Physica B 406 (2011) 789–793

Contents lists available at ScienceDirect

Physica B

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

Structural and magnetic behaviour of aluminium doped barium hexaferrite nanoparticles synthesized by solution combustion technique

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ARTICLE INFO

Article history:
Received 30 September 2010
Received in revised form
24 November 2010
Accepted 28 November 2010
Available online 5 December 2010

Keywords:
Nanocrystalline
solution combustion
Barium hexaferrite
Magnetization

ABSTRACT

Nanocrystalline M-type Al^{3+} substituted barium hexaferrite samples having generic formula $BaFe_{12-x}Al_xO_{19}$ (where $x=0.00$, 0.25, 0.50, 0.75, 1.00) were synthesized by the solution combustion technique. The precursors were prepared using stoichiometric amounts of Ba^{2+}, Fe^{3+} and Al^{3+} nitrate solutions with citric acid as a chelating agent. The barium nitrate to citric acid ratio was taken as 1:2 and pH of the solution was kept at 8. The sintered samples were characterized by XRD, EDAX, SEM, TEM and VSM techniques. Pure barium hexaferrite shows only single phase hexagonal structure while samples at $0.25 \leq x \geq 1.00$ show α-Fe_2O_3 peaks with M-phase of barium hexaferrite in the X-ray diffraction pattern. The lattice parameters (a and c) obtained from XRD data decreases with increase in aluminium content x. The particle size obtained from X-ray diffraction data is in the nanometer range. The magnetic behaviour of the samples was studied using vibrating sample magnetometer technique. The saturation magnetization (M_s) and magneton number (n_B) decrease from 38.567 to 21.732 emu/g and from 7.6752 to 4.2126$\mu_{B,}$ respectively, with increase in Al^{3+} substitution x from $x=0.0$ to 1.0.

1. Introduction

Nanomaterials represent a novel class of materials in which a significant fraction of atoms is present on the surface, which induces properties distinctly different from those of normal polycrystalline materials [1,2]. Recently, attention has been drawn towards nanocrystalline ferrites because of their wide applications in industry and technology [3].

Divalent ions like Ba, Sr and Pb have approximately the same ionic radii as that of the divalent oxygen ions and these elements constitute the hexagonal M-type ferrites. The M-type hexaferrite $MFe_{12}O_{19}$ (M=Ba, Sr or Pb) are important ferromagnetic oxides from the point of view of their applications on large scale. Because of their magnetic properties such as high intrinsic coercivity, large crystal anisotropy, etc. these materials can be used as permanent magnets, recording media and as components in microwave and high frequency devices [4]. Besides, these materials are very stable, and have low cost and high electrical resistivity [5].

Among the family of M-type hexagonal ferrite barium hexaferrite ($BaFe_{12}O_{19}$) is a hexagonal (M-type magnetoplumbite, space group P63/mmc) ferromagnetic ceramic material with easy magnetization along c-axis. It is widely applied due to its low production cost combined with excellent magnetic properties. It has high Curie temperature, high coercive force and magneto crystalline anisotropy along c-axis, and is also chemically stable and corrosion resistant. This has enabled the production of magnetic recording media, ferrofluids, sensors and microwave absorbing materials [6–10]. Barium hexaferrite has been applied as ceramic magnets in loud speakers and rotors in small DC motors [6]. The preparation technique of $BaFe_{12}O_{19}$ powder plays an important role in determining magnetic and structural properties [9].

According to the literature survey the barium hexaferrite particles were prepared by various methods such as the hydrothermal method [11], glass crystallization method [12], microemulsion [13], co-precipitation method [14] and citrate precursor [15]. However a number of difficulties in obtaining high purity ultrafine and homogeneous particles of barium hexaferrite with narrow size distribution were observed. Recently, to overcome these difficulties, advanced combustion techniques were used to synthesize complex oxide materials and ferrites [16–19].

In the present paper, we have focused on the synthesis of nanosize barium hexaferrite powders by the solution combustion technique. This is a novel technique with a unique combination of the chemical process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel giving a voluminous and fluffy product with large surface area. This solution combustion process is less complicated than the others and hence it is used for the preparation of barium hexaferrite samples in the present work. In the present study, the stoichiometric proportion of metal nitrate to citric acid has been used to prepare the barium hexaferrite samples. Pure nanocrystalline $BaFe_{12}O_{19}$ has been studied by many workers.

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doi:10.1016/j.physb.2010.11.094

However non-magnetic Al^{3+} substituted nanocrystalline $BaFe_{12}O_{19}$ has not been studied in detail. In order to understand the role of non-magnetic aluminium in the barium hexaferrite matrix an investigation was done in the present work.

2. Experimental

Nanocrystalline aluminium substituted barium hexaferrite samples were prepared by the solution combustion technique. AR grade barium nitrate $Ba(NO_3)_2$, ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ and aluminium nitrate $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in minimum amount of deionised water. Citric acid ($C_6H_8O_7$) was then added to the prepared aqueous solution to chelate Ba^{2+} and Fe^{3+} ions in the solution because among all other fuels citric acid has better complexing ability, low ignition temperature (i.e. 200–250 °C) and controlled combustion reaction with nitrates. After optimizing the pH of the mixed solution it was kept at 8 by adding ammonia solution. The mixed solution was evaporated to dryness by heating at 100 °C on a hot plate with continuous stirring and finally formed a very viscous brown gel. This viscous brown gel was ignited by increasing the temperature up to 150 °C and the loose powder of the samples was obtained. Finally, using the TGA- DTA data analysis (not shown here) the as-burnt powder when sintered at 900 °C for 8 h gives the nanosize nature of the aluminium substituted barium hexaferrite evidenced by X-ray diffraction and transmission electron microscopy.

