combustion reaction has been determined using the relation:

$$\Delta H_{combustion} = \left(\sum \Delta H_f \right)_{products} - \left(\sum \Delta H_f \right)_{reactants}$$

The combustion reactions have been found to occur on the dehydration of gel at a temperature above the ambient. However, for simplification in the calculation of exothermic heat, the reaction temperature has been assumed to be 298 K. The heat evolved in the combustion will raise the temperature of the products. In a complete combustion reaction, total reactant is converted into product in a very small time scale. With this condition, the system has been assumed to be adiabatic and the adiabatic flame temperature can be calculated by solving the equation:

Table 1
The oxidizing valences of the oxidants and the reducing valences of glycine fuel [23].

Compound	Derivation	Valency oxidizing (−) reducing (+)
Oxidizers		
$Fe(NO_3)_3 \cdot 9H_2O$	3 + 3.[0 + 3.(−2)]	−15
$Ca(NO_3)_2 \cdot 4H_2O$	2 + 2.[0 + 3.(−2)]	−10
$La(NO_3)_3 \cdot 6H_2O$	3 + 3.[0 + 3.(−2)]	−15
Fuel		
Glycine ($C_2H_5NO_2$)	2.(4)+5.(1)+0 + 2(−2)	9