PHYSICAL CHARACTERISTICS AND MAGNETIC PROPERTIES OF BAFE12O19/SRTIO3 BASED COMPOSITES DERIVED FROM MECHANICAL ALLOYING

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Abstract. Barium hexaferrite and strontium titanate are well established permanent magnet and piezoelectric materials which are technologically and scientifically attractive due to their potential for various applications in the field of magnetic electronics functional materials. However, the material properties for both require a careful control of grain structure as well as microstructure design to meet a specific application. In this work, we report some results of materials characterization especially particles and grains which were promoted during mechanical milling of a BaFe12O19/SrTiO3 composite system. These are including mean particle size characterization by Particle Size Analyzer and mean grain size determination by means of line broadenning analysis employing a step scanning counting in XRD apparatus for composite powders at various milling time up to 60 hours. It was found that the particle size of composite powders initially increased due to laminated layers formation of a composite and then decreased to an asymptotic value of ~8 μm as the milling time extended even to a relatively longer time. However, based on results of line broadening analysis the mean grain size of the particles was found in the nanometer scale. We thus believed that mechanical blending and milling of mixture components for the composite materials has promoted heterogeneous nucleation and only after successive sintering at 1100 oC the milled powder transformed into particles of nanograin. In thireport, microstructure as well as magnetic properties for the composite is also briefly discussed.

Keywords: particle size, grain size, barium hexaferrite, strontium titanate, mechanical milling

INTRODUCTION

Barium and strontium hexaferrites are well-known permanent magnet materials which have attracted extensive attentions due to their great technical importance . The two type of

materials have high magnetic anisotropy values, high Curie temperatures, relatively large values of total magnetization with excellent chemical stability and thus meet almost all requirement for permanent magnets. Combine with their low electrical conductivity, the materials found additional application in the areas of electric and electronic not excluding the application at high frequency range e.g. microwave devices and radar absorbing materials (RAM) [3,4]

Another kind of functional materials like Strontium titanate, SrTiO3 (STO) has been extensively studied and widely used as a ceramic material for electric and electronic applications . STO series have high dielectric constants; low dielectric losses, stable even at high temperatures and frequencies seem to be promising in the field of magnetic in addition to that of electric and electronics .

The convenient method for the production of fine and nanocrystalline materials is mechanical milling by a ball- milling technique which has also being adapted to the preparation of barium hexaferrite and strontium titanate. The technique is considered simple and less costly able to produce powders which compose of very fine particles in the range of single-domain particles (~1 μm) [7,8]. In this work, we report some results of materials characterization especially particle and grain sizes which were promoted during mechanical milling of a BaFe12O19/ SrTiO3 composite system. Discussion are including results of mean particle size characterization by a Laser Particle Size Analyzer and mean grain size determination by means of line broadening analysis employing a step scanning counting in the X- ray diffraction (XRD) apparatus. Magnetic properties of composite materials were also studied through a hysteresis loop obtained from the measurements.

METHODS

First, composite components respectively SrTiO3 (coded STO) and BaFe12O19 (coded BHF) were prepared through mechanical alloying route employing a planetary ball mill with ball to powder ratio 10:1 for 60 hrs. Stoichiometric quantities of the analytical-graded precursors BaCO3, SrCO3, Fe2O3 and TiO2 with purity better than 99 % were mixed and milled in a planetary ball mill. Milled powders of various milling time for respective composition were taken and successively analyzed by a Laser Particle Size Analyzer (PSA) Coulter LS100.. The milled powders were also sintered at temperature 1100 °C for 3 hrs. Additional analysis by XRD with Co $K\alpha$ radiation was performed on un overlapping diffraction peak employing step scanning and calculation for crystallite size determination using *Debye Scherer* formula . To obtain accurate results, the peak diffraction data taken through the step-scanning with the diffraction peaks do not overlap. Intensity data during scanning 2 seconds taken for each step of the diffraction angle 0.005°. Diffraction peak width, B is given by equation 1 and the average crystallite size *(D)* obtained from equation 2.

$$B = \frac{0.9\lambda}{D\cos\theta} + \eta\tan\theta$$

$$B\cos\theta = \frac{0.9\lambda}{D} + \eta\sin\theta$$

Where, λ is the X-ray wavelength, η is the strain in the materials and θ is the Bragg angle, while the peak width B obtained after the correction due to instrument broadening according to equation 3.

$$B = \sqrt{B_0^2 - B_s^2}$$

Where, Bo is the Full Width at Half Maximum (FWHM) of the test sample. Bs is the FWHM standard samples that used an in silicon (Si). Secondly, a composite STO: BHF with 1:1 in weight fraction in which the 60 hrs milled STO and BHF powders were co-milled for 100 hrs. The milled mixture was then pressed into a cylindrical dies of 25 mm diameter to form a green pellet. The pellet was sintered at 1100 °C for 3 hrs towards dense composites. Magnetic properties were evaluated using a composite material Permagraph equipped with an external magnetic field up to 2.3 T.

