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Synthesis and Characterization of Magnetic Barium Ferrite-Silica Nanocomposites

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ABSTRACT

Hexagonal bariumferrite ($BaFe_{12}O_{19}$, BaM) has been studied intensively for many years due to their importance as permanent magnets, high density magnetic recording media and microwave devices. The magnetic and electromagnetic absorption properties of BaM can be improved by the partial substitution of nonmagnetic materials like SiO_2, Al_2O_3, ZrO_2, etc., to make composites. In this work, we prepared BaM-SiO_2 nanocomposites by using mechanical alloying in a planetary mill followed by heat treatment near to phase transition. Relationship of BaM and SiO_2 used were 40:60, 50:50, 6 0:40 and 70:30 % by volume. The magnetic properties and microstructure were characterized for different milling times and heat-treatments. Vibrating Sample Magnetometer (VSM), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) were used as the main characterization techniques to study as-milled and heat-treated powders. The results indicate that 15 h of milling were enough to avoid the generation of hematite phase and to get a good dispersion of barium ferrite particles in the ceramic matrix. For milling periods beyond 15 h, the XRD patterns showed the presence of hematite phase caused by the decomposition of BaM. The purpose of the annealing process was to refine the nanocomposite structure to obtain monodomains on the BaM grains and to modify the magnetic properties. The BaM-SiO_2 nanocomposites heat treated at 900°C showed that the magnetization (M_s) and coercivity (H_c) were enhanced with respect to lower BaM volume fractions. The agglomerate size observed through scanning electron microscopic analysis was around 150 nm with a good BaM dispersion into the SiO_2 matrix. The highest saturation magnetization of 43 emu/g is obtained for the composition $60BaFe_{12}O_{19}$-$40SiO_2$ heat treated at 900°C.

Keywords: Barium ferrite, Magnetic properties, Ball- milling

1. Introduction

Hexagonal barium ferrite ($BaFe_{12}O_{19}$), often denoted as M-type BaM, is used for numerous applications such as permanent magnets, particulate media for magnetic recording and microwave devices due to its excellent chemical and physical properties such as large magnetocrystalline anisotropy, high curie temperature, mechanical hardness, excellent chemical stability, relatively large saturation magnetization and corrosion resistivity [1]. The magnetic properties of these materials depend mostly on their grain size and phase purity which is very much depends on their preparation methods. Their magnetic properties arise from the interactions between metallic ions occupying particular positions relative to the oxygen ions in its crystalline structure. The magnetic properties of $BaFe_{12}O_{19}$ can be improved by elemental substitutions of Ba^{2+} or Fe^{3+} sites or both, or by doping or compositing with other materials [2,3]. The preparation method determines mainly the structural and magnetic properties. There exist many methods to synthesize barium ferrite and its composites including the traditional ceramic sintering route, sol-gel method, hydrothermal, chemical co-precipitation, sputtering techniques etc [4-8].

Mechanical milling is a solid state technique and is used extensively for the synthesis of a wide range of nanostructured materials and powder particle refinement through mechanical assisted reactions [9] and has also been used in the synthesis of magnetic powders [10]. Milling induces rigorous plastic deformation due to the gradual refinement of the internal structure of the powders to nanometer level, which affects the magnetic properties of magnetic materials. The magnetic and electromagnetic absorption properties of BaM can be improved by the partial substitution of nonmagnetic materials like SiO_2, Al_2O_3, ZrO_2 etc to make composites. In this work, we report synthesis and characterization studies of the different ratio of $BaFe_{12}O_{19}$-SiO_2 composites by high energy ball milling, and the effect of milling time and annealing temperature on the microstructure and magnetic properties of ceramic-BaM nanocomposites is discussed.

