Journal of Molecular Structure 1106 (2016) 460–467

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Structural, magnetic and dielectrical properties of Al–Cr Co-substituted M-type barium hexaferrite nanoparticles

R.C. Alange [a], Pankaj P. Khirade [b], Shankar D. Birajdar [b], Ashok V. Humbe [b], K.M. Jadhav [b, *]

[a] Department of Physics, Shri. Madhavrao Patil Mahavidyalaya, Murum, Omerga, Osmanabad, M.S., 413605, India
[b] Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, M.S., 431001, India

ARTICLE INFO

Article history:
Received 31 August 2015
Received in revised form
31 October 2015
Accepted 2 November 2015
Available online 7 November 2015

Keywords:
Hexaferrite
Magnetic properties
XRD
SEM
Dielectrical properties

ABSTRACT

Al^{3+} and Cr^{3+} co-substituted barium hexaferrite $BaCr_xAl_xFe_{12-2x}O_{19}$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) nanoparticles were prepared by using sol–gel auto combustion method. X-ray diffraction (XRD) confirmed the formation of M-type hexagonal crystal structure with some additional peaks of Fe_2O_3. Various structural parameters such as lattice constants (a and c), unit cell volume (V), X-ray density (ρ_x), bulk density (ρ_m) and porosity (P) were determined using XRD data. The lattice constant (a), X-ray density (ρ_x) and porosity (P) decreases with increase in Fe content x. The grain size determined from scanning electron microscopy (SEM) images is in the nanometer range. Fourier transform infrared spectroscopy (FTIR) confirmed the formation of hexagonal ferrite structure for all the calcined samples. The M–H curves recorded at room temperature using pulse field hysteresis loop tracer technique exhibited typical hysteresis loop indicating that the sample exhibits ferromagnetic nature. The large coercivity (H_c) values indicate the nanocrystalline nature of the present samples. The coercivity (H_c), saturation magnetization (M_s), remanence magnetization (M_r) and magneton number (n_B) decreases with increase in Al–Cr content x. The dielectric parameters such as dielectric constant (ε'), dielectric loss (ε'') and loss tangent ($tan\ \delta$) were measured at room temperature in the frequency range 50 Hz to 5 MHz. All the dielectrical parameters show compositional as a function of frequency dependences. At lower frequencies, it is observed that the dielectric constant (ε'), dielectric loss (ε'') and loss tangent ($tan\ \delta$) are high.

1. Introduction

Nowadays, hexagonal ferrites are one of the promising materials, that has been attracted a considerable attention in the field of technological applications. A barium ferrite with general chemical formula $BaFe_{12}O_{19}$ with space group P63/mmc and magnetoplumbite structures has been widely used as a hard magnetic material since it was discovered by Philips [1–3]. Barium ferrite has been widely investigated owing to its interesting properties such as excellent chemical stability, corrosion resistivity, high magnetic properties, low cost etc. It also has some distinct properties such as high saturation magnetization, high coercivity, high magnetocrystalline anisotropy and Curie temperature (Tc) and therefore widely used as a magnetic material in the various permanent magnet applications [4–7].

The M-type $BaFe_{12}O_{19}$ hexagonal ferrite in pure and substituted form is well suited to applications in magnetic recording media, microwave communication, microwave dark room, anti-electromagnetic wave radiation because of its large coercivity due to its magnetocrystalline anisotropy, fine grain structure and excellent chemical stability [8–14]. Barium ferrite in pure and substituted form has been synthesized by conventional ceramic synthesis routes using respective oxides or carbonates by two stage sintering process at 1200–1300 °C by various researchers [15,16].

In order to get high-powered barium hexaferrite, researchers are trying their best to obtain pure crystalline mono-domain particles of $BaFe_{12}O_{19}$, different synthesis techniques have been developed, such as sol–gel technique [17], microemulsion [18], hydrothermal reaction [19], glass crystallization [20], salt-melt technique [15,21] etc. Particularly, sol–gel technique is a most commonly used method which can be used to prepare high-powered nanocrystalline barium hexaferrite.

Recently, many studies have been performed by many researchers to improve the magnetic properties by varying the grain

* Corresponding author.
E-mail address: drjadhavkm@gmail.com (K.M. Jadhav).

http://dx.doi.org/10.1016/j.molstruc.2015.11.004
0022-2860/

size or shape of the barium hexaferrite [22–24]. Furthermore, some of researches have carried out a synthesis of various new shapes of $BaFe_{12}O_{19}$ structures such as nanorods, nano-fibers, thin films etc [25–28]. In general, $BaFe_{12}O_{19}$ is synthesized using conventional ceramic and chemical synthesis methods. In order to improve its magnetic characteristics, it is important to control the particle size, closed to a single domain with homogeneity. Therefore, the chemical synthesis with a bottom-up approaches such as the co-precipitation, hydrothermal synthesis, sol–gel, low temperature combustion and self-assembly methods are the best synthesis methods for nanocrystalline $BaFe_{12}O_{19}$ [29–36].

In the literature, reports are available for the synthesis and characterization of barium hexaferrite substituted with various cations like Al, Ce, Co, Ti, Zn [37–40]. These studies revealed that the structural, electrical and magnetic properties of barium hexaferrite are strongly influenced with the substitution of multivalent cations. No systematic investigations of the structural, morphological, electrical, dielectrical and magnetic properties of Al and Cr co-substituted $BaFe_{12}O_{19}$ were reported in the literature to our knowledge.

The substitution of Al^{3+} and Cr^{3+} ions in the crystal structure of barium ferrite can significantly affect on magnetic properties by changing the magneto-crystalline anisotropy field. Here, by replacing the Fe^{3+} ions by Al^{3+} and Cr^{3+} ions, we expected to obtain the barium ferrite that possess high anisotropy field. Also, the electrical and dielectric properties are expected to be significantly high.

