Materials Research. 2011; 14(4): 505-507
DOI: 10.1590/S1516-14392011005000069

Structural and Photocatalytic Characterization of $BaFe_2O_4$ Obtained at Low Temperatures

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Received: March 16, 2011; Revised: August 8, 2011

Barium monoferrite $BaFe_2O_4$ classified as permanent magnet stands out among other ceramic magnets due to its high chemical stability, corrosion resistance and low production cost. In addition, experiments conducted on photocatalytic degradation of methyl orange and UV transmittance by spectrophotometry have shown that this material has photocatalytic properties. The spinel ferrite is of importance in many technological areas such as computing, communications and security. Several techniques for synthesis have been studied to optimize the properties of this material. The synthesis of $BaFe_2O_4$ by conventional processes often occurs at temperatures above 1000 °C. In this work, we obtained the phase $BaFe_2O_4$ at low temperatures (600 °C) from the combustion reaction using nitrates and maleic anhydride as metal complexing agent. Techniques of X-ray diffraction, specific surface area, thermogravimetry analysis and photocatalytic analysis were employed to characterize the products obtained.

Keywords: *barium monoferrite, combustion reaction, photocatalysis*

1. Introduction

Barium ferrite is often used in the manufacture of permanent magnets, magnetic storage media, magneto materials and pigments, as well as in the absorption of electromagnetic waves[1,2]. The great interest in ferrites is mainly due to the high abundance of reagents and low cost of production. This material has high capacity of magnetization, high coercivity, high chemical stability[1], as well as photocatalytic properties[1]. The degradation by photocatalysis is based on the irradiation of a photocatalyst, usually an inorganic N-type semiconductor[3]. Reducing or oxidizing reactions promoted by radiation energy are able to oxidize organic compounds to CO_2 and H_2O and to reduce the metals involved in the case[4]. The mixture of precursors at elevated temperatures ($\geq$1000) is considered a trivial process for obtaining a barium ferrite[5]. However, the use of high temperatures during synthesis or subsequent heat treatment provides a natural loss of fine particles in the product[6]. We searched to find a method that is simple, economical and which basically keeps the characteristics of the powder as much under controlas possible (purity, chemical homogeneity, shape and size of particles). The combustion method presents some advantages over other methods: the reagents are simple compounds and do not require any special equipment, the doping can be easily introduced, and the agglomeration of powders remains limited[7]. Moreover, it has proven to be quite promising to obtain nanostructured ferrite powders[5,7,8]. This research had as main objectives to examine the photocatalytic activity of $BaFe_2O_4$ powders obtained via the combustion reaction using maleic anhydride and metal nitrates as precursors, and to evaluate the behavior of crystalline phases and surface area obtained by thermal treatments.

2. Experimental

The following precursors were used to obtain fine powders: iron nitrate $Fe(NO_3)_3$. $9H_2O$ (Vetec), barium nitrate $Ba(NO_3)_2$. $6H_2O$ (Vetec) and maleic anhydride (Synth), all compounds with high purity. Initially, the nitrates were dissolved in a minimum amount of deionized water (enough to dissolve) and subjected to thermal agitation at about 60 °C. The complexing agent was added and the system remained for several minutes under agitation to ensure homogenization. Subsequently, the precursor solutions were brought to an electric furnace (Sanchis), preheated at 400 °C, where the self-ignition of the system occurred. The prepared solutions have the stoichiometric composition between oxidizing and reducing agents. The as-synthesized sample obtained was named BFAS. After synthesis, the as-synthesized powders were thermally treated at 500, 600, 700, 800, 900 and 1000 °C for 1 hour, whose nomenclatures were established as BF500, BF600, BF700, BF800, BF900 and BF1000, respectively.

