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The effect of different carbon reducing agents in synthesizing barium ferrite/magnetite nanocomposites

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HIGHLIGHTS

- Barium ferrite/magnetite nanocomposites synthesized via in-situ partial reduction.
- Carbon black, graphite and carbon nanofiber were compared as reducing agents.
- Carbon black makes the reduction process of iron oxide to progress to $Fe_{1-x}O$ stage.
- Carbon black had better reducing power than graphite and carbon nanofiber.

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ABSTRACT

Carbon can be used as a reducing agent in mechano-chemical reactions in mechanical milling. Some carbon sources have stronger reducing power in comparison to others. In this research mixtures of barium ferrite with different carbon sources (carbon black, graphite and carbon nanofiber) were milled in a high energy mechanical milling machine. The effect of carbon source reducing characteristics on the barium ferrite partial reduction was studied. Phase analysis, particles morphology and magnetic properties were investigated via XRD, HRTEM, and VSM, respectively. Phase analysis showed that the partial reduction of $BaO.6(Fe_2O_3)$ via carbon black progressed to $Fe_{1-x}O$ stage in molar ratio of C:O = 1.1 in the milling mixture. Carbon black had the best reducing power and then graphite was better reducing agent compared to carbon nanofiber. The 40 h milled sample with carbon black reached the highest saturation magnetization of 174.65 emu/g after vacuum heat treatment at 900 °C. HRTEM images showed that nanocrystals of Fe_3O_4 forms after 40 h milling of barium ferrite with graphite.

1. Introduction

The reducibility of metal oxides is measured by the content of removed oxygen per weight unit per time. Oxides with a high content of oxygen may not be reduced to the metallic species by direct reduction in one stage. In these oxides, some intermediate oxides form during the reduction process. Considering iron oxides, Fe_2O_3 is reduced to iron through intermediate iron oxides of Fe_3O_4 and FeO [1]. The production of metals from the lowest oxides might be possible using a reducing agent.

As the product of the reduction process increases in content, the reduction reaction rate decreases. The formed product on the reactants surfaces is a barrier for diffusion of un-reacted species. The reaction rate depends on the collision rate of the reactants atoms. In the cases that suitable reactants are present, by mechanical milling which results in a reduction of particle size, the surface area and hence, reaction rate increases [2].

Barium ferrite with a chemical formula of $BaFe_{12}O_{19}$ or BaO.6 (Fe_2O_3) is a hard magnetic ceramic oxide which has found several applications due to its high coercivity, high saturation magnetization, elevated Curie temperature, low production cost, and chemical stability. The intrinsic properties of the ferrites depend on their structure [3]. Several new synthesis methods for production of fine, ultrafine and nanoparticles of barium ferrite, including sol-gel [4,5], sol-gel combustion [6], microwave-assisted sol-gel auto-combustion [7], coprecipitation [8,9], hydrothermal [10], microemulsion [11], carbon combustion [12], self-propagating high-temperature synthesis [13], and electrospinning for production of nanofibers [14] have been applied in the recent years.

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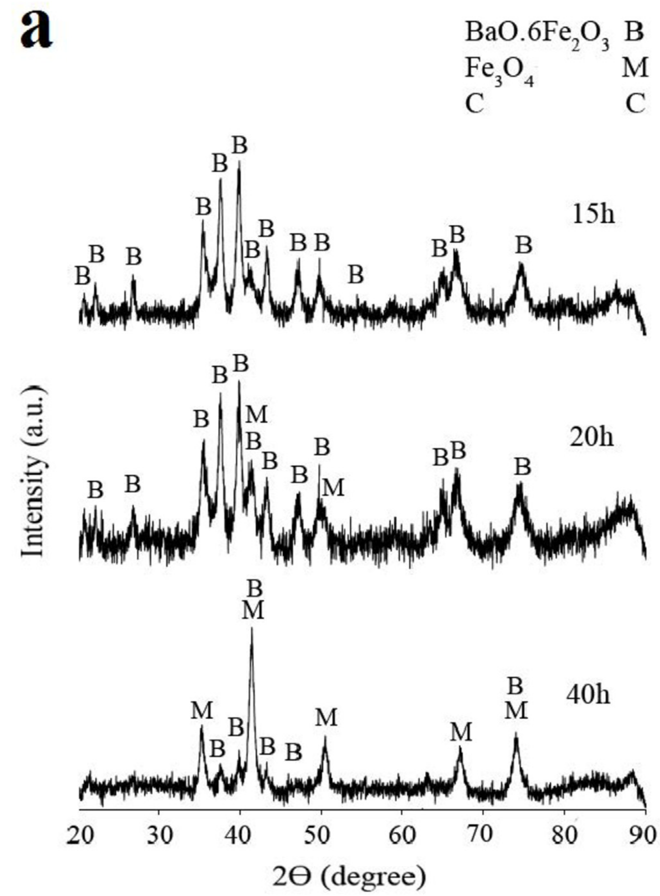

Fig. 1. The XRD patterns of barium ferrite and carbon black mixtures milled for different times; a) C:O = 0.9, b) C:O = 1 and c) C:O = 1.1.