2. Experimental

Barium ferrite -silica nanocomposites were synthesized by mechanical alloying in a planetary mill. The raw materials consisted of BaM and SiO_2 powders of analytical grade reagent with a particle size of ~5 μm BaM and 1 μm SiO_2. Relationship of BaM and SiO_2 used were 40:60, 50:50, 60:40 and 70:30 % by volume. Stoichiometric mixtures of the above chemicals were placed in a zirconia containers together with 20mm diameter zirconia balls as milling media (ball to powder ass ratio =10:1). Dry mechanical milling was carried out in air in a planetary ball mill (RESTCH, model PM400) by using a rotating speed of 350rpm, followed by heat treatment near to phase transition. The milling were done for 30 hrs in steps of 5 hrs and the obtained powder after every 5 hrs were heat treated at different temperatures (500, 900,1000 and 1200° C). Phase evolution on milling and the heat treated sample powders were analyzed by using X-ray powder diffraction in Philips X'pert Diffractometer using Ni-filtered CuK_α

radiation (λ=1.5418Å) in the range of 2θ =20-80°. The morphological features of the particle were observed using a scanning electron microscope (SEM) Philips XL 30ESEM. The purpose of heat treatment was to refine the structure of the resulting nanocomposites and create mono-domains in the barium ferrite particles to modify the magnetic properties. The magnetic properties of the samples were measured at room temperature by using a vibrating sample magnetometer (Lakeshore model 7300/9300 VSM) with an applied field up to 1.3T.

3. Results and discussion

The structural evolution and phase formation of the composite after milling and heat treatment has been examined by X-ray diffraction. Figure 1 (a) shows the X-ray diffraction patterns of barium ferrite-silica composite samples milled for 5h and heat treated at 500°C. It shows the presence of only bariumferrite and silica phases. But compared to figure 1 (a), the X-ray diffraction of the same sample milled for 30 h and heated at 500°C (figure 1(b)) shows an increase in amorphization (broadening of the peak) and a decrease in the intensity of the peaks. In addition to that, the presence of hematite phase also observed after 30h of milling.

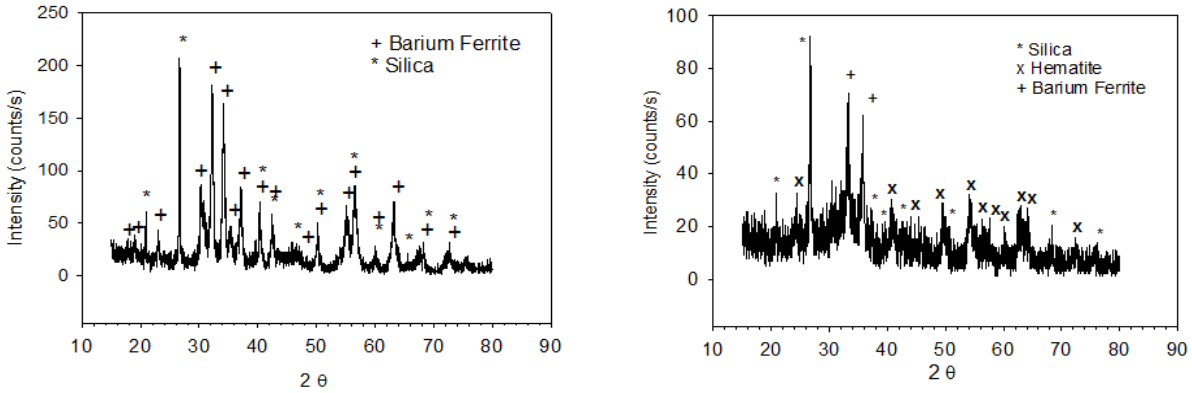

Figure1. X-ray diffraction patterns of 60%BaM-40%SiO_2 sample milled for 5h (a) and 30h (b) and heat treated at 500°C.

