

Effect of high energy milling on the synthesis temperature, magnetic and electrical properties of barium hexagonal ferrite



M. Manikandan, C. Venkateswaran*

Department of Nuclear Physics, University of Madras, Guindy Campus, Chennai 600 025, India

ARTICLE INFO

Article history:

Received 17 May 2013

Received in revised form

29 November 2013

Available online 24 January 2014

Keywords:

High-energy ball milling

Hexagonal ferrite

Single magnetic domain

Hard ferrimagnet

ABSTRACT

Nanoparticles of barium hexagonal ferrite ($\text{BaFe}_{12}\text{O}_{19}$) have been synthesized by initial high energy milling of the precursors and sintering subsequently. X-ray Diffraction pattern reveals the hexagonal phase with a crystallite size of 42 nm. Scanning Electron Micrograph (SEM) shows the size of nanoparticles to lie in the range of single domain particles. X-ray Photoelectron Spectroscopy (XPS) indicates Fe in +3 state and an associated surface peak indicates its presence at different environments. Vibrating Sample Magnetometer measurements (VSM) illustrate ferrimagnetism with high coercivity and non-saturation of hysteresis behavior up to 8500 Oe. The initial high energy milling confines the particle size to the nanoscale which leads to high coercivity. Temperature dependent magnetization shows a sharp peak before transition which is the characteristic of the single domain magnetic behavior. Resistivity plot shows a decreasing trend with temperature. Two thermal activation energy values of 0.81 eV and 0.29 eV indicate the existence of two different conduction processes. The frequency dependent dielectric constant plot shows a semiconducting behavior. The dielectric loss plot shows a drastic change at high temperature due to the anion vacancies in addition to four types of polarization.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Spinel, garnet and hexagonal ferrites are technologically important ceramic magnetic materials used in radio frequency, microwave and magnetic device applications owing to their high electrical resistivity, low magnetic loss and stability [1,2]. When the particle size is reduced to nanoscale they exhibit novel and/or enhanced physical and chemical properties which are different and in most cases superior to their bulk counterparts [3]. Among the ferrite family, hexagonal ferrites are microwave-absorbing material due to their significant value of permeability (> 1), high value of magnetization and planar anisotropic behavior at microwave frequencies [3]. Conventional spinel ferrites do not function well in the microwave range due to drop in the permeability. Barium ferrite with hexagonal structure ($\text{BaFe}_{12}\text{O}_{19}$) consists of spinel S blocks ($\text{Fe}_{11}\text{O}_{16}$)⁺ that are rotated 180° with respect to one another and separated by an atomic plane containing the Ba atoms called R blocks (BaFeO_3)⁻ with the iron atoms distributed within five sites, viz. three octahedral, one tetrahedral and one bipyramidal. This plane of atoms breaks the crystal symmetry resulting in the hexagonal structure and large magnetocrystalline anisotropy energy. Remarkably, the magnetic anisotropy field is 1000

times greater than some spinel ferrites [4,5]. Due to large magnetocrystalline anisotropy, high Curie temperature, excellent chemical stability and corrosion resistivity, $\text{BaFe}_{12}\text{O}_{19}$ is widely used as a permanent magnetic material in electronic applications and it is also being studied for recording applications [6].

The magnetic and dielectric characteristics of hexagonal ferrites strongly depend on the synthesis method and processing conditions, which influence the particle size distribution, morphology and microstructure of particles. When the size of particles is below a certain critical value (~ 460 nm), each particle is said to be a single magnetic domain. The technological applications, such as high-density hard disk data storage and integrated magnetoelectronic non-volatile magnetic memory, require the ferrite particles to be single magnetic domains along with narrow size distribution [3,7,8]. Hence, several non-conventional methods have been adopted to prepare high quality ultrafine pure barium ferrite particles; for instance ammonium nitrate melt technique [9], hydrothermal technique [10], alcohol-assisted spray-pyrolysis [11] and acetone-aided co-precipitation method [12]. Amongst these, ball milling assisted ceramic method is simple and efficient. The initial milling process reduces the phase formation temperature over the solid state reaction (~ 1473 K) method. There are a few reports on the synthesis and characterization of $\text{BaFe}_{12}\text{O}_{19}$ prepared using this method [13–16] where in the authors use a milling speed of 120 rpm [13], 95 rpm [14], milling time of 80 h [16], 16–62 h [14] and sintering temperatures higher than 1373 K

* Corresponding author.