In order to enhance magnetic or microwave absorbing properties of barium ferrite, different types of barium ferrite containing composites have been produced [15–27]. One of the applied methods for improving magnetic properties of hexaferrites is gas heat treatment technique. It has been reported [e.g. Refs. [28–31]] that by heat treating of barium, strontium and/or rare earth metal hexaferrites powder in the presence of carbon, nitrogen, carbon and nitrogen, hydrogen, or carbon and hydrogen containing gases, a magnetic structure with decreased values of coercivity forms.

The barium ferrite decomposes to Fe_2O_3 by mechanical milling [32]. Therefore, the resulting Fe_2O_3 can be reduced partially to magnetite (Fe_3O_4) by carbon as a reducing agent in mechanical milling medium. This will form $BaFe_{12}O_{19}/Fe_3O_4$ nanocomposites. In this research different types of carbon, i.e. graphite, carbon black and carbon nanofiber, as reducing agents are compared for partial reduction of barium ferrite to lower iron oxides. The effect of partial reduction on magnetic properties of the resulted composites is investigated.

1.1. Experimental procedure

Barium ferrite (reagent grade, Sigma-Aldrich, particle size ≤ 44 μm), graphite (reagent grade, Sigma-Aldrich, particle size ≤ 20 μm), carbon black (reagent grade, Sigma-Aldrich, particle size ≤ 45 μm) and carbon nanofiber (industrial grade, length < 200 μm and diameter < 100 nm) were purchased as starting materials. Barium ferrite with different carbon sources was mechanically milled in a planetary high energy milling machine with a rotating speed of 300 rpm. The ball to powder mass ratio was kept constant as 35 in all experiments. Samples were milled in a dry condition under closed lid air atmosphere. The vial and ball mass were measured before and after each experiment in order to calculate the

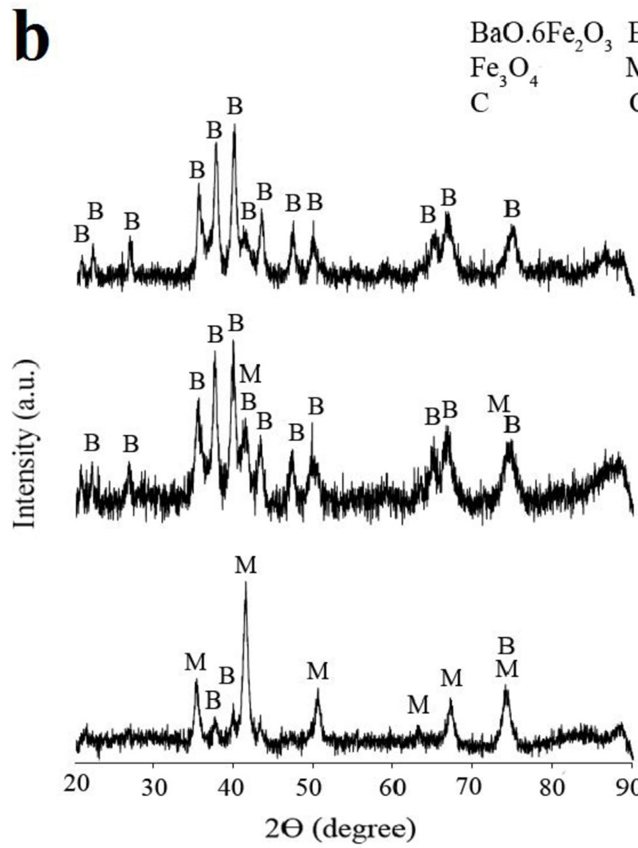

Fig. 1. (*continued*)

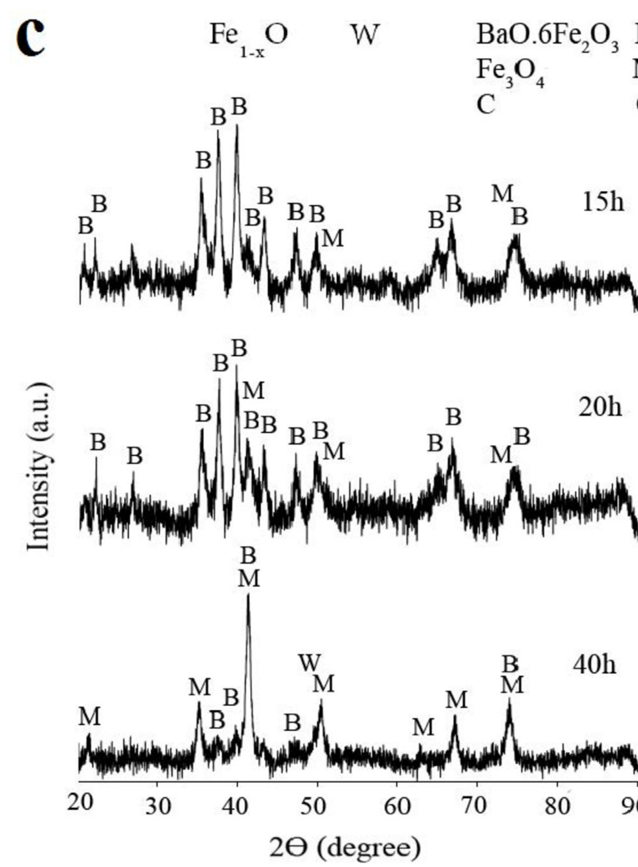

Fig. 1. (*continued*)