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Impedance spectroscopy and investigation of conduction mechanism in $BaMnO_3$ nanorods

Khizar Hayat [a], M.A. Rafiq [a,*], S.K. Durrani [b], M.M. Hasan [a]

[a] Nanostructured Materials and Devices Group, Department of Chemicals and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, P.O. Nilore, Islamabad 45650, Pakistan

[b] Material Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad 45650, Pakistan

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ABSTRACT

$BaMnO_3$ nanorods were synthesized at 200 °C and atmospheric pressure using the composite-hydroxide mediated method. X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy were used to investigate the structure, size, morphology, phase purity and elemental composition of $BaMnO_3$ nanorods. Electrical characterization of $BaMnO_3$ pellet was performed at 300–400 K and in the frequency range 200 Hz–2 MHz. Temperature dependence of AC conductivity suggests that the $BaMnO_3$ pellet behaves as a semiconducting material and conduction across the pellet can be explained by the correlated barrier hopping model. Impedance analysis was performed using the equivalent circuit model $(R_1Q_1C_1)(R_2C_2)$ and it suggests a single relaxation process in the $BaMnO_3$ pellet at a particular temperature. The analysis reveals that the $BaMnO_3$ pellet behaves like an *n*-type semiconductor material due to the presence of oxygen vacancies and some disorder. Modulus spectroscopy also supports the impedance results.

1. Introduction

In recent years, barium manganite ($BaMnO_3$), a perovskite-based material, has been studied extensively. $BaMnO_3$ properties can be tailored by doping different elements at barium (Ba) and/or manganese (Mn) lattice sites. By doping, this material has been investigated for its giant magnetoresistive effect, [1–6] antiferromagnetism, [7] high permittivity, [8] giant magneto-elastic coupling, [9] multiferroic behavior and large non-linear optical response [10–12]. Nanocrystalline $BaMnO_3$ has distinct physical and chemical properties as compared with bulk $BaMnO_3$. Field effect transistors using one-dimensional nano-manganites can be easily fabricated for realization of highly sensitive magnetic nanosensors. Wang et al. [6] used $BaMnO_3$ nanorods to sense oxygen (O_2) gas. They found that $BaMnO_3$ nanorods display *n*-type semiconductor behavior as a result of oxygen vacancies. The nanorods show high gas sensitivity due to the small size and high specific surface area of nanorods. However, electrical properties of $BaMnO_3$ nanorods have not received much attention. Electrical properties are of extreme importance because understanding of electron transport helps us to find potential applications for such materials.

In this paper we use the composite-hydroxide mediated (CHM) method to synthesize $BaMnO_3$ nanorods. Synthesis was performed at ~200 °C and atmospheric pressure. Structural characterization of these nanorods was performed using X-ray diffraction (XRD) analysis and Scanning Electron Microscopy (SEM). Elemental information of synthesized samples was obtained using the Energy Dispersive X-ray (EDX) technique. The synthesized material was in the form of a powder and was converted to cylindrical pellets for electrical measurements. AC electrical measurements were performed using an Agilent E4980A LCR meter at temperatures from 300 to 400 K. The frequency of the AC signal was varied from 200 Hz to 2 MHz. Results of impedance analysis show that as prepared $BaMnO_3$ pellet behaves as an *n*-type semiconductor material. Further it was revealed that there is some disorder present in the $BaMnO_3$ pellet due to the presence of oxygen vacancies. The disorder decreased with increase in temperature of the pellet. Analysis of AC conductivity shows that the conduction mechanism in the $BaMnO_3$ pellet is thermally activated, which can be explained by the correlated barrier hopping (CBH) model.

2. Experimental details

2.1. Synthesis of $BaMnO_3$ nanorods

$BaMnO_3$ nanorods were prepared by the composite-hydroxide mediated method. CHM is one of the simplest, most versatile and cost-effective approaches available for obtaining crystalline and chemically pure samples at low temperatures and atmospheric

* Corresponding author. Tel.: +92 51 2208014; fax: +92 51 2208070.
E-mail address: fac221@pieas.edu.pk (M.A. Rafiq).

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pressure with few residual impurities, as compared with conventional high temperature solid-state reaction techniques [13]. The synthesis was performed by the following steps:

(i) 100 g of mixed hydroxides (NaOH/KOH=51.5:48.5) was placed in a self-made 250 ml Teflon vessel with a cover to prevent it from contamination. (ii) A mixture of $BaCl_2.2\,H_2O$ and MnO_2, 2 mmol each, was used as the raw material for the reaction. (iii) The raw material was placed on the top of the hydroxides in the vessel. The vessel was then placed in a furnace preheated to 200 °C. (iv) After the hydroxides were completely molten, the covered vessel containing hydroxides was shaken thoroughly to ensure uniformity of mixed reactants. (v) After 48 h of reaction, the vessel was taken out and cooled to room temperature in air. The solid product was dissolved in deionized water and stirred for more than 2 h to completely dissolve the hydroxides. The product was filtered and washed with hot water to remove the hydroxide from the surface of the nanorods. The synthesized product was dried at 110 °C overnight.

A cylindrical pellet of 10 mm diameter, 0.5 g mass and approximately 1.95 mm thickness was prepared by uniaxial pressure in a hydraulic press at 5 ton load for 1 min. The green pellet was sintered in air at a fixed temperature of 600 °C for 8 h. A constant heating rate of 5 °C/min was maintained during the heating. The sintered pellet was cooled in air to room temperature by placing it in a furnace.

