Journal of Alloys and Compounds 766 (2018) 25–32

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Processing, dielectric and impedance spectroscopy of lead free $BaTiO_3$-$BiFeO_3$-$CaSnO_3$

Sushrisangita Sahoo [a], Sugato Hajra [b, *], Manojit De [c], Kalyani Mohanta [d], R.N.P. Choudhary [d]

[a] Department of Physics, Siksha O Anusandhan (deemed to be University), Bhubaneswar, Indiaa
[b] Department of Electronics and Instrumentation, Siksha O Anusandhan (deemed to be University), Bhubaneswar, India
[c] Department of Pure and Applied Physics, Guru Ghasidas Central University, Bilaspur, India
[d] Department of Ceramic Engineering, Indian Institute of Technology- Banaras Hindu University, Varanasi, India

ARTICLE INFO

Article history:
Received 5 April 2018
Received in revised form
22 June 2018
Accepted 23 June 2018

Keywords:
Solid state reaction
Electrical properties
Composite
Raman
Magnetic

ABSTRACT

The paper presents the fabrication and characterization of structural and electrical properties of an electronic composite of three perovskites: $BaTiO_3$, $BiFeO_3$ and $CaSnO_3$ in a fixed ratio of 80/13/07 (i.e., 0.80($BaTiO_3$)-0.13($BiFeO_3$)-0.07($CaSnO_3$) (referred as BTO-BFO-CSO-7)) using standard experimental techniques. Analysis of room temperature X-ray diffraction spectra helps to determine the crystal system and unit cell dimensions (lattice parameters) of the sample. The dielectric and impedance spectroscopy was used to study the resistive (impedance, complex electrical modulus and electrical transport properties) and insulating (dielectric) characteristics of the prepared electronic material at various frequencies (10^2–10^6 Hz) and temperatures (20–450 °C). Study of the Nyquist plot confirms the presence of temperature dependent bulk (grain) effect only and negative temperature coefficient resistance in the BTO-BFO-CSO-7 composite. Analysis of conductivity spectra reveals that the charge transfer by hopping contributes to the electrical transport process. The dielectric relaxation of the sample is studied using complex modulus spectra. This study also helps to understand the mechanism of the electrical transport process, which depicts a non-Debye type of conductivity relaxation. The magnetic hysteresis loop (M – H) shows a remanent magnetization of 0.031 emu/g.

1. Introduction

In the days of modernization, smart materials, including ferroelectro-magnetics, ferroics, piezoelectrics, optical fibers and shape-memory alloys are tailored by external stimuli. The main reason of being smart may be due to its application for specific uses exhibiting certain nature more than its usual properties. Multiferroic materials are a special class of smart materials which contains two or more ferroic domains (ferroelectric, ferromagnetic, ferroelastic, etc.) in a single-phase system. Such type of materials has a great potential for fabrication of devices (i.e., sensors, storage devices, spintronic device, etc.) and diversely in industries, like automotive, defense, aerospace and robotics [1–3]. In an extended meaning, this class of materials is capable of switching the electrical field with the virtue of magnetic field as well as the spontaneous magnetization, switched by means of an applied electric field [4]. One of the promising multiferroic materials at room temperature is bismuth ferrite, $BiFeO_3$ (BFO). It has a ferroelectric transition temperature of 830 °C and anti-ferromagnetic transition temperature of 370 °C [5]. It is observed that BFO has difficulty in getting proper ferroelectric hysteresis loop due to large leakage current and low resistivity. At room temperature, due to semi-conducting nature of BFO, the experimental data also show low values of dielectric constant, high loss and low spontaneous polarization [6]. In order to resolve these inherent problems of BFO, the fabrication of solid solutions/composites, suitable doping/substitution at the cation sites and the development of new techniques to get single phase of BFO has extensively been attempted [7–9]. It has also been found that the preparation of pure BFO has a significant presence of the secondary phase/impurity ($Bi_{40}Fe_2O_{63}$ or $Bi_{36}Fe_2O_{57}$) leading to a controversial composition. For increasing the structural stability of BFO, the fabrication of BFO-ABO_3 (A = mono to -divalence ions, B = tri to hexavalence ions) system has been found very important for scientific as well technological