The characterization of the resulting powders after heat treatment was performed by means of X-ray diffraction (XRD) to verify the presence of crystalline phases. For this purpose the X-ray diffractometer Philips X'Pert MPD was used, equipped with graphite monochromator and fixed anode operated at 40 kV and 40 mA, which uses a radiation wavelength (λ = 0.154056 nm) of Cu-Kα. The Autosorb Quantachrome (Nova 1000) was used for determining the specific surface area by N_2 adsorption using the BET method. The photocatalytic activity analysis uses an equipment consisting of 12 lamps of 8 W (λ = 365 nm), a Dreschel glass flask with a silicone septum for sample withdrawal, an air bubbler and a magnetic stirrer. The photoactivity of the samples was determined following the photodegradation of a solution containing 20 ppm of methylorange under UVA irradiation up to 80 minutes. For this analysis, samples were collected every 10 minutes and their absorbance was determined by UV-Vis spectrophotometry (Biospectro). The thermal analysis (TGA/SDTA - Metler Toledo 851e) was performed using O_2 atmosphere with a heating rate of 10 K/min up to 900 °C.

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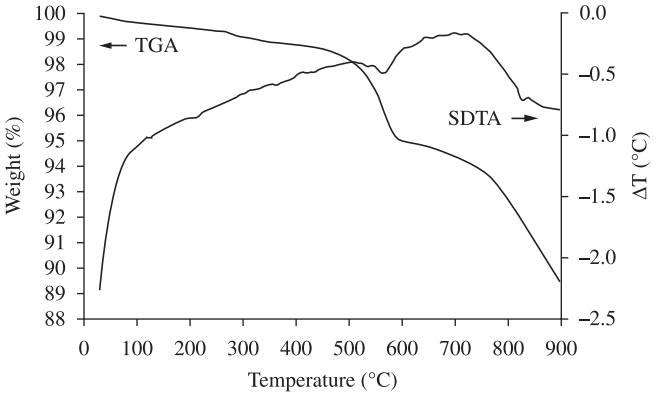


Figure 1. TGA as-obtained sample BFAS.

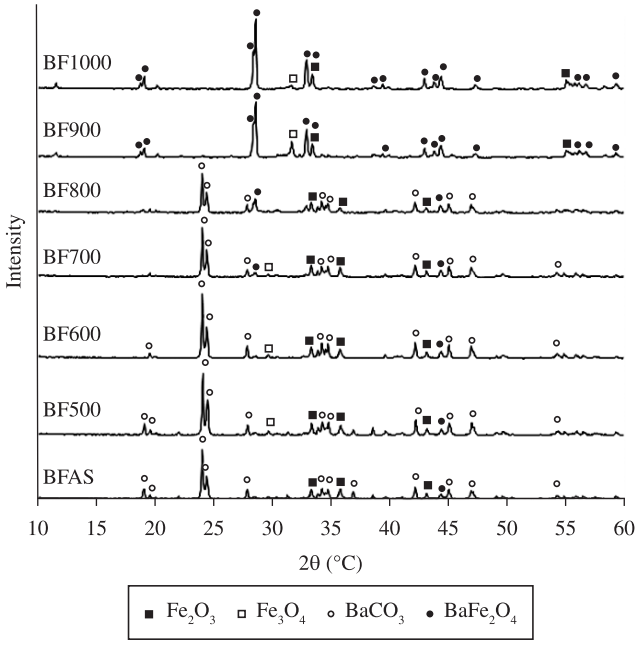
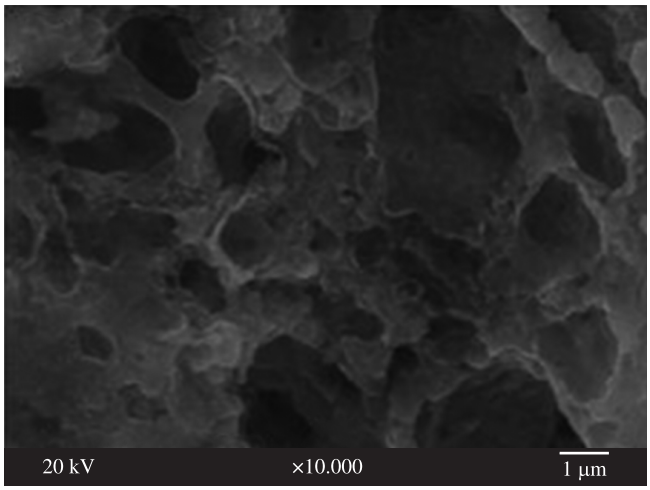


Figure 2. X-ray diffraction patterns of as-synthesized sample and samples subjected to heat treatment for 1 hour.