RESULTS AND DISCUSSION

In Figures 1 (a) and (b) the diffraction profiles of sintered mechanically alloyed of respectively BHF and STO materials are shown. Identification of the diffraction peaks ensured that the all peaks are matched with that of BaO.6 (Fe2O3) magnetic phase with a hexagonal crystal structure. Likewise, all diffraction peaks in the profile of Figure 1(b) corresponding very well to that of SrTiO3 phase with a cubic crystal structure. Thus, results of identification have confirmed that preparation of BHF and STO materials by a mechanical milling followed by a sintering at temperature of 1100 °C have succeeded very well to form single phase materials with respective phases.

Figures 2 (a) and (b) are showing results of evaluation for mean particle and crystallite sizes of STO and BHF samples respectively. All the sample powders go through the four stages of the mechanical alloying process, namely: (1) initial stage; (2) intermediate stage ;(3) final stage; (4) completion stage . It shows that mean particle sizes of Mechanically milled for both STO and BHF materials in initial or early stages of milling are characterized by the increase in the mean size due to incorporation of particles of component compounds. The largest mean particle size for both were achieved after 10 hrs milling times. However, the mean particle size of STO (~16 μm) is almost double when compared with that of BHF (~ 12 μm).
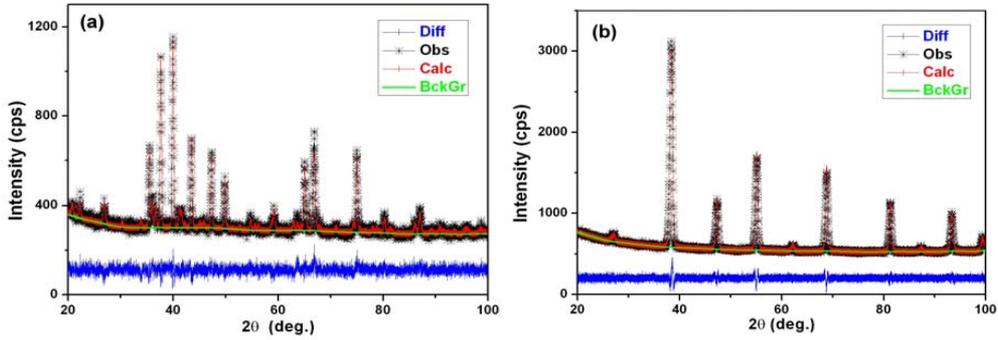
FIGURE 1. Diffraction profile of (a) BHF and (b) STO materials after sintering at 1100 0C.
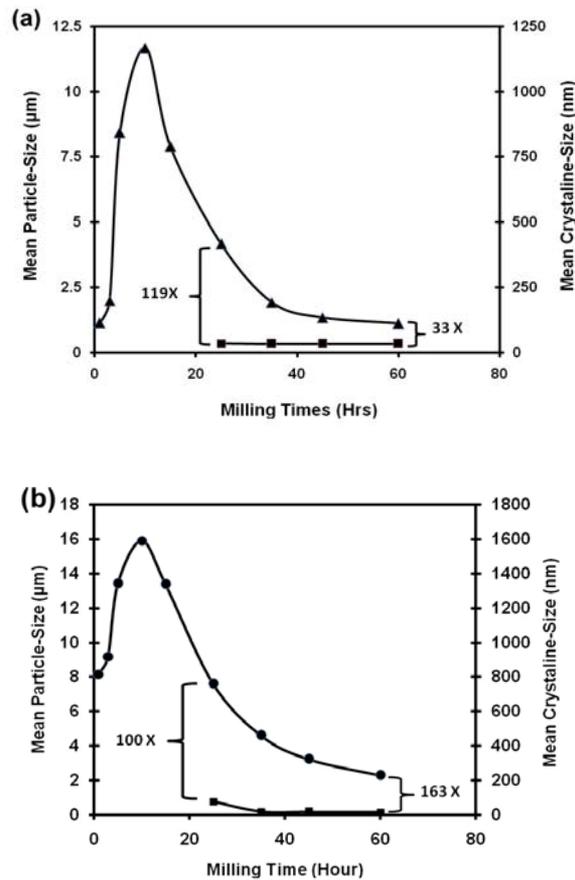
FIGURE 2. (a) Mean Particle-Size (▲) and Crystalline-Size (■) BHF, (b) Mean Particle-Size (●) and Crystalline-Size (■) STO

