Journal of Alloys and Compounds 616 (2014) 319–322

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Effect of process parameters on the phase formation, particle size and magnetic properties of MnBi nanoparticles prepared by mechanochemical synthesis

N.V. Rama Rao *, G.C. Hadjipanayis

Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA

ARTICLE INFO

Article history:
Received 20 May 2014
Received in revised form 2 July 2014
Accepted 13 July 2014
Available online 19 July 2014

Keywords:
MnBi nanoparticles
Mechanochemical process

ABSTRACT

Nanoparticles of MnBi are obtained from Bi_2O_3 and Mn by mechanochemical synthesis. The effect of excess dispersant (CaO) in mechanochemical synthesis and the temperature of subsequent thermal treatment on phase formation, particle size and magnetic properties of MnBi nanoparticles is investigated by means of X-ray diffraction analysis, scanning electron microscopy and magnetometry. With increase of excess dispersant, the average particle size decreases and the particles are observed to be more separated. Saturation magnetization (M_s) was found to decrease with increase of excess dispersant, while the coercivity (H_c) increases with the increase of dispersant up to 40 wt.% and thereafter it decreases. The formation of MnBi phase increases as the heat-treatment temperature is increased; however, the average particle size increases from nano to micrometer (200 nm to 2 μm).

1. Introduction

Since the high performance permanent magnets based on rare earths are becoming expensive due to the limited rare earth supply, the development of rare earth free permanent magnets for modern technologies is essential [1–3]. Out of all rare earth free magnets, the MnBi compound has emerged as a potential candidate because of its large magnetocrystalline anisotropy ($K \approx 10^7$ erg cm^{-3}) and relatively high magnetization [4]. Due to the MnBi phase diagram constrains, synthesis of single phase MnBi is difficult as it forms through peritectic reaction and fabrication of bulk magnet from powders resulted in lower magnetic performance single phase magnet, especially in the energy product [$(BH)_{max}$] [5–7]. Exchange coupled nanocomposite magnets have shown a path to improve the performance of single phase magnets further [8,9]. Preparation of high anisotropic hard magnetic nanoparticles is vital for the development of nanocomposite magnets as these nanoparticles act as the building blocks. Wet chemical methods were unsuccessful in synthesizing MnBi nanoparticles [10,11]. One promising method for obtaining these nanoparticles is the mechanochemical synthesis from oxide systems in the presence of a dispersant. In our recent work, we demonstrated that mechanochemical process could be used to synthesize separated and crystallographically anisotropic MnBi nanoparticles with size of 100–300 nm [12]. The process parameters such as the amount of dispersant CaO, ratio of Ca/O and Bi/Mn, and heat treatment temperatures have been found to be critical factors in controlling the phase formation, the particle size and magnetic properties. The aim of the present work is to investigate the effect of process parameters on the particle size, phase formation and magnetic properties of MnBi nanoparticles.

2. Experiment

MnBi nanoparticles were synthesized by mechanical milling of mixtures of Bi_2O_3 (99.6%, <1 μm) and Mn (99.5%, 45 μm) in the presence of reducing element Ca (99.5%, <1 mm) and dispersant CaO (98%, 1 μm). Extra 20 wt.% Ca was added to ensure a complete reduction of elements. The ratio of Ca/O (1.2) and Bi/Mn (0.3) were optimized to obtain the best results. The amount of excess CaO dispersant was varied from 15 to 45 wt.% in order to study its effect on the magnetic properties. The other experimental details and washing procedure was reported in our previous paper [12]. The samples were annealed in two steps; in the first step, samples were annealed between 800 °C and 1200 °C for 3–10 min and then quenched. After that, a second step annealing was carried out at 300 °C for 15 h for all the samples. X-ray diffraction (XRD) (Rigaku, Ultima IV, Cu Kα) was used to determine the phases present in the samples. XRD patterns were analyzed using the FULLPROF program based on the Rietveld method to quantify the amount of phases in the samples. Microstructural characterization of the powders was carried out using scanning electron microscopy (SEM) (JEOL, JSM-6335F). Magnetic hysteresis loops of the field aligned powders were measured using a vibrating sample magnetometer (Quantum Design, VersaLab) after magnetizing in a pulse field of 80 kOe.

* Corresponding author.
E-mail address: nvrrao@udel.edu (N.V. Rama Rao).

http://dx.doi.org/10.1016/j.jallcom.2014.07.107
0925-8388/

3. Results and discussion

3.1. Effect of excess dispersant CaO on phase formation, particle size and magnetic properties

The amount of excess CaO was varied from 15 to 45 wt.% keeping all the other process parameters the same. The samples were annealed at 800 °C/10 min and quenched; then a second step of long term annealing was carried out at 300 °C for 15 h. All the samples were washed and characterized. Fig. 1 shows the XRD patterns of the washed MnBi nanoparticles prepared with varying amount of excess CaO (15–45 wt.%). XRD patterns indicate that the LTP MnBi forms along with Bi as major phase. The detailed structural studies on one of the sample (CaO = 30 wt.%) were reported in our previous article [12]. The fraction (wt.%) of MnBi and Bi phases were estimated from XRD patterns using Rietveld method. The magnetic MnBi phase was calculated to be in the range of 15–30 wt.% in the samples and the maximum fraction of MnBi phase was observed for the samples with CaO of 30 wt.%. Since diffusion of Bi and Mn through the CaO matrix is necessary to form the MnBi nanoparticles, a further increase of CaO results in a lower fraction of MnBi phase due to the suppression of diffusion. SEM images of the particles prepared with different CaO amounts are shown in Fig. 2. It can be seen that more separated particles are formed for higher dispersant (CaO) concentration and the particle are in the size range 100–300 nm. Also, the average particle size was observed to decrease with increase of dispersant.