Figure 2 shows X-ray diffraction patterns of the samples milled for different hours and heat treated at different temperature of different compositions, (a) 30h milling for BaM-SiO_2 ratio 60:40 heat treated at 900°C (b) 30h milling for the ratio 50:50 at 900°C, (c) 15h milling for the ratio 60:40 at 900°C, (d) 15h milling for the ratio 60:40 at 1000°C and (e) 5h milling for the ratio 50:50 at 900°C. It shows as the milling time increases from 5h to 15h, the intensities of the diffraction pattern have diminished and peaks become broadened due to the refinement of the particles. The sample milled for 15h and heat treated at 1000°C (Figure 2 d) shows the major peaks of hematite phase. The sample of BaM-SiO_2 ratio 50:50 heat treated at 900°C also shows an increase amount diffraction peaks of hematite phase. From the figure 2, we can see from different compositional variation, milling time and heat treatment, the sample of BaM-SiO_2 ratio 60:40 milled for 15h and heat treated at 900°C shows the better structural

properties, though the same sample also exhibit a small quantity of hematite phase and in this case it doesn't have any negative effect as it occurs in very small quantities. The influence of volumetric concentration indicated that not always the great quantity of ferrite leads to better magnetic properties and it plays an important role in the degree of dispersion of the BaM in the ceramic matrix. The result shows that for BaM-SiO_2 samples of ratio 50:50 and 60:40, 900°C is enough to promote the structural rearrangement of Ba and Fe ions with short milling times and when the temperature increases to 1000°C leads to the partial decomposition of BaM to hematite phase.

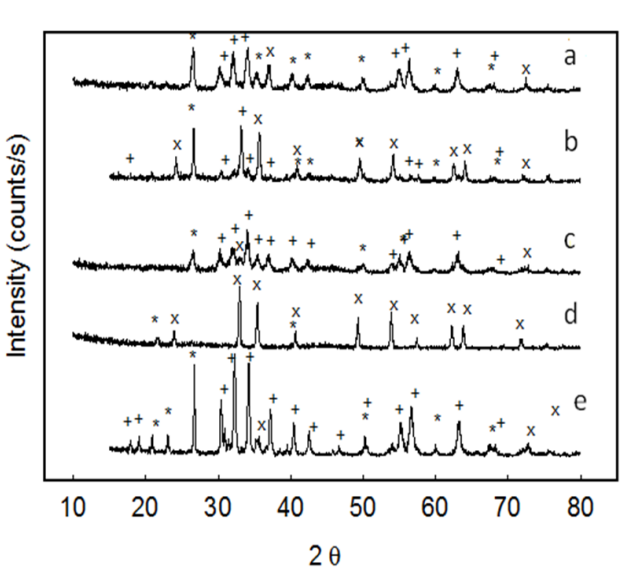

Figure 2. X-ray diffraction patterns of the samples milled for different hours and heat treated at different temperature for different compositions, (a) 30h milling for the ratio 60:40, heat treated at 900°C, (b) 30h milling for the ratio 50:50 at 900°C, (c) 15h milling for the ratio 60:40 at 900°C, (d)15h milling for the ratio 60:40 at 1000°C and (e) 5h milling for the ratio 50:50 at 900°C, (phases of silica (*), barium ferrite (+) and hematite (×))

To observe the distribution of phases and the dispersion of magnetic material in the ceramic host, samples were heat treated at 1200°C and analyzed by scanning electron microscopy in the secondary electron mode (a) and back scattering mode (b) and is shown in figure 3. From the figure we can see a two phase microstructure and also a good dispersion of a phase in another one. The back scattered electron mode gives us idea of compositions based on contrast and we can realize from the figure the existence of two phases. In this mode, the phase with lower atomic weight will appear more obscure, such as silica in the present case and consequently the clear phase will be of barium ferrite. The agglomerate size observed through scanning electron microscopic analysis was around 150 nm with a good BaM dispersion into the SiO_2 matrix.

