Results in Physics 8 (2018) 578–583

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Neodymium cobalt oxide as a chemical sensor

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ARTICLE INFO

Article history:
Received 28 October 2017
Received in revised form 24 December 2017
Accepted 30 December 2017
Available online 3 January 2018

ABSTRACT

Chemical sensing and electrical transport properties of neodymium coblate, $NdCoO_3$, was investigated in this work. It was prepared by using co-precipitation method. Pure neodymium chloride and cobalt chloride were mixing in the presence of sodium hydroxide and the obtained co-precipitated powder was calcined at 850 and 1000 °C. The synthesized composites, as-grown ($NdCoO_3$-I), calcined at 850 °C ($NdCoO_3$-II), and calcined at 1000 °C ($NdCoO_3$-III) were studied in details in terms of their morphological and structural properties. The X-ray analysis confirmed that the synthesized products are well crystalline possessing single phase orthorhombic crystal system of space group *Pbnm* **(62)**. The crystallite size of $NdCoO_3$-I, $NdCoO_3$-II, and $NdCoO_3$-III is 22, 111, and 338 nm, respectively which reflect that crystallite size is increasing with increase in firing temperature. The DC resistivity was measured as a function of temperature in the temperature range from room temperature up to 200 °C. All $NdCoO_3$ are semiconductor in this range of temperature but showed different activation energy which strongly depends on the crystallite size of the products. The activation energy decreased with increase in crystallite size, 0.798, 0.414 and 0.371 eV for $NdCoO_3$-I, $NdCoO_3$-II, and $NdCoO_3$-III, respectively. Thus resistivity increases with increase in crystallite size of $NdCoO_3$. All $NdCoO_3$ products were tested as chemical sensor for acetone by electrochemical approaches and showed excellent sensitivity. Among the $NdCoO_3$ samples, $NdCoO_3$-III showed the highest sensitivity (3.4722 $\mu Acm^{-2}\,mM^{-1}$) compared to other compositions and gradually decreased to 3.2407 $\mu Acm^{-2}\,mM^{-1}$ with decreasing the crystallite size of $NdCoO_3$-II. It is also observed that the sensitivity drastically decreased to 0.76253 $\mu Acm^{-2}\,mM^{-1}$ in the case of $NdCoO_3$-I. It is introduced an efficient route for the detection of environmental unsafe chemicals by electrochemical approach for the safety of healthcare and environmental fields in broad scales.

Introduction

Monitoring the environment for hazardous chemicals is one of the important topics to save our environment clean and safe. So progress in materials for chemical and gas sensor detection took considerable scientific attention. In a chemical or gas sensor one can realize a change in electrical or optical output as a result of chemical and physical interactions with chemicals/gases. In particular, the chemical sensors [1–4] are useful in various safety applications where, we can determine any leakage. It is well known that perovskite oxides with ABO_3 formula were used as a gas sensor materials due to their stability in thermal and chemical atmospheres [5–7]. The deficient in oxygen in semiconducting oxide materials is responsible for the change in resistance of an oxide sensor due to the adsorbed surface species [5]. Nanostructured perovskite materials can improve the sensing properties of the sensor due to high surface-to-volume ratio characteristics. Knowledge of nanoscale perovskite sensing materials have been achieved a great attraction to serve as a novel gas sensing materials at the lower working temperatures. For high-temperature applications, perovskite oxides are very rich materials, where they have high melting and decomposition temperatures, furthermore they can provide microstructural and morphological stability to improve reliability and long-term sensor performance [8]. The $EuFe_{0.9}Co_{0.1}O_3$ oxides exhibit good gas sensing properties to acetone gas at the operating temperature of 280 °C [9]. According to Mekam et al., the hybridization between the transition metal cation and Oxygen atoms in the orthorhombic perovskites, is essential to weaken the short-range repulsion and allow the distortion. Besides, the rare earth cation can modify the ground state and nature of the transition by hybridizing with the valence state, that may indirectly cause change in the transition metal – oxygen

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https://doi.org/10.1016/j.rinp.2017.12.079
2211-3797/

interactions [10]. The electrical properties of any material are an important factor which help us to understand the transport phenomenon and related properties. To distinguish between the possible mechanisms, namely, band transfer, thermionic emission, thermally assisted tunneling and variable range hopping, the general behavior of the electrical resistivity must be determined. The DC electrical resistivity measurements as a function of temperature of $Eu_{0.65}Sr_{0.35}Mn_{0.7}Fe_{0.3}O_3$ and $Eu_{0.65}Sr_{0.35}Mn_{0.3}Fe_{0.7}O_3$ were reported in Refs. [11,12] this temperature dependence of the resistivity curve showed the semiconductor behavior where, resistivity decreases with increasing temperature. According to Parfenov et al., [13] electrical resistivity-temperature dependence of $Nd_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ samples except $Nd_{0.65}Sr_{0.35}MnO_3$ manganite showed the activation temperature dependence of the specific resistance typical of semiconductors. Thermal conductivity of $NdCoO_3$ studied by Pillai [14] in the temperature range from 300 to 1200 K. The excitonic conductivity arising from the interactions of the t_{2g}–e_g states of cobalt ions in the oxides are showed with maxima at 1030 and 975 K, respectively, corresponding with their semiconductor-metal transition temperatures. Effect of Ni doping on the structural and electrical properties of $NdCoO_3$ was investigated by [15] where the conductivity measurements were carried out to investigate transport behavior of compounds. They found a drastic improvement of the room-temperature conductivity of $NdCo_{1-x}NixO_3$ (x = 0.1, 0.2) compared with the pure compound which explained in terms of decrease in band gap. By fitting Arrhenius and variable range hopping (VRH) models they explained behavior in different regions of temperature. The present work highlighted on the selective and sensitive chemical sensing and the electrical transport properties of neodymium coblate, $NdCoO_3$, and their correlation with crystal structure.