Fig. 3 shows the half hysteresis loops of the washed particles, prepared with varying amount of excess CaO, measured parallel to the alignment direction. The magnetization of all the samples is nearly saturated in a field of 30 kOe. The coercivity (H_c) and saturation magnetization (M_s) values extracted from Fig. 3 are plotted in Fig. 4 as a function of CaO amount. As evident from Fig. 4, M_s decreases with the increase of CaO. On the other hand, the H_c increases with increase of CaO up to 40 wt.% and thereafter

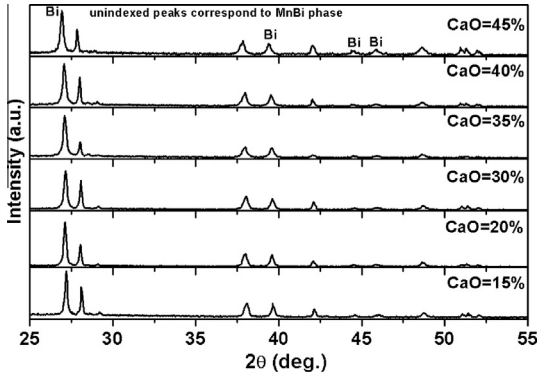

Fig. 1. XRD patterns of washed samples synthesized with varying amount (15–45 wt.%) of excess dispersant CaO.

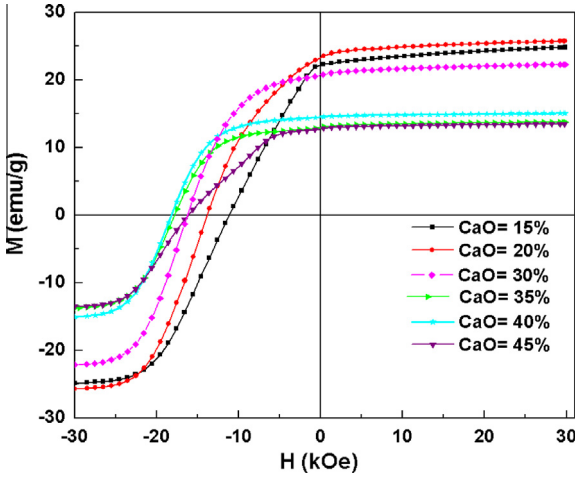

Fig. 3. Half hysteresis loops of washed particles synthesized with different excess dispersant CaO (measured parallel to the alignment direction).

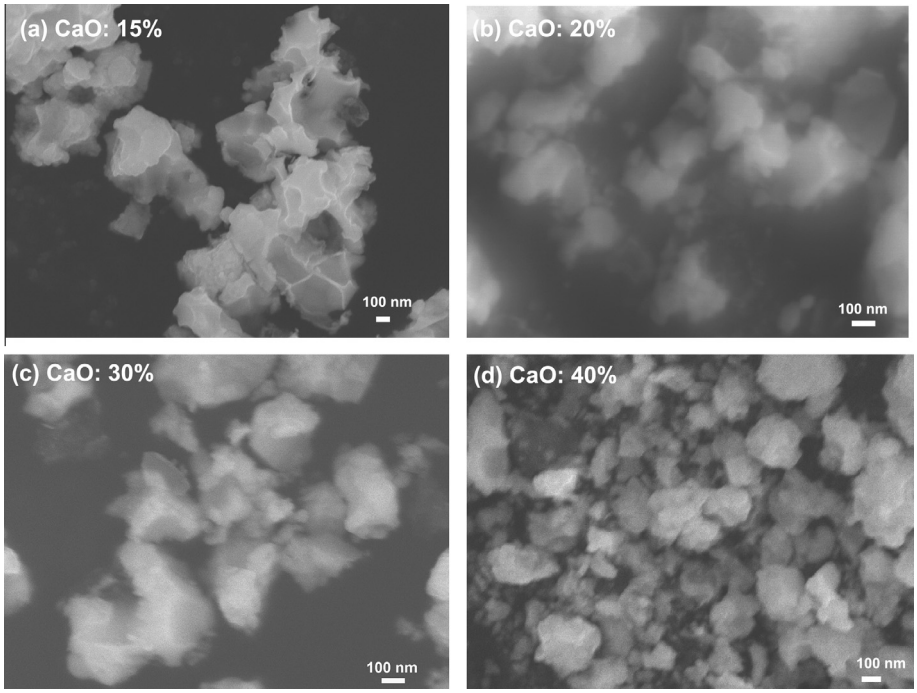

Fig. 2. Typical SEM images of washed particles synthesized with different excess dispersant CaO.