Thus, it will be interesting to study the structural, microstructural, electrical and magnetic properties of Al and Cr co-substituted barium ferrite ($BaCr_xAl_xFe_{12-2x}O_{19}$) nanoparticles. In this work, structural, morphological, magnetic and dielectrical properties of Al and Cr doped $BaCr_xAl_xFe_{12-2x}O_{19}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) nanocrystalline hexagonal ferrite are reported.

2. Experimental methods

2.1. Preparation of $BaCr_xAl_xFe_{12-2x}O_{19}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) hexaferrite nanoparticles

Analytical Reagent (AR) grade barium nitrate $Ba(NO_3)_2 \cdot 6H_2O$, ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$, aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$, chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ and citric acid ($C_6H_8O_7 \cdot H_2O$) as a fuel were used as starting materials. According to the composition of $BaCr_xAl_xFe_{12-2x}O_{19}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$), all the nitrates were separately dissolved in a minimum amount of de-ionized water and stirred on a magnetic stirrer for ten minutes. All the solutions were mixed together and stirred on a magnetic stirrer until the nitrates were completely dissolved. The metal nitrate to citric acid ratio was taken as 1:3. The solutions were stirred with continuous stirring on magnetic stirrer; drop by drop ammonia solution was added to adjust the pH value to 7. Then the solution was heated on a hot plate at 80 °C with constant stirring until gel was formed. Instantaneously gel ignites with the formation of large amounts of gas, resulting in to light weight voluminous powder. The resulting precursor powder was annealed at 900 °C for 10 h to obtain pure $BaCr_xAl_xFe_{12-2x}O_{19}$ hexaferrite powder. The various steps involve in the synthesis of $BaCr_xAl_xFe_{12-2x}O_{19}$ using sol–gel auto combustion method is shown in Fig. 1.

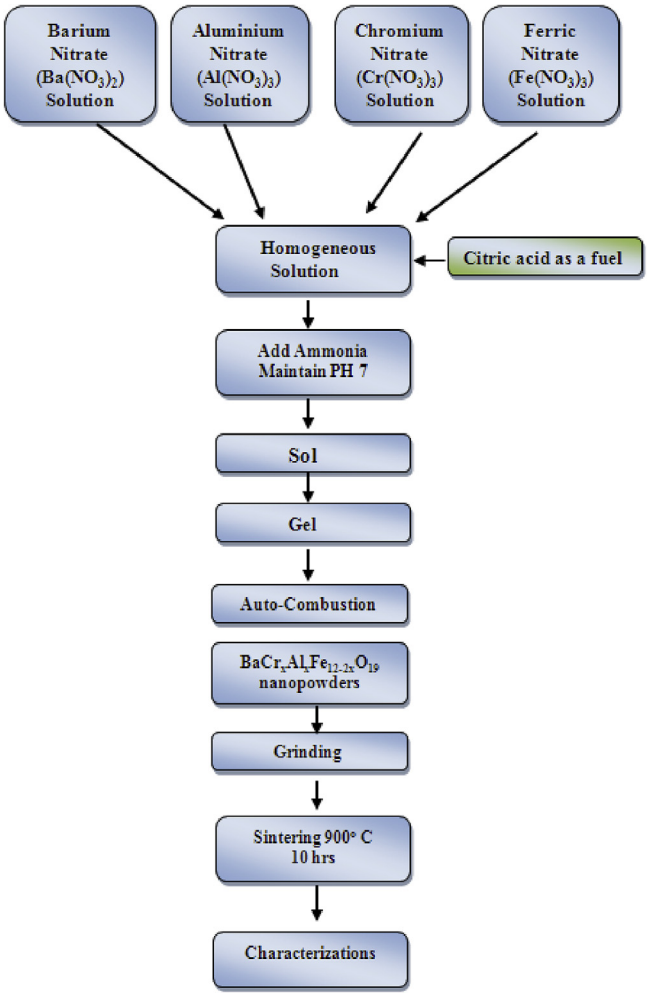

Fig. 1. Flowchart of sol–gel auto combustion synthesis of $BaCr_xAl_xFe_{12-2x}O_{19}$ nanoparticles.

2.2. Measurements and characterizations

The prepared $BaCr_xAl_xFe_{12-2x}O_{19}$ samples in nanosize form were characterized by standard techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrum (EDS). X-ray diffraction (XRD) technique was employed to characterize the prepared $BaCr_xAl_xFe_{12-2x}O_{19}$ nanoparticles using PANalytical X'pert pro difractometer. The XRD patterns were recorded at room temperature in the 2θ range of 20° to 80° using Cu-Kα radiation ($\lambda = 1.5405$ Å). Scanning electron microscopy (model JEOL JSM-6360) technique was used to study the surface morphology of the samples operated at 20 kV. Using SEM data grain size and morphology of the prepared $BaCr_xAl_xFe_{12-2x}O_{19}$ nanoparticles was studied. The Fourier transform infrared spectroscopy (FTIR) of the prepared samples were recorded in the region 3000–450 cm^{-1} on PerkinElmer spectrum –100 spectrophotometer using KBr as a reference material. The magnetic properties were measured using pulse field hysteresis loop technique (Magnata Company) at room temperature. The dielectric properties of all the samples were measured using LCR-Q meter (HIOKI 3532-50-JAPAN) as a function of the frequencies (50 Hz–5 MHz). The dielectric constant, dielectric loss and dielectric loss tangent were obtained.

3. Results and discussions

3.1. X-ray diffraction (XRD)

X-ray diffraction patterns for all the synthesized samples are shown in Fig. 2. X-ray diffraction analysis revealed that all the diffraction peaks seen in the XRD pattern well matches with the