* Corresponding author.
E-mail address: sugatofl@outlook.com (S. Hajra).

https://doi.org/10.1016/j.jallcom.2018.06.284
0925-8388/

importance. Some of past investigation shows that the BFO-$PbTiO_3$ [10] composite has enhanced electrical polarization and reduced leakage current, BFO-$DyFeO_3$ [11] composite reveals enhanced dielectric properties, whereas BFO-$BaTiO_3$ [12] revels both ferroic order and low loss (less than 3%). Yang et al. fabricated BFO-BTO-YIG composites and reported the basic crystal structure, proper (less leaky) P-E loop and enhanced electrical and magnetic properties [13]. Out of many perovskites, some members of alkaline-earth stannate family have been used to fabricate its composites with bismuth ferrite for the enhancement of dielectrsic properties, manufacturing of thermally stable capacitors and photo-catalysis. In both the states (i.e., doped or pure), such type of materials is considered as a base material for gas detection sensors which involves various gas like H_2, Cl_2, NO_2, CO, HC [14]. Despite such potential applications, some alkaline earth stannate composites have not been examined extensively except a few. Mandal et al. [15] reported the processing and electrical properties of $CaSnO_3$ porous sample. But, the correlation of such prepared material was not established with BFO-BTO solid solutions. The porous sample prepared by them cannot be a better capacitor material, because the electric charge carriers will sink in the pore leading to a reduced grain to grain connectivity. The availability of pores within the sample will lead to the interaction with humidity. In this context, firstly, we have added a small amount (7 wt %) of $CaSnO_3$ in the BTO (major)-BFO(minor) system which leads to high reactivity and a reduction in the reaction temperature.

Taking the environmental concerns, the elimination of lead compounds from device engineering leads to focus on the synthesis, and characterization (phase evolution, microstructure, molecular and electrical properties (conductivity, impedance, modulus, and dielectric) of an electronic composite of three perovskites in a 80/13/07 ratio (i.e., 0.8($BaTiO_3$)-0.13($BiFeO_3$)-0.07($CaSnO_3$) = BTO-BFO-CSO-7).

2. Experimental

The fabrication of BTO-BFO-CSO-7 was carried out by a standard mixed-oxide route using starting materials; $BaCO_3$ (M/S Loba Chemie Co Ltd, 99% pure), Fe_2O_3 (M/S Loba Chemie Co Ltd, 98% pure), Bi_2O_3 (M/S Central Drug House Pvt Ltd, 99% pure), TiO_2 (M/S Loba Chemie Co Ltd, 98% pure), SnO_2 (M/S Loba Chemie Co Ltd, 99.9% pure), $CaCO_3$ (M/S Sigma-Aldrich, 99.99% pure). These raw powders of oxides and carbonates were carefully weighed in required stoichiometry. The starting materials were mixed in a wet medium (methanol) and then dry grounding in agate mortar. To maintain the loss during high temperature heating 2 wt % of extra Bi_2O_3 was introduced during preparation of the sample. Commercially available Al_2O_3 crucible was utilized for calcinations of mixed powder at 950 °C for 12 h in an air atmosphere. The calcined powder was blended with polyvinyl alcohol (PVA) 5 wt % for the preparation of pellets. Subsequently, the obtained powder was pressed into disc shape (12 mm diameter and 1.5 mm thickness) using uni-axial pressure not more than 4×10^6 Nm^{-2}. After that, the green pellets were fired at 1050 °C for 4 h in ambient air using a computer programmable heat furnace. To obtain temperature-frequency dependent electrical parameters of the above ceramic samples, both smooth, flat surfaces of the disc type compacted material had been painted using air-drying conducting silver paste and annealed at 120 °C for 4 h to make the sample dried.