Experimental details

$NdCoO_3$ was prepared using co-precipitation method by dissolving the pure chlorides of neodymium, and cobalt in 100 mL distilled water then pure sodium hydroxide was added with the proper molar ratio. All together were stirred using magnetic stirring until we get the pH of our solution to be 12–13. The stirring process is maintained at 80 °C for 12 h then cooled down to the room temperature. Co-precipitated $NdCoO_3$ washed in distilled water until removing any powder of NaCl. The under investigation compounds in this work were fired at 850 °C and 1000 °C for 12 h. XRD measurements were performed with Cu radiation using a PANalytical X'pert Pro MPR diffractometer to check the formation of the required structure. The micrograph and elemental analysis measurements were carried out using Field Emission Scanning Electron Microscope FE-SEM – JEOL (JSM-5600) with acceleration voltage 15 kV and magnification of ×43,000. DC resistivity as a function of temperature was measured in the temperature range from room temperature up to 200 °C. Electrochemical I–V observation was executed at room condition by using the Keithley electrometer, where fabricated electrode and Pd-wire were used as working and counter electrode respectively.

Fabrication of senor

Silver electrode of surface area ~0.0216 cm^{-2} is coated with as-grown ($NdCoO_3$-I), calcined at 850 °C ($NdCoO_3$-II), and calcined at 1000 °C ($NdCoO_3$-III) using conducting binder such as butyl carbitol acetate and ethyl acetate (Fig. 1). All together are kept in the oven at 60 °C for 12 h until the film become completely uniform and dry. It is used as a working electrode and Pd wire is used as a counter electrode. Acetone is diluted in de-ionized water at different concentrations and used as a target analyte. Phosphate

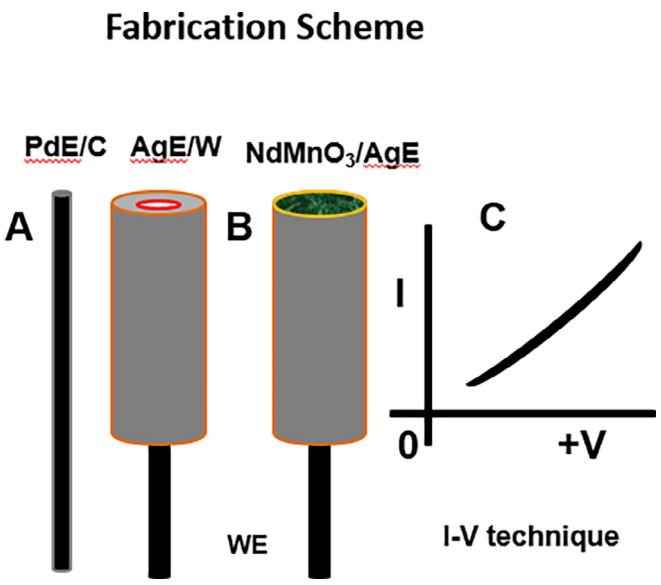

Fig. 1. 257175914400 Fabrication scheme of $NdCoO_3$ coated AgE for chemical sensor development.

buffer solution (PBS, 0.1 M, pH 7.0) is prepared by mixing 0.2 mol of Na_2HPO_4 and 0.2 mol of NaH_2PO_4 solutions in 100.0 mL of de-ionized water. Amount of 0.1 M PBS was kept constant as 10.0 mL for all measurement. The pH of the solution is kept constant because increase in pH affects the efficiency of the electrochemical experiment which may be due increase in ion carriers. PBS was used for total investigations of chemical sensor development and its performance. The different samples of $NdCoO_3$ coated electrode has been primarily investigated in absence of Acetone by I–V technique. After injecting the acetone drop-wise (100.0 μL) into bulk solution, the similar technique is used to measure the conducting current against applied voltage. The ratio of voltage and current (slope) is calculated as a measure of acetone sensitivity.

Results and discussions

XRD diffraction patterns of $NdCoO_3$ as prepared and annealed at 850 °C and 1000 °C are shown in Fig. 2a. Sample $NdCoO_3$ I (as grown) is not completely formed but after firing at 850 °C for $NdCoO_3$ II and 1000 °C for $NdCoO_3$ III samples it is clear that both samples are completely crystalline and both patterns are refined using Fullprof program [16], see Fig. 2b. It is quite clear that all reflections belong to the orthorhombic crystal system of *Pbnm* space group (No. 62) where the maximum refection intensity at 112 planes is observed and no other phases are exist. The lattice parameters are listed in Table 1. The Nd atoms occupy (x, 1/4, z) position while Co atoms occupy (0, 0, 1/2) position and surrounded by octahedral oxygen atoms. The oxygen atoms in this compound are distributed as following; four of them occupy the (x, 1/4, z) position and eight have (x, y, z) position. The bond lengths between Co—O and Co—O—Co angles were calculated and they are listed in Table 1.

There are slightly differences in the positions of Nd-Co-O atoms in $NdCoO_3$-II, and $NdCoO_3$-III, which still possess the same phases. This difference leads to change in distortion. Jahn-Teller distortion is given by the octahedral distortion parameter Δd which defined as [17].

$$\Delta d = \frac{1}{6}\sum_{n=1}^{6}\left[\frac{(dn-d)}{d}\right]^2$$