E-mail address: cvunom@hotmail.com (C. Venkateswaran).

[13–15,17]. However it will be seen that the phase formation temperatures were high even when milled for prolonged hours at speeds ≤ 120 rpm. High temperature sintering in turn leads to the formation of larger particles of $\text{BaFe}_{12}\text{O}_{19}$. Moreover, $\text{BaFe}_{12}\text{O}_{19}$ is reported along with secondary phases like $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 and BaFe_2O_4 . The studies show that the presence of secondary phases also affects the magnetic and dielectric properties. Some reports [13,15] indicate decrease in the magnetic and dielectric properties due to low milling speed and extended milling time. Short milling time also yields coarse particles, which become larger after annealing at high temperature, leading to a decrease in coercivity and dielectric constant [14,15]. In addition to the milling speed, time and sintering temperature, ball to powder ratio also plays a role in the preparation of single domain particles of $\text{BaFe}_{12}\text{O}_{19}$.

A comparatively high milling speed of 250 rpm and an optimum milling time of 5 h used in the present study considerably lowers the sintering temperature to yield single domain particles of $\text{BaFe}_{12}\text{O}_{19}$ without any secondary phases. The magnetic and dielectric properties of the synthesized $\text{BaFe}_{12}\text{O}_{19}$ are also studied as a function of temperature, as such a study had not been reported earlier. Further, the oxidation state of Fe, dc conductivity and resistivity studies provide an indepth understanding of the single domain system.

2. Experimental

Stoichiometric proportion of barium carbonate and iron oxide were milled using zirconia vials and balls with a ball to powder ratio of 16:1 at a speed of 250 rpm for 5 h. The milled powders were pressed into pellets of 12 mm diameter, sintered at 1223 K in air for 5 h and subsequently furnace-cooled to room temperature.

X-ray Diffraction (XRD) of the prepared sample was carried out using $\text{Cu-K}\alpha$ radiation. The crystallite size was calculated using Scherrer's formula. Surface morphological features were observed using a FEI Quanta FEG 200 High Resolution Scanning Electron Microscope (HR-SEM). X-ray Photoelectron Spectroscopy (XPS) measurement was done using DAR400-XM 1000 (OMICRON Nanotechnology, Germany) equipped with dual Al/Mg anodes as the X-ray source. The Mg anode was used to obtain the survey and elemental spectra. The spectra were calibrated using C 1s peak at 284.5 eV to exclude the charging effect on the sample. Magnetic studies were made using Vibrating Sample Magnetometer (VSM) (EG&G PARC 4500, USA). The electrical conductivity and dielectric measurements were carried out in the temperature range 393–693 K and in the frequency range of 1 kHz to 1 MHz using an impedance analyzer (Solatron 1260 Impedance/Gain-phase Analyzer).

3. Results and discussion

3.1. Structural and surface morphological studies

Fig. 1 shows the XRD pattern of the synthesized sample. The formation of $\text{BaFe}_{12}\text{O}_{19}$ phase having hexagonal structure with the space group $\text{P6}_3/\text{mmc}$ is evident from the pattern. Initial high energy ball milling mechanically activates the precursors and helps in decreasing the temperature for phase formation. The refined cell parameters, $a=5.848(2)$ Å, $c=23.09(6)$ Å, and the corresponding unit cell volume ($V=684$ Å³) match closely with those of JCPDS file no: 78-0133. The crystallite size calculated using the Scherrer's formula is ~ 42 nm.