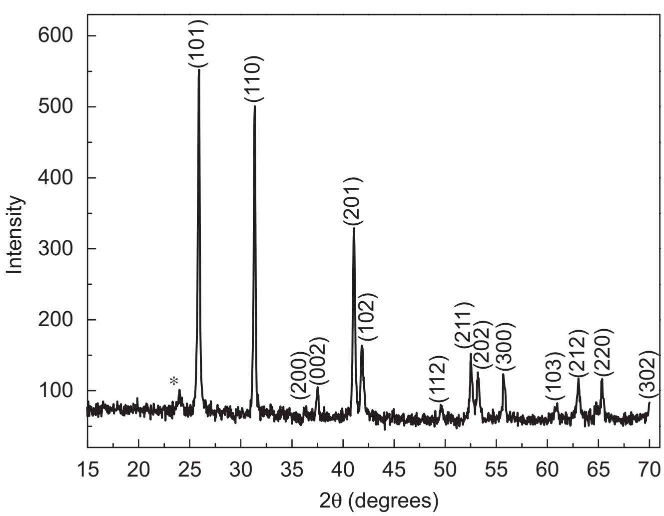

Fig. 1. XRD pattern of $BaMnO_3$ nanorods.

2.2. Structural characterization

Fig. 1 shows the XRD pattern of $BaMnO_3$ nanorods at room temperature using the Bruker D8 Discover diffractometer equipped with Cu Kα radiation. The observed XRD pattern shows that the powder is predominantly a single phase 2H-$BaMnO_3$ compound. However a small impurity peak is observed at $2\theta=24^\circ$. This is due to potassium (K), as confirmed by EDX. 2H-$BaMnO_3$ has lattice constants $a=b=5.6991$ Å and $c=4.8148$ Å, consistent with the JCPDS Card no. 26-0168, $P6_3/mmc$ (1 9 4).

Fig. 2a shows a Scanning Electron Micrograph of $BaMnO_3$ nanorods obtained using a JSM-5910 JEOL, Japan. $BaMnO_3$ nanorods have an average diameter of ~100 nm. The lengths of these rods vary from ~1 to 2 μm. Fig. 2b shows the compositional analysis of the sample carried out with energy dispersive X-ray spectroscopy (EDXS). The EDXS result shows the presence of a very small amount (1.72–2.40% of potassium (K), which confirms the XRD result. This impurity may be removed by excessive washing.

3. Results and discussion

3.1. Impedance spectroscopy

Impedance measurements were performed in the frequency range 200 Hz–2 MHz using an Agilent E4980A LCR meter and in the temperature ranges 300–400 K. Fig. 3 shows the Nyquist plots (real part of complex impedance Z' vs imaginary part of complex impedance Z'') of the pellet. A single semicircular arc is observed at each temperature. The Centre of each semicircle is below the real axis (Z') due to the presence of temperature dependent multirelaxation processes. This means that the $BaMnO_3$ pellet exhibits non-Debye behavior. At lower frequencies a tail (or spike) is observed. This may be due to electrode/electrolyte polarization [14–16]. The impedance results were analyzed using ZView software. The inset in Fig. 3 shows the equivalent circuit used to represent electrical properties of the pellet. The equivalent circuit comprises two RC circuits in series. A constant phase element (CPE=Q) is introduced in parallel to the R_1C_1 circuit to cater to non-ideal behavior of the system. This non-ideal behavior may be due to the presence of disorder in the pellet. The circuit

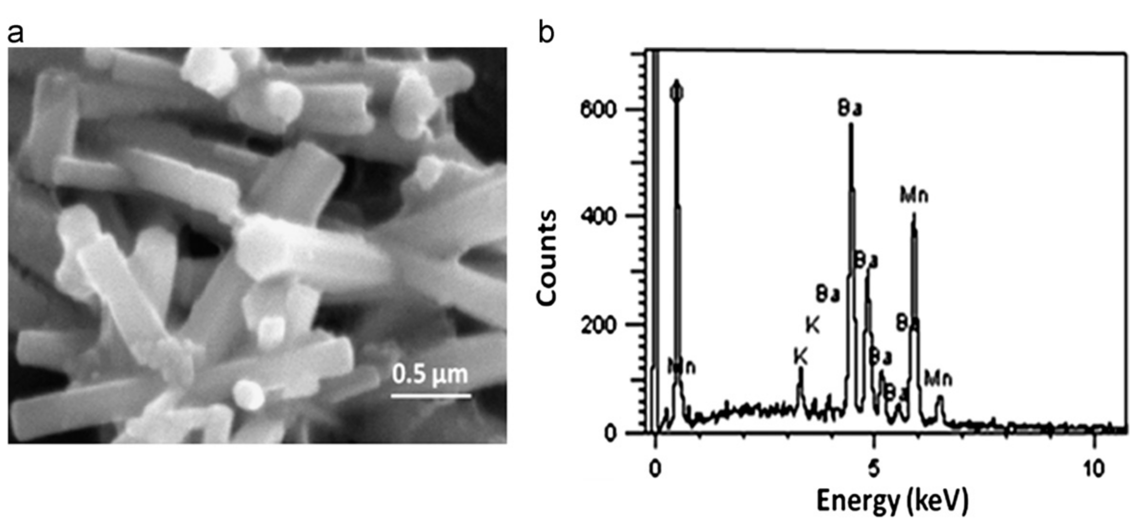

Fig. 2. (a, b) SEM micrographs of $BaMnO_3$ nanorods