To check the formation of the prepared sample, preliminary analysis of crystal structure and data with X-ray radiation at RT (room temperature) using a powder diffractometery (Rigaku Miniflex, Japan, wavelength λ = 0.15405 nm, scanning angles on a 2θ scale ($20^0 \le \theta \le 80^0$) and scanning rate of 3°/min) has been carried out. The microstructure analysis of the gold -sputtered pellet surface was carried out with the help of the scanning electron microscope (M/S Inspect S50, Magnetgatan, Sweden). The energy dispersive spectrum (EDS) and color mapping of the sample were evolved from the texture of the sample using Oxford Instruments. The room temperature Raman analysis was carried out with the help of STR-500 Micro-Raman spectrometer. The X-ray photoelectron spectroscopy (XPS) was performed to determine the valence state of Fe using photoelectron spectrometer from VSW Scientific Instruments. To study the field and temperature dependence of electrical characteristics, such as, capacitance, impedance, electrical modulus, transport (conduction) and related properties of the fabricated sample was obtained by an LCR/PSM (model 1735, N4L) meter in the frequency range of 10^2–10^6 Hz as a function of temperature (20–500 °C). A digital multimeter was utilized to measure the voltage and converted into temperature using K-type thermocouple chart. Room temperature magnetic hysteresis loops were measured using a vibrating sample magnetometer (VSM, Lake-Shore Model 7410).

3. Results and discussion

3.1. Crystal data and morphology

To check the phase purity, the crystal structure determination, and lattice parameters X-ray diffraction analysis was undertaken. Fig. 1 exhibits the X-ray diffraction (XRD) pattern of BTO-BFO-CSO-7 which analysis confirms the coexistence of BTO-BFO and CSO phases in the fabricated composite. It shows a number of sharp peaks which are totally different from that of raw materials. Analysis of XRD pattern confirms the presence of desirable phases (i.e. both BTO-BFO and CSO) in the composites with few unknown impurity phases. As the structure of the studied material is not known, all the XRD peaks of the experimental data were matched with JCPDS file of $BaTiO_3$, $BiFeO_3$, $CaSnO_3$ bearing card number 01-075-2122 [16], 01-073-0548 [17], 00-031-0312 [18] respectively. The CSO addition in the BTO-BFO composite leads to the formation of secondary/impurity phases mostly due to the coexistence of two different crystal structures of prepared sample or due to a possible crystallization of a new and/or different phase. Analysis of the crystal data favors the orthorhombic structure of the prepared sample which is consistent with our previously reported paper [19]. The lattice parameters of the prepared distorted perovskite system are as follows: a = 11.514 Å, b = 3.931 Å, c = 16.894 Å and

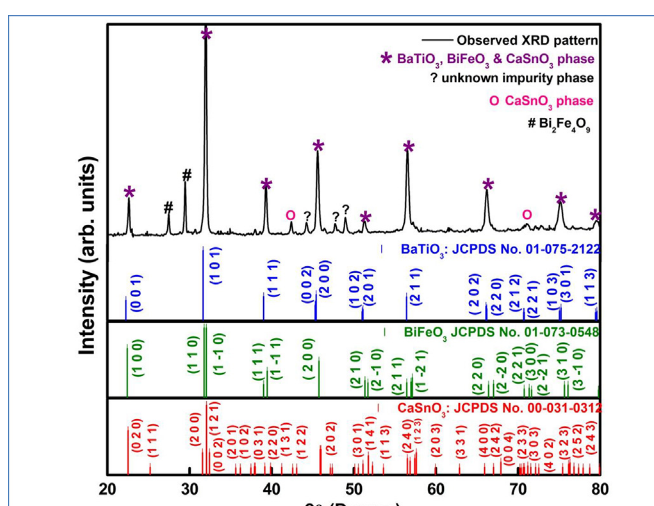

Fig. 1. Room temperature XRD of BTO-BFO-CSO-7 sample.