(a) (b)

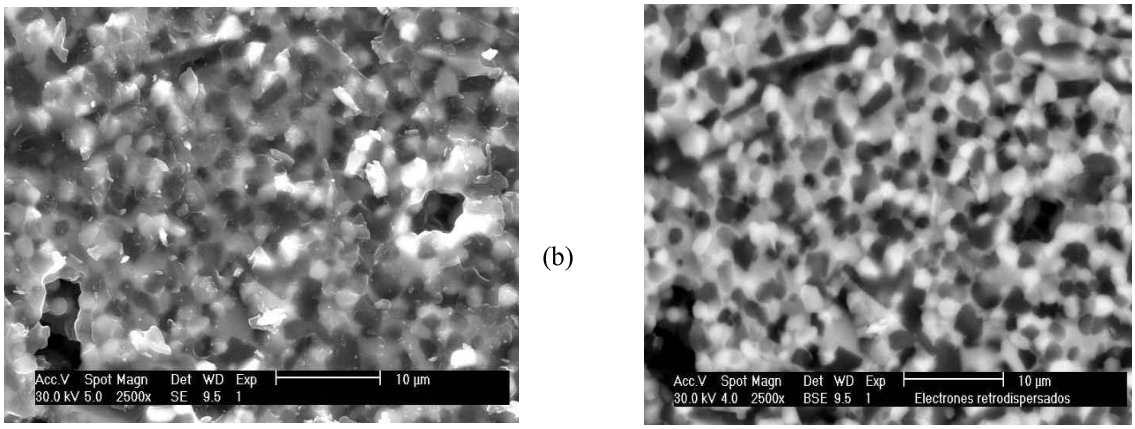

Figure.3 . Scanning electron micrographs of the 15h milled powder pressed and heat treated at 1200°C for the 60%BaM-40%SiO_2 sample (a) secondary electron and (b) back scattering mode.

Figure 4 shows the dependence of saturation magnetization (a) and coercivity (b) as a function of heat treatment temperature from 500 to 1000°C for the samples 60%BaM-SiO_2 and 40%BaM-SiO_2 with 15h of milling. Figure 4 shows the temperature treatment have an effect on the magnetization and coercivity of the material. Figure shows the sample 60%BaM-SiO_2 reached a saturation magnetization of 43emu/g at 900°C; however, for the sample 40%BaM-SiO_2 a maximum saturation magnetization of 33emu/g is obtained at the same temperature. In addition, as the annealing temperature is increased to 1000°C, a negative effect is seen on the magnetization as it reduces to 10emu/g in both samples. This is attributed to the formation of increase α-Fe_2O_3 phase with increase in annealing temperature

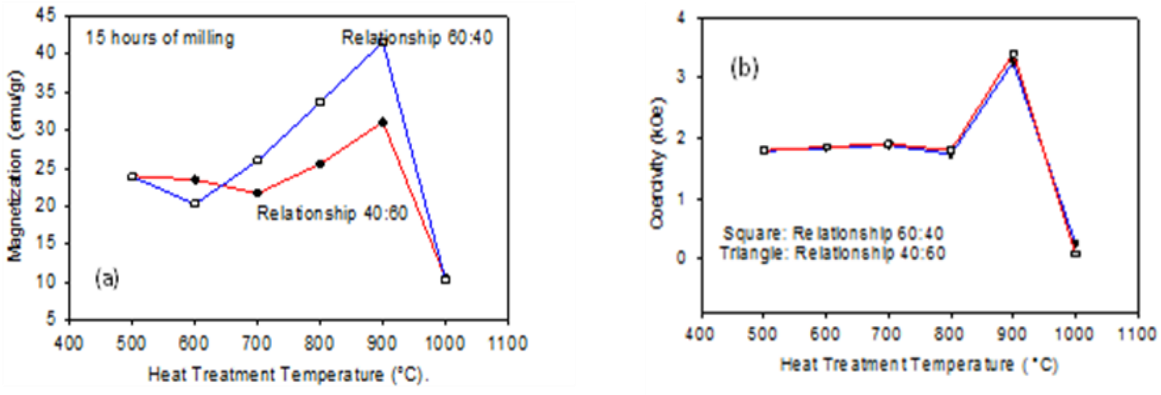

Figure 4. The dependence of saturation magnetization (a) and coercivity (b) as a function of heat treatment temperature for the samples 60%BaM-SiO_2 and 40%BaM-SiO_2 with 15h of milling.

to 1000°C as is also shown by the XRD spectrum of the samples heat treated at 1000°C. Figure 4(b) shows the dependence of coercivity as a function of different heat treatment temperatures. Coercivity also shows a similar trend as that of saturation magnetization. In the range 500-800°C that the samples presented an Hc values close to 2kOe. The sample heat treated at 900°C shows an increase in coercivity value of 3.5kOe for the ratio 60:40 and 3.4 kOe for the ratio 40:60. Both the samples show a value less than 0.5kOe for the samples treated at 1000°C.