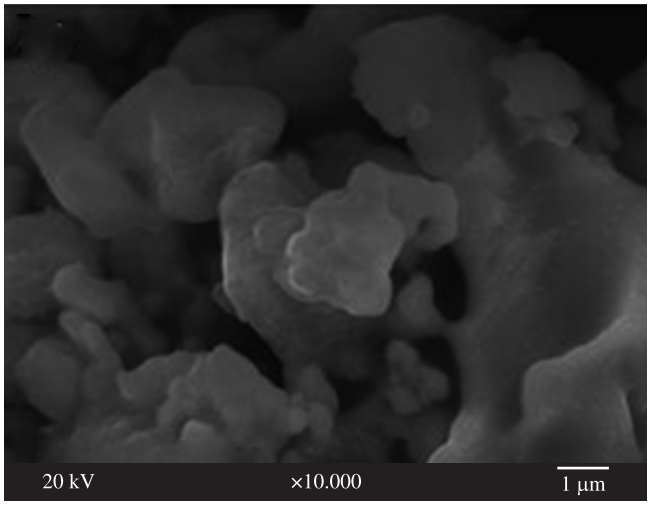
3. Results and Discussion

Figure 1 shows the thermal analysis (TGA/SDTA) of as-obtained sample BFAS. The TGA curve presents a continuous weight loss until 900 °C, probably due to residual organics and carbonates. The SDTA curve presents a peak, suggestive of an exothermic reaction around 550 °C, probably associated with the decomposition of carbonates formed during the combustion synthesis of the nitrates and the oxidizing agent.

In fact, the XRD analysis (Figure 2) of the samples as-synthesized and heat treated suggests the presence of secondary phases such as barium carbonate ($BaCO_3$) between 500 °C and 800 °C. Between 900 °C and 1000 °C the presence of barium ferrite ($BaFe_2O_4$) becomes the main phase, but the samplealso presents some peaks of iron oxides. Castro et al.[7] also obtained $BaFe_2O_4$ via combustion synthesis and even after heat treatment at 700 °C for 2 hours they also observed secondary phases such as $BaCO_3$ and Fe_3O_4. Additional heat treatment above 900 °C promotes the decomposition of residual carbonates and the formation of $BaFe_2O_4$. Qiu et al.[1], also obtained barium ferrite and hematite phases before annealed at 850 °C employing the combustion synthesis.



(a)



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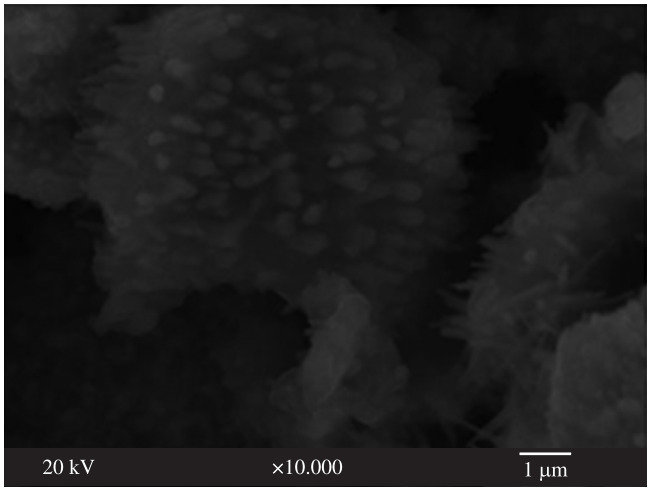

(c)

Figure 3. SEM micrographs of samples: a) as-synthesized at 400 °C; b) heat treated at 1000 °C; and c) heat treated at 1000 °C with magnetic particles.

Table 1. Relationship between annealing temperature (T) and specific surface area (S_{BET}) samples at different temperatures.