Extention of milling time beyond 10 hrs have decreased progressively the mean size towards a settle value. Long terms of mechanical treatment during advanced stages of mechanical alloying

have caused particles experiencing embitterment due to accumulation of internal stresses . Continuous plastic deformations to the brittle particles should cause further reduction in particle size towards an average value of ~ 1 μm and eventually settle down to that value even if the deformation continues to grow after the duration of 60 hrs milling time.

Including in Figures 2 (a) and (b) are results of the evaluation of mean crystallite size in milled particles after heat treated at 1100 °C. There was no significant changing in mean crystallite sizes as represented by four different samples of different particle size in both of STO and BHF based samples. However, the mean crystallite size of STO was almost double (~ 14 nm) when compared with that of BHF (~ 34 nm). In addition, ratio between mean particle size and crystallite size at 60 hrs milling time for both STO (163 times) and BHF (33 times) was also almost double. Thus, the mean crystallite size is controlled by mean particle size. This was particularly true to the particles which milled 60 hrs and beyond.

On the light of results described above, it follows that the process of integration of mechanical treatment which accompanied by sintering at 1100 °C has promoted the formation of particles containing respectively STO and BHF phase nanocrystallites. In this case the rate of decrease in particle size is relatively higher than the rate of decrease in crystallite size due to mechanism of particle size reduction and the crystallite growth is not the same. Results for both mean particle and crystallite size of the two type of samples clearly demonstrated that crystallites or grains which promoted by mechanical alloying were in a nano regime in which the grains with sizes below 100 nm were commonly found in STO and BHF based samples.

Similar preparation procedures as described was then applied to composite materials of BHF-STO system. Result of identification once again confirmed that composite samples were consisted of stable phases of respective component in Figure 3.
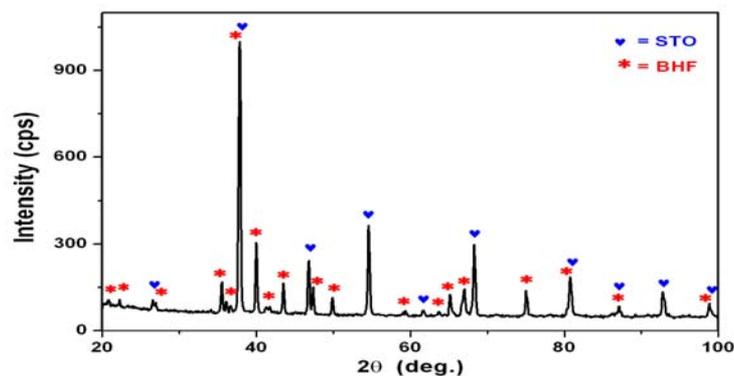
FIGURE 3. : X-ray diffraction profile of BHF/STO (1:1) composite materials after sintering at 1100 °C

The trace exhibits a pattern consisting of a mixture of BHF and STO diffraction traces. No additional phases were identified in the composites which indicate no phase decomposition take place during heat treatments. Our measurement indicated that the lattice constant of BHF in Figure 1(a) which derived from refine a and c values respectively 5.888 Å and 23.218 Å whereas the lattice constants of BHF in a composite were respectively 5.873 Å and 23.118 Å in Figure 3. Thus, there is a slightly different especially in the c value of BHF in a composite. For STO which derived from refined data of Figure 1 (b) was 3.905 Å and that of STO in a composite (Fig. 3) was 3.904 Å. There is almost no different in lattice constant between STO and STO in a composite.

