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Characterization and magnetic properties of $Nd_xBi_{1-x}Fe_{0.95}Co_{0.05}O_3$ nanopowders synthesized by combustion-derived method at low temperature

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ABSTRACT

$Nd_xBi_{1-x}Fe_{0.95}Co_{0.05}O_3$ ($x=0$, 0.05, 0.10, 0.15) nanopowders were prepared by a combustion-derived method. The Rietvelt fitting of the X-Ray diffraction data from the $Nd_xBi_{1-x}Fe_{0.95}Co_{0.05}O_3$ (NBFCO) powders showed nanopowders with rhombohedral $BiFeO_3$ crystalline structure (R3c) for $x \leq 10$ and a partial structural transition to orthorhombic phase (Pnma) for $x=0.15$. The differential thermal analysis and thermogravimetric analysis (DTA/TGA) showed a crystallization temperature of 180 °C. Transmission electronmicroscopy (TEM) images revealed that the NBFCO nanopowders were composed of fine particles under 60 nm. From Raman spectroscopy, a band of disordered anion lattice was observed at 653 cm^{-1}. In spite of the antiferromagnetic nature of bulk $BiFeO_3$, the NBFCO nanopowders obtained displayed a ferromagnetic hysteresis loop, with coercivity about 0.1 T and remanent magnetization of 1.02–4.33 A m^2/kg were obtained at room temperature. This ferromagnetic behavior is due to increasing and uncompensated spins at the surface and the canted internal spin by the tilt of FeO_6 octahedral units. We have developed a novel synthetic route for the preparation of ferromagnetic BFO-derived nanopowder materials by a surfactant-assisted combustion-derived method.

1. Introduction

Recently, $BiFeO_3$ (BFO) derived materials have attracted much attention due to being the only multiferroic compound that exhibits simultaneous ferroelectric and G-type antiferromagnetic orders over a broad range above room temperature (Curie temperature > 800 °C, Neel temperature = 370 °C) [1–6]. As a partially covalent oxide, BFO has a rhombohedrally distorted perovskite structure belonging to a space group of R3c [7]. Nevertheless, it exhibits weak magnetism at room temperature due to a spiral magnetic spin cycloid with a periodicity of ~62 nm [6]. So far, most studies on BFO have been performed on two-dimensional epitaxial thin films grown on various substrates [8–11], where epitaxial strain is manifested so as to alter some important properties including crystal lattice structure, polarization, and magnetization. However, more recent approaches have been focusing on polycrystals as well as substrate-free nanostructures such as low-dimensional nanostructures, especially zero-dimensional materials like nanoparticles (NPs) [12–17]. Meanwhile, studies on finite size effect of BFO have been carried out by different authors and some interesting properties (e.g., shift of Neel temperature, gas sensing properties, etc.) have been reported [18–22]. Previous studies had demonstrated that synthesis of BFO NPs through a traditional solid-state method produces poor reproducibility and causes formation of coarser powders as well as Bi_2O_3/$Bi_2Fe_4O_9$ impurity phase [6]. Until now, several chemical routes (e.g. hydrothermal treatment, mechanochemical synthesis method, and sol–gel methodology, etc.) have been successfully employed for fabricating BFO nanoparticles. However, these approaches have certain shortcomings such as impurities found in the final products. Ghosh *et al.* reported a ferrioxalate precursor method to synthesize BFO NPs through solutions of some specific salts at a temperature of 600 °C [23]. Despite the efforts made through enhancing sintering temperature to avoid impurities, a small amount of Bi_2O_3 was found in the final product. Han *et al.*

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have accomplished the morphologies tunable synthesis of bismuth ferrites using hydrothermal method [24]. The resulting size of BFO NPs was sometimes large (up to several hundred nanometers) though no impurities were found in the final products. Using the same method, Chen *et al.* prepared pure phase BFO nanocrystallites at 200 °C using KOH concentration of 4 M. In this study, impurity phases of $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ were easily formed with only a slight change in the KOH concentration [25]. Selbach et al. synthesized BFO NPs through a modified Pechini method using nitrates as metal precursors [26]. Although pure phase BFO was obtained in this study, contaminant produced by decomposition of the precursor was present. Ghosh *et al.* synthesized nanosized bismuth ferrite using a soft chemical route with tartaric acid as a template material and nitric acid as an oxidizing agent [27]. However, the crystallinity of the resulting BFO NPs was unsatisfactory and the existence of an impure Bi_2O_3 amorphous phase in the host was evident at low temperature product of 400 °C. To deal with the issues mentioned above, our recent research suggests that if an excess oxidant agent is to be added to the solution, crystallinity of BFO NPs could be improved. Herein, we reported a general wet chemical route for synthesizing uniform BFO NPs at about 180 °C. To our best knowledge, this is the lowest temperature employed in the literature for BFO fabrication with the exception of certain high pressure techniques such as hydrothermal or solvothermal methods. In addition, the magnetic properties were also investigated for BFO NPs with different size distributions.

