Journal of Asian Ceramic Societies 2 (2014) 416–421

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Contents lists available at ScienceDirect

Journal of Asian Ceramic Societies

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

Combined structural, electrical, magnetic and optical characterization of bismuth ferrite nanoparticles synthesized by auto-combustion route

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ARTICLE INFO

Article history:
Received 16 July 2014
Received in revised form 28 August 2014
Accepted 2 September 2014
Available online 20 September 2014

Keywords:
$BiFeO_3$
Chemical synthesis
Nanoparticles
Dielectric properties
Ferroelectricity

ABSTRACT

Phase-pure multiferroic bismuth ferrite (BFO) nanoparticles were synthesized by energy efficient, simple and low temperature sol–gel followed by auto-combustion route. Highly crystalline and well-shaped BFO nanoparticles of size about 50 nm were observed in TEM. Thermal analysis was used to optimize the calcination temperature as 500 °C. An endothermic peak at 834 °C has been detected in the DTA curve, representing the Curie temperature. The dielectric anomaly around Neel temperature (T_N) was observed signifying the magnetoelectric coupling. The BFO nanoparticles were found to be highly resistive ($\rho \sim 3 \times 10^9$ Ω-cm) and had very low leakage current of the order of μA/cm^2, which resulted from phase purity. A significantly enhanced weak ferromagnetism was observed due to smaller particles size and remnant magnetization and coercive field were 0.067 emu/g and 185 Oe, respectively. *P–E* loop confirmed the ferroelectric behavior of BFO nanoparticles. The direct band gap energy was calculated to be 2.2 eV from UV–vis studies.

1. Introduction

Ferroic materials that exhibit spontaneous and switchable internal ordering have great importance due to a wide range of functional applications and their interesting fundamental physics [1]. Multiferroic combines two or more primary ferroic orderings out of ferroelectricity, ferromagnetism and ferroelasticity [1–4]. The most interesting thing about these materials is their magnetoelectric coupling, as a result of which electric polarization can be swapped by magnetic field and vice versa. This coupling multiplies the degrees of freedom, due to which multiferroics can be used in the field of highly dense non-volatile memory devices, spintronics, telecommunication and sensors [4–8].

Mostly studied single-phase ABO_3 type perovskite multiferroics are $BiFeO_3$ (BFO), $BiMnO_3$ (BMO) and some rare earth manganites like $YMnO_3$ [9]. Out of these, BFO is the only promising candidate that retains ferroelectric ($T_C \sim 825$ °C) along with G-type antiferromagnetic (Neel temperature, $T_N \sim 360$ °C) orderings fairly above room temperature. It possesses rhombohedrally distorted perovskite structure with space group R3c, which can also be described by hexagonal system of basis with lattice parameters $a_{hex} = 5.58$ Å and $c_{hex} = 13.90$ Å [5]. It shows small residual magnetization as a result of canting of spins from their perfect antiparallel direction, which is greatly enriched in nanoparticles of size less than period of cycloid modulation, i.e. 62 nm [10]. Also, it has a small band gap lying in visible region, so it finds potential application as a visible light photo-catalyst [11].

Although BFO is mostly investigated multiferroic, its practical applications are limited on account of high leakage current, which is caused by defects and compositional instability [12]. It is synthesized in various forms like single crystals, ceramics, nanoparticles/crystals and thin films [13–15]. However, stoichiometric phase-pure synthesis is a challenging task. Conventionally, it is synthesized by solid-state reaction of Bi_2O_3 and Fe_2O_3 at high temperature, but reaction kinematics suggests that the temperature range for stability is very small and deviation from this range leads to impurity phases like $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ [16]. Furthermore, bulk form of BFO offers insignificant electric and magnetic moments. So, it is beneficial to synthesize in the form of BFO nanoparticles and thin films.

Various low temperature wet chemical methods, like hydrothermal, co-precipitation, micro-emulsion technique, modified Pechini's method, mechanochemical, sol–gel and solution combustion route, have been reported for the synthesis of BFO nanoparticles/ceramics [17–22]. Besides, several literature describe

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Peer review under responsibility of The Ceramic Society of Japan and the Korean Ceramic Society.

http://dx.doi.org/10.1016/j.jascer.2014.09.001

auto-combustion route but it is rare to find collective studies for structural, electrical, magnetic and optical properties of BFO nanoparticles [23–25]. It is known that the phase purity is needed for obtaining better magneto-electric properties of BFO. Therefore, the objective of this work is to synthesize stoichiometric phase-pure BFO nanoparticles at low temperature via auto-combustion route which is a simple and energy efficient method, and to investigate structural, electrical, magnetic and optical properties while maintaining nanoparticle nature of BFO intact. In the process, we have got enhanced properties than previous reports, particularly in case of temperature-dependent dielectric study in which an anomaly nearby T_N signifying the magnetoelectric coupling is observed.

2. Experimental

2.1. Sample synthesis

Bismuth ferrite (BFO) nanoparticles were synthesized by low temperature sol–gel followed by auto-combustion route, which was based on modified Pechini's method. In this method, $Bi(NO_3)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ (Sigma Aldrich, purity >99%) were used as starting materials according to the stoichiometry. First, bismuth nitrate was dissolved in 1 N nitric acid at 60 °C, and then iron nitrate was added to it while maintaining the heating and stirring to make a homogeneous solution. Citric acid as a chelating agent was added in 2:1 molar ratio with metal ions and the solution was stirred vigorously for another 2 h. As-obtained light brownish solution was kept on hot plate till it became viscous resin. While continuous heating, dried resin auto-ignited and released large amounts of gases and became a dark brownish powder, which was further ground and calcined at 500 °C for 3 h to get pure phase of BFO.