Sample	T (°C)	S_{BET} ($m^2.g^{-1}$)
BFAS	400	9.40
BF500	500	4.65
BF600	600	7.62
BF700	700	3.34
BF800	800	6.73
BF900	900	8.67
BF1000	1000	9.92

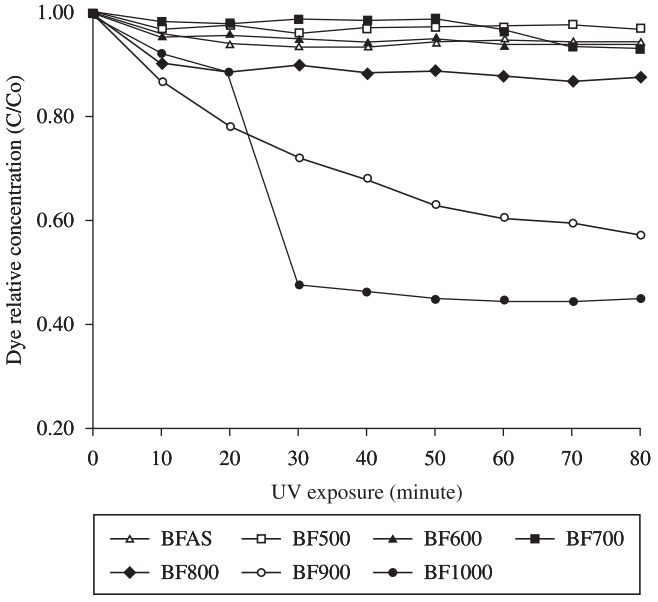

Figure 4. Transmittance of the samples with different temperatures of heat treatments.

Figure 3a presents an SEM image of the as-synthesized sample. It is possible to observe a large amount of microscopic pores, with the typical structure of the materials obtained by combustion synthesis. The distribution of holes forms a cluster system, presenting irregular shapes of different sizes and deformed surfaces. The formation of these clusters is probably due to the intense forces of van der Waals attraction between particles. However, in Figure 3b it is possible to notice the beginning of the coalescence process and the formation of aggregates. Figure 3c shows some areas comprising aligned acicular-shape magnetic particles. Some small spherical particles inside the acicular zone could also be observed. This could indicate there was not enough opportunity to convert all magnetite to hematite[8].

Table 1 lists the temperature of heat treatment correlated with the specific surface area (S_{BET}) of the samples. The results show that the samples have similar specific surface area values varying from 3.3 to 9.9 $m^2.g^{-1}$. It is possible, however, to observe that samples BF900 and BF1000 have the highest surface area among the heat treated samples.

Figure 4 shows the results of photocatalytic degradation of methylorange in the presence of the different samples. Samples BFAS, BF500, BF600, BF700 and BF800 showed low values of dye degradation. According to Yang et al.[3] the low photocatalytic activity of these samples is mainly due to the presence of $BaCO_3$ and low crystalline phases present in these samples, as corroborated by the analysis of XRD (Figure 2). Higher photoactivity was obtained for the BF900 and BF1000 samples, where the specific surface area is higher and the presence of $BaFe_2O_4$ is more evident (Figure 2). It is well established that $BaFe_2O_4$ is a photocatalyst and that $BaCO_3$ and isolated iron oxides do not promote photodegradation. Indeed, the main factor in the photoactivity of any catalyst is the presence of amorphous or low crystalline phases that act as electron traps, avoiding the free radical formation and, furthermore, dye degradation. In the XRD results it is possible to notice that the identification (formation) of $BaFe_2O_4$ peaks is only observed for samples annealed at 900 and 1000 °C. This correlates well with the photocatalytic results that show that these specific samples have by far the highest photoactivity.

4. Conclusions

The combustion synthesis in the solution using maleic anhydride as fuel showed a favorable process for obtaining $BaFe_2O_4$. However, when the sample was subjected to heat treatment at temperatures below 1000 °C, secondary phases such as $BaCO_3$, Fe_2O_3 and Fe_3O_4 were observed. As for the photocatalytic activity, it was observed that samples annealed at 900 and 1000 °C showed considerable photocatalytic activity, presumably because of the presence of well-defined crystalline phases and higher surfaces areas. The presence of carbon and secondary phases of low crystallinity possibly intervened in the photocatalytic activity of the other samples. Thus, it was possible to combine the highest surface area (9.92 $m^2.g^{-1}$) and the presence of $BaFe_2O_4$ with the best photocatalytic performance.

Acknowledgements

The authors acknowledge CNPq for financial support.

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