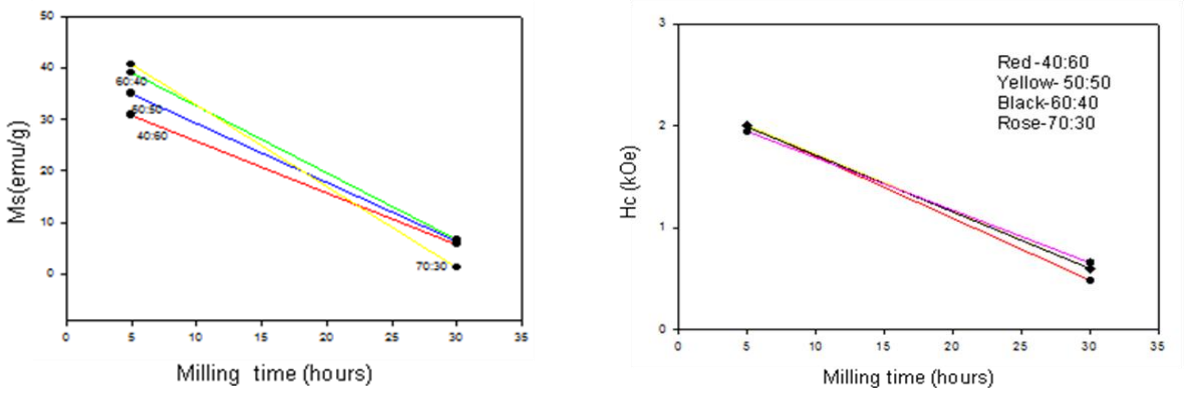

Figure 5. Effect of saturation magnetization Ms (a) and Coercivity (Hc) (b) as a function of milling time for different compositions treated at 500°C

The effect of magnetization and coercivity as a function of milling time for different compositions treated at 500°C is shown in Figure 5. It is noted that the system 70:30 has the highest value of magnetization for 5h milled sample (Figure 5(a)). The effect of increasing milling time reduces the magnetization of all samples due to the presence of α-Fe_2O_3 as well as the distortion of crystal lattice. The coercivity as a function of milling time (Figure 5 (b)) shows all the system have same value at 5h of milling and it decreases with milling time. The low value of coercivity at 30h of milling is due to presence of large number of defects in the network which does not disappear at 500°C. The milling clearly affects the distortion of the network for short and long milling hours and it is the combined action of the distortion and decomposition of BaM in to hematite (α-Fe_2O_3) and probably amorphous BaO. The latter could not be detected by X-ray, which suggests its not crystalline nature. Hematite is antiferromagnetic in nature; this means that it does not have a net magnetization. As its content increases with the time of milling the magnetization decreases due to the dissolution of ferrimagnetic phase (BaM). The coercive field strength does not depend on the presence of α-Fe_2O_3.

Figure 6 shows the saturation magentization and coercity as a function of milling time from 5 to 30 h for the samples 60%BaM-40%SiO_2 and 50%BaM-50%SiO_2 heat treated at 900°C. As we can see from the figure milling time have a strong influence on the magnetic properties. Figure shows an opposite trend for both factors, saturation magnetization decreases with milling time whereas coercivity increases. Maximum value of saturation magnetization is obtained for the BaM-SiO_2 ratio 60:40 (43emu/g), but for the ratio 50:50 at the same conditions saturation magnetization obtained is only 41emu/g. Also the higher coercivity is obtained for the sample with the ratio 60:40 (4.5kOe) but for the relation 50:50, the coercivity value is only 4.2kOe. The milling time causes an increase in coercivity because the particle size reduces with milling time and size is close to critical domain (mondomain) and is directly related to the increase in processing time. The values obtained for the samples milled for 15 h and subsequent heat treatment at 900°C are located in the values of 3.3kOe, which are acceptable for the purpose of magnetic recording.