2.2. Characterization

The dried resin was subjected to TG-DTA analysis with Netzsch-409STA apparatus at a heating rate of 10 °C/min under nitrogen flow to obtain an optimum temperature range for the calcination. Structure and phase study of BFO nanoparticles were carried out by XRD with PANanalytical Diffractometer (Model: X'Pert Pro; Cu-Kα_1, λ = 1.5405 Å) at room temperature. Morphology of nano-sized particles was studied by TEM (Tecnai 300 kV Ultra twin; FEI Company). *J–E* characteristic for leakage current analysis was obtained by applying a DC field and using a computer controlled Keithley Source Meter (Series 2400). Ferroelectric hysteresis loop was traced by an indigenously built Sawyer–Tower circuit (Marine India) driven by a lock-in amplifier. Dielectric measurement was carried out by the four-point probe system on Agilent E4980A LCR meter in the temperatures range of 30–460 °C and at frequencies ranging from 20 Hz to 2 MHz. These all characterizations were performed on 0.5 mm thick pellet of BFO nanoparticles, annealed at 500 °C for 2 h on which high-grade silver paste was coated uniformly to serve as electrodes. The magnetic hysteresis loops of the powder samples within a field range of ±2.2 T were measured at room temperature using a vibrating sample magnetometer (JDAW-2000D VSM). The UV–vis absorption spectra of the BFO nanoparticles were measured on Varion Cary-100 UV–vis spectrophotometer.

3. Results and discussion

3.1. Thermal analysis

Thermal analysis (TG-DTA) was used to get appropriate temperature range of calcination for obtaining pure phase of bismuth ferrite. For this, as-obtained precursor was heated up to a temperature of 900 °C with heating rate of 10 °C/min in a continuous flow of N_2 gas. TG curve (Fig. 1a) showing weight of dried resin decreased in a step-like manner up to temperature of 450 °C. There is a sudden dip at temperature of 146 °C, accompanied with a large exothermic peak in DTA, which indicates the starting of combustion of metal citrate complex that formed during reaction and other organic materials. So, large amount of energy and gases like CO_2, NO_2, etc. were released. Then, there is a plateau region from 450 °C to 650 °C, which is the most suitable range of temperature for calcination. This auto-combustion route of BFO synthesis is based on principles of propellant chemistry [25], where a high-energy redox reaction takes place. As formation of oxide requires enormous energy, a high temperature is required for the reaction to begin. However, in this method, energy is supplied at molecule level by the combustion of complex carbonized ions, which get used for formation of oxide without attaining a high temperature.

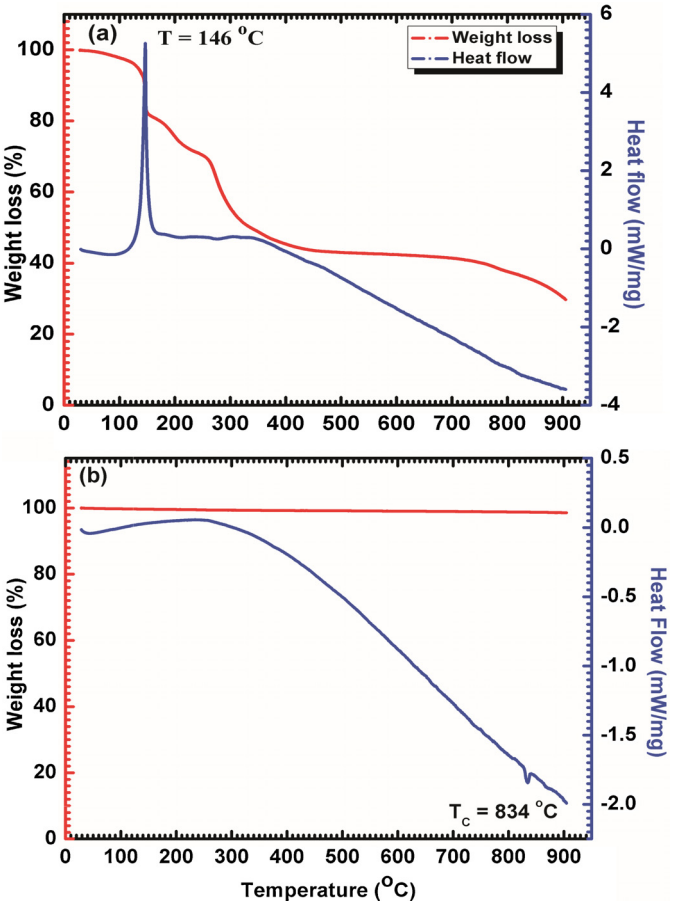

Fig. 1. TG-DTA curves of (a) as-obtained precursor and (b) BFO nanoparticles calcined at 500 °C.

Fig. 1b shows the TG-DTA curve of BFO nanoparticles calcined at 500 °C, where straight TG curve (no weight loss) confirms the quite stability on heating of BFO nanoparticles throughout the temperature range. An endothermic peak at ~834 °C in DTA curve may be due to change in the crystal structure of BFO which clearly indicates the Curie temperature (T_C).

3.2. Structural analysis

The room temperature powder X-ray diffraction pattern of BFO nanoparticles calcined at 500 °C is shown in Fig. 2. All the diffraction peaks are indexed with various ($h\,k\,l$) planes according to hexagonal system of basis. The position of each peak was found to be in