The results of particle and crystallite sizes evaluation for phase constituent magnetic and electric composites are summarized in Figure 4. The same trend was also obtained on the change in the average size of particles during mechanical. However, destruction of particles in the composite system into finer particle size required a relatively long period of milling time. The results in Figure 4 show the mean particles size of composite after mechanical incorporation of 100 hrs is ~ 4 µ m. Post-sintering of composite materials has promoted phases belong to respectively BHF and STO with the mean crystallite size of each almost the same was ~ 27 nm. Mechanical milling of each composite components for 100 hrs have promoted crystal embryo containing particles prior to stages of sintering due to plastic deformation experienced by particles during a relatively long terms period milling.
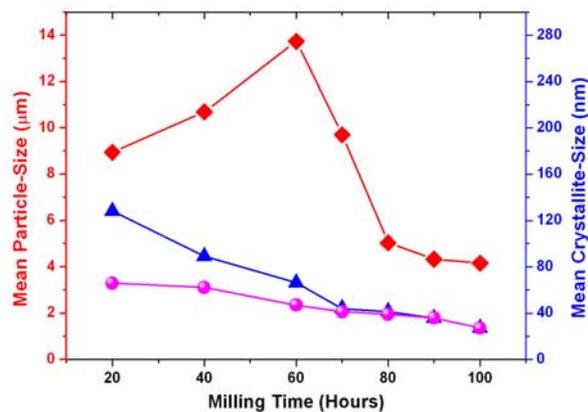
FIGURE 4. Mean Particle-Size Composite of BaFe12O19/SrTiO3 (♦); and Mean Crystallite-Size Balfe12O19 (▲) and SrTiO3 (•) in Composite of BaFe12O19/ SrTiO3.

The results of the evaluation of particle size and crystallite size as shown in Figures 2 and 4 have clearly indicated that the mean size of crystallites in particles is a particle size control. Data once again show the change in crystallite size goes with a relatively slow pace compared

to the size of the particles. One of factors that influencing the mean size of crystals of a material is a sintering temperature and duration of detention during sintering (holding time) through the mechanism of crystal growth. Nevertheless, effects of sintering temperatures and holding times for particles and crystal growth kinetics are currently being studied and thus cannot be reported in this paper.
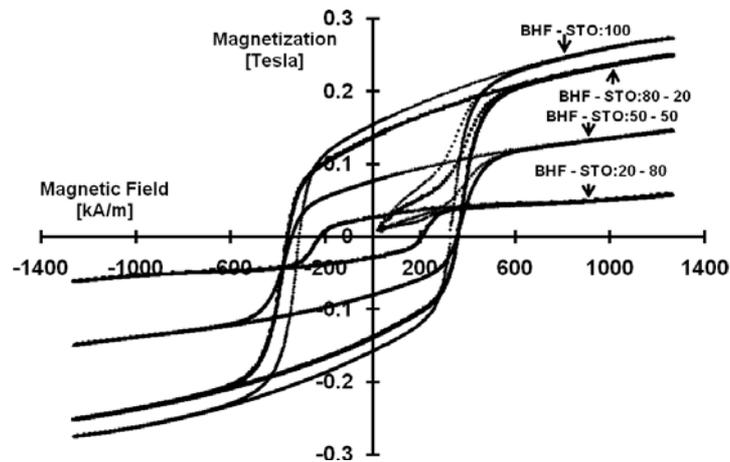
FIGURE 5. The hysteresis loop of composite BaFe12O19/SrTiO3.

In Figure 5, the hysteresis loops of composite samples are shown. The loops were typical of BHF which characterized by almost a similar value of intrinsic coercivity but a difference in remanent magnetization. Remanent magnetization value of composite samples decreased with increasing fraction of STO components obviously due to phase belong to STO is nonmagnetic. This also means that the fraction of magnetic components in the composite is therefore reduced. Based on the data in Figure 5 the hysteresis loops, remanent value of BHF sample is ~ 0.156 T. Remanent magnetization value of BHF-STO composite sample with a composition of 80-20, 50-50, and 20-80 respectively are 0.14 T, 0.08 T, and 0.03 T is about 80%, 50%, and 20% of the value of remanent magnetization of the sample BHF. Thus the remanent magnetization of the composite sample is determined by the fraction of magnetic component only.

CONCLUSIONS

From the research results as presented and discussed in this paper some conclusions can be drawn that the integration process of both the mechanical components of composite materials and composite material itself produces fine particles measuring 2-8 microns and size cannot be sized more refined again even though the duration mechanical integration is extended. Heating of the particles results in the mechanical integration of the sintering temperature of 1100 °C promote the formation of crystallites with nanometer-scale size and material make the

integration of mechanical and sintering the material with a particle containing nanocrystallite. Composite sample prepared in this way consists of clusters of particles of each constituent phase were randomly distributed in the composite. Magnetic properties of the composite sample is still largely determined by the material components that have a magnetic phase.

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