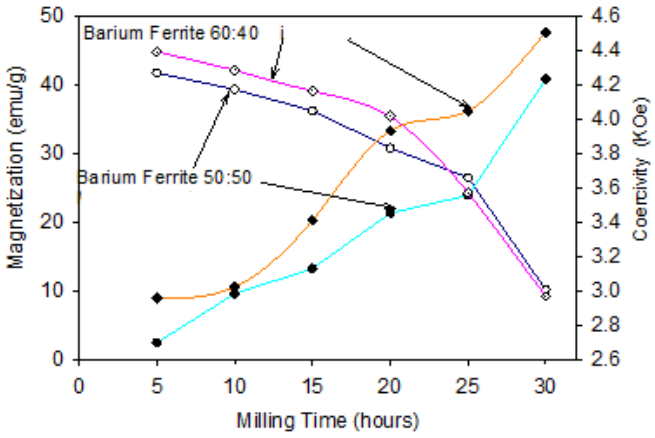

Figure 6. The saturation magnetization (□○) and coercivity (■●) as a function of milling time for the samples 60%BaM-40%SiO_2 and 50%BaM-50%SiO_2 heat treated at 900°C

Figure 7 shows the hysteresis loops for the sample 60%BaM-40%SiO_2 milled for 15h and heat treated at 700, 800, 900, 950 and 1000°C. The highest magnetization is obtained for the sample heat treated at 900 and 950°C. It was observed an increase in magnetization as the temperature increases from 700-950°C and afterwards a sharp drop at 1000°C, because the magnetic properties of the bariumferrite-silica nanocomposites changed significantly at 1000°C due to the presence of hematite (α-Fe_2O_3) phase. The coercivity also increased with heat treatment, as shown in the second quadrant of the hysteresis curve.

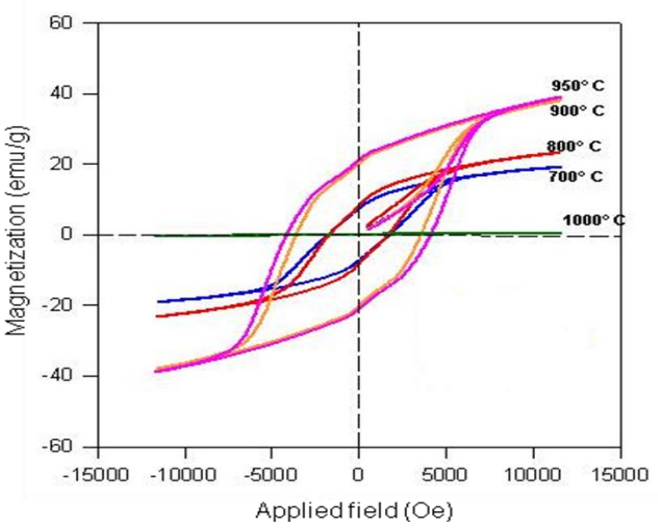

Figure 7. Hysteresis loops for the sample 60%BaM-40%SiO_2 milled for 15h and heat treated at 700,800,900,950 and 1000°C

4. Conclusions

In this work we synthesized barium ferrite and silica nanocomposite by high energy ball milling. The study was done with different compositional ratio of BaM and SiO_2, milling time and annealing temperature. X-ray diffraction study shows that the sample with compositional ratio 60%BaM-40%SiO2 with 15h of milling and 900°C heat treatment is enough for obtaining well dispersed phase of BaM on the ceramic matrix with better magnetic properties. The values obtained for the samples milled for 15 h and subsequent heat treatment at 900°C are located in the values of 3.3kOe, which are acceptable for the purpose of magnetic recording.

5. Acknowledgements

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6. References

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