Scanning Electron Micrograph is shown in Fig. 2. The surface of the sample shows the formation of individual nanoparticles of crystalline nature as well as their agglomeration. The particle size obtained from the image is in the range of 70–93 nm. This value is

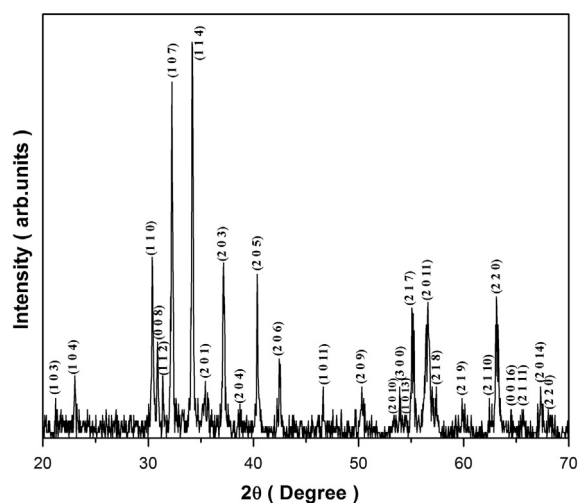


Fig. 1. X-ray diffraction pattern of $\text{BaFe}_{12}\text{O}_{19}$.

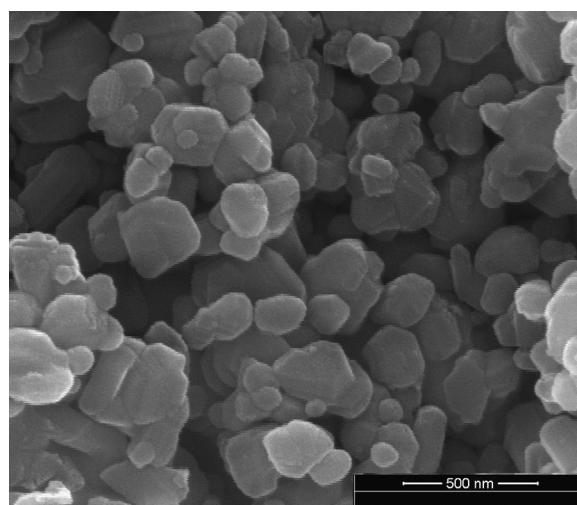


Fig. 2. HR-SEM of $\text{BaFe}_{12}\text{O}_{19}$ showing the nanoparticles distribution.

much smaller than the critical value of 460 nm reported by Rezsescu et al. [18], for single magnetic domain structure. The obtained particle size is also very low compared to the predicted critical particle size (0.5 μm) for barium hexaferrites [7]. These confirm the single domain nature of the sample and the initial high-energy milling of the precursors helps the formation of single domain magnetic particles.

3.2. XPS analysis

The electronic state of Fe present in $\text{BaFe}_{12}\text{O}_{19}$ was determined through X-ray photoelectron spectroscopy. The survey spectrum (Fig. 3(a)) indicates the presence of Ba, Fe and O peaks. The C 1s peak (284.5 eV) was used as the reference for charge correction. Fig. 3(b) shows the deconvolution of Fe spectrum done using CASA XPS software with a mixture of Gaussian and Lorentzian function and Shirley function for background. The $2p_{3/2}$ peak at 710.5 eV corresponds to Fe_2O_3 (Fe^{3+}) [19] and the satellite peak (718.8 eV) is 8.2 eV from the main $2p_{3/2}$ peak (710.5 eV), indicating the presence of Fe^{3+} . Moreover, the peak at 714.1 eV corresponds to surface peak [20], which can be attributed to the reduction in co-ordination of Fe (i.e. in hexaferrite, Fe is present in five non-equivalent crystallographic sites, three octahedral, one tetrahedral and one site surrounded by five oxygen atoms forming a trigonal bipyramid). As the co-ordination of Fe^{3+} ion decreases, the

Download English Version:

<https://daneshyari.com/en/article/1799855>

Download Persian Version:

<https://daneshyari.com/article/1799855>

[Daneshyari.com](https://daneshyari.com)