2. Experiments

All of the reagents were of analytical grade and used without further purification. Following a typical procedure, bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$, iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$, cobalt nitrate $Co(NO_3)_2 \cdot 4H_2O$, and neodimium nitrate $Nd(NO_3)_3 \cdot 9H_2O$ were weighed in stoichiometric proportions and dissolved in deionized water and 1 mL of glacial acetic acid to completely disolve the bismuth nitrate. Then glycine (NH_2CH_2COOH) and TX-100 were added to the solutions to make the combustion precursor solution. The light-yellow-colored solution was heated under vigorous stirring, when almost dried, it was transferred to an alumina crucible continuously stirred and heated at 250 °C in the hot plate until combustion. Subsequently, powder was leached with 50 mL of HNO_3 1 M for 5 min magnetically stirred (600 RPM), and then the powders were filtered in vacuum and washed three times with water and ethanol, then dried at 80 °C for 1 h to obtain well-crystallized BFO NPs with controllable sizes. For comparison, another group of powders were synthesized by modifying a typically soft chemical route by using excess citric acid as chelating agents [27].

The slurry (intermediate product, before combustion) was subjected to thermal analysis in order to determine the subsequent sintering temperature with simultaneous Thermogravimetric Analysis & Differential Thermal Analysis (TG–DTA) system

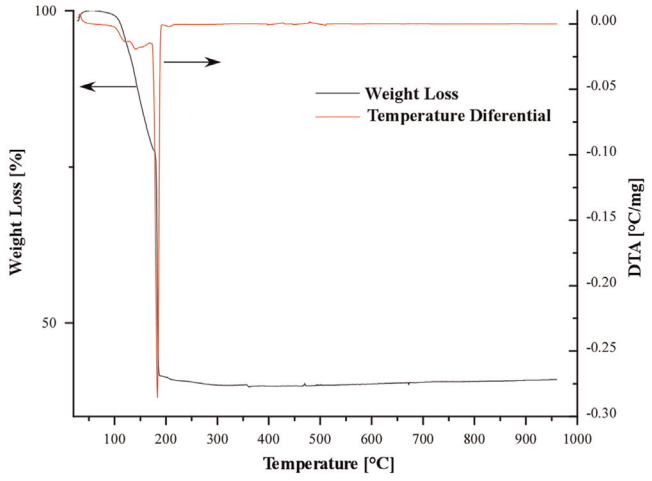

Fig. 1. Thermogram of the $Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$ precursor powder prepared via combustion method at 250 °C.

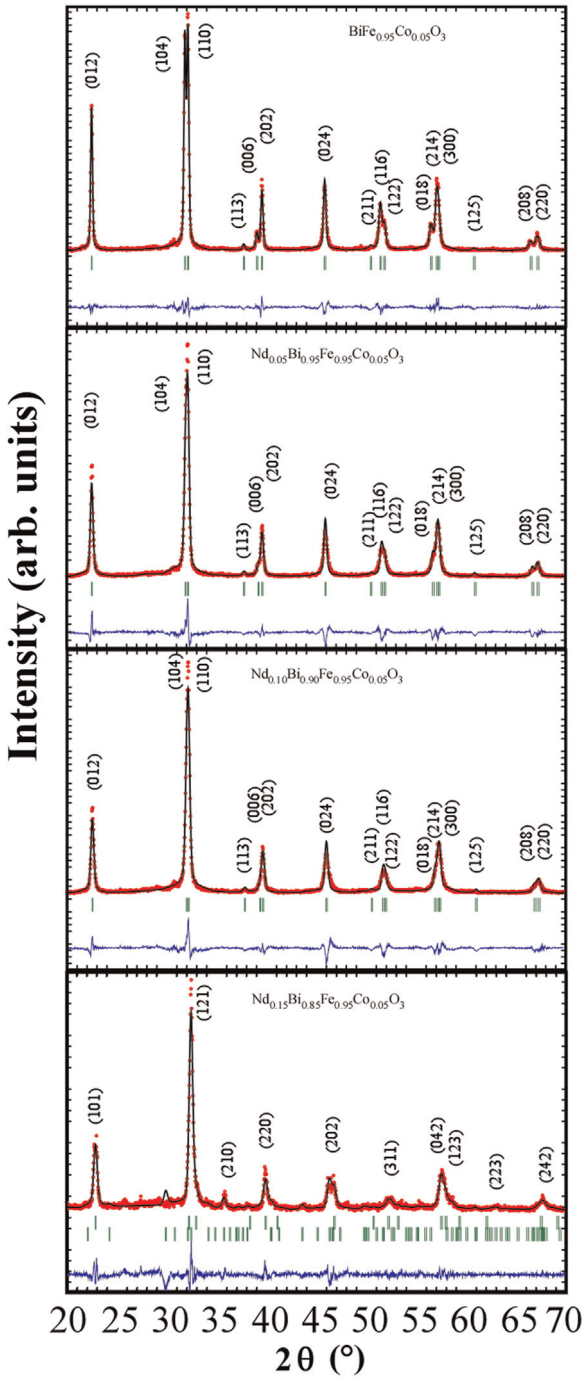

Fig. 2. X-Ray diffraction (XRD) patterns of the modified combustión synthetized $Nd_xBi_{1-x}Fe_{0.95}Co_{0.05}O_3$ (x=0–0.15) powders. For x=0–0.10 the index marker represent the reflections of $BiFeO_3$ rombohedral (R3c) spacegroup (JCPDS file 01-072-2112). For x=0.15 the index markers from the bottom represent the reflections of $NdFeO_3$ orthorombic (Pnma) spacegroup (JCPDS file 01-088-0477), and $BiFeO_3$ rombohedral (R3c) spacegroup (JCPDS file 01-072-2112), respectively.