The phase identification of the prepared samples was performed with the help of a Philips X-ray diffractometer (Model PW-3710) using CuKα radiation ($\lambda = 1.5405$ Å). Lattice parameters a and c for all the samples were calculated by the following formula using the XRD data [20]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

where 'd' is the inter planar spacing and (h k l) are the Miller indices.

The stoichiometric proportion of the constituent ions was examined through energy dispersion of the X-ray analysis (EDAX) technique. The surface morphology of the prepared samples was studied using the scanning electron microscopy (Model JEOL-JSM 63604) technique as well as the transmission electron microscopy technique. Magnetic parameters such as saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) were obtained at room temperature by the vibrational sample magnetometer (VSM) technique with a maximum applied field of 9 kOe.

3. Results and discussions

3.1. Structural aspects

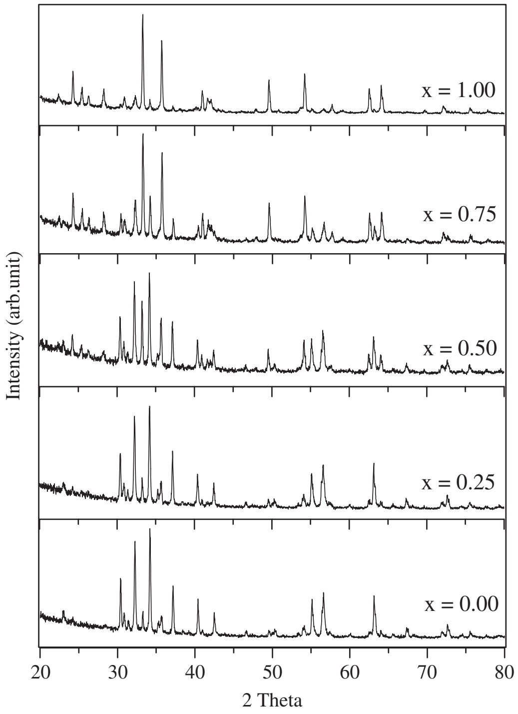

Fig. 1. X-ray diffraction patterns of $BaFe_{12-x}Al_xO_{19}$ samples.

Table 1
Lattice constants 'a' and 'c', c/a ratio and cell volume (V) of $BaFe_{12-x}Al_xO_{19}$ samples.

Composition 'x'	Lattice constant (Å)		c/a	V (Å)^3
	a	c		
0.00	5.8862	23.1437	3.9318	694.434
0.25	5.8734	23.0787	3.9293	689.475
0.50	5.8668	23.0687	3.9320	687.628
0.75	5.8644	23.0499	3.9304	686.506
1.00	5.8637	23.0332	3.9281	685.844

Table 2
X-ray density (d_x), bulk density (d_m), porosity (P), particle size (t) and grain size (G) of $BaFe_{12-x}Al_xO_{19}$ samples.

Composition 'x'	d_x (g/cm^3)	d_m (g/cm^3)	P (%)	t (nm)	G (nm)
0.00	5.315	3.284	38.20	62.20	74
0.25	5.318	3.639	31.56	58.58	64
0.50	5.298	3.725	29.68	54.25	58
0.75	5.271	3.325	36.92	48.15	52
1.00	5.242	3.468	33.82	42.52	47

The powder X-ray diffraction patterns of $BaFe_{12-x}Al_xO_{19}$ samples with $x = 0.00$–1.00 in steps of 0.25 are shown in Fig. 1. The $BaFe_{12}O_{19}$ ($x = 0.00$) sample shows a single phase hexagonal structure while other XRD patterns of the remaining samples show α-Fe_2O_3 as a secondary phase. The XRD pattern for pure $BaFe_{12}O_{19}$ is in good agreement with JCPDS data (card no. 78-0133). Using the JCPDS data the peaks of the XRD pattern were indices for the hexagonal structure. The lattice parameters were calculated for each plane and the average of all are taken as a final lattice constant. The peaks observed due to amorphous response at lower angle having very less intensity cannot be taken into consideration while calculating the lattice parameter. The X-ray intensity keeps decreasing with increase in Al^{3+} substation of x. However, the change in the relative intensities of the patterns may be related to occupation of the crystallographic sites of the crystal lattice. The value of lattice parameters decreases with increase in Al^{3+} substitution as shown in Table 1. This is attributed to the smaller ionic radii of the Al^{3+} ions (0.52 Å) than that of the Fe^{3+} (0.67 Å) ions. Using the XRD data the unit cell volume (V_{cell}), bulk density (d_m) and X-ray density (d_x) of the sample were calculated. The percentage porosity of all the samples was also calculated using the relation between bulk density and X-ray density, and the values are presented in Table 2 [21]. The decrease in porosity indicates that the doped elements may have enhanced the process of densification of the barium hexaferrite matrix. The X-ray density (d_x) decreases with increase in Al^{3+} substitution x of the sample, which is considered due to the small ionic radii of Al^{3+} ions compared to